III. MINERAL COMMODITIES

A. INDIVIDUAL MINERAL COMMODITY REVIEWS

ALUMINA & ALUMINUM

A. Commodity Summary

Aluminum, the third most abundant element in the earth's crust, is usually combined with silicon and oxygen in rock. Rock that contains high concentrations of aluminum hydroxide minerals is called bauxite. Although bauxite, with rare exceptions, is the starting material for the production of aluminum, the industry generally refers to metallurgical grade alumina extracted from bauxite by the Bayer Process, as the ore. Aluminum is obtained by electrolysis of this purified ore.[1]

The United States is entirely dependent on foreign sources for metallurgical grade bauxite. Bauxite imports are shipped to domestic alumina plants, which produce smelter grade alumina for the primary metal industry. These alumina refineries are in Louisiana, Texas, and the U.S. Virgin Islands.[2] The United States must also import alumina to supplement this domestic production. Approximately 95 percent of the total bauxite consumed in the United States during 1994 was for the production of alumina. Primary aluminum smelters received 88 percent of the alumina supply. Fifteen companies operate 23 primary aluminum reduction plants. In 1994, Montana, Oregon, and Washington accounted for 35 percent of the production; Kentucky, North Carolina, South Carolina, and Tennessee combined to account for 20 percent; other states accounted for the remaining 45 percent. The United States is the world's leading producer and the leading consumer of primary aluminum metal. Domestic consumption in 1994 was as follows: packaging, 30 percent; transportation, 26 percent; building, 17 percent; electrical, 9 percent; consumer durables, 8 percent; and other miscellaneous uses, 10 percent. The 1994 production of aluminum was 3,300,000 metric tons while the production capacity was 4,163,000 metric tons per year.[3] Exhibits 1 and 2 list the names and locations of the domestic alumina and aluminum production plants. In addition, 1992 production capacities have been provided in Exhibit 2 for some of the aluminum producers.

EXHIBIT 1

SUMMARY OF ALUMINA PROCESSING FACILITIES

Facility Name	Location	Process Methods
ALCOA	Point Comfort, TX	Bayer
Kaiser (1992 alumina prod. was 1.06 mt[4])	Gramercy, LA	Bayer
Martin	St. Croix, VI	Bayer
Ormet	Burnside, LA	Bayer
Reynolds	Corpus Christi, TX	Bayer

---

[1] "Aluminum and Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. II, 1991, pp. 190-212.

[2] Patricia A. Plunkert and Errol D. Sehnke, "Aluminum, Bauxite, and Alumina," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 183-203.

[3] Patricia Plunkert, "Aluminum," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 16-17.

[4] Patricia Plunkert, 1992, Op. Cit., pp. 183-203.

EXHIBIT 2

SUMMARY OF ALUMINUM PROCESSING FACILITIES

Facility Name	Location	Type of Operations	1992 Production Capacity[5] (1000 metric tons)
ALCOA	Warrick, IN Massena, NY Badin, NC Alcoa, TN Rockdale, TX Wenatchee, WA	Hall-Heroult Hall-Heroult Hall-Heroult Hall-Heroult Hall-Heroult Hall-Heroult	Unknown Unknown Unknown Unknown Unknown Unknown
ALUMAX	Mt. Holly, SC	Hall-Heroult	275
Alcan Aluminum Corp.	Henderson, KY	Hall-Heroult	Unknown
Columbia Aluminum Corp.	Goldendale, WA	Hall-Heroult	Unknown
Eastico	Frederick, MD	Hall-Heroult	Unknown
Intalco	Ferndale, WA	Hall-Heroult	Unknown
Kaiser Aluminum Corp.	Spokane, WA Tocoma, WA	Hall-Heroult Hall-Heroult	Unknown Unknown
Columbia Falls Aluminum Corp.	Columbia Falls, MT	Hall-Heroult	Unknown
National South Wire	Hawesville, KY	Hall-Heroult	Unknown
Noranda	New Madrid, MO	Hall-Heroult	215
Northwest	The Dalles, OR	Hall-Heroult	82
Ormet	Hannibal, OR	Hall-Heroult	Unknown
Ravenswood	Ravenswood, WV	Hall-Heroult	Unknown
Reynolds	Massena, NY Troutdale, OR Longview, WA	Hall-Heroult Hall-Heroult Hall-Heroult	123 121 204
Venalco	Vancouver, WA	Hall-Heroult	Unknown

---

[5] Ibid.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Free moisture in crude bauxite, as mined, may range from five to 30 percent. To produce dry bauxite, most of the free moisture is removed by heating crude bauxite in rotary drying kilns. Calcined bauxite is produced by heating bauxite to reduce total volatile matter, including chemically combined water, to less than one percent. Approximately two tons of crude ore is required to produce one ton of calcined bauxite.

Alumina tri-hydrate is used for the production of the pure aluminum chemicals, high quality refractories, and other high aluminum products, while aluminum is used for the preparation of the purest aluminum chemicals. Alumina and bauxite are the principal raw materials for the production of aluminum chemicals such as aluminum sulfate, aluminum chloride, aluminum fluoride, sodium aluminate, and aluminum acetate.[6]

Metallurgical grade alumina (i.e., 30 to 60 percent aluminum oxide)[7] is extracted from bauxite by the Bayer process and aluminum is obtained from this purified ore by electrolysis via the Hall-Heroult process. These processes are described below. Exhibits 3 and 4 present process flow diagrams for the Bayer process and the Hall-Heroult process.

2. Generalized Process Flow Diagram

Bayer Process

A process flow diagram of the Bayer process is shown in Exhibit 3. The primary purpose of a Bayer plant is to process bauxite to provide pure alumina for the production of aluminum. All bauxite refineries share five common process steps: (1) ore preparation; (2) bauxite digestion; (3) clarification; (4) aluminum hydroxide precipitation; and (5) calcination to anhydrous alumina. Additional operations include steam and power generation, heat recovery to minimize energy consumption, process liquor evaporation to maintain a water balance, impurity removal from process liquor streams, classification and washing of trihydrate, lime causticization of sodium carbonate to sodium hydroxide, repair and maintenance of equipment, rehabilitation of residue disposal sites, and quality and process control. Each step in the process can be carried out in a variety of ways depending upon bauxite properties and optimum economic tradeoffs. Each of these steps is discussed in further detail below.[8]

Ore Preparation

Bauxite mining processes depend largely on the nature of the ore body. If the ore is not uniform, contains an excessive amount of kaolin, or is difficult to handle due to the moisture content, blending operations, physical beneficiation, and bauxite drying are used. Grinding is designed to produce feed material small enough to ensure easy alumina extraction, yet coarse enough to avoid clarification problems with bauxite residue. Uniform, consistent, easily digested bauxite slurry is formed by blending properly ground bauxite slurry in slurry storage "surge" tanks prior to digestion.[9]

---

[6] V.J. Hill, "Bauxite," from Industrial Minerals and Rocks, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 135-147.

[7] Aluminum Company of America. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[8] "Aluminum Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. II, 1991, pp. 254-261.

[9] Ibid.

Bauxite Digestion

Digestion extracts and solubilizes the available aluminum mineral from the bauxite. In digestion, which is performed in steel vessels, autoclaves, or tubular reactors, hot spent liquor reacts with the aluminum minerals in the bauxite to form soluble sodium aluminate ($NaAlO_3$)[10]. Virtually all other constituents are rejected as undissolved solids. Other important reactions that occur in digestion are desilication, causticization of liquor, and precipitation of impurities. The reactive silica in bauxite, such as that in kaolin, reacts with the caustic solution to form soluble sodium silicate, which then reacts at digester temperature to form an insoluble sodium aluminum silicate known as "desilication product." Causticization, the reaction of hydrated lime with sodium carbonate to regenerate sodium hydroxide and precipitate calcium carbonate, is an important part of the Bayer process chemistry. Na_2CO_3 is formed in Bayer liquors by caustic degradation of the organics in bauxite and by absorption of carbon dioxide during exposure of process liquors to the atmosphere. Although poor lime efficiency and alumina losses during digestion as calcium aluminates have led to the practice of "outside" causticization of dilute pregnant liquors in the residue washing area of the plant, digestion lime additions are still made to control impurities such as phosphorus pentoxide.[11]

Clarification

Clarification is necessary to separate bauxite residue solids from the supersaturated pregnant liquor near its boiling point. Coarse particles, called sand because of their high silica content, are usually removed by cycloning followed by washing on sand classifiers prior to disposal. Iron oxide, silica, and other undigested portions of the ore are also removed in settling, thickening, and filtration units, and sent to treatment and disposal units. These wastes are commonly called red and brown muds; these two wastes are RCRA special wastes and therefore are not subject to LDR regulations.[12] In most plants, the fine fraction of residue is settled in raking thickeners with the addition of flocculants to improve the clarity of thickener overflow. The concentrated thickener underflow is washed before disposal in countercurrent decantation washers, on vacuum drum-type filters, or a combination of both. Thickener overflow is filtered to remove the final traces of solids and ensure product purity. Kelly-type pressure filters are most widely used, but some plants use sand filters in which the liquor is filtered by gravity through a bed of properly sized sand. Filtered solids are removed from filter press cloth by hosing and are elutriated from the sand by backwashing.[13]

Aluminum Hydroxide Precipitation

Precipitation is the heart of the Bayer process where recovery of the $Al(OH)_3$ from process liquors occurs in high yield and product quality is controlled. In 1988, practically all of the hydroxide was obtained by Bayer processing and 90 percent of it was calcined to metallurgical grade alumina (Al_2O_3). The liquor is usually seeded with fine gibbsite seed from previous cycles to initiate precipitation. Precipitation can be continuous or batch. Modern plants use the continuous system. Slurry leaving precipitation is classified into a coarse fraction and one or more fine fractions, usually by elutriation in hydroclassifiers. In smelting grade alumina plants, the coarse fraction, called primary product, is sent to calcination; the fine fractions, called secondary and tertiary seed, are recycled to be grown to product size.[14]

---

[10] Aluminum Company of America. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[11] Ibid.

[12] U.S. Environmental Protection Agency, "Aluminum Production," from Report to Congress on Special Wastes from Mineral Processing, Vol. II, Office of Solid Waste, July 1990, pp. 3-1 - 3-15.

[13] "Aluminum Compounds," Op.Cit., pp. 254-261.

[14] Ibid.

Calcination to Anhydrous Alumina

Calcination, the final operation in the Bayer process for production of metallurgical grade alumina, is performed either in rotary kilns or fluid bed stationary calciners. Prior to calcination, the process liquor is washed from the $Al(OH)_3$ using storage tanks and horizontal vacuum filters. During heating, the trihydroxide undergoes a series of changes in composition and crystal structure but essentially no change in particle shape. The product is a white powder and consists of aggregates of differing sizes.[15]

Evaporation and Impurity Removal

Evaporation over and above that obtained in the cooling areas from flashed steam is usually required to maintain a water balance by accounting for the dilution arising from residue and $Al(OH)_3$ washing, free moisture in the ore, injected steam, purge water, and uncontrolled dilutions. Evaporation also serves to concentrate impurities in the liquor stream such as sodium oxalate (a product of organics degradation), facilitating the removal of these impurities.[16]

Hall-Heroult Process

Reduction

Since the development of the Hall-Heroult process, nearly all aluminum has been produced by electrolysis of alumina dissolved in a molten cryolite based bath. Molten aluminum is deposited on a carbon cathode, which serves also as the melt container. Simultaneously, oxygen is deposited on and consumes the cell's carbon anodes. The overall all reaction is[17]:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3\ CO_2$$

Cryolite is the primary constituent of the Hall-Heroult cell electrolyte. Because of its rarity and cost, synthetic cryolite is substituted. Synthetic cryolite is manufactured by reacting hydrofluoric acid with sodium aluminate from the Bayer process. Once the smelting process is in operation, no cryolite is needed because cryolite is produced in the reduction cells by neutralizing the Na_2O brought into the cell as an impurity in the alumina using aluminum fluoride. Thus, the operating cells require inputs of aluminum fluoride. Aluminum fluoride is produced in a fluidized bed by the reaction of hydrofluoric acid gas and activated alumina made by partially calcining the alumina hydrate from the Bayer process. Alumina fluoride is also made by the reaction of fluosilicic acid, a by-product of phosphoric acid production, and aluminum hydroxide from the Bayer process. The aluminum fluoride solution is filtered, and AlF_3 is precipitated by heating, then is flash dried and calcined.

The equivalent of 3-4 kg of fluoride per metric ton of aluminum produced is absorbed from the bath into the cell lining over the lining's 3 to 10 year life. The most common method of recovery treats the crushed lining using dilute NaOH to dissolve the cryolite and other fluorides. The solution is filtered and Na_3AlF_6 is precipitated by neutralizing the NaOH using carbon dioxide. The aluminum industry in the United States uses about 15 kg of fluoride ion per metric ton aluminum, 10-25 percent of which is lost. The remainder, consisting of cryolite generated in reduction cells and of bath in scrap cell linings, is stored for future use. New fluoride for the aluminum industry comes largely from fluorspar and phosphate rock.

---

[15] Ibid.

[16] Ibid.

[17] Ibid.

EXHIBIT 3

THE BAYER PROCESS

(Adapted from: Development Document for Effluent Limitations, 1989.)

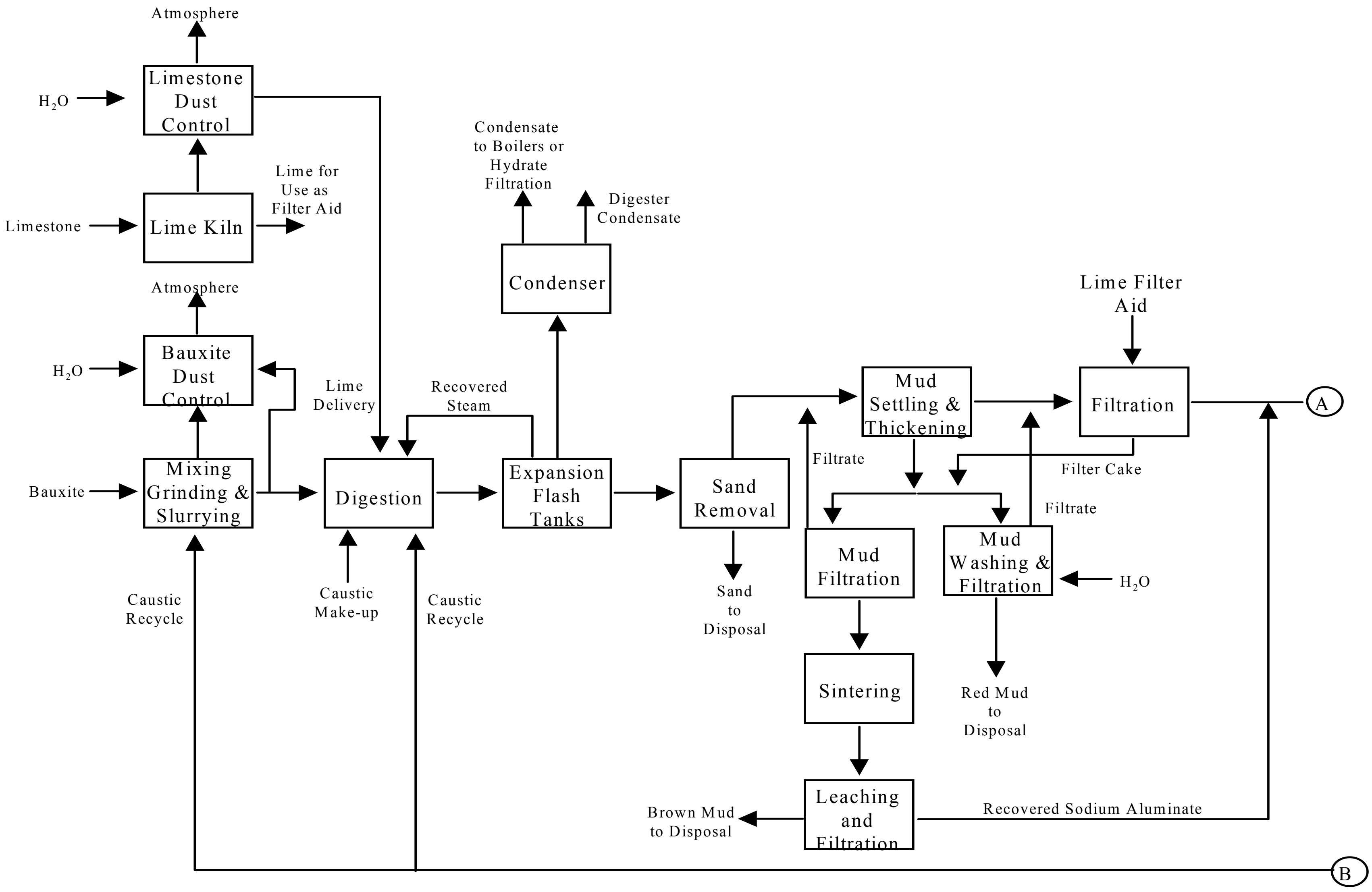


EXHIBIT 3 (Continued)

THE BAYER PROCESS

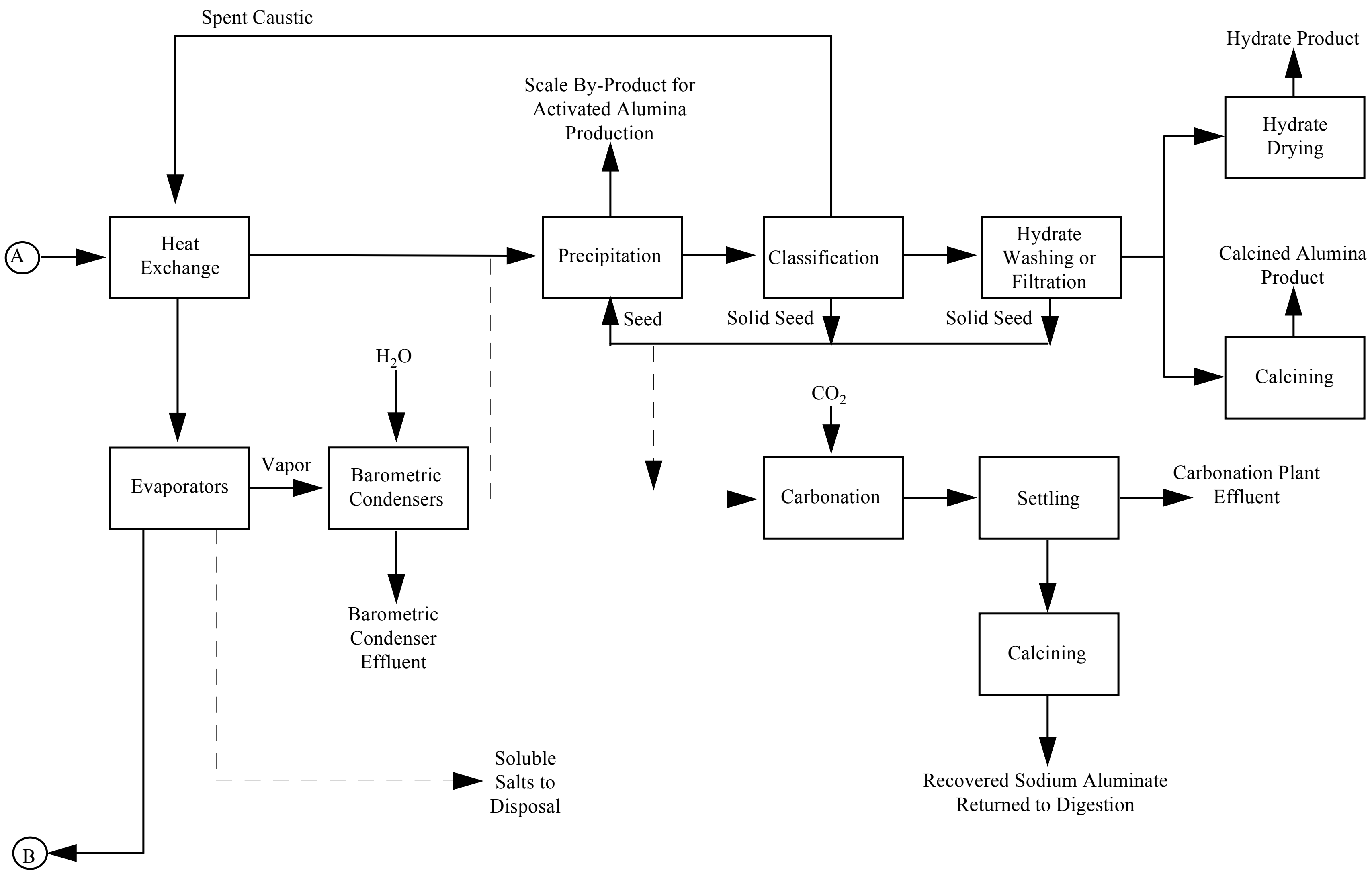
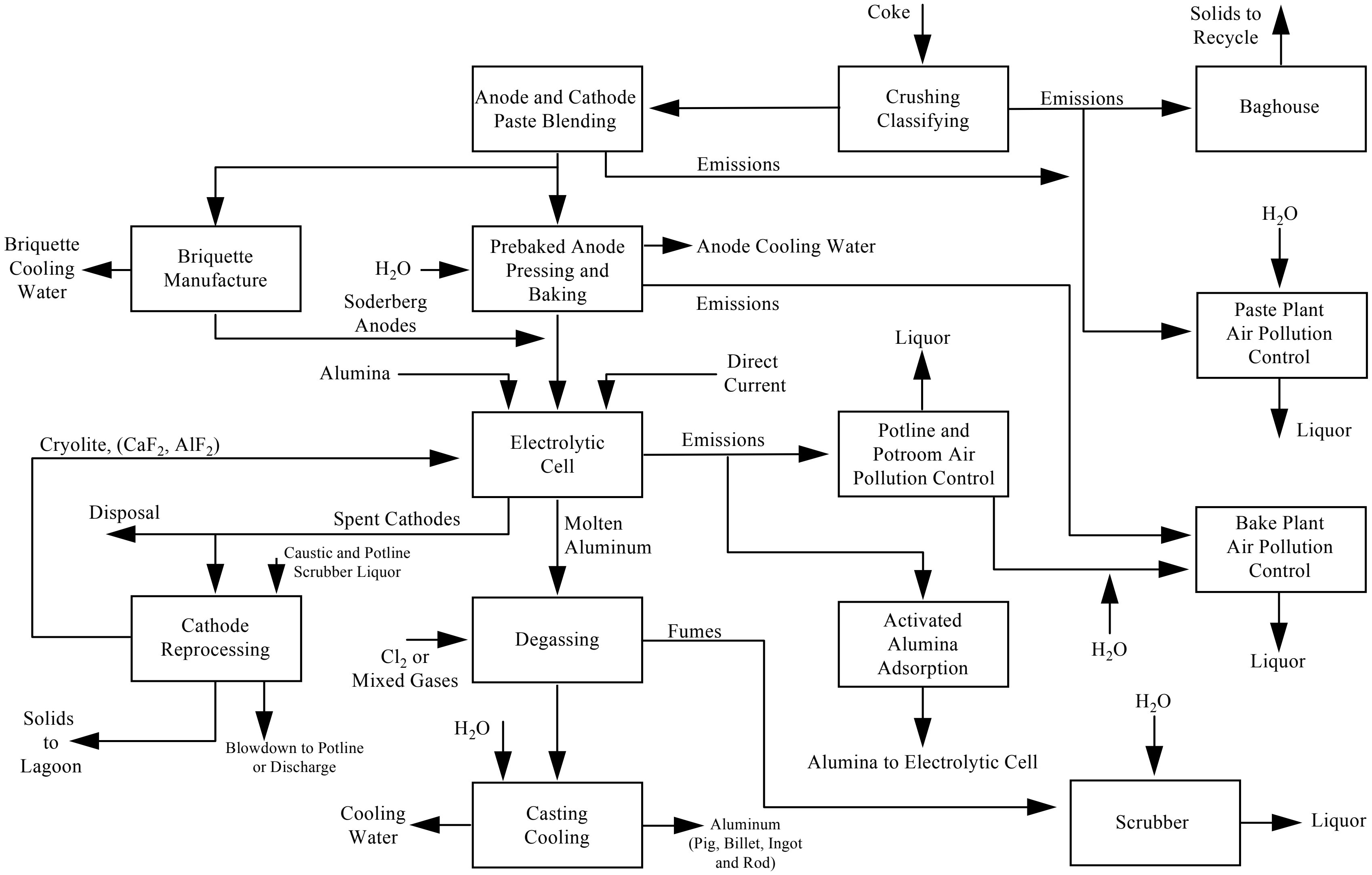


EXHIBIT 4

THE HALL-HEROULT PROCESS

(Adapted from: Development Document for Effluent Limitations Guidelines, 1989.)



Fluxing and Degassing

The molten aluminum collected in the bottom of the electrolytic pots is tapped and conveyed to holding furnaces for subsequent refining and alloying. Refining consists of fluxing to remove impurities and degassing to reduce entrapped hydrogen gas in the molten aluminum. These two operations are often performed prior to casting. Degassing is performed by injecting chlorine, nitrogen, argon, helium, and mixtures of chlorine and inert gases into the molten aluminum. Hydrogen desorbs into the chlorine bubble due to the partial pressure difference between the elements. The addition of a gas to the melt also mixes the aluminum to assure that all materials added concurrently for alloying are distributed evenly in the molten aluminum. Chlorine gas reacts with trace element impurities to form insoluble salt particles. These salt particles and the metal oxide impurities rise to the surface of the molten bath through specific gravity differences and flotation, respectively. The impurities collect at the surface of the molten metal and are skimmed and removed from the furnace.[18]

Casting

Casting is generally the final step at most aluminum reduction plants. The most common methods for casting include: pig and sow casting, direct chill casting, continuous rod casting, and shot casting.

Stationary casting is used to cast *pigs and sows* (ingots). In this method of casting, the molds are stationary and the contact cooling water (if used) generally evaporates.[19]

There are two methods of *direct chill casting*, vertical and horizontal. Vertical direct chill casting is characterized by continuous solidification of the metal while it is being poured. The length of the ingot or billet cast using this method is determined by the vertical distance it is allowed to drop rather than by mold dimensions. Molten aluminum is tapped from the smelting furnace and flows through a distributor channel into a shallow mold. Noncontact cooling water circulates within this mold, causing solidification of the aluminum. As the solidified aluminum leaves the mold, it is sprayed with contact cooling water to reduce the temperature of the forming ingot or billet. The cylinder descends into a tank of water, causing further cooling of aluminum as it is immersed. When the cylinder reaches its lowest position, pouring stops, the ingot is removed, and the process is repeated to create another ingot. Horizontal chill casting is performed in much the same manner as vertical chill casting. The main difference is that the cast aluminum is conveyed from the mold in the horizontal direction rather than vertically.[20]

In *continuous rod casting*, a ring mold is fitted into the edge of a rotating casting wheel. Molten aluminum is then poured into the mold and cools as the mold assembly rotates. After the wheel has rotated about 160 degrees, the pliable aluminum bar is released. Immediately following release from casting, the rod is transported on conveyers to a rolling mill where the diameter of the rod is reduced.[21]

In *shot casting*, aluminum shot is used as a deoxidant. Molten metal is poured into a vibrating feeder, where droplets of molten metal are formed through perforated openings. The droplets are cooled in a quench tank.[22]

---

[18] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Vol II, Office of Water Regulations Standards, May 1989.

