

LEAD

A. Commodity Summary

Lead ore is mined domestically in several states. Seven lead mines in Missouri, along with mines in Alaska, Colorado, Idaho, and Montana yield most of the total ore production. (BOM, 1995, p. 94) In 1990, primary lead was processed at three integrated smelter-refineries in Glover, Boss, and Herculaneum, Missouri, a smelter in East Helena, Montana, and a refinery in Omaha, Nebraska. (U.S. EPA, 1990, p. 10-1) The integrated plant in Boss, Missouri is no longer operational. (BOM, 1995, p. 94; personal communication with Kenneth Buckley, Doe Run Company, April 18, 1994)

Expected yield from domestic mines was 365,000 metric tons (mt) of lead (in concentrates) in 1994. Expected primary lead production from domestic and imported ores totaled 330,000 mt and 30,000 mt, respectively, in 1994. In addition, domestic secondary production from lead scrap totaled 880,000 mt in 1993, up from 842,000 mt in 1989. United States lead reserves totaled 10 million mt in 1993. (BOM, 1995, pp. 94-95)

In 1990, total domestic primary lead production capacity was estimated to be 577,000 mt per year. However, this figure represented the aggregate of one smelter, one refinery, and three integrated smelter-refineries. (U.S. EPA, 1990, p. 10-2) Only four primary lead facilities are currently operational (BOM, 1995, p. 94). Exhibit 1 presents the names and locations of the lead mining, smelting, and refining facilities located in the United States. The lead mines shown were active as of 1990. As available, Exhibit 1 also presents information on potential site factors indicating whether the facility is located in a sensitive environment.

Lead was consumed by approximately 200 domestic manufacturing plants in 1993. The major end use was in transportation, with about 70 percent consumed in the manufacture of batteries, fuel tanks, solder, seals, and bearings. Electrical, electronic, and communications uses (including batteries), ammunition, TV glass, construction (including radiation shielding), and protective coatings consumed more than 25 percent. The remainder was used in ballast and weights, ceramics and crystal glass, tubes and containers, type metal, foil, wire, and specialized chemicals. Overall, lead acid batteries accounted for about 80 percent of lead consumption. (BOM, 1995, pp. 94-95).

B. Generalized Process Description

1. Discussion of Typical Production Processes

Primary lead facilities in the United States employ pyrometallurgical methods to produce lead metal. Treatment of lead ores begins with crushing, grinding, and concentrating. Pelletized concentrates are fed with other materials (e.g., smelter material formerly classified as byproducts, coke) to a sinter unit. The sinter process agglomerates fine particles, drives off volatile metals, converts metal sulfides to metal oxides and sulfates, and removes sulfur as sulfur dioxide (SO₂). The exit gas stream from the sinter machine is cleaned and routed to an acid plant to produce concentrated sulfuric acid. The sintered material is then introduced into a blast furnace along with coke and fluxes. (SAIC, 1991b, p. 2)

Inside the blast furnace, the lead is reduced (smelted), and the molten material separates into four layers: lead bullion; "speiss" and "matte," two distinct layers containing recoverable quantities of copper and other metals; and blast furnace slag. The speiss and matte are sold to operators of copper smelters for metals recovery, and the slag is stored and partially recycled. The bullion is drossed (agitated and cooled in a drossing kettle) to remove lead and other metal oxides, which form a layer of dross that floats on the bullion. The dross, composed of roughly 90 percent lead oxide, along with other elements, is skimmed and sent to a dross furnace for recovery of non-lead mineral values. Slag and residual lead from the dross furnace are returned to the blast furnace. The remaining material is sold to operators of copper smelters for recovery of copper and precious metals. The lead bullion may then be decopperized before being sent to the refining stages. (U.S. EPA, 1990, p. 10-2)