[19] Ibid.

[20] Ibid.

[21] Ibid.

[22] Ibid.

Anode Paste Plant

Fabrication of anodes takes place in the anode paste plant where coal tar pitch and ground petroleum coke are blended together to form paste. During electrolysis, the prebaked anode is gradually consumed and becomes too short to be effective. The resulting anode "butts" are recycled for use in the paste plant. Operations in the paste plant include crushing, screening, calcining, grinding, and mixing. The paste is then formed into briquettes or into green prebaked anodes. In this stage, briquettes and green anodes are essentially the same, differing only in size. Briquettes are formed through an extrusion process in which the paste is forced through a die and then chopped into small pieces using a dicer. Green anodes, which are much larger than briquettes, are formed by pressing paste into a mold. Vibration may also be used. After forming, cooling water is used to quench the briquette or anodes to facilitate handling.

Anode Bake Plant

Anodes used in prebaked potline cells are baked prior to their use in the potline. Two basic furnace types are used to bake anodes, ring furnaces and tunnel kilns. In the ring furnace, green anodes are packed into pits with a blanket of coke or anthracite filling the space between the anode blocks and the walls of the pits. A blanket of calcined petroleum coke also fills the top of each pit above the top layer of anodes to help prevent oxidation of the carbon anodes.

Each pit is baked for a period of about 40-48 hours. The flue system of the furnace is arranged so that hot gas from the pits being baked is drawn through the next section of pits to gradually preheat the next batch of anodes before they are baked. Air for combustion is drawn through the sections previously baked, cooling them. The baked anodes are then stripped from the furnace pits.

In the tunnel kiln, a controlled atmosphere is maintained to prevent oxidation of the carbon anodes. Green anode blocks are loaded on transporter units that enter the kiln through an air lock, pass successively through a preheating zone, a baking zone, and a cooling zone, and leave the kiln through a second air lock. The refractory beds of the cars are sealed mechanically to the kiln walls to form the muffle chamber and permit movement of the units through the kiln. The muffle chamber is externally heated by combustion gases and the products of combustion are discharged through an independent stack system. Effluent gases from the baking anodes may be introduced into the fire box so as to recover the fuel value of hydrocarbons and reduce the quantity of unburned hydrocarbons. Baked anodes are delivered to air blast cleaning machines using fine coke as blasting grit. Fins, scrafs, and adherent packing are removed by this treatment, and the baked anodes are then transferred to the rod shop where the electrodes are attached.[23]

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

Several diverse research initiatives have been carried out to reduce the quantity and/or toxicity of the numerous production wastes generated in the alumina/aluminum industry. Spent potliner wastes (SPL) from aluminum reduction (Hazardous Waste Number K088) have become one of the aluminum industry's biggest environmental concerns. Reynolds Metals Company (Reynolds) developed a process for detoxifying SPL in which the SPL was blended with limestone and an antiagglomeration agent and thermally treated in a rotary kiln. The process is successful in destroying cyanides and reducing the concentration of soluble fluorides in the kiln residue. The cyanides are destroyed by oxidation and the majority of soluble fluoride salts are converted to stable, insoluble calcium fluoride by reaction with limestone. The process was developed and utilized for more than 2 years on an industrial scale at Reynolds' idled Hurricane Creek Alumina Plant in Bauxite, AR. More than 300,000 tons of SPL reportedly were treated successfully during this period.[24] In fact, Reynolds received a RCRA delisting variance for this waste stream.

---

[23] Ibid.

[24] Patricia Plunkert, 1992, Op. Cit., pp. 183-203.

On April 8, 1996, EPA finalized land disposal restrictions for K088 and established treatment standards based on the Reynolds process described above. While the Agency determined at that time that adequate treatment capacity was available, for several logistical and other reasons, the Agency decided to grant a nine-month capacity variance for K088, until January 8, 1997. Some of the logistical barriers to complying with the LDRs included pretreament requirements, such as grinding or crushing, that generators of waste would need to meet prior to sending the wastes to the treatment facility. Also, some facilities generating K088 needed time to work out such logistical issues as transportation, pretreatment capacity, and contracting for treatment capacity. Shortly following the Agency's decision to grant the extension, several aluminum producers petitioned for a full two-year capacity variance and modification of the treatment standards. The petition cited problems that had been identified with the Reynolds process. In response to the petition, the Agency extended the capacity variance for an additional six months, to July 8, 1997. A further extension was granted to October 8, 1997. No further action was taken by the Agency when that variance expired; LDRs and the the treatment standards promulgated in April 1996 therefore became effective on October 8, 1997.

An alternative treatment known as the COMTOR process was developed at Comalco's Research Center in Melbourne, Australia. The process has three stages--feed preparation, calcination, and fluoride recovery. Crushing the SPL before treatment reportedly improved the rate and quality of the detoxification process. The COMTOR process utilized a new type of calciner, known as a Torbed. Calcination reportedly was the most effective method for reducing the leachable cyanide content of the SPL. Ash treatment recovered the fluoride values for recycling directly to the electrolytic cell. Once the cyanide was destroyed and the fluorides either recovered or stabilized, the residue reportedly passed the standard leach tests and was no longer considered toxic.[25]

The Florida Institute of Phosphate Research (FIPR) reportedly has developed a dewatering process that may achieve promising results on red mud waste streams from the Bayer process operations. The FIPR process consists of adding pulp fibers with a polyacrylamide flocculant. The fibers assist in the formation of large flocs that have the physical stability to withstand normal industrial dewatering techniques.[26]

Biological methods of converting sodium oxalate, generated from the Bayer process production of alumina, have been tested. The use of micro-organisms to dispose of sodium oxalate was said to be far simpler and cheaper than the currently employed burning and landfilling methods of disposal.[27]

Manganese dioxide treatment has been found to cause a beneficial decrease in the soda content of the alumina and that a small reduction in the total organic carbon levels with this treatment also may be significant in improving the viscosity of the liquor.[28]

4. Beneficiation/Processing 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.

---

[25] Ibid.

[26] Ibid.

[27] Ibid.

[28] Ibid.

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.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between bauxite ore preparation and bauxite digestion because the bauxite ore is vigorously attacked (digested) by a strong chemical agent, thereby destroying the physical structure of the mineral, to produce sodium aluminate. 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 below the mineral processing waste streams generated downstream of the beneficiation/processing line, 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

Water softener sludge. The 1991 total waste volume generation rate for this waste stream was 2,000 metric tons per year.[29] Because this waste is not a mineral processing waste, the Agency did not evaluate it further.

2. Mineral Processing Wastes

Alumina Production

Existing data and engineering judgment suggest that the materials listed below from alumina production do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

Evaporator Salt Waste. The 1991 total waste volume generation rate for this waste stream was 2,000 metric tons per year.[30]

Bauxite Residue. The 1991 total waste volume generation rate for this waste stream was 137,000 metric tons per year.[31] Placement in impoundments behind retaining dikes built around clay-lined ground is commonly used for disposal of bauxite residue. Leaks into aquifers have motivated the installation of underdrains between the residue and a clay-sealed, plastic-lined lake bottom. Another method of disposal is called semidry disposal, dry-stacking, or the drying field method. This method takes advantage of the thixotropic nature of the residue. The

---

[29] U.S. Environmental Protection Agency, Newly Identified Mineral Processing Wastes Characterization Data Set, Vol. I, Office of Solid Waste, August 1992, pp. I-2 - I-8.

[30] Ibid.

[31] Ibid.

residue is concentrated by vacuum filtration or other means to 35-50 percent solids. Using agitation and/or additives, the viscosity of the concentrated slurry is reduced so it can be pumped to the disposal area where it flows like lava. The slurry is called nonsegregating because neither water nor sand separate from it. As viscosity increases, the flow stops. There is no free water on the surface of the impoundment, so the deposited residue dries and cracks whenever it is not raining. When the percent solids approaches 70-75 percent, bulldozers can work on the deposit.[32]

Waste Alumina. The 1991 total waste volume generation rate for this waste stream was 7,000 metric tons per year.[33]

Spent Cleaning Residue. The 1991 total waste volume generation rate for this waste stream was 3,000 metric tons per year.[34]

Pisolites. Kaiser, in Gramercy, LA reported generating 72,920 metric tons of this waste in 1988. Reportedly, this waste was either sold for construction of farm roads or sent to a pisolite storage pile which is lined with an in-situ clay barrier.[35]

Wastewater. There are four sources of wastewater from bauxite production--(1) digester condensate, (2) barometric condenser effluent, (3) carbonation plant effluent, and (4) mud impoundment effluent. Digester condensate may be recycled to product wash or boiler water. Barometric condensate is a good quality, somewhat alkaline water. Mud impoundment effluent is recycled or discharged. These wastewaters are not expected to be hazardous. Waste characterization data are presented in Attachment 1.

Red and brown muds result from the clarification step of the Bayer process and are RCRA exempt special wastes. The 1991 total waste generation rate for this waste stream was 2,800,000 metric tons per year.[36] The red and brown muds are routed to large on-site surface impoundments known as red and brown mud lakes. In these lakes, the red and brown muds settle to the bottom and the water is removed, treated, and either discharged or reused. The muds are not removed, but are accumulated and disposed in place. The muds dry to a solid with a very fine particle size. The impoundments that receive the muds typically have a surface area of between 44.6 and 105.3 hectares. The depth of the impoundments ranges from 1 to 16 meters and averages 7 meters. As of 1988, the quantity of muds accumulated on-site ranged from 500,000 to 22 million metric tons per facility, with an average of 9.7 million metric tons per facility.[37]

Red and brown muds contain significant amounts of iron, aluminum, silicon, calcium, and sodium. Red muds may also contain trace amounts of elements such as barium, boron, cadmium, chromium, cobalt, gallium, vanadium, scandium, and lead, as well as radionuclides. The types and concentrations of minerals present in the muds depend on the composition of the ore and the operating conditions in the digesters.

---

[32] "Aluminum Compounds," Op. Cit., pp. 254-261.

[33] U.S. Environmental Protection Agency, 1992, Op. Cit., pp. I-2 - I-8.

[34] U.S. Environmental Protection Agency, Op. Cit., 1992, pp. I-2 - I-8.

[35] RTI Survey, Kaiser, Gramercy, LA, 1988, ID# 100339.

[36] Ibid.

[37] U.S. Environmental Protection Agency, Op. Cit., 1990, 3-1 - 3-15.

Aluminum Production

APC dust/sludge is a possible waste stream from aluminum production operations, including electrolysis, fluxing, degassing, and anode production. Emissions may consist of unreacted chlorine and aluminum chloride gas, aluminum oxide, sulfur, fluoride, hydrocarbons, and organics.[38] 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.

Flue Dust. The 1991 waste generation rate was 39,000 metric tons per year.[39] 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.

Sweepings. The 1991 waste generation rate was 23,000 metric tons per year.[40] 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.

Electrolysis Waste. Electrolysis wastes include fluoride emissions and hydrocarbon fumes. Both sodium tetrafluoroaluminate gas and entrained liquid solidify to form fluoride particulates. Treatment consists of dry scrubbers that catch particulates and sorb HF on alumina that is subsequently fed to the cells. Nearly all the fluoride evolved is fed back into the cell.[41] Hydrocarbon fumes are generally disposed of by burning. This waste is generated at a rate of 58,000 metric tons per year (adjusted from a 1991 reported value to reflect recent changes in the sector) and may be toxic for lead.[42] This waste was formerly classified as a sludge.

Baghouse Bags and Spent Plant Filters. The 1991 waste generation rate was 19,000 metric tons per year.[43] 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.

Skims and Discarded Drosses.[44] The Aluminum Association has provided the Agency with information about skims and drosses. They stated these materials are byproducts, generated as part of the aluminum melting process. Specifically, when exposed to the atmosphere, a thin layer of aluminum oxide forms on the molten aluminum's surface (i.e., scrap aluminum being melted is coated with aluminum oxide). This oxide material is the starting point for byproducts derived from melting aluminum. The oxide layer increases during stirring, transferring, fluxing, and pouring operations, and floats to the surface of the molten aluminum. It builds up in troughs, furnaces, and crucibles during the casting process, and free aluminum becomes mixed and entrapped with the oxide. Dross is the solidified material, generally consisting of oxides of aluminum and other alloying materials, formed when molten aluminum reacts with the atmosphere or moisture. Skim are accumulations of oxide with entrapped metal, formed on the metal surface after melting from oxide films introduced as surface oxides on all charge components. Skims and drosses were formerly categorized by EPA as characteristic byproducts.

---

[38] U.S. Environmental Protection Agency, 1989. Op. Cit., Vol. II.

[39] Ibid.

[40] Ibid.

[41] "Aluminum Alloys," 1992, Op. Cit., pp. 190-212.

[42] U.S. Environmental Protection Agency, 1992, Op. Cit., pp. I-2 - I-8.

[43] Ibid.

[44] The Aluminum Association. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

In 1994, the U.S. aluminum industry generated approximately 439,000 metric tons of skims and drosses. Approximately 80,000 metric tons were reclaimed on-site, while an estimated 350,000 metric tons went off-site for reclamation. On a facility-specific basis, one company processed 76,900 metric tons of aluminum byproducts which it generated, sending other volumes off-site for further processing to companies which specialize in aluminum byproduct recovery. Recycling of aluminum skims and drosses is very common, and economically feasible with metal contents as low as eight percent. Depending on the material and processes employed, recovery rates may exceed 60 percent. For example, in 1994, one recovery facility processed 90,500 metric tons of byproducts at an average recovery rate of 60 percent. The facility then returned the recovered metal to its customers. The U.S. exports approximately 4,700 metric tons of aluminum byproducts annually, while aluminum companies import 13,600 metric tons of aluminum byproducts per year.

Anode Prep Waste. The 1991 waste generation rate was 20,000 metric tons per year.[45] 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.

Scrap Furnace Brick. The 1991 waste generation rate was 77,000 metric tons per year.[46] 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.

Cryolite Recovery Residue. The 1991 waste generation rate was 30,000 metric tons per year.[47] Historical management of this waste has included disposal in an unlined surface impoundment.[48] This waste may contain high levels of lead. Existing data and engineering judgment suggest, however, that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Cast House Dust. This waste is generated at a rate of 19,000 metric tons per year (adjusted from a 1991 reported value to reflect recent changes in the sector) and may contain toxic levels of cadmium and mercury.[49] This waste may be recycled and was formerly classified as a sludge. Attachment 1 presents waste characterization data for casthouse dust.

Spent Potliners. This waste is a listed hazardous waste (K088). The 1991 waste generation rate was 118,000 metric tons per year.[50] This waste stream may contain toxic levels of arsenic, cyanide, and selenium as well as detectable levels of cadmium, chromium, barium, lead, mercury, silver, and sulfates. This waste is generally managed through landfilling, indefinite "storage," or cathode reprocessing. Cathode reprocessing serves a hazardous waste treatment function by reducing waste volume, and incidentally recovering cryolite. Cathode reprocessing consists of grinding the spent potliners in a ball mill and then leaching with caustic to solubilize fluoride. Undigested cathode material is separated from the leachate using sedimentation and then sent to lagoons. Sodium aluminate is then added to the leachate to initiate the precipitation of cryolite and a second solid-liquid separation is performed to recover cryolite, which can be reused in the electrolytic cell. Lime is added to the supernatant to precipitate calcium fluoride and a third solid-liquid separation is performed. The resulting supernatant is then routed back to the front of the process and used for leaching. Blowdown from the system varies from plant to plant but it is

---

[45] Ibid.

[46] Ibid.

[47] Ibid.

[48] 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, pp. 3-4--3-6.

[49] U.S. Environmental Protection Agency, 1992, Op.Cit., pp. I-2 - I-8.

[50] Ibid.

universally used as potline scrubber liquor make-up when wet potline scrubbers are used. It is also common to route potline scrubber liquor through the cathode reprocessing circuit. In this way, fluoride concentrations of the scrubber liquor are controlled and recycling is possible. Spent potliners are listed wastes, KO88.

Sludge. This waste is generated at a rate of 80,000 metric tons per year (adjusted from a 1991 reported value to reflect recent changes in the sector). Management of this waste includes disposal in an unlined surface impoundment.[51] Attachment 1 presents waste characterization data for this waste stream. 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.

Treatment plant Effluent. 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 characterization data are presented in Attachment 1.

Miscellaneous 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 characterization data are presented in Attachment 1.

D. Non-uniquely Associated Hazardous Wastes

Cooling tower blowdown was generated at a rate of 8,000 metric tons per year in 1991.[52] Because this waste stream is non-uniquely associated, the Agency did not evaluate it further. 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 naptha), and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous), and other lubricants.

E. Summary of Comments Received by EPA

New Factual Information

Two commenters provided new information on the processes used in the alumina/aluminum sector (COMM65, COMM77). This new information has been incorporated into the Agency's sector report, as appropriate.

Sector-specific Issues

None.

---

[51] 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, pp. 3-4--3-6.

[52] Patricia Plunkert, 1992, Op. Cit.

BIBLIOGRAPHY

"Aluminum and Alloys." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. II. 1991. pp. 190-212

"Aluminum Compounds." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. II. 1991. pp. 254-261.

Hill, V.J. "Bauxite." From Industrial Minerals and Rocks. 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 135-147.

McCawley, Frank and Luke H. Baumgardner. "Aluminum." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 9-30.

Plunkert, Patricia. "Aluminum." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 16-17.

Plunkert, Patricia A. and Errol D. Sehnke. "Aluminum, Bauxite, and Alumina." From Minerals Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 183-203.

RTI Survey, Kaiser, Gramercy, LA, 1988, ID# 100339.

Sehnke, Errol. "Bauxite." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 26-27.

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. Vol. I. August 1992. pp. I-2 - I-8.

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. Vol. III. August 1992. pp. 1-2 - 1-45.

U.S. Environmental Protection Agency. "Alumina Production." From Report to Congress on Special Wastes from Mineral Processing. Vol. II. Office of Solid Waste. July 1990. pp. 3-1 - 3-15.

U.S. Environmental Protection Agency. Developement Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Vol. II. Office of Water Regulations Standards. May 1989.

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. pp. 3-4--3-6.

ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER - ALUMUMINA/ALUMINUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.0005	0.298	1.5	20/20	-	-	-	0/0	-	-
Arsenic	0.001	0.333	1.5	20/20	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.0001	0.033	0.4	20/20	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.001	0.057	0.2	20/20	-	-	-	0/0	1.0	0
Chromium	0.004	0.074	0.6	20/20	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.01	0.285	1.6	20/20	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.008	0.491	5	20/20	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0001	0.001	0.0062	19/19	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.004	0.682	4	20/20	-	-	-	0/0	-	-
Selenium	0.0005	2.488	44	20/20	-	-	-	0/0	1.0	0
Silver	0.0005	0.075	0.36	20/20	-	-	-	0/0	5.0	0
Thallium	0.0005	0.191	0.69	20/20	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.01	0.168	1	20/20	-	-	-	0/0	-	-
Cyanide	0.002	39.44	180	22/22	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - CASTHOUSE DUST - ALUMINA/ALUMINUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM					
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	TC Level	# Values In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	7.5	7.5	7.5	1/1	0.42	0.42	0.42	1/1	-	-
Arsenic	32	32	32	1/1	0.001	0.001	0.001	0/1	5.0	0
Barium	10	10	10	1/1	0.28	0.28	0.28	1/1	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	7.2	7.2	7.2	1/1	3.5	3.5	3.5	1/1	1.0	1
Chromium	110	110	110	1/1	0.086	0.086	0.086	1/1	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	510	510	510	1/1	0.25	0.25	0.25	1/1	-	-
Iron	93000	93000	93000	1/1	0.47	0.47	0.47	1/1	-	-
Lead	17	17	17	1/1	0.024	0.024	0.024	1/1	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	1100	1100	1100	1/1	19	19	19	1/1	-	-
Mercury	0.0001	0.0001	0.0001	0/1	0.84	0.84	0.84	1/1	0.2	1
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	260	260	260	1/1	0.74	0.74	0.74	1/1	-	-
Selenium	0.92	0.92	0.92	1/1	0.001	0.001	0.001	0/0	1.0	0
Silver	1.9	1.9	1.9	1/1	0.15	0.15	0.15	1/1	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	120	120	120	1/1	0.58	0.58	0.58	1/1	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	18	18	18	1/1	-	-
Fluoride	-	-	-	0/0	61	61	61	1/1	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	27000	27000	27000	1/1	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - TREATMENT PLANT EFFLUENT - ALUMINA/ALUMINUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.0005	0.3438	1.1	15/15	-	-	-	0/0	-	-
Arsenic	0.002	0.3326	1.9	15/15	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.001	0.0191	0.06	15/15	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.002	0.0690	0.2	15/15	-	-	-	0/0	1.0	0
Chromium	0.004	0.0434	0.24	15/15	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.006	0.0975	0.744	15/15	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.02	0.2222	0.6	15/15	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0001	0.0019	0.0213	14/14	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.005	0.1985	0.56	15/15	-	-	-	0/0	-	-
Selenium	0.001	0.3743	3	15/15	-	-	-	0/0	1.0	0
Silver	0.002	0.1416	0.7	15/15	-	-	-	0/0	5.0	0
Thallium	0.001	0.2288	0.69	15/15	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.056	0.2561	2	15/15	-	-	-	0/0	-	-
Cyanide	0.004	37.0253	200	17/17	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - MISCELLANEOUS WASTEWATERS - ALUMINA/ALUMINUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.0005	0.377	2	11/11	-	-	-	0/0	-	-
Arsenic	0.01	0.512	2.3	11/11	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.0005	0.019	0.08	11/11	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.001	0.037	0.1	11/11	-	-	-	0/0	1.0	0
Chromium	0.004	0.029	0.2	11/11	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.008	0.299	1.3	11/11	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.01	0.438	3	11/11	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0001	0.001	0.003	11/11	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.005	0.326	1	11/11	-	-	-	0/0	-	-
Selenium	0.001	3.964	40	11/11	-	-	-	0/0	1.0	0
Silver	0.002	0.129	0.5	11/11	-	-	-	0/0	5.0	0
Thallium	0.0005	0.189	0.73	11/11	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.02	0.108	0.6	11/11	-	-	-	0/0	-	-
Cyanide	0.004	95.24	180	11/11	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SLUDGE - ALUMINA/ALUMINUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM					
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	TC Level	# Values In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.64	1.68	3	3/5	0.032	0.032	0.032	1/1	-	-
Arsenic	0.72	7.18	16	5/5	0.001	0.014	0.026	1/2	5.0	0
Barium	4	31.2	78	5/5	0.01	0.024	0.037	2/2	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.0465	1.04	2	3/5	0.001	0.013	0.025	1/2	1.0	0
Chromium	1.3	13.7	33	5/5	0.002	0.005	0.008	2/2	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.38	95.40	380	5/5	0.001	0.011	0.021	2/2	-	-
Iron	730	2386	5300	5/5	0.27	0.300	0.33	2/2	-	-
Lead	5	30.98	63	5/5	0.001	0.002	0.003	1/2	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	0.41	24.96	60	5/5	0.12	0.235	0.35	2/2	-	-
Mercury	0.0001	0.06	0.32	3/5	0.0001	0.0002	0.0002	1/2	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	15	224	520	5/5	0.045	0.045	0.045	1/1	-	-
Selenium	0.05	0.32	0.78	4/5	0.001	0.004	0.006	1/2	1.0	0
Silver	0.04	1.02	2	3/5	0.001	0.002	0.002	1/2	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	1.4	82.48	320	5/5	0.011	0.056	0.1	2/2	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	2	436	870	2/2	-	-
Fluoride	-	-	-	0/0	0.48	48.74	97	2/2	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	2.2	12.60	23	2/2	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-
	-	-	-	0						

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

ANTIMONY

A. Commodity Summary

According to the U.S. Bureau of Mines, antimony metal and oxide are produced by seven companies domestically. Additionally, a small amount of antimony is recovered domestically as a byproduct of smelting lead and silver-copper ores. Exhibit 1 presents the names, locations, and type of processes used by the facilities involved in the primary production of antimony metals and oxides. Estimated apparent domestic consumption was 45,000 metric tons during 1994. Antimony is used mainly in flame retardants, transportation (including batteries), chemicals, ceramics, and glass.[1]

Antimony is generally found in association with other elements in complex ores as the sulfide mineral stibnite. Antimony is made available commercially as antimony trioxide. Most of the antimony trioxide produced is derived from imported original sources.

EXHIBIT 1

SUMMARY OF ANTIMONY FACILITIES

Facility Name	Location	Type of Operations
Amspec Chemical Corp	Gloucester, NJ	Pyrometallurgical
Ant. Process (inactive)	Moscow, TN	Pyrometallurgical
Anzon, Inc.	Laredo, TX	Pyrometallurgical
ASARCO Incorporated	Omaha, NE	Pyrometallurgical
ASARCO (inactive)	El Paso, TX	Electrowinning
Chemet (inactive)	Moscow, TN	Pyrometallurgical
Laurel Ind.	LaPorte, TX	Pyrometallurgical
M&T Chemical (inactive)	Baltimore, MD	Pyrometallurgical
McGean Chemical	Cleveland OH	Pyrometallurgical
Sunshine Mining Company	Kellogg, ID	Electrowinning
US Antimony Corp.	Thompson Falls, MT	Pyrometallurgical

---

[1] Antimony Specialist, "Antimony," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, p. 18.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Primary antimony production usually arises as a byproduct or coproduct of mining, smelting, and refining other antimony-containing ores such as tetrahedrite (a complex silver-copper-antimony-sulfide ore) or lead ore.[2]

2. Generalized Process Flow Diagram

Antimony can be produced using either pyrometallurgical processes or a hydrometallurgical process. As shown in Exhibits 2 through 7, for the pyrometallurgical processes, the method of recovery depends on the antimony content of the sulfide ore. For example, the lowest grades of sulfide ores, containing 5-25% antimony, are volatilized as oxides; ores containing 25-40% antimony are smelted in a blast furnace; and 40-60% antimony ores are either liquated or treated by iron precipitation. As shown in Exhibit 6, the rich oxide ores that result from either volatilization, smelting, or liquation can be reduced directly in a reverberatory furnace. Exhibit 7 outlines the process used to refine the antimony metal resulting from pyrometallurgical process.

Alternatively, antimony can be recovered hydrometallurgically by leaching and electrowinning as shown in Exhibit 8.[3] Currently, the Sunshine Mining Company in Kellogg, Idaho is the only domestic mine that employs the hydrometallurgical process.

Pyrometallurgical Recovery

Oxide Volatilization. As indicated in Exhibit 2, low grade ore is recovered through oxide volatilization. The ore is roasted with coke or charcoal in a rotary kiln or shaft furnace. As a result of the roasting step, sulfur is burned away and removed in the waste gases and antimony trioxide, which condenses, can be recovered in flues, condensing pipes, or a Cotrell precipitator. The resultant oxide is briquetted and reduced to metal.[4] The largest producer of antimony metal from roasting is Anzon in Laredo, Texas.