EXHIBIT 1

SUMMARY OF LEAD MINING, SMELTING, AND REFINING FACILITIES

Facility Name	Location	Type of Operations	Poter	ntial Factors Related to Sensitive Environments
ASARCO	East Helena, MT	Smelting		ity is partially located within a 100-yr. floodplain, a and, and a fault area
				roximately 3,500 residents live within one mile of the ity boundary
			• The bound	nearest residence is located 100 yards from the facility dary
			(slag	h from the bottom of special mineral processing waste) management units to water in the uppermost usable fer is 38 feet
				aquifer is located between the ground surface and the rmost usable aquifer; this aquifer is contaminated
			slag	ace water monitored upstream and downstream of the management units has exceeded national ambient ice water quality criteria for lead
			exce	bient air monitored near the slag management units has eded the NAAQS for lead (arithmetic 3-month average, ug/m^3)

Facility Name Type of Operations Potential Factors Related to Sensitive Environments Location ASARCO Glover, MO Smelting and Refining ۲ Facility is partially located in karst terrain One residence is located within one mile of the facility, • approximately one-half mile from the facility boundary Depth from the bottom of the slag management units to • water in the uppermost usable aquifer is 5 feet at its highest seasonal level and 30 feet at the lowest seasonal level Ground water monitoring wells located downgradient from ٠ the slag management units have shown exceedances of the NPDWS for cadmium and the NSDWS for zinc and total dissolved solids Omaha, NE Refining • Facility is partially located in a 100-yr. floodplain and a fault ASARCO area Approximately 4,400 residents live within one mile of the • facility boundary ۲ The nearest residence is located approximately threequarters of a mile outside the facility boundary • Ambient air monitored near the slag management units has exceeded the NAAOS for lead (arithmetic 3-month average, $1.5 \,\mu g/m^3$) ASARCO Leadville Unit Leadville, CO Mining

EXHIBIT 1 (Continued)

EXHIBIT 1 (Continued)

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
Doe Run Co.	Herculaneum, MO	Smelting and Refining	 Facility located within 100-yr. floodplain Approximately 1,000 residents live within 1 mile of the facility boundary Nearest residence is 21 yards from the facility boundary The active on-site surface impoundment is located 142 yards from the nearest residence outside the facility boundary The depth from the bottom of the on-site solid waste management units to water in the uppermost usable aquifer is approximately 80 feet, at its highest and lowest levels.
Fourth of July Mine	Yellow Pine, ID	Extraction	
Galena Mine	Mullan, ID	Extraction	
Glass Mine	Pend Oreille County, WA	Extraction	
Greens Creek Mine	Admiralty Island, AK	Extraction	
Lucky Friday Mine	Mullan, ID	Extraction	
Magmont Mine	Bixby, MO	Extraction	
Montana Tunnels Mine	Jefferson County, MT	Extraction	
Red Dog Mine	Kotzebue, AK	Extraction	
Sunnyside Mine	Silverton, CO	Extraction	
Sweetwater Mine	Bunker, MO	Extraction	

EXHIBIT 1 (Continued)

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
Viburnum Mines (6 mines):	Iron, Reynolds, and Washington Counties,	Extraction and Beneficiation	
Brushy Creek Casteel	MO		
Fletcher Viburnum 28			
Viburnum 29 Buick			
West Fork Mine	Bunker, MO	Extraction	

Lead refining operations generally consist of several steps, including (in sequence) softening, desilverizing, dezincing, bismuth removal, and final refining. Various other saleable materials also may be removed from the bullion during these steps, such as gold and oxides of antimony, arsenic, tin, and copper. During final refining, lead bullion is mixed with various fluxes and reagents to remove remaining impurities (e.g., calcium, magnesium, and lead oxide). The lead is cooled and the impurities rise to the surface and are removed as slag; this slag may be recycled to the blast furnace. The purified bullion is then cast into ingots. (U.S. EPA, 1990, pp. 10-2, 10-3)

Recently, researchers at the former U.S. Bureau of Mines developed bench-scale alternative processes for producing lead. These techniques consist of hydrometallurgical methods (e.g., leaching and solvent extraction). Results of this research are discussed below, under <u>Hydrometallurgical Beneficiation</u>.

2. Generalized Process Flow Diagram

Exhibit 2 contains a process flow diagram that illustrates the steps used in primary lead production, and includes several waste streams. Process variations are indicated by dashed arrows. Slag from primary lead processing is a special waste, and hence is not subject to regulation under RCRA Subtitle C. In addition, material flow diagrams showing the source and fate of materials for ASARCO's Glover, MO and Helena, MT facilities are provided in Exhibits 3 and 4, respectively.