Blast Furnace Smelting. As shown in Exhibit 3, the blast furnace smelting process used to recover antimony from intermediate (25-40%) grades of oxide and sulfide ores, flue dust, liquation residues, mattes, briquetted fines, and rich slags is similar to the blast furnace method used to process lead. A low pressure, high smelting column, water-jacketed blast furnace is used. The slag is separated from the antimony metal and sent to waste or reprocessing.[5]

Sulfur Liquation. As indicated in Exhibit 4, liquation is used to recover antimony from high grade ores. The ores can be heated either in batch mode in a perforated pot, or in continuous mode using a reverberatory furnace. This process separates the antimony sulfide from the gangue. The liquated product is known as crude or needle antimony, which can either be distributed as antimony sulfide or converted to recover antimony metal. Either iron precipitation or oxide reduction can be used to recover metallic antimony from the sulfide.[6]

---

[2] Thomas O. Llewelyn, "Antimony," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, p. 225.

[3] "Antimony," Kirk-Othmer Encyclopedia of Chemical Technology, 1992, 4th ed., Vol. III, p. 370.

[4] Ibid.

[5] Ibid., p. 371.

[6] Ibid.

EXHIBIT 2

ANTIMONY OXIDE VOLATILIZATION PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, pp. 3-31 - 3-45)

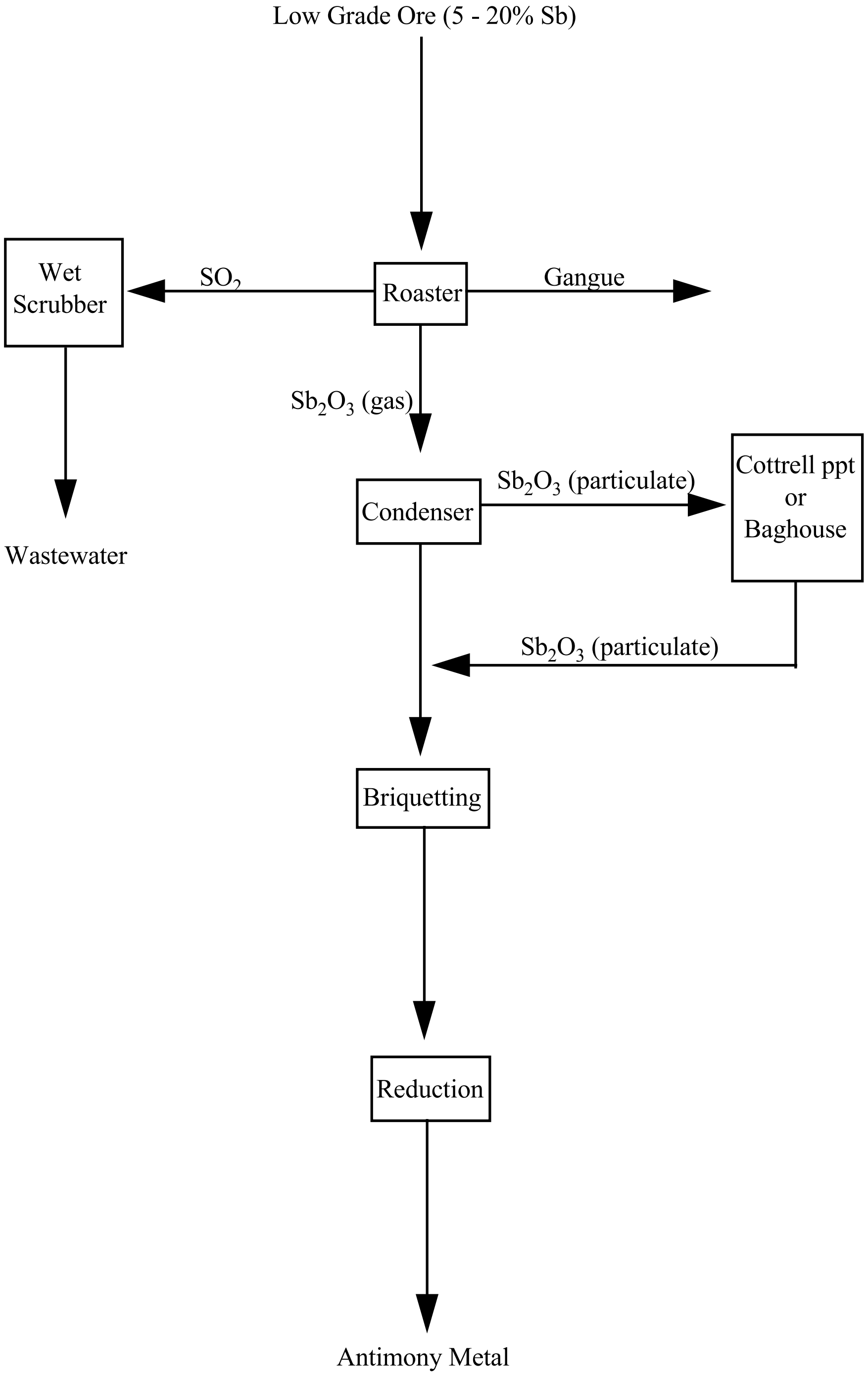


EXHIBIT 3

ANTIMONY SMELTING

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, pp. 3-31 - 3-45.)

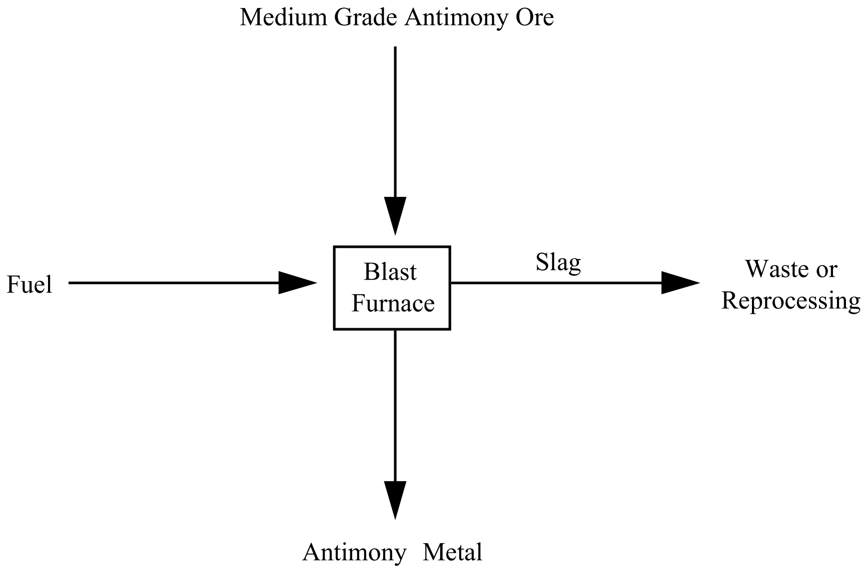


EXHIBIT 4

ANTIMONY LIQUATION PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, pp. 3-31 - 3-45.)

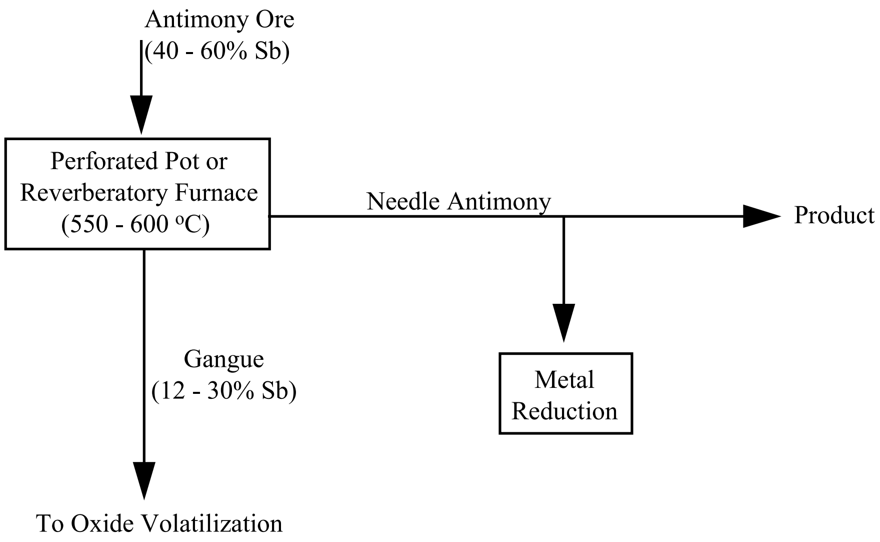


EXHIBIT 5

ANTIMONY IRON PRECIPITATION REDUCTION PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, pp. 3-31 - 3-45.)

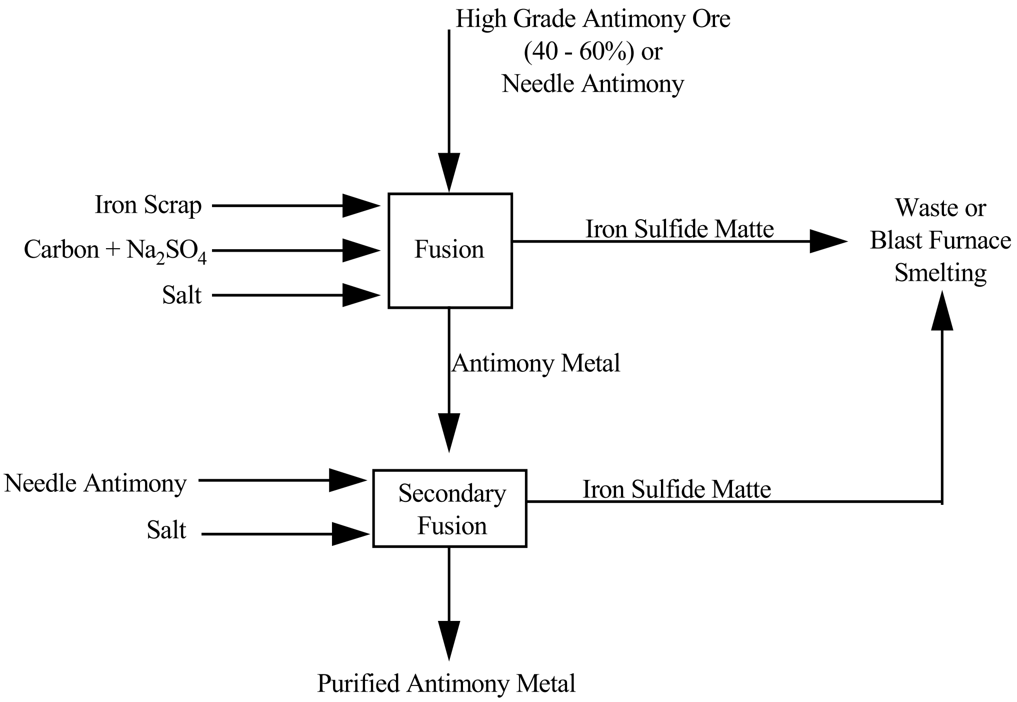
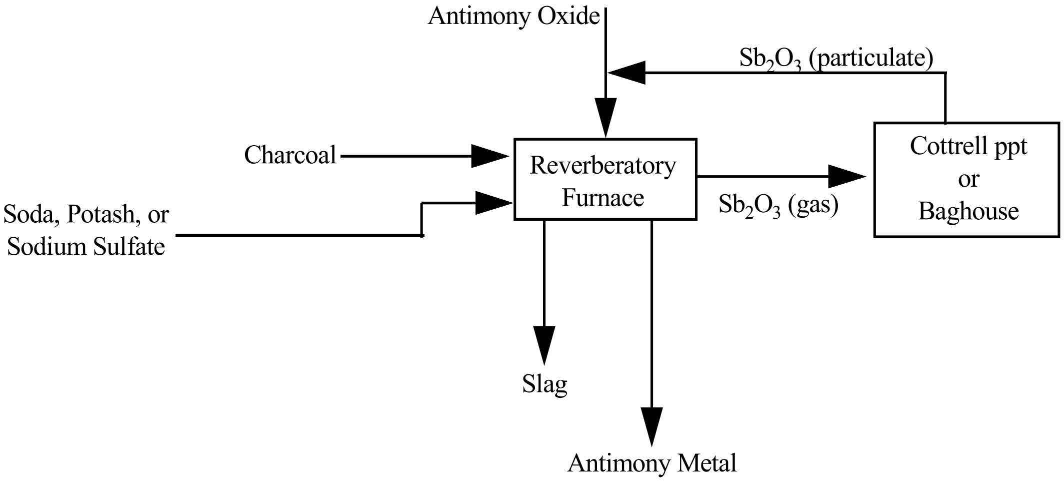


EXHIBIT 6

ANTIMONY OXIDE REDUCTION PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, pp. 3-31 - 3-45.)



Iron Precipitation. Iron precipitation is used to convert crude antimony sulfide to metallic antimony. As Exhibit 5 illustrates, the molten antimony sulfide is heated in combination with iron scrap, carbon, and Na_2SO_4. The process uses iron as the reductant to replace antimony in the molten antimony sulfide. Sodium sulfate and carbon are added to produce sodium sulfide. Alternatively, salt is added to form a fusible light matte with iron sulfide and facilitate the separation of the metal. Because the resultant metal contains high concentrations of iron and sulfur, a second fusion with liquate antimony and salt is used to produce a purified antimony metal.[7]

Oxide Reduction. Antimony trioxide or other antimony oxides are reduced with charcoal in reverberatory furnaces as shown in Exhibit 6. The addition of an alkaline flux of soda, potash, and sodium sulfate dissolves residual sulfides and gangue and also minimizes volatilization. During this process, the loss of antimony due to volatilization necessitates the use of Cotrell precipitators or baghouses to recover the antimony trioxide for reprocessing. During this process, a slag is produced and separated from the antimony metal.[8]

Refining. Metal resulting from pyrometallurgical reduction requires refining to remove arsenic, sulfur, iron, and copper impurities. Exhibit 7 presents a typical flow process diagram for the refining process. The iron and copper concentrations can be reduced by adding stibnite or a mixture of sodium sulfate and charcoal to form an iron-bearing matte. The matte is skimmed from the surface of the molten metal, after which the metal is treated with an oxidizing flux of caustic soda or sodium carbonate and niter (sodium nitrate) to remove arsenic and sulfur. Although lead is not readily removed from antimony, material containing lead may be used for lead based alloy applications.[9]

Hydrometallurgical Recovery

Antimony can also be recovered using the hydrometallurgical process outlined in Exhibit 8, which involves leaching followed by electrowinning and autoclaving. The hydrometallurgical process is based on the knowledge that: (1) an alkaline sodium sulfide solution acts as an effective solvent for most antimony compounds and (2) most other metals are insoluble in such a solution (excluding arsenic, tin, and mercury).[1010] The Sunshine Mining Company is the only domestic antimony facility that uses this hydrometallurgical technique. The Sunshine facilities are a complete mine-to market operation. In addition to their antimony plant, their operations include a mill, a silver-copper refinery, and a functional mint. Their antimony facility produces both antimony metal and sodium antimonate. The process at this facility involves: (1) leaching and filtration, (2) electrowinning, and (3) autoclaving and tails treatment.

Leaching and Filtration. The ore concentrates from the mill are leached in a batch process in a heated, pressurized vat. Some of the concentrates are blended, prior to leaching, with coke, sodium sulfate, and sodium carbonate and then melted in a furnace. The resultant material is then leached with a sodium hydroxide solution. Other concentrates are combined with sodium sulfide and sulfur and leached with a sodium hydroxide solution without prior melting. This leach solution is created by combining the barren catholyte (depleted electrolyte from downstream electrowinning), elemental sulfur, sodium sulfide, and sodium hydroxide. The solution matrix then solubolizes the antimony and any arsenic present that is not in the form of arsenopyrite, producing soluble thio compounds including $NaSbS_2$, Na_3SbS_3, Na_3SbS_4, and Na_3AsS_3. The solids can then be separated from the leaching

---

[7] Ibid.

[8] Ibid.

[9] Ibid., pp. 372-373.

[10] Corby G. Anderson, Suzzann M. Nordwick, and L. Ernest Kyrs, "Processing of Antimony at the Sunshine Mine," from Residues and Effluents - Processing and Environmental Considerations, The Minerals, Metals, & Materials Society, 1991, p. 349-366.

EXHIBIT 7

ANTIMONY REFINING

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, pp. 3-31 - 3-45.)

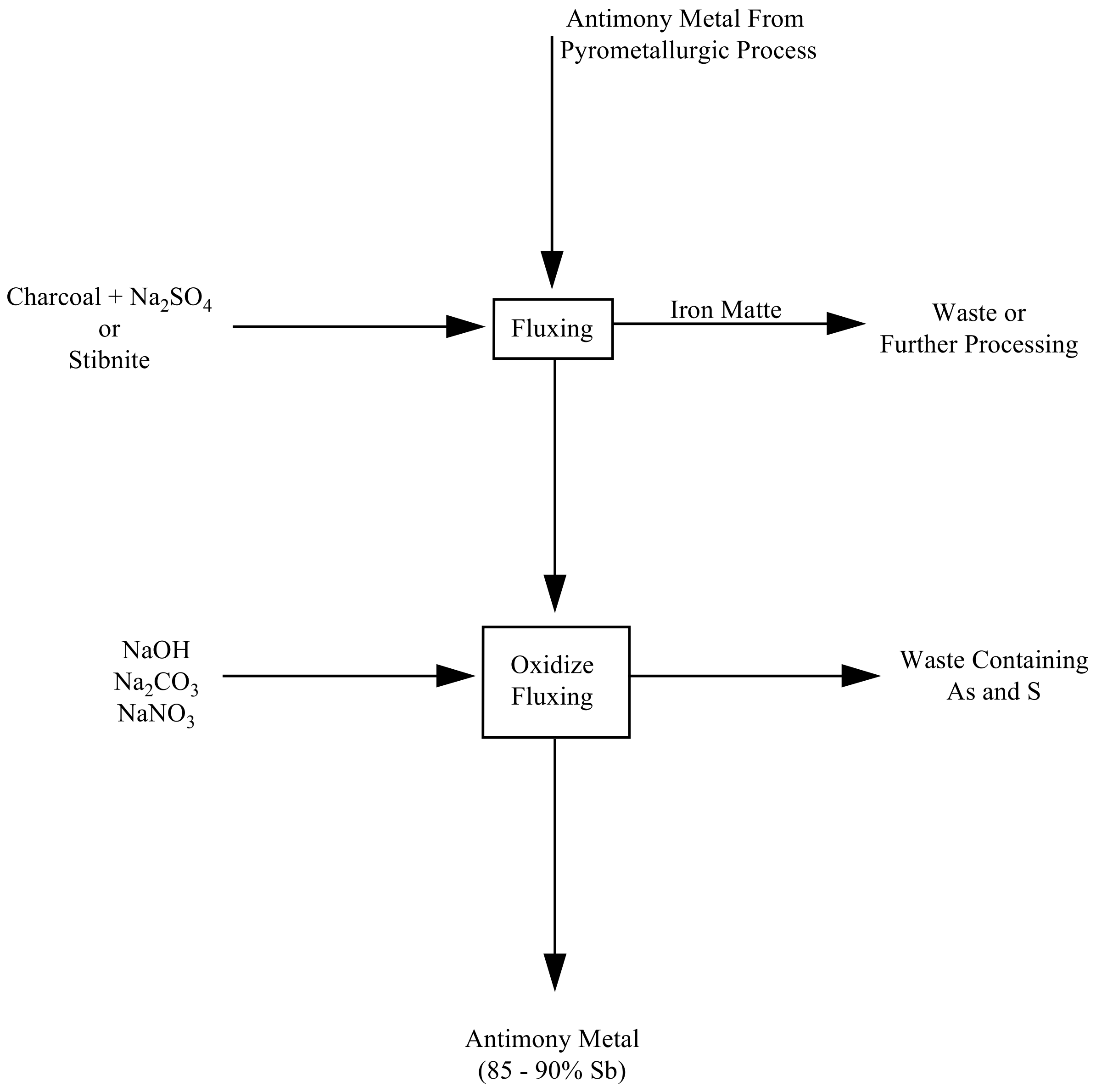
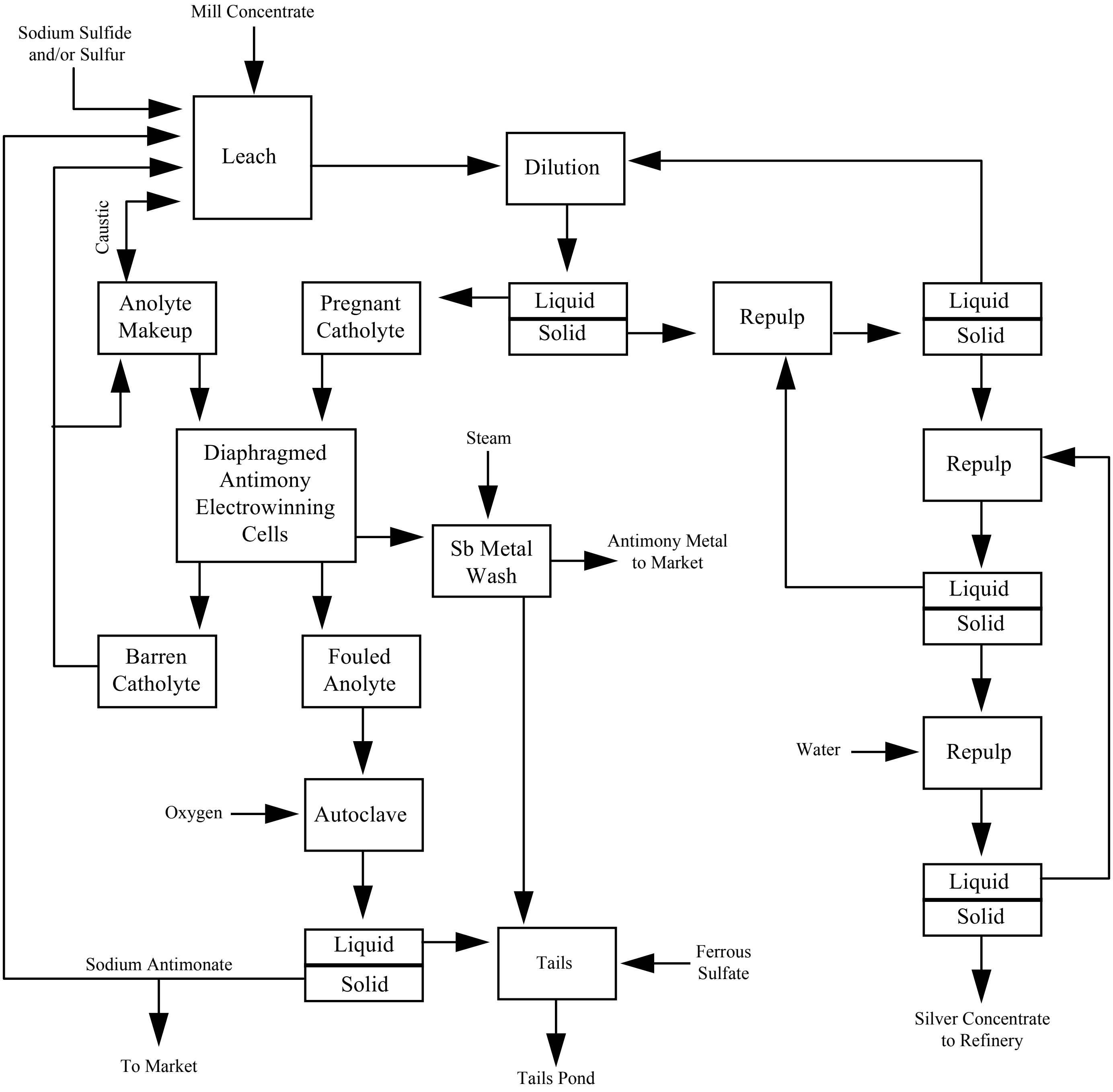


EXHIBIT 8

HYDROMETALLURGICAL ANTIMONY PRODUCTION PROCESS

(Adapted from: Residues and Effluents - Processing and Environmental Considerations, 1991, pp. 349 - 366.)



solution by thickening and filtration. The leached residue is either disposed of or processed further to recover other metals.[11]

As shown in Exhibit 7, when the leaching is complete, the resultant slurry is diluted to enhance solid separation from the alkaline solution. Dilution involves the use of water recovered from downstream repulping. After dilution the slurry consists of an antimony bearing pregnant catholyte solution and a high grade silver-copper residue. The solid-liquid separation takes place by conventional settling and thickening. Both primary and secondary thickeners are used with a repulp stage occurring in between. Including this first repulping step, there three total repulping steps involved in the Sunshine Mine recovery process. Residue from the secondary thickener is repulped a second time and then recovered with a disc filter. The mixture is then sent through a third and final repulping stage during which fresh water enters the process. The final filtration step involves a drum filter. The wash water flows from the drum filter back through to the second repulping stage. From the second repulping step, the wash water flows through the disc filter and back to the first repulp step and from there the water is sent back to the leach stage for use in the dilution step. The three repulping steps allow for maximum recovery of the leached antimony and provide a copper-silver residue that is free from alkaline sulfur compounds that might interfere with acid pressure leaches downstream when the resultant solid filter cake is sent to the Sunshine silver refinery.[12]

Electrowinning. As shown in Exhibit 8, the pregnant solution from the leaching process is used as feed for the electrowinning circuit. Antimony metal is deposited on the cathode as a brittle, non-adherent layer which is periodically stripped and washed. The resultant product is either sold or sent for further processed to antimony trioxide.

Because the products of oxidation at the anode interfere with the deposition of antimony at the cathode, two different and physically separated solutions are used. The catholyte, in this case the pregnant solution from the leaching process, surrounds the cathode and the anolyte, a combination of barren catholyte and sodium hydroxide solution, surrounds the anode. Mixing of the two solutions is minimized by the use of a canvas barrier or diaphragm. The canvas barrier has small pores that allow the solutions to come into contact, maintaining the integrity of the electrical circuit.

The recovered metal is washed by blowing steam into a tank containing hot water and the metallic antimony. This step removes any solutions or soluble solids that have adhered to the metal during the plating process. This wash water is sent to tails treatment and can be autoclaved to recover sodium antimonate. After drying, the antimony metal product is packaged and sold to secondary smelters for use as a lead hardener or for antimony oxide production.[13]

After the antimony has been removed, the barren catholyte can be recycled to the process through one of two methods. In the process where the ore is melted prior to leaching, the spent electrolyte is spray dried and the dried salts are captured in a baghouse for reuse during the blending step. In the other process where the concentrates are leached without melting them first, the barren catholyte solution is recycled directly into the leaching process. Site-specific information indicates that the fouled anolyte is removed and treated by autoclaving to recover sodium antimonate, which is then recycled to the leaching process. The resultant antimony metal can be converted to antimony trioxide in a fuming furnace.[14]

---

[11] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Vol. IV, Office of Water Regulations Standards, 1989, p. 2062.

[12] Corby G. Anderson, 1991, Op. Cit., p. 355.

[13] Corby G. Anderson, 1991, Op. Cit., p. 360.

[14] U.S. Environmental Protection Agency, 1989. Op. Cit., p. 2063.

Autoclaving. Sodium antimonate ($NaSbO_3$) is produced by autoclaving the antimony-bearing fouled anolyte solution from the electrowinning process. Residual caustic sodas are also present in the fouled anolyte and can be recovered. Oxygen autoclaving, heating the solution under pressure in the presence of oxygen, is used to produce the sodium antimonate. The elevated temperature and pressure drive the oxidation reaction and result in the formation of insoluble sodium antimonate which is separated from the remaining liquid by sedimentation and decanting. The resultant sodium antimonate either recycled back to the leaching step or sold depending on market conditions.[15]

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

None Identified.

4. Beneficiation/Processing Boundary

Since antimony is generally recovered as a co-product or a by-product of other metals, all of the wastes generated during antimony recovery are mineral processing wastes. 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 antimony is recovered as a co-product or a by-product of other metals, mining wastes are addressed in the descriptions of the initial ore/mineral. For a further description of these wastes see the report for lead presented elsewhere in this background document.

2. Mineral Processing Wastes

The following wastes have been identified as generated during the oxide volatilization process.

Gangue. Gangue generated from roasting during the oxide volatilization process may contain traces of antimony and other heavy metals. Gangue generated from either smelting or other higher grade recovery processes may be sent to oxide volatilization for further antimony recovery, since that process is designed for lower grade ores. 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. The wastewater generated from the wet scrubber process following oxide volatilization may contain sulfur and some heavy metals. 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.

The following wastes have been identified as generated during the smelting and refining portions of the antimony recovery process. 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 waste generation rates.

APC Dust/Sludge. 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.

Sludge from Treating Process Waste Water. 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.

---

[15] Corby G. Anderson, 1991, Op. Cit., p. 361.

Refining Dross. 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.

Slag and Furnace Residue. The slag generated during the oxide reduction process may contain residual soda, potash, or sodium sulfate. The waste generation rate for this waste stream is reported to be 32,000 mt/yr. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead.

Waste Solids. Wastes produced from fluxing during the refining process contain arsenic (As) and sulfur (S). 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.

Hydrometallurgical Recovery

Leach Residue. The leach residue contains antimony, sulfur, sodium, pyrite, silica, and stibnite.[16] In the antimony plant in Kellogg, Idaho, a hot alkaline sulfide solution is used to dissolve antimony and most arsenic species from the ore concentrate, leaving a leach residue containing less than one percent antimony.[17] 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.

Gangue (Filter Cake). At the Kellogg plant, slurry from the leach tanks is diluted and then thickened and filtered in a series of repulp-filtration steps. The resulting filter cake, containing 18-20 percent moisture, becomes feed material at the silver refinery. Filtered leach solution containing antimony (primarily as sodium thioantimonate) is fed to the antimony electrowinning circuit.[18] 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.

Stripped Anolyte Solids. Electrowinning "tails" consist of fouled anolyte and cathode wash water. The fouled anolyte is heated and pressurized with oxygen in a 1,500 gallon autoclave to recover sodium antimonate before being sent to the tailings pond.[19] The waste generation rate for this waste stream is reported to be 190 metric tons/yr. This waste stream is fully recycled and is classified as a by-product. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for arsenic.

Spent Barren Solution. Barren catholyte solution is recycled back to the leach step and to the anolyte make up water added prior to the electrowinning step. 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.

Autoclave Filtrate. The liquid phase from the autoclave, which contains sodium arsenate and residual antimony is treated with solid ferrous sulfate to precipitate arsenic as $Fe_3(AsO_4)$ and antimony as Sb_2S_3 at a pH of 8 to 8.5. Quicklime is then added to precipitate residual iron in the solution. The resulting anolyte slurry is then commingled with mill tailings and pumped to an unlined on-site surface impoundment. Natural sedimentation removes solids under the liquid outflow which is discharged under an NPDES permit.[20] The low, medium, and high annual waste generation rates were estimated as 380 metric tons/yr, 32,000 metric tons/yr, and 64,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste stream may be partially recycled and

---

[16] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 2062.

[17] Gary Light, ICF, Incorporated, "Report on July 1993 Mineral Processing and Incinerator Site Visits," Draft memorandum to Bengie Carroll, August 10, 1993, p. 2-1.

[18] Ibid., p. 2-2.

[19] Ibid.

[20] Ibid.

may exhibit the characteristics of toxicity (arsenic, cadmium, lead, and mercury) and corrosivity. This waste stream is classified as a spent material. Waste characterization sampling data for this waste stream is included as Attachment 1.

D. Non-uniquely Associated Wastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

BIBLIOGRAPHY

Anderson, Corby G., Nordwick, Suzzann M., and Kyrs, L. Ernest. "Processing of Antimony at the Sunshine Mine." From Residues and Effluents - Processing and Environmental Considerations. The Minerals, Metals, & Materials Society. 1991. p. 349-366.

"Antimony." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. III. 1992. pp. 367-382.

Antimony Specialist. "Antimony." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 18-19.

Llewellyn, Thomas O. "Antimony." From Minerals Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 223-226.

Light, Gary. ICF Incorporated. "Report on July 1993 Mineral Processing and Incinerator Site Visits." August 10, 1993.Draft memorandum to Bengie Carroll.

U.S. Environmental Protection Agency. Development Document for Effluent Limitation Guidelines and Standards for Nonferrous Metals Manufacturing Point Source Category. Vol V. Office of Water Regulations Standards. May 1989. p. 2079

U.S. Environmental Protection Agency. "Antimony." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. Office of Solid Waste. p. 3-31 - 3-45.

ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - AUTOCLAVE FILTRATE - ANTIMONY

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM					
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	TC Level	# Values In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	3.7	40.59	120	8/8	-	-	-	0/0	-	-
Arsenic	260	1977.75	3700	8/8	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	-	-	-	0/0	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.002	0.069	0.3	8/8	-	-	-	0/0	1.0	0
Chromium	-	-	-	0/0	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.2	0.391	0.8	8/8	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.01	0.458	3.05	8/8	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.015	5.30	12.6	7/7	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	-	-	-	0/0	-	-	-	0/0	-	-
Selenium	-	-	-	0/0	-	-	-	0/0	1.0	0
Silver	-	-	-	0/0	-	-	-	0/0	5.0	0
Thallium	-	-	-	0/0	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.01	0.110	0.27	8/8	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

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 to concentrations of 90-95%. This crude trioxide is either pyrometallurgically

---

[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.

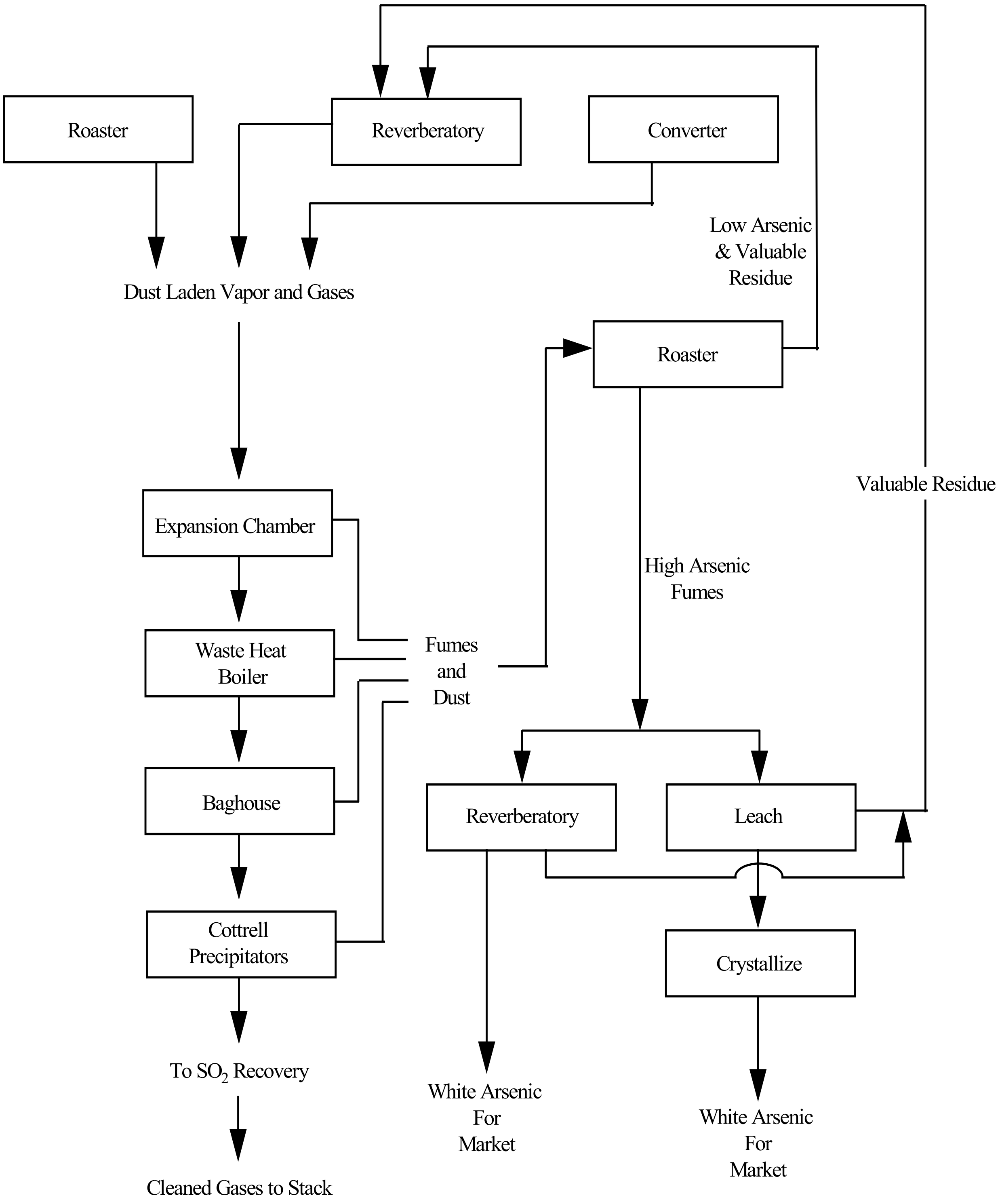
[5] "Arsenic and Arsenic Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. III, 1992, pp. 626-628.

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

EXHIBIT 1

ARSENIC TRIOXIDE PRODUCTION PROCESS

(Adapted from: "Arsenic and Arsenic Alloys," 1992, Op. Cit., p. 627.)



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) Processes

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.

D. Non-uniquely Associated Wastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

---

[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.

BERYLLIUM

A. Commodity Summary

Beryllium (Be) is used as an alloy, oxide, or metal in electronic components, electrical components, aerospace applications, defense applications, and other applications.[1] Beryllium is processed into three forms -- beryllium alloys (principally beryllium-copper); beryllium oxide or beryllia ceramic; and metallic beryllium.[2] Beryllium-copper alloys account for about 75 percent of the United States annual consumption of beryllium on a metal equivalent basis. These alloys, most of which contain about two percent beryllium, are used because of their high electrical and thermal conductivity, high strength and hardness, good fatigue and corrosion resistance, and non-magnetic properties.[3] Beryllia ceramic is specified for its electrical insulating properties and its unusual ability to conduct heat. Metallic beryllium offers light weight, strength, stiffness, specialized nuclear properties, and the ability to dissipate heat rapidly.[4]

Beryllium is a recognized constituent in some 40 minerals. However, only two minerals -- beryl, an aluminosilicate ($3BeO \bullet Al_2O_3 \bullet 6SiO_2$) containing 5 to 13 percent beryllium oxide (BeO), and bertrandite ($Be_4Si_2O_7(OH)_2$), which occurs as tiny silicate granules containing less than one percent BeO -- are commercially available as beryllium ores.[5] A BeO content of 10 percent is considered necessary for the economic extraction of beryllium from beryl and bertrandite ores. Bertrandite ores are considered a commercially viable source of beryllium because of the large reserves present, the ability to mine it in an open pit, and the fact that beryllium may be extracted by leaching with sulfuric acid. In fact, the majority of beryllium produced is now obtained from bertrandite.[6]

The major deposits of beryllium in the United States are bertrandite deposits in the Spor Mountains of Utah. Brush Wellman, Inc. bought the mineral rights to these deposits and began mining in the 1960's.[7] Its plant near Delta, Utah, is the only commercial beryllium extraction and production plant operating in the Western world.[8] The Delta plant uses both beryl and bertrandite ores as inputs for the production of beryllium hydroxide. Although bertrandite ore is mined on-site using open-pit methods, the beryl ore is imported primarily from Brazil. However, beryl deposits also occur in China, Argentina, India, Russia, and some African countries. Beryl is usually obtained as a by-product from mining zoned pegmatite deposits to recover feldspar, spodumene, or mica.[9] Two other facilities process the beryllium hydroxide to produce beryllium metal, alloy or oxide. Exhibit 1 presents the name,

---

[1] Deborah A. Kramer, "Beryllium," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 28.

[2] Brush Wellman, Inc. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

[3] U.S. Bureau of Mines, "Beryllium in 1992," Mineral Industry Surveys, April 1993, p. 3.

[4] Brush Wellman, Inc. Op. Cit.

[5] Brush Wellman, Comments of Brush Wellman Inc. on EPA's Proposed Reinterpretation of the Mining Waste Exclusion, December 30, 1985, p. 1.

[6] "Beryllium and Beryllium Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, p. 126.

[7] "From Mining to Recycling," Metal Bulletin Monthly — MBM Copper Supplement, 270, 1993, p. 27.

[8] Deborah A. Kramer, January 1995, Op. Cit., p. 28.

[9] "Beryllium and Beryllium Alloys," 1992, Op. Cit., p. 126.

location, the type of processing, input material and product for each of the beryllium processing facilities. Exhibit 2 presents general site information on the Delta, UT facility.

EXHIBIT 1

SUMMARY OF PRIMARY AND SECONDARY BERYLLIUM ORE PROCESSORS[a]

Facility Name	Location	Type of Process	Input Material	Products
Brush Wellman	Delta, UT	Primary	Ores	$Be(OH)_2$
Brush Wellman	Elmore, OH	Secondary	$Be(OH)_2$	Be Metal and Alloys
NGK Metals	Revere, PA	Secondary	$Be(OH)_2$	Be Metal

[a] - Personal Communication between ICF Incorporated and Deborah Kramer, U.S. Bureau of Mines, October 1994.

EXHIBIT 2

SITE INFORMATION

Facility Name	**Facility Location**	**Potential Factors Related to Sensitive Environment**
Brush Wellman, Inc.	Delta, Utah	• Brush Wellman mill located 10 miles north of Delta, Utah; mine located 50 miles west of the mill. • Nearest resident lives 5 miles from Brush Wellman facility • Brush Wellman facility is not located in: a 100-year floodplain, an area designated as wetland, Karst terrain, fault area, or an endangered species habitat • No public drinking water wells are located within 5 miles of the Brush Wellman facility • Private drinking water wells are located within 1 mile of the Brush Wellman facility

B. Generalized Process Description

1. Discussion of Typical Production Processes

Brush Wellman extracts bertrandite ore at a mine site located approximately 50 miles northwest of Delta, Utah. The ore is transported to a mill located 10 miles north of Delta and is treated using a counter-current extraction process to produce beryllium sulfate, $BeSO_4$. A second route, using the Kjellgren-Sawyer process, treats the beryl ore and provides the same beryllium sulfate intermediate. The intermediates from the two ore extraction processes are combined and fed to another extraction process. This extraction process removes impurities solubilized during the processing of the bertrandite and beryl ores and converts the beryllium sulfate to beryllium hydroxide, $Be(OH)_2$. The beryllium hydroxide is either sold, or sent off-site to either be converted to beryllium fluoride, BeF_2, which is then catalytically reduced to form metallic beryllium, converted to beryllium oxide, or converted to beryllium alloys.

2. Generalized Process Flow Diagram

Exhibit 3 (Parts 1-3) presents a generalized process flow diagram for the production of metallic beryllium. Each part of the process is described in greater detail below.

Part 1: Extraction of Beryllium as Beryllium Sulfate

Processing of bertrandite and imported beryl ores takes place at the Brush Wellman plant in Delta, Utah. Even though beryllium is extracted from both ores as beryllium sulfate, there are significant differences in the two extraction procedures. For example, the beryl extraction procedure requires five 15-foot diameter thickeners, while the bertrandite process uses eight 90-foot diameter thickeners.[10]

Bertrandite Ore. The bertrandite ore is crushed, sized, and wet milled to provide a pumpable slurry of particles below 840 µm.[11] The slurry is leached with sulfuric acid, H_2SO_4, at moderate temperatures (about 95°C) to solubilize the beryllium. The resulting beryllium sulfate solution is separated from unreacted solids using thickeners and counter-current decantation (CCD). The solids from the thickener underflow are discarded to a tailings pond.[12]

Beryl Ore. In contrast to bertrandite, beryl ore contains beryllium in a tightly bound crystalline structure. Therefore, in order to effectively leach the beryllium with sulfuric acid, it is first necessary to destroy the crystalline structure. The Kjellgren-Sawyer process is used commercially to extract beryllium from beryl. In this process, the ore is crushed, melted at 1650°C, and quenched by pouring the molten ore into water. The resulting noncrystalline glass (frit) is heat treated at 900-950°C to further increase the reactivity of the beryllium component. After grinding to <74 µm, a slurry of the frit powder is reacted with concentrated sulfuric acid at 250-300°C to produce soluble beryllium sulfate and aluminum sulfate, $Al_2(SO_4)_3$.[13] The spent solid fraction is separated from the beryllium sulfate solution using thickeners and CCD and discarded to a tailings pond.

Beryllium sulfate leach solutions from the bertrandite and beryl CCD thickeners are combined in a surge tank and pumped to another tank where sulfuric acid is added. The solution is then pumped to a filter which is pre-coated with diatomaceous earth. The clarified filtrate solution from the filter (called extraction feed) is pumped to another surge tank before being introduced into the next step of the process, the production of beryllium hydroxide. The filter cake from the filter is continuously scraped off, repulped with fresh water, and pumped to the leach output where it is recycled to the CCD thickeners for beryllium recovery.[14]

In the past, the beryllium sulfate solution produced from the extraction of beryl ore was neutralized with ammonia in order to separate the bulk of the aluminum as ammonium alum. The ammonium alum crystals were then removed by centrifugation. Organic chelating agents, such as the sodium salt of ethylenediaminetetraacetic acid (EDTA) and triethanolamine, were added to the alum-free solution in the presence of sodium hydroxide to form a

---

[10] U.S. Environmental Protection Agency, "Beryllium," 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes, 1988, p. 3-47.

[11] Crushing, sizing, and wet milling are shown as physical processing in Exhibit 1.

[12] Brush Wellman, Comments of Brush Wellman Inc. on EPA's Proposed Reinterpretation of the Mining Waste Exclusion, Revised November 21, 1988, p. 8.

[13] Crushing, melting, quenching, heat treating, and grinding are shown as physical treatment in Exhibit 1.

[14] Brush Wellman, Inc. Comment submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

solution of sodium beryllate. Heating the solution to just below its boiling point precipitated a granular beryllium hydroxide that was recovered by continuous centrifugation.[15]

Part 2: Production of Beryllium Hydroxide from Beryllium Sulfate

During the extraction processes performed on the bertrandite and beryl ores, elements other than beryllium (e.g., aluminum, iron, and magnesium) are solubilized and must be removed in order to prevent product contamination. Therefore, extraction feed solution is pumped from the surge tank to the solvent extraction circuit. Solvent extraction is a closed-loop circuit consisting of three steps: loading, stripping, and acid conversion. The loading step consists of ten pairs of mixer and settler tanks. To liberate the beryllium from the extraction feed, the extraction feed is mixed with kerosene containing di(2-ethylhexyl)phosphate in each mixer tank and allowed to separate by gravity in each settler tank, where beryllium-laden organic liquid floats to the top. This is done sequentially through all ten mixer/settler pairs with aqueous liquid moving downcurrent from the first extraction mixer tank to the last settling tank, while the organic liquid moves upcurrent from the last mixer tank to the first settling tank. The aqueous liquid that leaves the end of the loading step of the solvent extraction circuit is known as raffinate, and it contains all of the magnesium (Mg) and most of the aluminum (Al) found in the beryllium sulfate extraction feed solution. The raffinate is pumped to a surge tank where any residual organic liquid is allowed to separate. The raffinate is then pumped to a water collection tank where it is combined with other wastewater streams and pumped to the tailings disposal tank, and then to the tailings pond. None of the raffinate is recycled.

The beryllium-laden organic liquid that comes out of the loading step of the solvent extraction circuit is called loaded organic. It is pumped to a surge tank and then to two pairs of mixer/settler tanks which comprise the stripping step of the solvent extraction circuit. The loaded organic is contacted with a small volume of aqueous ammonium carbonate in the mixer tanks, and allowed to separate in the settler tanks. The ammonium carbonate solution strips the beryllium, any remaining aluminum, iron, and uranium from the loaded organic, and results in an ammonium-beryllium carbonate solution with a ten-fold higher beryllium concentration than the loaded organic. The ammonium-beryllium carbonate solution is pumped to a surge tank before being introduced into the iron hydrolysis step. The remaining organic liquid from the stripping step is termed stripped organic.

The stripped organic has a basic pH from the stripping step and is converted to an acid pH for reuse in the loading step of the solvent extraction circuit. This is done in the acid conversion step of the solvent extraction circuit. In this step, the stripped organic is treated in two pairs of mixer/settler tanks by contacting it with aqueous sulfuric acid solution. The acidified, or converted, organic is pumped to two surge tanks prior to being recycled to the loading step of the solvent extraction circuit. The aqueous liquid from the acid conversion step is a wastewater called converted aqueous feed (CAF) and is pumped to the raffinate surge tank for discard. None of the CAF is recycled.[16]

Heating the ammonium beryllium carbonate solution to 95°C liberates part of the ammonia (NH_4) and carbon dioxide (CO_2) and causes the precipitation of beryllium carbonate, $BeCO_3$. The beryllium carbonate is separated on a rotary drum filter and may be drummed as an intermediate product. However, the beryllium carbonate may also be reslurried in deionized water and processed to beryllium hydroxide. Heating the beryllium carbonate slurry to 165°C in a pressure vessel liberates the remaining carbon dioxide and the resulting beryllium hydroxide is recovered by filtration.[17]

---

[15] "Beryllium and Beryllium Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. IV, 1978, p. 808.

[16] Brush Wellman, Inc. January, 26, 1996. Op. Cit.

[17] Ibid.

EXHIBIT 3

Process Flow Diagram for Production of Metallic Beryllium (Part 1 of 3)

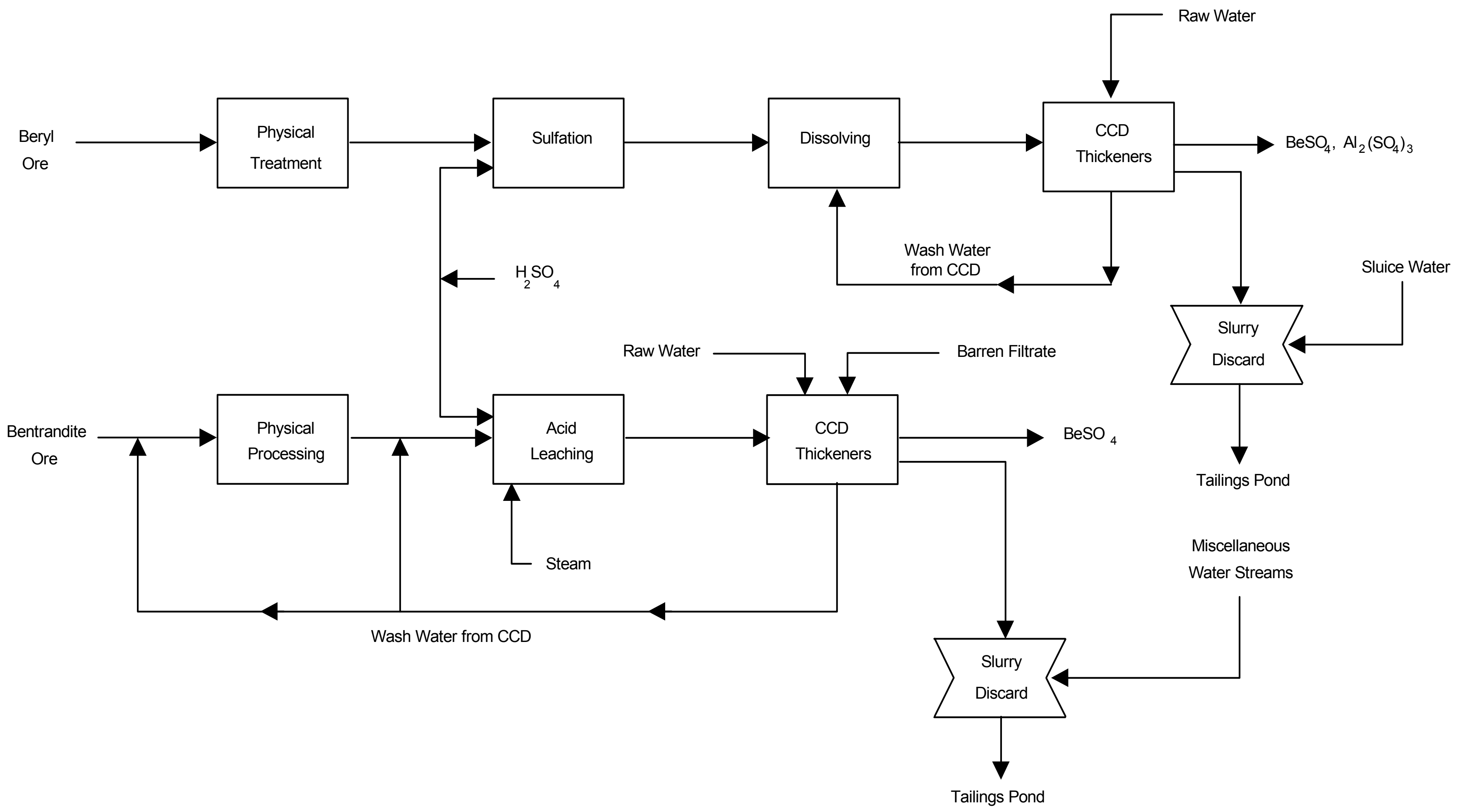
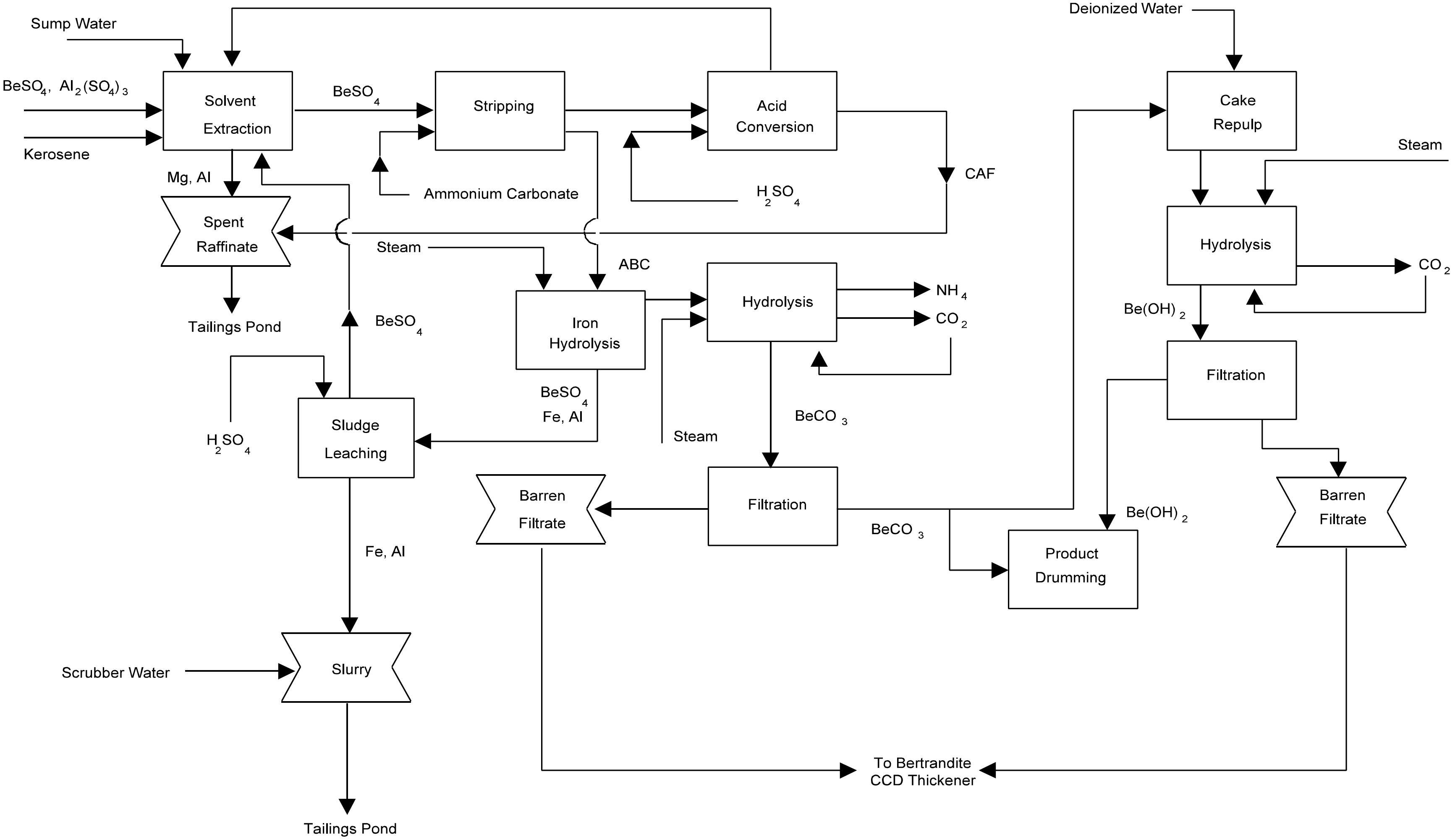


EXHIBIT 3

Process Flow Diagram for Production of Metallic Beryllium (Part 2 of 3)

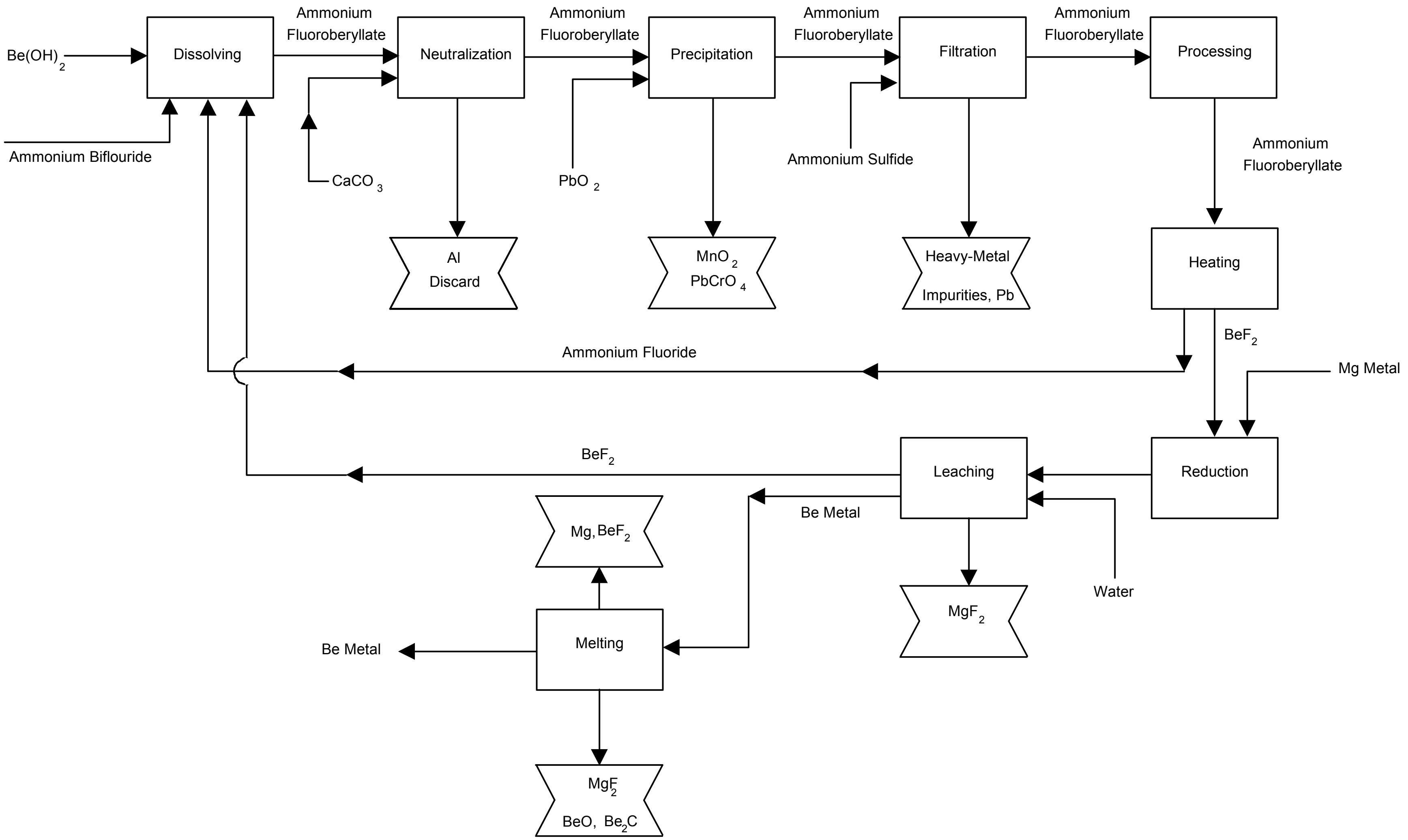


ABC = Ammonium Beryllium Carbonate

CAF = Converted Aqueous Feed

EXHIBIT 3

Process Flow Diagram for Production of Metallic Beryllium (Part 3 of 3)



Beryllium hydroxide production is the starting point for all further beryllium processing. Following hydroxide extraction, separate production processes are involved in producing the three basic beryllium lines (i.e., metallic beryllium, beryllium alloys, and beryllia).

Part 3: Production of Beryllium Metal, Oxide, and Alloys

Production of Metallic Beryllium. Brush Wellman uses the Schwenzfeier process to prepare a purified, anhydrous beryllium fluoride for reduction to beryllium metal. The first step of this process involves dissolving beryllium hydroxide in ammonium bifluoride to yield a solution of ammonium fluoroberyllate at pH 5.5. The solution is neutralized by adding aquaammonia. Then, solid calcium carbonate, $CaCO_3$, is added and the solution is heated to 60°C to remove aluminum before filtering. After filtration, ammonium sulfide is added to the filtrate to remove any heavy-metal impurities. Following the filtration step, ammonium fluoroberyllate is crystallized by co-current evaporation under vacuum. The crystals are continuously removed by centrifugation and washed lightly, while the mother liquor and washings are returned to the evaporator.[18] The ammonium fluoroberyllate is charged into inductively heated, graphite-lined furnaces where it is thermally decomposed to beryllium fluoride and ammonium fluoride. The ammonium fluoride is vaporized into fume collectors for recycle to the dissolution operation, whereas the molten beryllium fluoride is removed from the bottom of the furnace and solidified as a glassy product on water-cooled casting wheels.[19]

The beryllium fluoride is then reduced by magnesium metal (Mg) at a stoichiometric ratio of 1 BeF_2 : 0.7 Mg. In this process, magnesium metal and beryllium fluoride are charged into a graphite crucible at a temperature of about 900°C. The excess beryllium fluoride produces a slag of magnesium and beryllium fluorides having a melting point substantially below that of beryllium metal. The excess BeF_2 prevents the formation of an oxide film on the beryllium particles and assists in the coalescence of the metal.[20]

When the exothermic reaction is completed, the reaction products are heated to about 1300°C to allow molten beryllium to separate and float on top of the slag. The molten beryllium and slag are then poured into a graphite receiving pot where both solidify. The reaction product is then crushed and water-leached in a ball mill. The excess beryllium fluoride quickly dissolves, causing disintegration of the reaction mass and liberation of the beryllium metal as spherical pebbles. The leach liquor in this step is continuously passed through the ball mill in order to remove the fine, insoluble magnesium fluoride (MgF_2) particles formed during the reduction reaction. The magnesium fluoride is ultimately separated from the leach liquor and discarded. The leach liquor, which includes the excess beryllium fluoride, is then recycled as part of the input for making ammonium fluoroberyllate. The beryllium metal pebbles contain 98 percent beryllium along with entrapped reduction slag and unreacted magnesium. To remove these impurities, the metal is melted in induction furnaces under a vacuum. The excess magnesium and beryllium fluoride from the slag vaporize and are collected in suitable filters. Nonvolatiles, such as beryllium carbide (Be_2C), beryllium oxide, and magnesium fluoride, separate from the molten metal as a dross that adheres to the bottom of the crucibles. The purified beryllium metal is poured and cast into ingots of 150-200 kilograms.[21]

Production of Beryllium Oxide. Exhibit 4 illustrates the production of beryllium oxide. Beryllium hydroxide is dissolved in water and sulfuric acid. The resulting beryllium sulfate solution is filtered to remove impurities. The solution flows to one of two evaporators followed by two crystallizers in parallel where beryllium sulfate crystals are formed. The crystals are separated from the mother liquor in a centrifuge, and the mother liquor is recycled to the beryllium hydroxide dissolver.

---

[18] Evaporation, centrifugation, and washing are shown as processing in Exhibit 1.

[19] "Beryllium and Beryllium Alloys", 1992, Op. Cit., pp. 129-130.

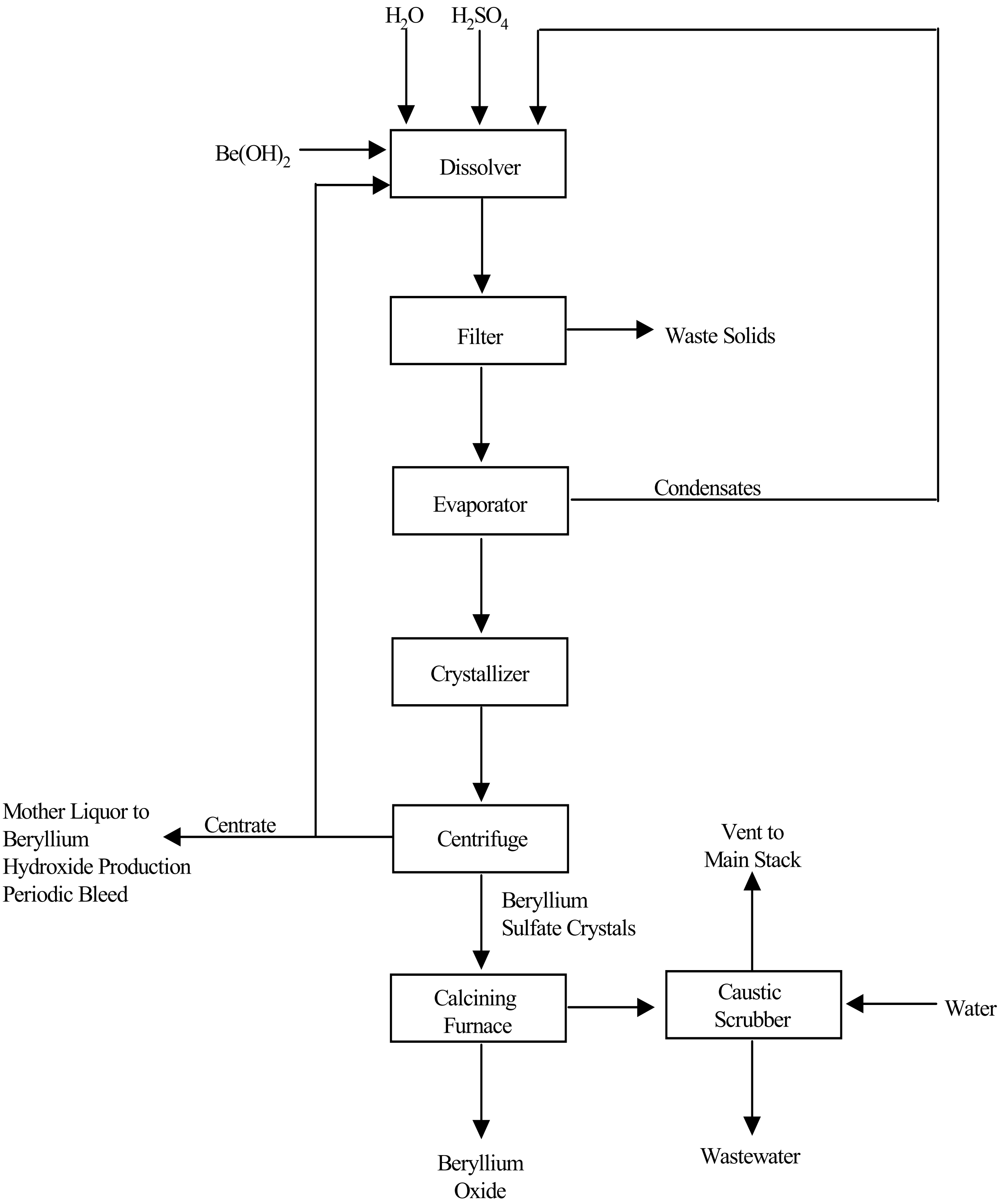
[20] Ibid., p. 130.

[21] "Beryllium and Beryllium Alloys," 1978, Op. Cit., p. 810.

EXHIBIT 4

PROCESS FLOW DIAGRAM FOR PRODUCTION OF BERYLLIUM OXIDE

(Adapted from: Development Document for Effluent Limitations Guidelines, 1989, p. 3647.)



The beryllium sulfate is calcined in gas fired furnaces at about 1100°C to beryllium oxide. The exhaust gas from the calcining furnace is scrubbed in caustic scrubbers to remove sulfur dioxide. The scrubber water is sent to treatment.[22]

Production of Beryllium-copper Alloys. Beryllium hydroxide, electrolytic copper, and carbon are combined in an electric arc furnace to make beryllium-copper master alloy. The resultant melt, containing about four percent beryllium is cast into ingots. Remelting master alloy ingots with additional copper and other alloying elements yields the desired beryllium-copper alloy, which is then cast into slabs or billets. Slabs of beryllium copper alloys are processed further into strip or plate, and billets are extruded into tube, rod, bar, and wire products.[23]

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

The Fluoride process, an alternative to the Kjellgren-Sawyer process, converts the beryllium oxide found in beryl ore to a water-soluble form by roasting with fluxes. In this process, pulverized beryl ore is roasted with sodium fluorosilicate at approximately 750°C to form slightly soluble sodium fluoroberyllate. The reaction products are extruded as wet briquettes and ground in a wet pebble mill. The sodium fluoroberyllate is then leached with water at room temperature. The filtered solution is treated with sodium hydroxide to form sodium beryllate, from which a filterable beryllium hydroxide is precipitated by boiling. The beryllium hydroxide can then be processed to metallic beryllium using the process discussed in Part 3.[24]

4. Beneficiation/Processing 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.

---

[22] U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category, Vol. VII, Office of Water Regulation Standards, May 1989, p. 3643.

[23] Deborah A. Kramer, "Beryllium Minerals," from Industrial Rocks and Minerals, 6th Ed., Society for Mining, Metallurgy, and Exploration, 1994, p. 152.

[24] "Beryllium and Beryllium Alloys," 1978, Op. Cit., pp. 808-809.

Bertrandite and Beryl Ore Processes

EPA determined that for the production of beryllium via the bertrandite and beryl ore processes, mineral processing occurs between solvent extraction and iron hydrolysis, due to the change in chemical composition that occurs during hydrolysis.[25] 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 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.

Other Beryllium Processing

Because other beryllium products are produced after either bertrandite ore processing or beryl ore processing, all of the wastes generated during these operations are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, please see the bertrandite ore and beryl ore process sections above.

C. Process Waste Streams

During the production of metallic beryllium from beryl and bertrandite ores, several waste streams are generated. Each waste stream is identified below, along with the portion of the process in which it is created. For each waste stream, any specific information regarding its physical and chemical characteristics is provided, as well as generation rates and management practices.

1. Extraction/Beneficiation Wastes

Part 1: Extraction of Beryllium as Beryllium Sulfate

Physical Processing/Treatment wastes. These wastes are generated by the physical processing or treatment of ore, and may include **tailings**, **gangue**, and **wastewater**. No other information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

Bertrandite thickener slurry. Approximately 370,000 metric tons of bertrandite thickener slurry were discarded to a tailings pond in 1992.[26] The pH of the bertrandite thickener slurry has been reported between 2.5 and 3.5.[27] The attached data in Attachment 1 indicate that the pH of bertrandite thickener slurry ranges from 2 to 3. Therefore, this waste may sometimes exhibit the hazardous characteristic of corrosivity. We used best engineering judgment to determine that this waste stream may be recycled to extraction/beneficiation units. Bertrandite thickener slurry was formerly classified as a by-product. This waste stream is combined with approximately 250,000 metric tons of miscellaneous water streams prior to disposal.[28] The miscellaneous water streams are generated during the bertrandite ore extraction process, but the origin of these streams is unknown. See Attachment 1 for waste characterization data.

---

[25] U.S. Environmental Protection Agency, Letter from Mr. Robert Tonetti, Acting Deputy Director, Waste Management Division, Office of Solid Waste to Mr. Richard Davis, Brush Wellman, Inc., March 15, 1990.

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

[27] Brush Wellman, 1988, Op. Cit., p. 8.

[28] RTI Survey 101006, National Survey of Solid Wastes From Mineral Processing Facilities, Brush Wellman Co., Delta, UT, 1989, p. 2-4.

Beryl thickener slurry. In 1992, beryl thickener slurry was discarded to a tailings pond at a rate of 3,000 metric tons/yr.[29] The beryl thickener slurry has a pH of 2.[30] Therefore, this waste exhibits the hazardous characteristic of corrosivity. We used best engineering judgment to determine that this waste stream may be recycled to extraction beneficiation units. Beryl thickener slurry was formerly classified as a by-product. This waste stream is combined with about 21,000 metric tons of sluice water prior to disposal.[31] The sluice water is used to transport the beryl ore to the start of the ore extraction processes. See Attachment 1 for waste characterization data.

Part 2: Production of Beryllium Hydroxide from Beryllium Sulfate

Spent raffinate. Approximately 380,000 metric tons of spent raffinate were discarded to a tailings pond in 1992. This waste exhibits the hazardous characteristics of toxicity (for selenium) and corrosivity.[32] The raffinate has a pH of 1.4.[33] This aqueous waste stream also contains magnesium and aluminum,[34] and may contain treatable concentrations of metal impurities, total suspended solids, and low levels of organics.[35] This waste stream is discarded to a tailings pond.[36] Spent raffinate was formerly classified as a spent material. This waste stream is combined with approximately roughly 33,000 metric tons of an **acid conversion stream** prior to disposal.[37] See Attachment 1 for waste characterization data.

Sump water. This waste is generated during the solvent extraction process that removes metal impurities from the beryllium sulfate solution. 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.

Acid conversion stream. This waste is the resultant aqueous liquid of the stripping step of the solvent extraction process and is referred to as converted aqueous feed. This waste stream is combined with spent raffinate and discarded to a tailings pond.[38] 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.

---

[29] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-2.

[30] Ibid., p. 6-61.

[31] RTI Survey 101006, 1989, Op. Cit., p. 2-4.

[32] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-2.

[33] Brush Wellman, 1988, Op. Cit., p. 11.

[34] "Beryllium and Beryllium Alloys", 1992, Op. Cit., p. 129.

[35] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 3569.

[36] Brush Wellman, Inc. January 25, 1996. Op. Cit.

[37] RTI Survey 101006, 1989, Op. Cit., p. 2-4.

[38] Brush Wellman, Inc. January 25, 1996. Op. Cit.

2. Mineral Processing Wastes

Part 2: Production of Beryllium Hydroxide from Beryllium Sulfate

Separation slurry. In 1992, the separation slurry was discarded to a tailings pond at a rate of 2,000 metric tons/yr.[39] The separation slurry has a pH of 3.[40] The slurry contains iron and aluminum which have been precipitated as hydroxides and carbonates from the aqueous ammonium beryllium carbonate stream.[41] This waste stream is combined with about 39,000 metric tons of scrubber water prior to disposal.[42] The scrubber water is probably basic because it is used to scrub the ammonia and carbon dioxide stream released during the heating of the ammonium beryllium carbonate. See Attachment 1 for waste characterization data.

Spent barren filtrate streams. The barren filtrate streams are produced during the filtration of beryllium carbonate and beryllium hydroxide. Approximately 88,000 metric tons of barren filtrate were discarded to a tailings pond in 1992. This waste exhibits the hazardous characteristic of toxicity for selenium.[43] The barren filtrate streams have a pH of 9.8.[44] EPA received conflicting data about whether this waste stream is recycled to the bertrandite CCD thickeners or is disposed, so we used best engineering judgment to determine that this waste stream is partially recycled. The streams were formerly classified as spent material. The barren filtrate stream from the filtration of beryllium carbonate operation contains uranium that was solubilized in the ore extraction processes. See Attachment 1 for waste characterization data.

Beryllium hydroxide supernatant. When beryllium is recovered from recycled customer material, internally generated residues, scrap, and recycled mother liquor from the beryllium oxide crystallization operations, the raw material is dissolved in sulfuric acid and beryllium and then precipitated with caustic as beryllium hydroxide. After gravity separation, the supernatant is discharged as a wastewater stream.[45] 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. See Attachment 1 for waste characterization data.

Part 3: Production of Beryllium Metal, Oxide, and Alloys

<u>Production of Metallic Beryllium</u>

The following waste streams are generated during the conversion of beryllium hydroxide to beryllium metal.

Neutralization discard. This waste stream contains precipitated aluminum. 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.

Precipitation discard. This waste stream contains precipitated manganese dioxide and lead chromate. 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.

Filtration discard. This waste stream contains lead and other heavy-metal impurities. Although no published information regarding waste generation rate or characteristics was found, we used the methodology

---

[39] U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-2.

[40] Brush Wellman, 1988, <u>Op. Cit.</u>, p. 9.

[41] "Beryllium and Beryllium Alloys," 1978, <u>Op. Cit.</u>, p. 807.

[42] RTI Survey 101006, 1989, <u>Op. Cit.</u>, p. 2-4.

[43] U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, p. I-2.

[44] Brush Wellman, 1988, <u>Op. Cit.</u>, p. 10.

[45] U.S. Environmental Protection Agency, 1989, <u>Op. Cit.</u>, p. 3660.

outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 23,000 metric tons/yr, and 45,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity for lead. This waste stream is not recycled.

Leaching discard. This waste stream contains insoluble magnesium fluoride. 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.

Dross discard. This waste stream contains nonvolatiles, such as beryllium oxide, magnesium fluoride, and beryllium carbide which separate from the molten beryllium metal during the final melting process. 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.

Melting emissions. This gaseous waste stream contains magnesium and beryllium fluoride which vaporized during the final melting process and collected on suitable filters. 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. Process condensates are generated from the ammonium beryllium fluoride crystallizer and the ammonium fluoride sludge filtrate evaporator. The condensed water is used as makeup for the fluoride furnace scrubbing system, for the beryllium pebble plant scrubbing system, for sludge washing, and general plant water usage such as floor washing. Periodic discharge from the process water pit is necessary to prevent dissolved solids build-up. The process wastewater has a neutral pH, and treatable concentrations of beryllium and fluoride. Ammonia and cyanide are also reported as present above treatable concentrations.[46]

Pebble plant area vent scrubber water. The beryllium pebble plant contains a ventilation system for air circulation. A wet scrubber is employed to clean the used air prior to venting to the atmosphere. Although the scrubber is recycled extensively, a blowdown stream is periodically discharged to the process water pit. Makeup water for the scrubber is obtained from the process water pit. This scrubber water has a slightly acidic pH, and treatable concentrations of beryllium and fluoride.[47] 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. See Attachment 1 for waste characterization data.

Chip treatment wastewater. Pure beryllium metal scrap in the form of chips is treated with nitric acid and rinsed prior to being vacuum cast along with beryllium pebbles into a beryllium metal billet. The spent acid and rinse water are discharged. This operation combines refining beryllium from secondary as well as primary sources.[48] 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, 50,000 metric tons/yr, and 1,000,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity for chromium. See Attachment 1 for waste characterization data. We also used best engineering judgment to determine that this waste stream may be partially recycled. This waste stream was formerly classified as a spent material.

Production of Beryllium Oxide

Scrubber liquor. This waste contains the sulfur dioxide removed from the furnace exhaust gas and sent to treatment. While over 90 percent of this stream is recycled, the rest is discharged as a wastewater stream. Scrubber liquor has a neutral pH, very high concentrations of dissolved solids (primarily sodium sulfate), and treatable

---

[46] U.S. Environmental Protection Agency, 1989, Op. Cit., p. 3661.

[47] Ibid., p. 3662.

[48] Ibid., p. 3661.

concentrations of beryllium, fluoride and suspended solids.[49] 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 solids. This waste stream contains the impurities filtered from beryllium sulfate solution. 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.

Production of Beryllium-copper alloys

No other information on waste characteristics, waste generation, or waste management of wastes generated during production of beryllium-copper alloys was available in the sources listed in the bibliography.

D. Non-uniquely Associated Wastes

Non-uniquely associated hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants.

E. Summary of Comments Received by EPA

New Factual Information

Four commenters provided new factual information on beryllium sector processes and waste streams. (COMM58, COMM59, COMM60, COMM64). This information has been incorporated into the commodity summary, process description, and waste stream description sections of this sector report.

Sector-Specific Issues

Three commenters indicated that the Agency had incorrectly placed the beneficiation/processing line in the beryllium sector. (COMM58, COMM60, COMM64) The commenters indicated that the Agency's placement of the beneficiation/processing line was inconsistent with prior Agency determinations. The Agency agrees that the beneficiation/processing line was incorrectly located in the initial draft of the sector report, and has revised the discussion of the beneficiation/processing boundary to reflect the decision made in the March 15, 1990 letter from Robert Tonetti, Acting Deputy Director, Waste Management Division, to Richard Davis of Brush Wellman, Inc.[50]

EPA received conflicting information about the disposition of spent barren filtrate. One commenter indicated that spent barren filtrate is recycled to the bertrandite CCD thickeners (COMM59). However, in comments on the Regulatory Impact Analysis, the same commenter indicated that spent barren filtrate is not recycled (COMM60). In the May 12, 1997 Second Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes, this same commenter indicated that a waste stream known as "finc barren filtrate" is recycled (Brush Wellman, Inc., 2P4P-00052). It is unclear whether "fine barren filtrate" and spent barren filtrate are the same waste stream because the commenter provided differing generation quantities for "fine barren filtrate" and "barren filtrate." Furthermore, a process flowsheet provided in the comment did not indicate direct recycling of barren filtrate to the CCD thickeners. In light of this conflicting information,

---

[49] Ibid., p. 3660.

[50] In the process of incorporating this change into two supporting documents of this Rulemaking (Regulatory Impact Analysis and Characterization of Mineral Processing Wastes and Materials), EPA inadvertently removed spent barren filtrate from cost and risk modeling analyses as a beneficiation waste. This waste is a processing waste because it is generated downstream of the initial mineral processing step of beryllium production, iron hydrolysis. EPA has corrected this error in the supporting documents.

EPA is assuming that this material is partially recycled as described in the spent barren filtrate waste stream description.

BIBLIOGRAPHY

"Beryllium and Beryllium Alloys." Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. Vol. IV. 1978.

"Beryllium and Beryllium Alloys." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992.

Brush Wellman. Comments of Brush Wellman Inc. on EPA's Proposed Reinterpretation of the Mining Waste Exclusion. December 30, 1985.

Brush Wellman. Comments of Brush Wellman Inc. on EPA's Proposed Reinterpretation of the Mining Waste Exclusion. Revised November 21, 1988.

Brush Wellman, Inc. Comments submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

"From Mining to Recycling." Metal Bulletin Monthly — MBM Copper Supplement. 270. 1993. p. 27.

ICF Incorporated. Brush Wellman: Mineral Processing Waste Sampling Visit — Trip Report. August 1989.

ICF Incorporated. "Notes from November 30, 1989 Meeting with Brush Wellman." Memorandum to Bob Hall from David Bauer. December 11, 1989.

Kramer, Deborah, A. "Beryllium." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 28-29.

Kramer, Deborah, A. "Beryllium Minerals." From Industrial Rocks and Minerals. 6th Ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 149-156.

Personal Communication between ICF Incorporated and Deborah Kramer, U.S. Bureau of Mines. October 20, 1994.

RTI Survey 101006. National Survey of Solid Wastes From Mineral Processing Facilities. Brush Wellman Co., Delta, UT. 1989.

U.S. Bureau of Mines. "Beryllium in 1992." Mineral Industry Surveys. April 1993.

U.S. Environmental Protection Agency. "Beryllium." 1988 Final Draft Summary Report of Mineral Industrial Processing Wastes. 1988. pp. 3-46 - 3-52.

U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Vol. VII. Office of Water Regulation Standards. May 1989.

U.S. Environmental Protection Agency. Newly Identified Mineral Processing Waste Characterization Data Set. Office of Solid Waste. August 1992.

ATTACHMENT 1

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - BETRANDITE THICKENER SLURRY - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	200.00	454.50	709.00	2/2	6.80	6.80	6.80	1/1	-	-
Antimony	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Arsenic	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	5.0	0
Barium	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	100.0	0
Beryllium	9.70	3,209.90	9,320.00	3/3	0.84	0.84	0.84	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0		
Cadmium	0.50	0.50	0.50	0/1	0.01	0.01	0.01	0/1	1.0	0
Chromium	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	5.0	0
Cobalt	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Copper	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Iron	7.00	186.00	365.00	2/2	0.12	0.12	0.12	1/1	-	-
Lead	17.20	17.20	17.20	1/1	0.03	0.03	0.03	0/1	5.0	0
Magnesium	300.00	340.00	380.00	2/2	16.00	16.00	16.00	1/1	-	-
Manganese	308.00	308.00	308.00	1/1	0.49	0.49	0.49	1/1	-	-
Mercury	0.0500	0.0500	0.0500	0/1	0.0001	0.0001	0.0001	0/1	0.2	0
Molybdenum	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Nickel	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Selenium	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	1.0	0
Silver	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	5.0	0
Thallium	25.00	25.00	25.00	0/1	0.25	0.25	0.25	0/1	-	-
Vanadium	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Zinc	65.30	65.30	65.30	1/1	1.19	1.19	1.19	1/1	-	-
Sulfate	1,900.00	2,450.00	3,000.00	2/2					-	-
Fluoride	-	-	-	0/0					-	-
Chloride	18.20	18.20	18.20	1/1					-	-
pH*	2.00	2.50	3.00	2/2				2/2	2<pH>12	1
Organics (TOC)	385.00	385.00	385.00	1/1					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - BERYL PLANT SLURRY DISCHARGE - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detected	Minimum	Average	Maximum	# Detected	Level	In Excess
Aluminum	0.62	0.62	0.62	1/1	0.22	0.22	0.22	1/1	-	-
Antimony	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Arsenic	0.30	0.30	0.30	1/1	0.13	0.13	0.13	1/1	5.0	0
Barium	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	100.0	0
Beryllium	0.05	4,660.02	9,320.00	2/2	0.19	0.19	0.19	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.005	0.005	0.005	0/1	0.005	0.005	0.005	0/1	1.0	0
Chromium	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	5.0	0
Cobalt	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Copper	0.05	0.05	0.05	0/1	0.15	0.15	0.15	1/1	-	-
Iron	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Lead	0.03	0.03	0.03	0/1	0.03	0.03	0.03	0/1	5.0	0
Magnesium	5.29	5.29	5.29	1/1	4.13	4.13	4.13	1/1	-	-
Manganese	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Mercury	0.0003	0.0003	0.0003	0/1	0.0001	0.0001	0.0001	0/1	0.2	0
Molybdenum	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Nickel	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Selenium	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	1.0	0
Silver	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	5.0	0
Thallium	0.25	0.25	0.25	0/1	0.25	0.25	0.25	0/1	-	-
Vanadium	0.05	0.05	0.05	0/1	0.05	0.05	0.05	0/1	-	-
Zinc	0.05	0.05	0.05	0/1	2.32	2.32	2.32	1/1	-	-
Sulfate	8,740.00	8,740.00	8,740.00	1/1					-	-
Fluoride	-	-	-	0/0					-	-
Chloride	155.00	155.00	155.00	1/1					-	-
pH*	2.00	2.00	2.00	1/1					2<pH>12	1
Organics (TOC)	579.00	579.00	579.00	1/1					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SPENT RAFFINATE - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	1570	1610	1650	2/2	3050	3050	3050	1/1	-	-
Antimony	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	-	-
Arsenic	3.05	3.05	3.05	1/1	1.19	1.19	1.19	1/1	5.0	0
Barium	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	100.0	0
Beryllium	2.62	5.52	8.00	5/5	2.83	2.83	2.83	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.01	0.01	0.01	0/1	0.10	0.10	0.10	1/1	1.0	0
Chromium	0.81	0.81	0.81	1/1	1.00	1.00	1.00	1/1	5.0	0
Cobalt	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	-	-
Copper	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	-	-
Iron	2.88	2.88	2.88	1/1	3.16	3.16	3.16	1/1	-	-
Lead	0.05	0.05	0.05	0/1	0.69	0.69	0.69	1/1	5.0	0
Magnesium	1690	1690	1690	1/1	1640	1640	1640	1/1	-	-
Manganese	60.70	60.70	60.70	1/1	61.10	61.10	61.10	1/1	-	-
Mercury	0.0001	0.0001	0.0001	0/1	0.0002	0.0002	0.0002	1/1	0.2	0
Molybdenum	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	-	-
Nickel	0.46	0.46	0.46	1/1	1.00	1.00	1.00	1/1	-	-
Selenium	0.41	0.41	0.41	1/1	1.00	1.00	1.00	1/1	1.0	1
Silver	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	5.0	0
Thallium	0.50	0.50	0.50	0/1	5.00	5.00	5.00	1/1	-	-
Vanadium	0.10	0.10	0.10	0/1	1.00	1.00	1.00	1/1	-	-
Zinc	141.00	141.00	141.00	1/1	125	125	125	1/1	-	-
Sulfate	55900	55900	55900	1/1					-	-
Fluoride	7000	7000	7000	1/1					-	-
Chloride	298.00	298.00	298.00	1/1					-	-
pH*	0.90	0.95	1.00	2/2					2<pH>12	2
Organics (TOC)	-	-	-	0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SEPARATION SLURRY - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	1110	1110	1110	1/1	54.10	54.10	54.10	1/1	-	-
Antimony	64.60	64.60	64.60	1/1	0.12	0.12	0.12	1/1	-	-
Arsenic	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	5.0	0
Barium	5.00	5.00	5.00	0/1	0.10	0.10	0.10	1/1	100.0	0
Beryllium	180.00	262.80	320.00	5/5	34.80	34.80	34.80	1/1	-	-
Boron	-	-	-	0/0	-	-	-	0/0		
Cadmium	0.50	0.50	0.50	0/1	0.02	0.02	0.02	1/1	1.0	0
Chromium	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	5.0	0
Cobalt	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Copper	5.00	5.00	5.00	0/1	0.11	0.11	0.11	1/1	-	-
Iron	28000	47300	66600	2/2	3.21	3.21	3.21	1/1	-	-
Lead	26.50	26.50	26.50	1/1	0.03	0.03	0.03	1/2	5.0	0
Magnesium	15.80	15.80	15.80	1/1	3.21	3.21	3.21	2/2	-	-
Manganese	5.00	5.00	5.00	0/1	0.13	0.13	0.13	1/1	-	-
Mercury	0.1300	0.1300	0.1300	1/1	0.0001	0.0001	0.0001	0/1	0.2	0
Molybdenum	10.70	10.70	10.70	1/1	0.05	0.05	0.05	0/1	-	-
Nickel	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	-
Selenium	12.80	12.80	12.80	1/1	0.05	0.05	0.05	0/1	1.0	0
Silver	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	5.0	0
Thallium	25.00	25.00	25.00	0/1	0.25	0.25	0.25	0/1	-	0
Vanadium	5.00	5.00	5.00	0/1	0.05	0.05	0.05	0/1	-	0
Zinc	28.30	28.30	28.30	1/1	1.60	1.60	1.60	1/1	-	-
Sulfate	8030	8030	8030	1/1					-	-
Fluoride	7.00	7.00	7.00	1/1					-	-
Chloride	-	-	-	0/0					-	-
pH*	3.00	3.08	3.15	2/2					2<pH>12	0
Organics (TOC)	475.00	475.00	475.00	1/1					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - BARREN FILTRATE - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	0.30	579.88	2,290.00	4/4	14.70	293.85	573.00	2/2	-	-
Antimony	1.35	3.18	5.00	1/2	0.79	0.90	1.00	2/2	-	-
Arsenic	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	5.0	0
Barium	0.05	2.53	5.00	0/2	0.15	0.58	1.00	2/2	100.0	0
Beryllium	7.90	48.04	76.30	5/5	2.66	15.03	27.40	2/2	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.03	0.26	0.50	1/2	0.02	0.06	0.10	2/2	1.0	0
Chromium	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	5.0	0
Cobalt	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Copper	0.10	2.55	5.00	1/2	0.05	0.53	1.00	1/2	-	-
Iron	0.20	222.13	886.00	4/4	0.34	108.67	217.00	2/2	-	-
Lead	0.03	7.56	15.10	1/2	0.03	0.27	0.52	1/2	5.0	0
Magnesium	2.72	516.36	1,030.00	2/2	2.48	147.74	293.00	2/2	-	-
Manganese	0.05	101.03	202.00	1/1	0.05	6.63	13.20	1/2	-	-
Mercury	0.0001	0.0251	0.0500	0/2	0.0001	0.0002	0.0002	1/2	0.2	0
Molybdenum	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Nickel	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Selenium	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	1.0	1
Silver	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	5.0	0
Thallium	0.25	12.63	25.00	0/2	0.25	2.63	5.00	1/2	-	-
Vanadium	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Zinc	0.76	57.38	114.00	2/2	0.78	13.29	25.80	2/2	-	-
Sulfate	710.00	14,705.00	28,700.00	2/2					-	-
Fluoride	81.00	121.00	161.00	2/2					-	-
Chloride	175.00	178.50	182.00	2/2					-	-
pH*	9.00	9.38	9.60	4/4					2<pH>12	0
Organics (TOC)	370.00	1,405.00	2,440.00	2/2					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - BERYLLIUM HYDROXIDE SUPERNATANT RAW WASTEWATER - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.003	0.003	0.003	1/1	-	-	-	0/0	-	-
Arsenic	0.003	0.003	0.003	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	12	12	12	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.004	0.004	0.004	1/1	-	-	-	0/0	1.0	0
Chromium	0.11	0.11	0.11	1/1	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	1.4	1.4	1.4	1/1	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.168	0.168	0.168	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0002	0.0002	0/0	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.12	0.12	0.12	1/1	-	-	-	0/0	-	-
Selenium	0.003	0.003	0.003	1/1	-	-	-	0/0	1.0	0
Silver	0.32	0.32	0.32	1/1	-	-	-	0/0	5.0	0
Thallium	0.002	0.002	0.002	1/1	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.19	0.19	0.19	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - PROCESS WASTEWATER - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.30	579.88	2,290.00	4/4	14.70	293.85	573.00	2/2	-	-
Antimony	1.35	3.18	5.00	1/2	0.79	0.90	1.00	2/2	-	-
Arsenic	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	5.0	0
Barium	0.05	2.53	5.00	0/2	0.15	0.58	1.00	2/2	100.0	0
Beryllium	7.90	48.04	76.30	5/5	2.66	15.03	27.40	2/2	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.03	0.26	0.50	1/2	0.02	0.06	0.10	2/2	1.0	0
Chromium	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	5.0	0
Cobalt	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Copper	0.10	2.55	5.00	1/2	0.05	0.53	1.00	1/2	-	-
Iron	0.20	222.13	886.00	4/4	0.34	108.67	217.00	2/2	-	-
Lead	0.03	7.56	15.10	1/2	0.03	0.27	0.52	1/2	5.0	0
Magnesium	2.72	516.36	1,030.00	2/2	2.48	147.74	293.00	2/2	-	-
Manganese	0.05	101.03	202.00	1/1	0.05	6.63	13.20	1/2	-	-
Mercury	0.0001	0.0251	0.0500	0/2	0.0001	0.0002	0.0002	1/2	0.2	0
Molybdenum	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Nickel	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Selenium	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	1.0	1
Silver	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	5.0	0
Thallium	0.25	12.63	25.00	0/2	0.25	2.63	5.00	1/2	-	-
Vanadium	0.05	2.53	5.00	0/2	0.05	0.53	1.00	1/2	-	-
Zinc	0.76	57.38	114.00	2/2	0.78	13.29	25.80	2/2	-	-
Sulfate	710.00	14,705.00	28,700.00	2/2					-	-
Fluoride	81.00	121.00	161.00	2/2					-	-
Chloride	175.00	178.50	182.00	2/2					-	-
pH*	9.00	9.38	9.60	4/4					2<pH>12	0
Organics (TOC)	370.00	1,405.00	2,440.00	2/2					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - PEBBLE PLANT AREA VENT SCRUBBER WATER - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.003	0.0030	0.003	2/2	-	-	-	0/0	-	-
Arsenic	0.042	0.0510	0.06	2/2	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	210	210	210	2/2	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.033	0.0335	0.034	2/2	-	-	-	0/0	1.0	0
Chromium	0.093	0.1165	0.14	2/2	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.5	0.5400	0.58	2/2	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.168	0.1680	0.168	2/2	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0003	0.0004	0.0004	2/2	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.064	0.0640	0.064	2/2	-	-	-	0/0	-	-
Selenium	0.003	0.0030	0.003	2/2	-	-	-	0/0	1.0	0
Silver	0.0005	0.0043	0.008	2/2	-	-	-	0/0	5.0	0
Thallium	0.002	0.0020	0.002	2/2	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.096	0.1130	0.13	2/2	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - CHIP TREATMENT WASTEWATER - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC Level	# Values In Excess
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects		
Aluminum	-	-	-	0/0	-	-	-	0/0	-	-
Antimony	0.003	0.003	0.003	1/1	-	-	-	0/0	-	-
Arsenic	0.003	0.003	0.003	1/1	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	3300	3300	3300	1/1	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.063	0.063	0.063	1/1	-	-	-	0/0	1.0	0
Chromium	7.4	7.4	7.4	1/1	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	1.4	1.4	1.4	1/1	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.2	0.2	0.2	1/1	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0002	0.0002	1/1	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.78	0.78	0.78	1/1	-	-	-	0/0	-	-
Selenium	0.003	0.003	0.003	1/1	-	-	-	0/0	1.0	0
Silver	0.04	0.04	0.04	1/1	-	-	-	0/0	5.0	0
Thallium	0.002	0.002	0.002	1/1	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	7.2	7.2	7.2	1/1	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SCRUBBER LIQUOR - BERYLLIUM

	Total Constituent Analysis - PPM				EP Toxicity Analysis - PPM				TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	-	0/0	-	-	-	0/0	-	0
Antimony	0.003	0.0067	0.015	6/6	-	-	-	0/0	-	-
Arsenic	0.003	0.0030	0.003	6/6	-	-	-	0/0	5.0	0
Barium	-	-	-	0/0	-	-	-	0/0	100.0	0
Beryllium	0.49	1.0733	2	6/6	-	-	-	0/0	-	-
Boron	-	-	-	0/0	-	-	-	0/0	-	-
Cadmium	0.004	0.0073	0.015	6/6	-	-	-	0/0	1.0	0
Chromium	0.042	0.0675	0.13	6/6	-	-	-	0/0	5.0	0
Cobalt	-	-	-	0/0	-	-	-	0/0	-	-
Copper	0.12	0.4100	1.5	6/6	-	-	-	0/0	-	-
Iron	-	-	-	0/0	-	-	-	0/0	-	-
Lead	0.16	0.1667	0.168	6/6	-	-	-	0/0	5.0	0
Magnesium	-	-	-	0/0	-	-	-	0/0	-	-
Manganese	-	-	-	0/0	-	-	-	0/0	-	-
Mercury	0.0002	0.0002	0.0002	6/6	-	-	-	0/0	0.2	0
Molybdenum	-	-	-	0/0	-	-	-	0/0	-	-
Nickel	0.019	0.0297	0.043	6/6	-	-	-	0/0	-	-
Selenium	0.003	0.0030	0.003	6/6	-	-	-	0/0	1.0	0
Silver	0.024	0.0655	0.1	6/6	-	-	-	0/0	5.0	0
Thallium	0.002	0.0020	0.002	6/6	-	-	-	0/0	-	-
Vanadium	-	-	-	0/0	-	-	-	0/0	-	-
Zinc	0.039	0.0553	0.087	6/6	-	-	-	0/0	-	-
Cyanide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfide	-	-	-	0/0	-	-	-	0/0	-	-
Sulfate	-	-	-	0/0	-	-	-	0/0	-	-
Fluoride	-	-	-	0/0	-	-	-	0/0	-	-
Phosphate	-	-	-	0/0	-	-	-	0/0	-	-
Silica	-	-	-	0/0	-	-	-	0/0	-	-
Chloride	-	-	-	0/0	-	-	-	0/0	-	-
TSS	-	-	-	0/0	-	-	-	0/0	-	-
pH *	-	-	-	0/0					2<pH>12	0
Organics (TOC)	-	-	-	0/0					-	-

Non-detects were assumed to be present at 1/2 the detection limit. TCLP data are currently unavailable; therefore, only EP data are presented.

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

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-70 - 2-76.)

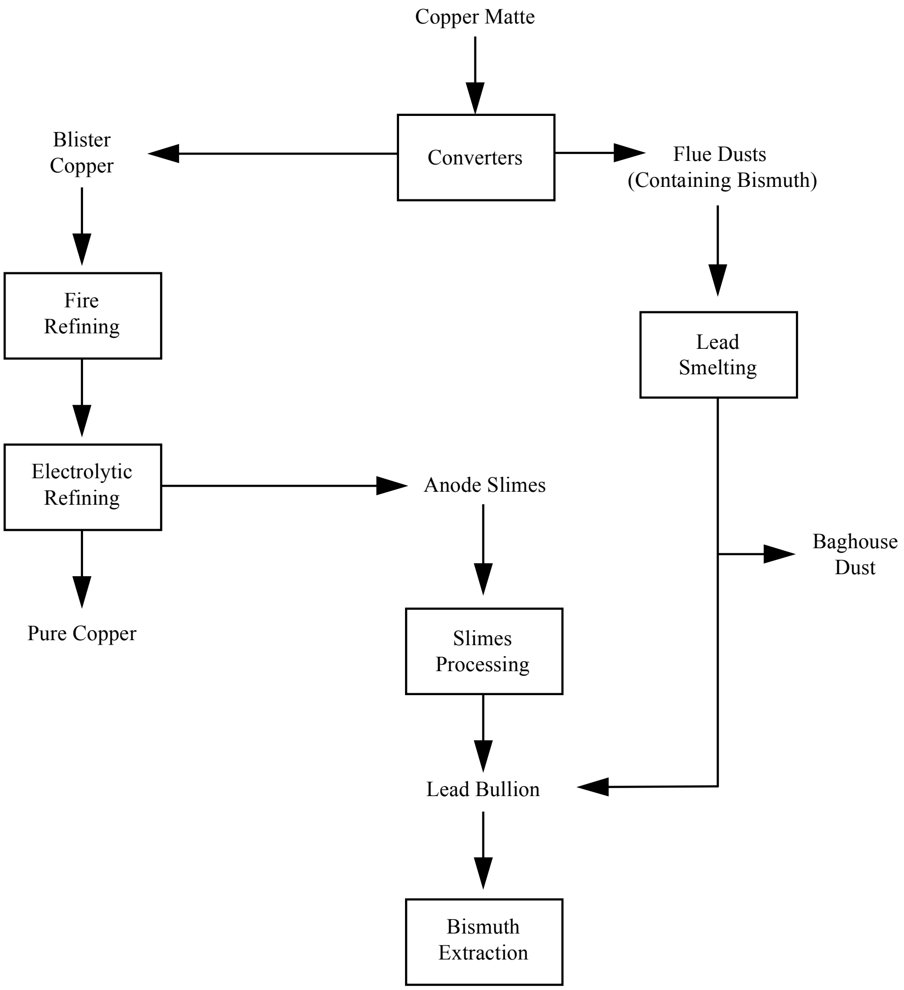
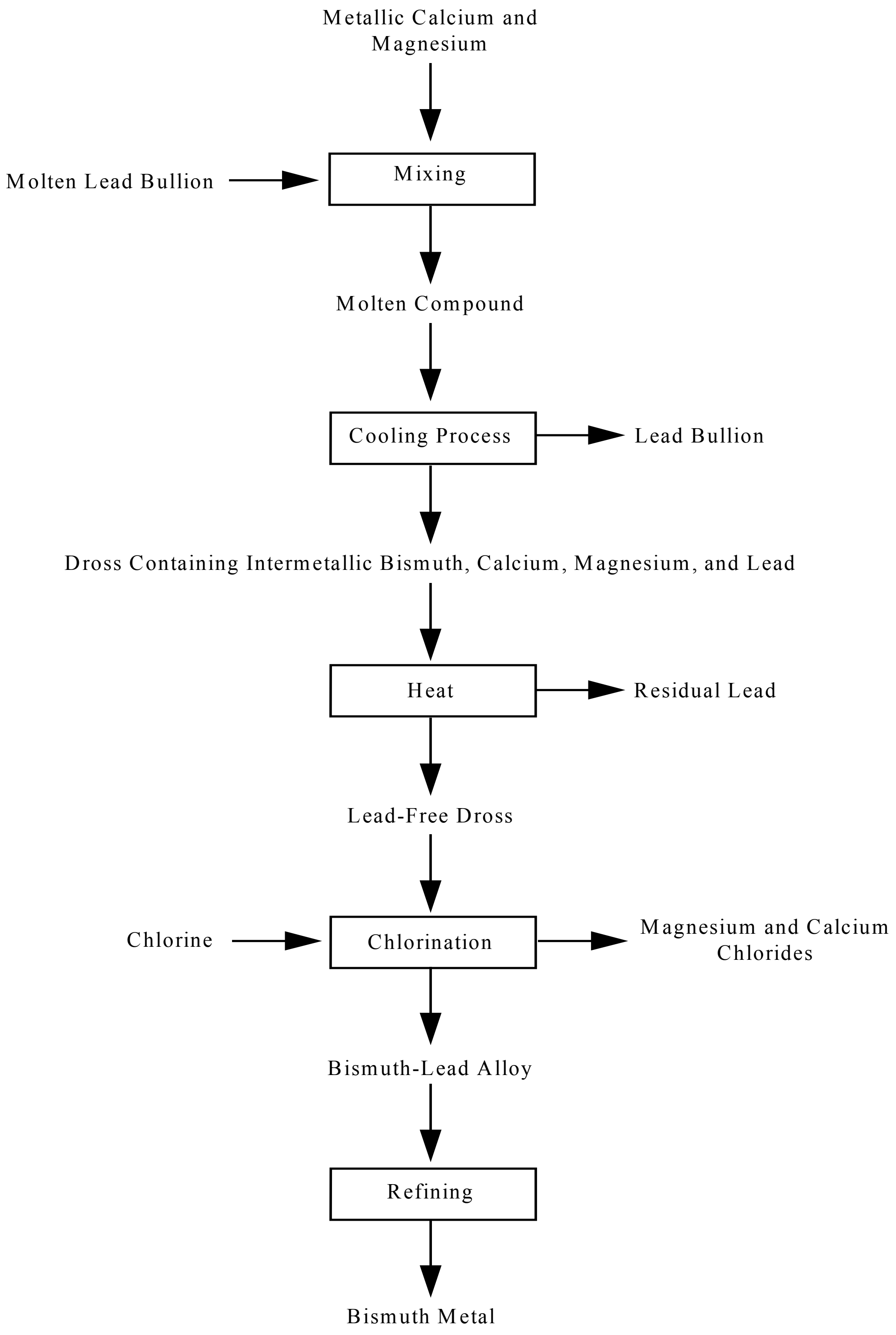


EXHIBIT 2

BISMUTH BETTERTON-KROLL PROCESS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-7- - 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) Processes

None Identified.

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

---

[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] Ibid.

EXHIBIT 3

BETTS ELECTROLYTIC EXTRACTION

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-70 - 2-76.)

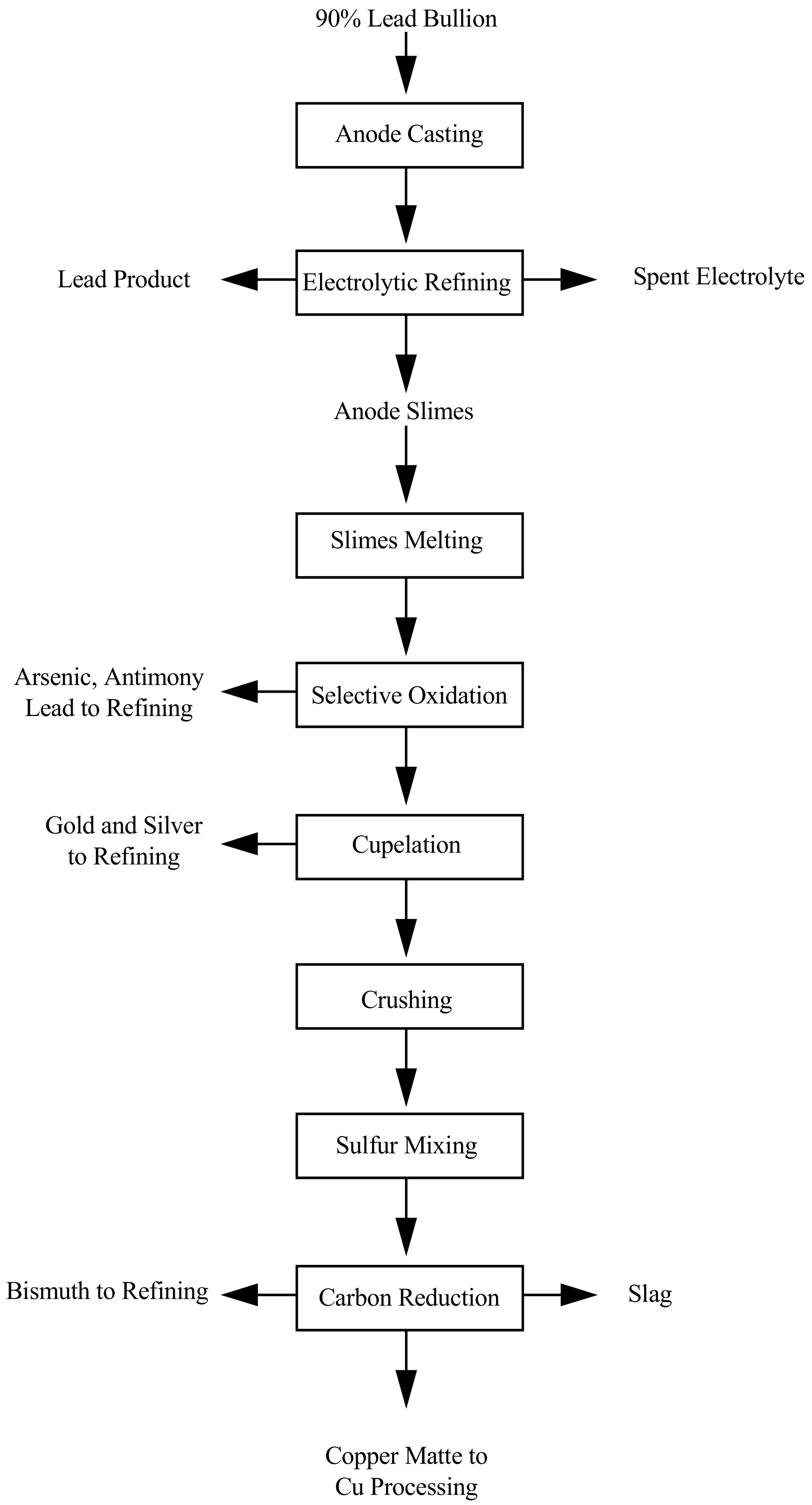


EXHIBIT 4

RECOVERY FROM BISMUTH BEARING MATERIALS

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-70 - 2-76.)

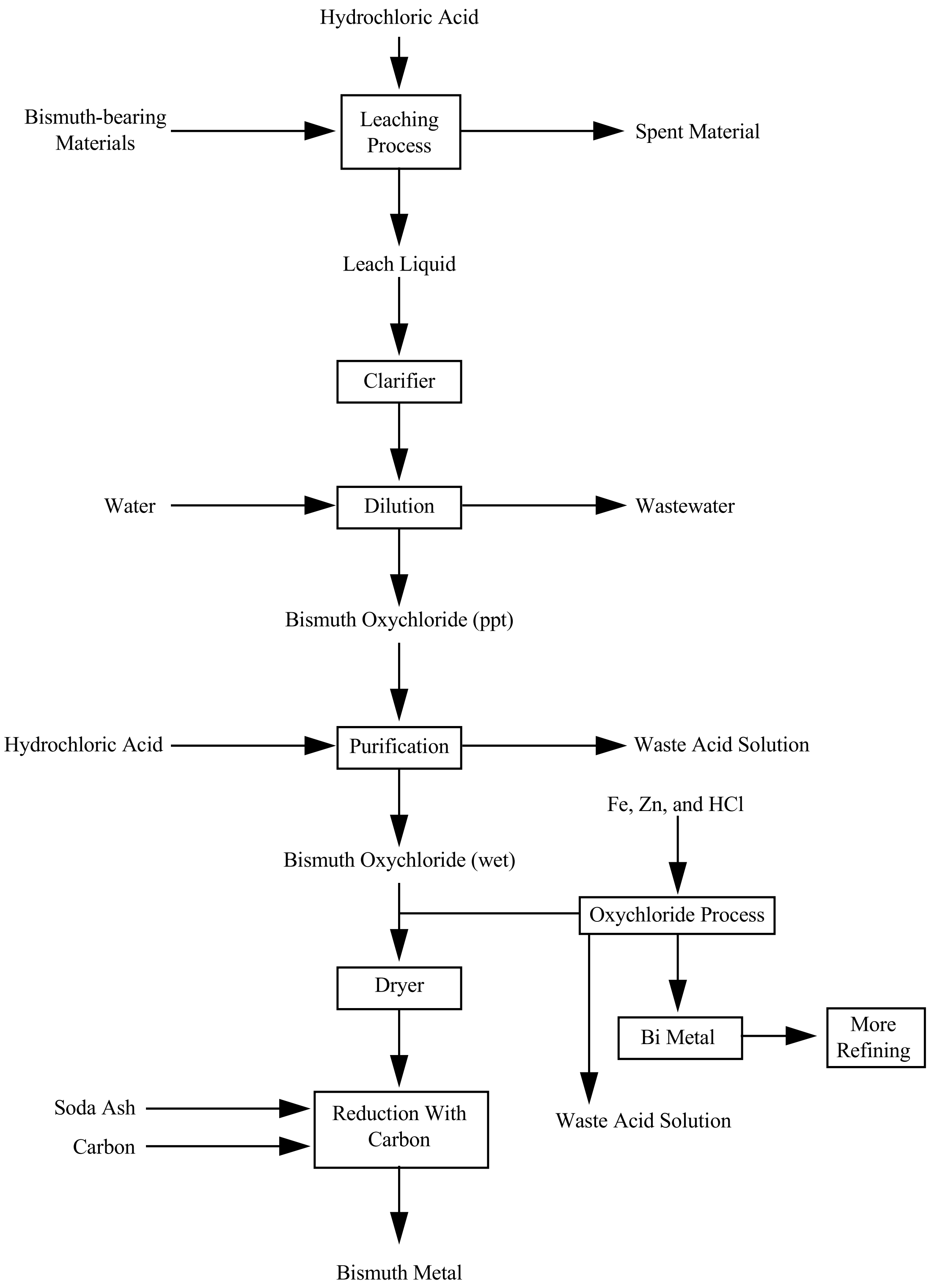
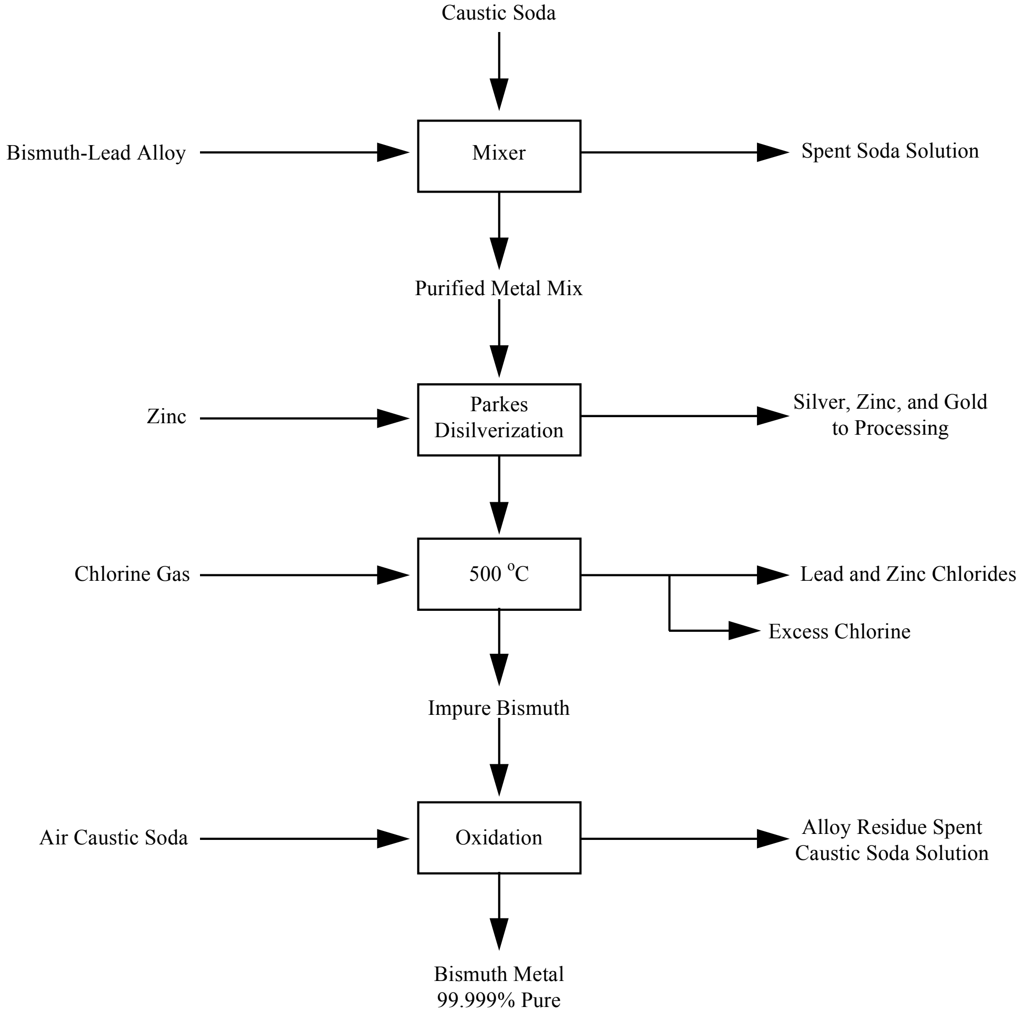


EXHIBIT 5

BISMUTH REFINING

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-70 - 2-76.)



processing waste. For a description of where the beneficiation/processing boundary occurs for this mineral comodity, 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. Non-uniquely Associated Wastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

BIBLIOGRAPHY

"Bismuth." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992. pp. 237-243.

Jasinski, Stephen M. "Bismuth." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 30-31.

Ojebuoboh, Funsho K. "Bismuth-production, properties, and applications." JOM, 44, No. 4. April 1992. pp. 46-49.

Stevens, Laurence G. and White, C.E.T. "Indium and Bismuth." Metals Handbook Volume 2. Properties and Selection: Nonferrous Alloys and Special-Purpose Materials. Tenth ed. 1990. pp. 750- 757.

U.S. Environmental Protection Agency. "Bismuth." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. Office of Solid Waste. pp. 2-70 - 2-76.

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

BORON

A. Commodity Summary

Borates are defined by industry as any compound that contains or supplies boric oxide. A large number of materials contain boric oxide, but the three most common boron containing minerals are borax, ulexite, and colemanite.[1] Kernite is a metamorphic phase of borax and is an important borax mineral. Borate production in the United States in centered mainly in the Mojave Desert in southern California. Borax and kernite are mined by U.S. Borax (located in Boron, California) and borate is also recovered from brines pumped from Searles Lake.[2] Kernite comprises more than one-third of the boron deposit in Boron, California.

Borax is the most important boron mineral for the borate industry. It crushes freely, and dissolves readily in water, and its solubility and rate of solution increase with water temperature. Kernite has a higher B_20_3 content than borax, but its excellent cleavage causes it to form fibers that mat and clog handling equipment. Being slowly soluble in water, kernite requires autoclaving or pre-refinery hydration for efficient conversion into refined products. It is currently used primarily as feed for the boric acid plant located in Boron, California.[3] Colemanite is the preferred calcium-bearing borate used by the non-sodium fiberglass industry. Although it has low solubility in water, it readily dissolves in acid.[4]

The major uses of borates include: fiberglass insulation, textile or continuous-filament glass fibers, glass, detergents and bleaches, enamels and frits, fertilizers, and fire retardants.[5] According to the U.S. Bureau of Mines, apparent domestic consumption of boric oxide in 1994 was estimated at 362 thousand metric tons.[6]

B. Generalized Process Description

1. Discussion of Typical Production Processes

There are two companies that operate borate recovery plants domestically, each using a distinctly different borate-containing source. The first plant near Searles Lake recovers borax from natural mineral-rich lake brines. The process at Searles Lake involves fractional distillation followed by evaporation. Borax is only one of the products recovered there; other products include sodium sulfate, lithium compounds, potash, and other salts. The second company, U.S. Borax, mines and processes crude and refined sodium borates, their anhydrous derivatives, and anhydrous boric acid at a plant in Boron, California.[7]

2. Generalized Process Flow Diagram

Exhibits 1 through 4 present the process flow diagrams for borate brine extraction and boric acid recovery. Exhibit 1 illustrates the processes used to prepare boric acid from ore in Boron, California. Exhibits 2, 3 and 4 present the methods used at two of the plants involved in the Searles Lake operations to recover borates from the brines deposits in California.

---

[1] Robert B. Kistler and Cahit Helvaci, "Boron and Borates," from Industrial Minerals And Rocks, 1994, p. 171.

[2] Ibid.

[3] Ibid.

[4] Ibid.

[5] Ibid., p. 183.

[6] Phyllis A. Lyday, "Boron," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, pp. 32-33.

[7] Phyllis A. Lyday, "Boron," from Minerals Yearbook Volume 1. Metals and Minerals, 1992, p. 249.

Borate Ore Processing

At the U.S. Borax facility in Boron, California, the ores are selectively mined, crushed, and stockpiled for production at two distinct facilities producing sodium borate and boric acid, respectively.

Sodium Borate Production. The principal ore used in the process, tincal, is soluble in water. After the ore is crushed, the tincal is dissolved in water. The resulting insolubles are then separated from the solution and the clarified liquor is fed to the crystallizers. Next, the crystals of sodium borate are separated from the weak solution which then can be recycled back to the dissolution step. The crystals are dried and can either be sold as borax or treated further to produce other borate materials.[8] One of the products prepared when the crystals are cooled is sodium borate decahydrate. If sodium borate pentahydrate is the desired product, the sodium borate decahydrate can be sent to further recrystallization. Anhydrous sodium borate can be produced by thermally dehydrating either the sodium borate decahydrate or sodium borate pentahydrate.[9] U.S. Borax also produces boric acid from ores, discussed below.

Boric Acid Production. Some of the solid sodium borate ore from the stockpile at the U.S. Borax facility is reacted with sulfuric acid and used as feed in the production of boric acid.[10] Exhibit 1 presents the process used to produce boric acid from the ore stockpile. Clays, sands and other impurities are also present in the ore. After the ore is crushed and ground, it is acid digested using sulfuric acid to produce two new compounds, sodium sulfate and boric acid. The clay and other insolubles are then removed from the aqueous stream. Rake classifiers separate out the larger material, while settling tanks and thickeners are used to remove the finer materials. The stream is then filtered further to remove any remaining insoluble materials. After filtration, the solution is pumped to crystallizers. In the crystallizers, the solution is cooled, forming a slurry containing solid boric acid crystals and a boric acid solution. Further filtration and centrifugation separate the solid boric acid, which can be dried and packaged for sale.[11] The remaining liquor can be further evaporated to recover a sodium sulfate co-product.

Brine Extraction

Operations at Searles Dry Lake in California involve the recovery of boron from brine deposits at three separate facilities: Trona, Argus, and Westend. Not all of these facilities are directly involved with the extraction of boron from brines. The Argus facility, for example, only produces soda ash, however, the carbonated liquid from this plant is used at the Westend plant. Borates can be recovered from concentrated brines prepared by either of two methods: carbonation or evaporation. Exhibit 2 presents the process flow diagrams for the method used at the Westend plant. Exhibit 3 presents the liquid-liquid extraction steps used at the Trona plant to process brine prepared by evaporation.

---

[8] U.S. Environmental Protection Agency, "Boron," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77-2-84.

[9] Versar, Inc., "Boron Derivatives," Multi-media Assessment of the Inorganic Chemicals Industry, Prepared for U.S. Environmental Protection Agency, August 1980, p. 2-5.

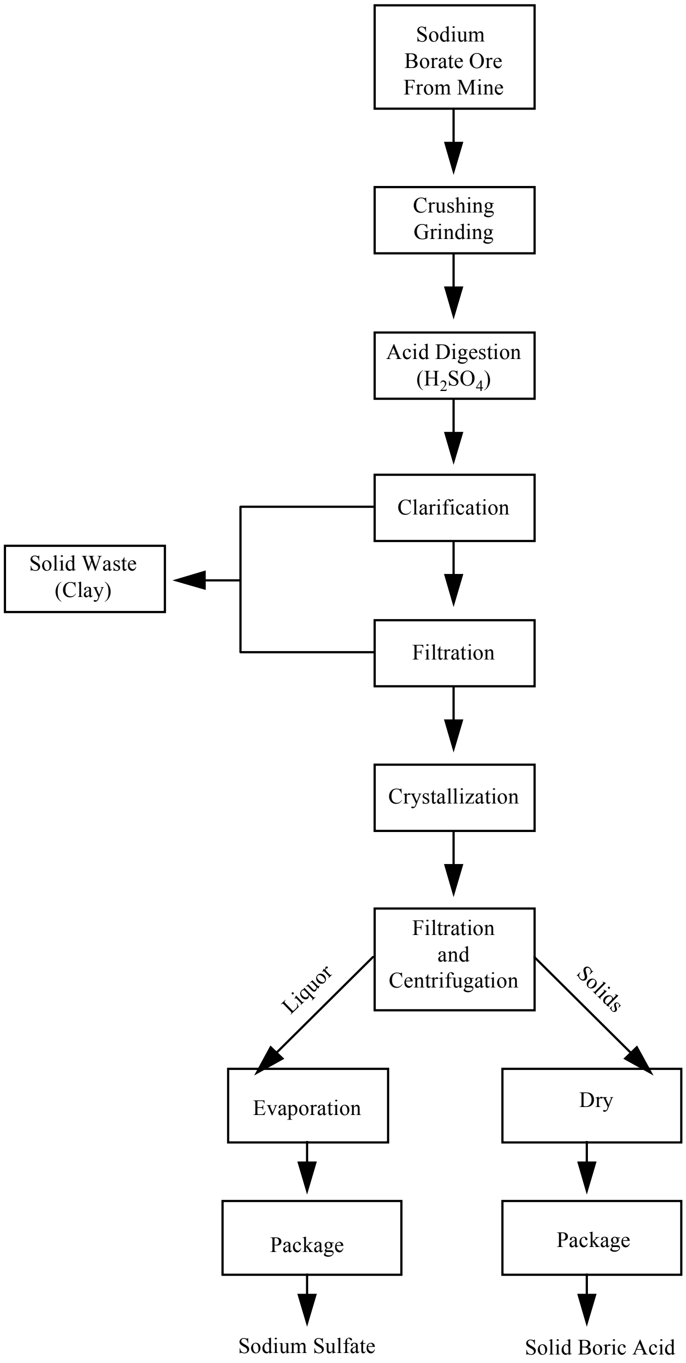
[10] Ibid.

[11] "Comments Regarding Classification of the Boric Acid Production Line at Boron Operation of United States Borax & Chemical Corporation," Memorandum and Enclosures from W.W. Cooper, Ph.D., Senior Environmental Scientist, U.S. Borax to Mr. Lynn E. Johnson, R.E.H.S., Toxic Substances Control Program. October 3 and 11, 1991.

EXHIBIT 1

BORIC ACID PRODUCTION AT BORON, CALIFORNIA

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77 - 2-84.)



Westend Plant (Carbonated Liquor). Carbonation is used at the Argus facility to supersaturate the brine solution with sodium bicarbonate. As shown in Exhibit 2, the carbonated liquor from this facility is used in combination with the brine solution at the Westend facility. The Westend facility produces anhydrous sodium borate, sodium borate pentahydrate, sodium borate decahydrate, boric acid, sodium sulfate, and sodium bicarbonate. At the Westend plant, after the sodium bicarbonate has precipitated out, the brine and carbonated liquor mixture is cooled to crystallize sodium borate decahydrate. The crude sodium decahydrate is filtered out from the liquor, which can be sent for further processing to the sulfate plant. The crude sodium borate decahydrate is then either heated to its melting point to remove hydrated water, thus producing anhydrous sodium borate, which can either be packaged and sold or sent to further processing or, acid digested using sulfuric acid to produce boric acid. Although not shown in the Exhibit 2, the sodium borate decahydrate can be redissolved and hydrated and then cooled to form either sodium borate decahydrate or sodium borate pentahydrate. If the anhydrous sodium borate is reacted with sulfuric acid instead, the resulting product is boric acid.[12]

Trona Plant (Evaporated Brine). Evaporation processes are used in the Searles Lake operations to remove sodium chloride from the brine and to concentrate other desired constituents of the brine prior to further processing. The brine is pumped initially to solar evaporation ponds and concentrated. As the brine is evaporated, the sodium chloride concentration increases until the $NaCl$ crystallizes out of solution. In addition, during the evaporation process, a rapid, controlled cooling selectively crystallizes various other salts including sodium bicarbonate and sodium sulfate. The concentrated brine from the evaporation ponds is then sent to the Trona plant for use as brine feedstock.[13]

Liquid-Liquid Extraction. The Trona facility uses a proprietary liquid-liquid extraction process to remove borate compounds from the brine (Exhibit 3). Specifically, during the process the brine is mixed with a chelating agent in a kerosene solution to remove the borates from the brine. Brine is pumped to the plant and emulsified. The emulsion is sent to a settling tank and through an API separator to break the emulsion and the extractant from the brine. The spent brine is returned to Searles Lake. The extractant is then combined with dilute sulfuric acid to convert the sodium borate to boric acid. This step produces a strip liquor containing boric acid, sodium sulfate, potassium sulfate, and sodium chloride. The strip liquor is then sent to a carbon filtration column to remove any remaining organic fractions. The filtered liquor is vacuum cooled in a boric acid crystallizer. The resulting boric acid crystals are centrifuged to separate them from the liquor, washed, dried, and packaged for sale. The resulting "mother liquor" is vacuum cooled further to crystallize the mixed sulfates, which are centrifuged to form a sulfate cake and sent to a potash production line.[14]

Potash/Borax Line. The potash/borax line is part of the Trona plant that produces pentahydrate borax, anhydrous borax, potassium chloride (potash), and potassium sulfates. As shown in Exhibit 4, brine is pumped to the plant from the evaporation ponds and sent to further evaporation. Following the evaporation, some of the concentrated brine is fed to tanks and vacuum cooled. Following this, the resultant halite is slurried, filtered, washed, and sent back to Searles Lake with the spent liquor. After the drying step, the solution is cooled and the potassium chloride that precipitates out can be sold as a product. The remaining brine is mixed with the sulfate cake from the liquid-liquid extraction process and potassium sulfate is precipitated. Following the precipitation of potassium chloride, the residual solution can be cooled to allow sodium borate pentahydrate to precipitate out from the remaining solution. This is then redissolved, hydrated, and filtered, producing dehydrated borax products (i.e., sodium borate decahydrate or sodium borate pentahydrate). The decahydrate borax can be further processed by heating to remove hydrated water, thus producing anhydrous sodium borate.[15] At Searles Lake the same processes

---

[12] California Department of Toxic Substances Control, "Searles Lake Mining Operation," Memorandum from William Soo Hoo, Chief Counsel to Van Housman, Office of Solid Waste, U.S. Environmental Protection Agency, August 1, 1991.

[13] Ibid.

[14] Ibid.

[15] Ibid.

EXHIBIT 2

BORATE BRINE PROCESSING AT SEARLES LAKE, CALIFORNIA WESTEND PLANT (CARBONATED LIQUOR FEEDSTOCK)

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77 - 2-84.)

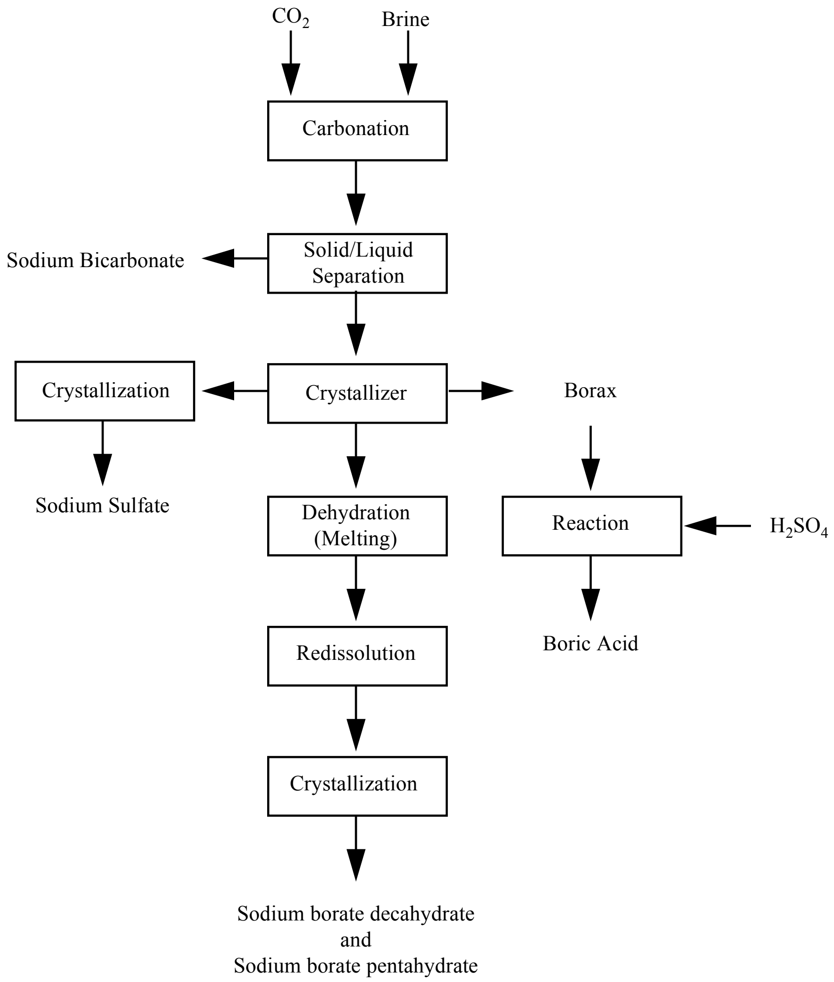


EXHIBIT 3

BORATE BRINE PROCESSING AT SEARLES LAKE, CALIFORNIA TRONA PLANT (LIQUID-LIQUID EXTRACTION)

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77 - 2-84.)

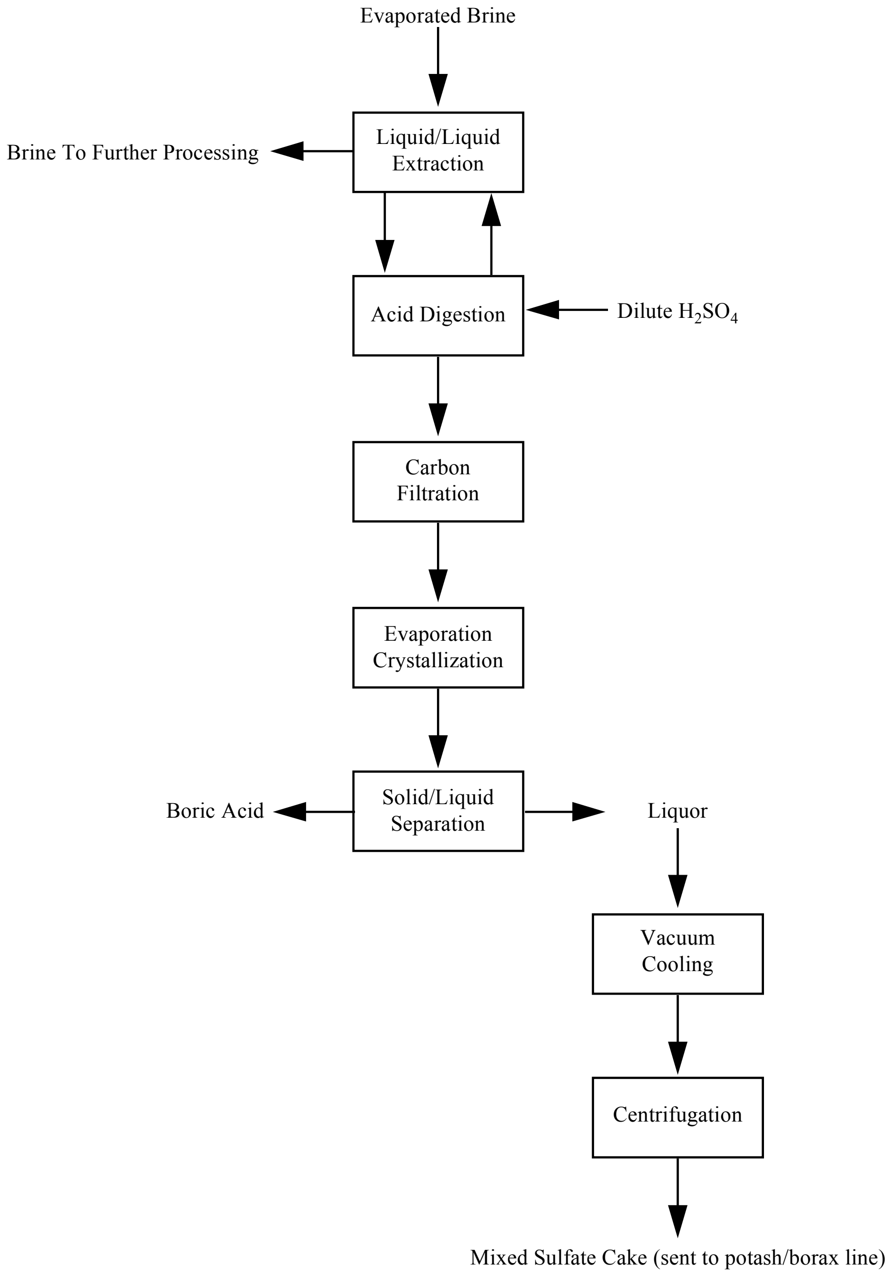
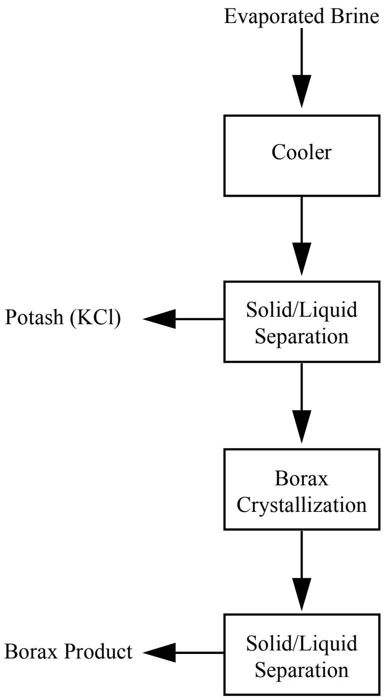


EXHIBIT 4

PRODUCTION OF POTASH AND BORAX AT SEARLES LAKE, CALIFORNIA TRONA PLANT

(Adapted from: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77 - 2-84.)



are also used to produce chemicals including sodium chloride, soda ash, and potassium chloride. These solids are precipitated from the brine solution as the solution evaporates.[16]

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

None Identified.

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 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.

EPA reviewed the processes used to produce sodium borate and boric acid from borate ores (at U.S. Borax) and from brines (at Searles Lake) and determined that the beneficiation/mineral processing line is crossed when sodium borate is digested using sulfuric acid to produce boric acid and sodium sulfate. Specifically, at the U.S. Borax facility, the beneficiation/mineral processing line occurs between the crushing and grinding of the solid sodium borate ore and acid digestion with sulfuric acid. At the Searles Lake, Westend Plant, the beneficiation/mineral processing line occurs when borax is removed from the crystallizer and reacted with sulfuric acid to produce boric acid. At the Searles Lake, Trona Plant, the beneficiation/mineral processing line occurs between the liquid/liquid extraction and acidification step. EPA identified these points in the processes as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the sodium borate occurs (sodium borate reacts with the sulfuric acid to produce two new chemicals - boric acid and sodium sulfate). Therefore, because EPA has determined that all operations following the initial “mineral processing” step in the production sequences are also considered mineral 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.

With regard to the production of potash and borax at the Searles Lake, Trona Plant, EPA determined that all of the processes may be classified as extraction or beneficiation activities. As a result, all of the wastes associated

---

[16] Versar Inc., 1980, Op. Cit., p. 2-7.

with the production of borates are considered to be extraction or beneficiation wastes and, thus, eligible for the Bevill Mining Waste Exclusion.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Borate Ore Processing

Gangue. Gangue solids are generated from the initial dissolution step during the production of sodium borate decahydrate. In 1980, these waste were reported as generally inert insolubles, although they contained 0.08 percent natural arsenic mineral realgar. The solid wastes from ore residues and evaporation wastes were sent to on-site lined evaporation ponds.[17]

Wastewater. Process wastewater from washing contains dissolved borax and other salts may be sent to lined evaporation ponds.[18]

From Brines

Spent Solvents, Crud, and Waste Brine. The brine extraction process generates waste brine and spent solvents. The plant extract or crud generated during the recovery of boron from brines at the Trona plant contains arsenic and halogens and is ignitable.[19]

Particulate Emissions. Particulates generated from drying operations are collected in dry bags and recycled. In 1980, the wastes were generated at approximately 14 kg per kkg of product.[20]

Boric Acid Production

Spent Sodium Sulfate. Crystallization produces sodium sulfate. 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.

2. Mineral Processing Wastes

Boric Acid Production

Spent Clay and Other Insolubles. No information is available.

Waste Liquor and Underflow Mud. Some of the liquor remaining after the boric acid is filtered off contains arsenic. In 1980, one site reported that the arsenic was present as a natural impurity in the ore used to make the sodium pentahydrate. Another site reported returning the arsenic-containing wastes to the original subterranean brine source. One commenter reported a combined generation rate for waste liquor and mud of 150,000 tons/yr and indicated that the TCLP analysis performed for arsenic is consistently well below 5 ppm.[21]Low, medium, and high

---

[17] Ibid.

[18] Versar, Inc., 1980, Op. Cit., p. 2-7.

[19] California Department of Toxic Substances Control, Memorandum from William Soo Hoo, Director, to Sylvia K. Lowrance, Office of Solid Waste, U.S. Environmental Protection Agency, May 8, 1992.

[20] Versar, Inc., 1980, p. 2-5.

[21] U.S. Borax. Comments submitted in response to the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

annual waste generation rates were estimated as 300 metric tons/yr, 150,000 metric tons/yr, and 300,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for arsenic. This waste is recycled and formerly was classified as a spent material. Existing data and engineering judgment suggest that waste liquor and underflow mud material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Spent Sodium Sulfate. Crystallization following acid digestion produces sodium sulfate. 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.

D. Non-uniquely Associated Wastes

There are no non-uniquely associated wastes in this specific sector. However, standard 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants.

E. Summary of Comments Received by EPA

New Factual Information

One commenter addressed the boron sector report (COMM 86). The commenter provided some technical corrections and some specific line edits for the report. These comments have been included, as appropriate, in the revised boron sector report.

Sector-specific Issues

None.

BIBLIOGRAPHY

"Boron." Kirk-Othmer Encyclopedia of Chemical Technology 4th ed. Vol. 4. 1992 pp. 360-364.

"Boron." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. Office of Solid Waste, U.S. Environmental Protection Agency. p. 2-77-2-84.

California Department of Toxic Substances Control. Memorandum from William Soo Hoo, Director, to Sylvia K. Lowrance, Office of Solid Waste, U.S. Environmental Protection Agency. May 8, 1992.

California Department of Toxic Substances Control. "Searles Lake Mining Operation," Memorandum from William Soo Hoo, Chief Counsel to Van Housman. Office of Solid Waste. U.S. Environmental Protection Agency. August 1, 1991.

"Chemicals From Brine." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992. p. 823.

"Comments Regarding Classification of the Boric Acid Production Line at Boron Operation of United States Borax & Chemical Corporation," Memorandum and Enclosures from W.W. Cooper, Ph.D., Senior Environmental Scientist, U.S. Borax to Mr. Lynn E. Johnson, R.E.H.S., Toxic Substances Control Program. October 3 and 11, 1991.

Kistler, Robert B. and Helvaci, Cahit. "Boron and Borates." From Industrial Minerals and Rocks. 1994. 6th ed. p. 171-186.

Lyday, Phyllis A. "Boron." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 32-33.

Lyday, Phyllis A. "Boron." From Minerals Yearbook Volume 1. Metals and Minerals. 1992. pp. 247-252.

BROMINE (from brines)

A. Commodity Summary

Bromine is a member of the halogen family of elements. Elemental bromine is highly reactive and occurs in nature only as bromide compounds. Sources of bromide include sea water, subterranean brines, saline lakes, oil and gas well brines, and evaporate chloride minerals including halite (NaCl), sylvite (KCl), and carnallite.[1] Bromide compounds are used in fire retardants, agriculture, petroleum additives (ethylene dibromide is an antiknock additive in leaded gasoline), and well drilling fluids. Domestic consumption of bromide was estimated to be 287 million kilograms in 1994.[2]

According to the U.S. Bureau of Mines, companies in Arkansas and Michigan were responsible for all elemental bromine production in 1993. Exhibit 1 presents the names, locations, and types of operations employed by the facilities involved in the production of bromine. The Dow Chemical Company (Dow) in Ludington, Michigan is not directly involved in the purification of bromine; however, Dow removes bromine from its magnesium brines because it is an impurity in their magnesium operation. Dow ships the recovered bromine to the Ethyl Corporation in Arkansas to be purified and prepared for sale.

EXHIBIT 1

SUMMARY OF BROMINE FACILITIES

Facility Name	Locations	Type of Operations
Dow Chemical Company	Ludington, MI	Brine extraction prior to production of magnesium chloride. Sent to Ethyl Corporation for purification.[a]
Ethyl Corp.	Magnolia, AR	Brine Extraction
Great Lakes Chemical Corp.	El Dorado, AR (3 plants)	Brine Extraction

[a] Personal communication between Jocelyn Spielman, ICF Incorporated and Phyllis Lyday, U.S. Bureau of Mines. October 5, 1994.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Commercial bromine production processes involve the oxidation of bromide to bromine, using chlorine as the oxidant. Most of the liberated bromine remains dissolved in the brine. The brine is then stripped of bromine and the bromine is then recovered from the stripping agent. Further purification by distillation is often a final step in the process.[3] Exhibits 2 and 3 present the generalized process flow diagrams for the production of bromine and each of the steps is described in further detail below.

2. Generalized Process Flow Diagram

---

[1] M.J. Wilhelm and K.C. Williams, "Bromine Resources," from Industrial Minerals and Rocks, 1994, 6th ed. p. 187.

[2] Phyllis Lyday, "Bromine," Mineral Commodity Summaries, 1995, U.S. Bureau of Mines, p. 34.

[3] "Chemicals from Brines," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, p. 823.

As shown in Exhibits 2 and 3, there are three principal steps involved in the production of bromine from brines: (1) skimming and acid stripping; (2) bromine extraction from the aqueous solution; and (3) condensation and purification of the bromine. Variations on this production process generally differ in the extraction step.[4]

Skimming and Acid Stripping

Skimming and Hydrocarbon Removal. The first step in bromine recovery is skimming the oil from the well brines and removing hydrocarbons. Following the skimming process, the brine solution undergoes acidification and stripping with the addition of sulfuric acid. Spent hydrogen sulfate (H_2S) is stripped from the solution and sent to sodium sulfate (Na_2S) recovery.

Acidification and Chlorination. Although bromine occurs in the form of bromide in sea water and in natural brine deposits containing chloride, additional chlorine may be added to oxidize bromide to bromine. Chlorine is used because it has a higher reduction potential than bromine.[5] As shown in Exhibit 3, acidification with H_2SO_4 can be part of the recovery process.

Extraction of Bromine

Bromine is extracted or stripped from the chlorinated solution using either steam (steaming out) or air (blowing out process). Steam is used when the concentration of bromine in the brine is greater than 1,000 ppm. The advantage of this method is that bromine can be condensed directly from the steam. Air is used when the bromine source is sea water because large volumes of stripping gas would be required, thereby making the use of steam too expensive. However, when air is used, bromine must be trapped in an alkaline or reducing solution to concentrate it.[6]

Steaming Out. As shown in Exhibit 3, brine is pumped to the top of a granite absorption tower filled with ceramic packing material. Steam and chlorine are pumped in from the bottom of the tower. The bromine is oxidized by the chlorine as it falls through the ceramic material. The chlorine replaces the bromine in the brine and the gaseous bromine rises to the top of the tower with the steam, where it is condensed to a liquid.[7]

Blowing Out. Generally, sea water contains bromine as either magnesium bromide or sodium bromide. When the source of the bromine is sea water, the blowing out method is used to strip the bromine from the brine. In the blowing out method, prior to reaching the tower, raw sea water is acidified with sulfuric acid followed by the addition of chlorine. Air is drawn into the base of the tower and rises as the bromine descends. Air containing bromine passes to the absorption tower, where the bromine reacts with sulfur dioxide to form hydrogen bromide.[8]

---

[4] "Bromine," Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed., Vol. IV, 1992, p. 548.

[5] Ibid., pp. 548-549.

[6] Ibid.

[7] Phyllis Lyday, "Bromine," from Minerals Yearbook Volume 1. Metals and Minerals, 1992, p. 259.

[8] Ibid., pp. 259-260.

EXHIBIT 2

BROMINE EXTRACTION FROM WELLS

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1992, pp. 547 - 550.)

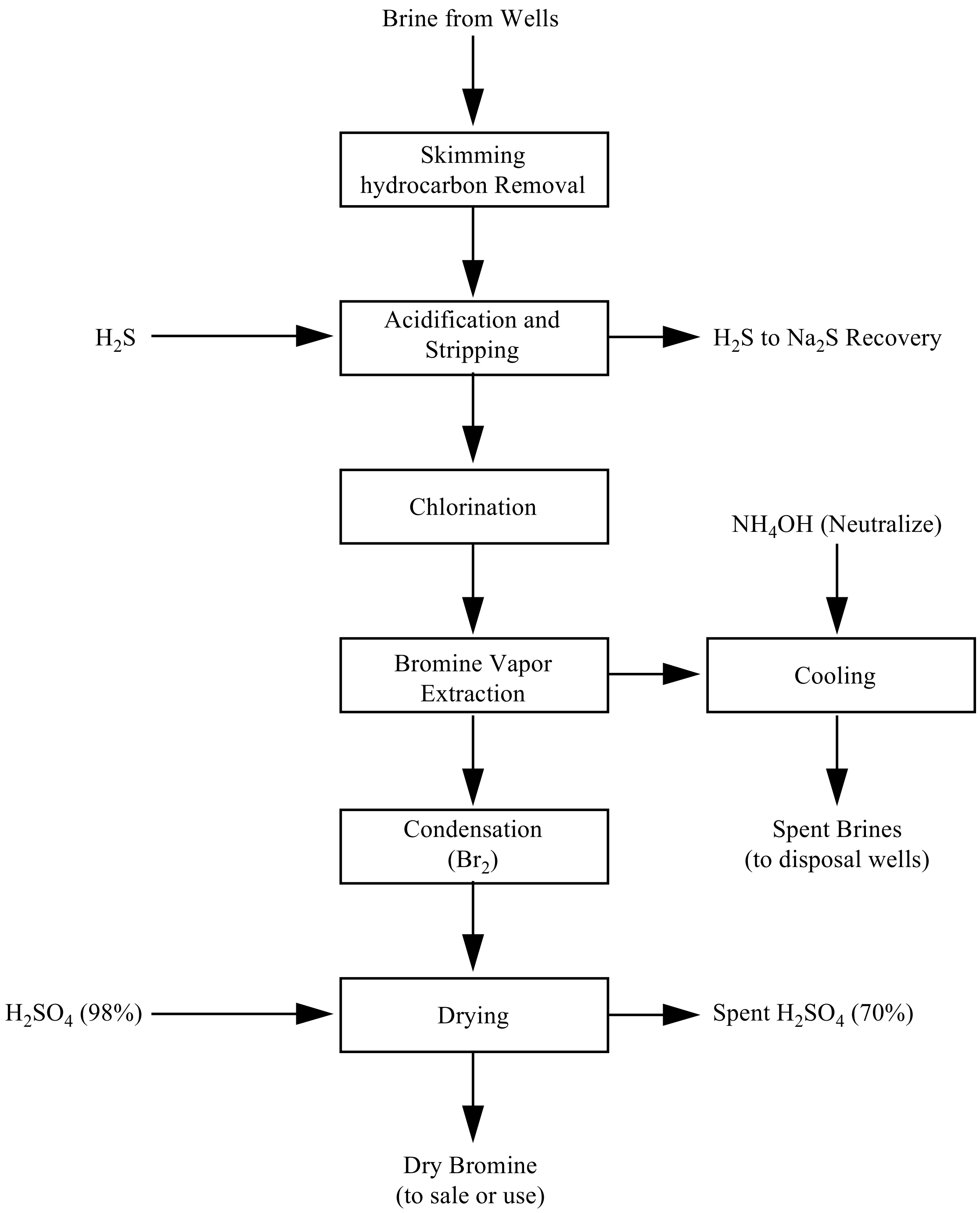
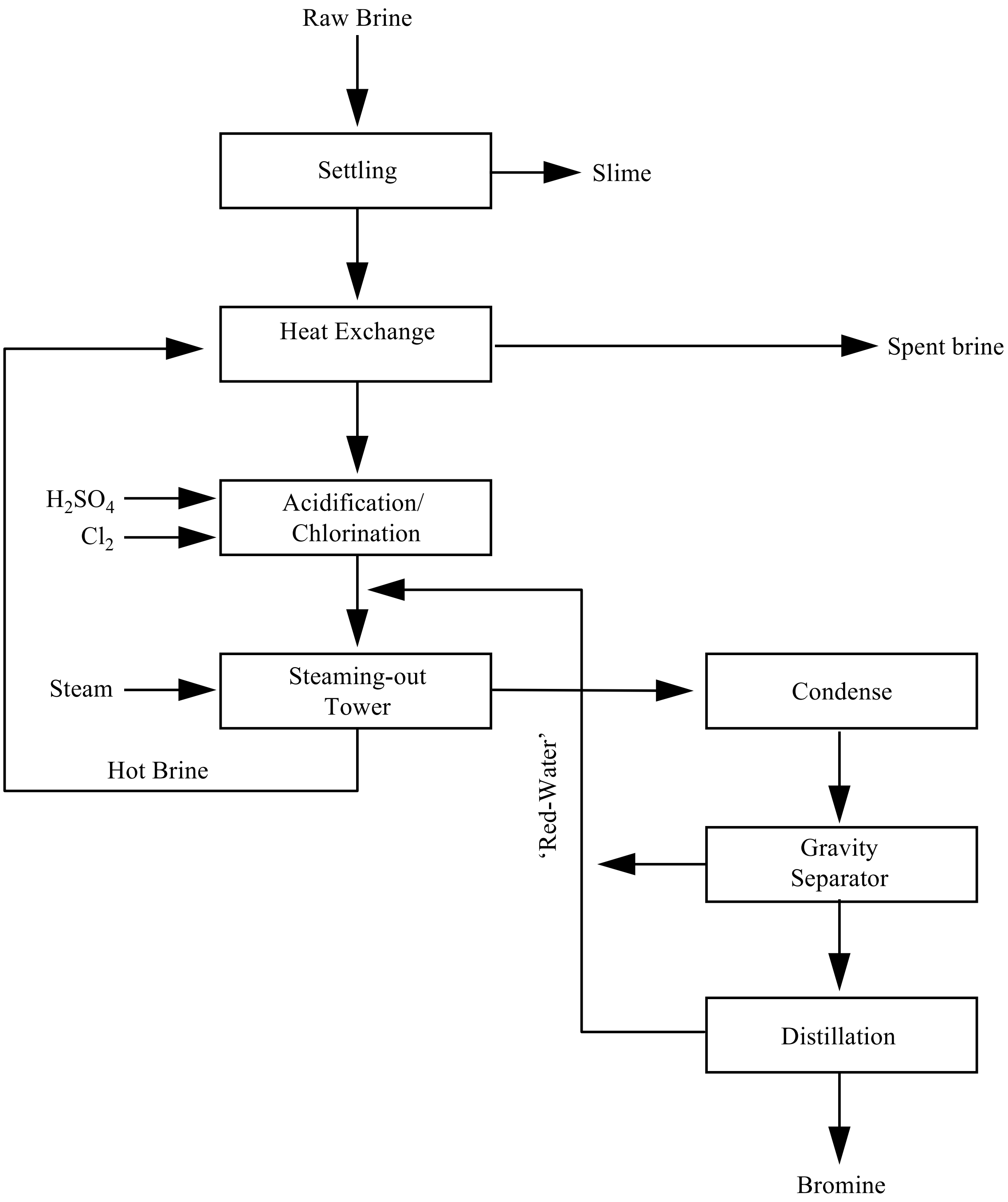


EXHIBIT 3

STEAMING OUT PROCESS FOR RECOVERY OF BROMINE FROM HIGH BROMIDE BRINES

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1992, pp. 547 - 550.)



Condensation and Purification of Bromine

Following either method of extraction, the brine stream can be separated from the emerging gas stream containing free bromine. The gas is then cooled to condense water and bromine. The spent brine from the vapor extraction process can be neutralized with the addition of NH_4OH and cooled. After removing the ammonia, spent brine can either be used in other processes, sent to disposal wells, or returned to the source.

Condensation. The condensation process varies depending on the extraction process used. After the steaming out method, the bromine is condensed directly from the steam. Following the blowing out method, the bromine can be separated by adding acid to the extracted solution and distilling with steam. The gaseous stream containing bromine can be condensed and purified.[9] The liquid resulting from the condensation step is separated and the recovered water is recycled back to the absorption tower.

Purification. Typically, following condensation the bromine is dried with sulfuric acid and then purified by distillation. As shown in Exhibit 2, a 98 percent H_2SO_4 can be added, resulting in the generation of a spent solution containing 70 percent H_2SO_4. The resultant dry bromine is sent to sale or use.

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

Recent patents describe a single-stage vacuum and a double-stage vacuum process for bromine recovery which modify existing recovery procedures. The single-stage vacuum is similar to the steaming out process, except that it is carried out under subatmospheric pressure. The double-stage vacuum re-strips the tail brines from the first stripping under greater vacuum. The use of a vacuum in these modified process eliminates the need to heat the brine with steam by matching the vapor pressure of the brines. Additional benefits of the vacuum modification include increased tower capacity, reduction in chlorine use, and reduction in the amount of lime needed to treat the spent brine.[10]

4. Beneficiation/Processing Boundary

EPA does not have enough information on this mineral commodity sector to determine where in the production sequence mineral processing begins.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Waste Brine. Waste liquids are generated during the vapor extraction and once these are neutralized and cooled they can either be sent to disposal wells or returned to the brine deposit. These spent brines may contain ammonia from the neutralizing step. Alternatively, waste brine can also be generated during the steaming out process in the form of a hot bromine-free liquor that emerges from the bottom of the tower. This liquor is neutralized with lime and discharged to a waste pond.[11]

Slimes. Slimes are generated from the settling step in the steaming out process.

Water Vapor. Some chlorine and water vapor are captured at the top of the tower during steaming out.

---

[9] Ibid., p. 260.

[10] "Bromine," Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. IV, 1992, p. 550.

[11] Phyllis Lyday, 1992, Op. Cit., p. 260.

2. Mineral Processing Wastes

Bromine is used to make several organic chemical compounds in operations in close proximity to the brine extraction process. EPA does not have enough information to determine where in the production sequence mineral processing begins.

D. Non-uniquely Associated Wastes

Non-uniquely associated and 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, and acidic tank cleaning wastes. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

BIBLIOGRAPHY

"Bromine." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992. pp. 547-550

"Chemicals From Brine." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. Vol. IV. 1992. p. 823.

Lyday, Phyllis. "Bromine." From Minerals Yearbook Volume 1. Metals and Minerals. 1992. pp. 259-270

Lyday, Phyllis. "Bromine." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 34-35

Personal Communication with Phyllis Lyday, Bromine Specialist, U.S. Bureau of Mines. October 5, 1994.

U.S. Environmental Protection Agency. "Bromine." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. Office of Solid Waste, pp. 2-85 - 2-88.

Wilhelm, M.J. and Williams, K.C. "Bromine Resources." From Industrial Minerals and Rocks. 6th ed. 1994. pp. 187-189.