Extraction and Beneficiation

Lead is mined (extracted) almost exclusively in underground operations, though a few surface operations do exist. The use of underground or surface mining techniques depends on the proximity of the ore body to the surface, and the individual characteristics of each ore body determine the exact mining method. (U.S. EPA, 1993b, p. 14)

Lead ores are beneficiated in a series of steps, beginning with milling, a multi-stage crushing and grinding operation. Crushing is usually a dry operation that utilizes water sprays to control dust. Primary crushing is often performed at the mine site, followed by additional crushing at the mill. The crushed ore is mixed with water and initial flotation reagents to form a slurry, then ground in rod and ball mills. The slurried ore may be ground in autogenous mills (in which the ore acts as the grinding medium) or semi-autogenous mills (in which steel balls are added to the ore). Hydrocyclones are used between each grinding step to separate coarse and fine particles; coarse particles are returned to the mill for further size reduction. (U.S. EPA, 1993b, pp. 15-16)

Ground ores are further beneficiated by flotation. Flotation is a technique by which particles of a mineral or group of minerals are made to adhere preferentially to air bubbles by the action of a chemical reagent. During or after milling, ore may be treated with chemicals (known as conditioners and regulators) to modify the pH of the ore pulp prior to flotation. Once conditioned, the ore is then slurried with fresh or salt water and various types of chemical reagents that promote separation of different metals (collectors, frothers, activators, and depressants). Flotation typically occurs in a series of steps, and multiple floats may be required to remove different mineral values from a polymetallic ore. The residues (tailings) from one float are often used as the feed for a subsequent float to concentrate another metal. (U.S. EPA, 1993b, pp. 16-20)

Flotation typically occurs in a series of cells, arranged from roughers to scavengers to cleaners (roughers make a coarse separation of values from gangue, and scavengers remove smaller quantities of the remaining values). Froth from the cleaner cells is sent to thickeners, in which the concentrate is thickened by settling. The thickened concentrate is pumped out, dewatered by a filter press, and dried. The concentrate is then fed to a sintering operation. (U.S. EPA, 1993b, pp. 18-23)

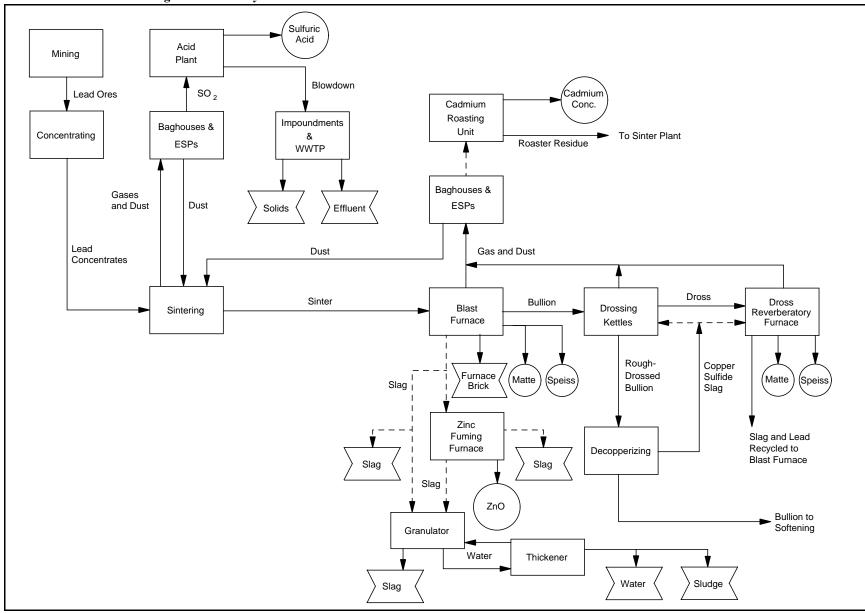


Exhibit 2. Process Flow Diagram of Primary Lead Production in the U.S.

Exhibit 2 (Continued).

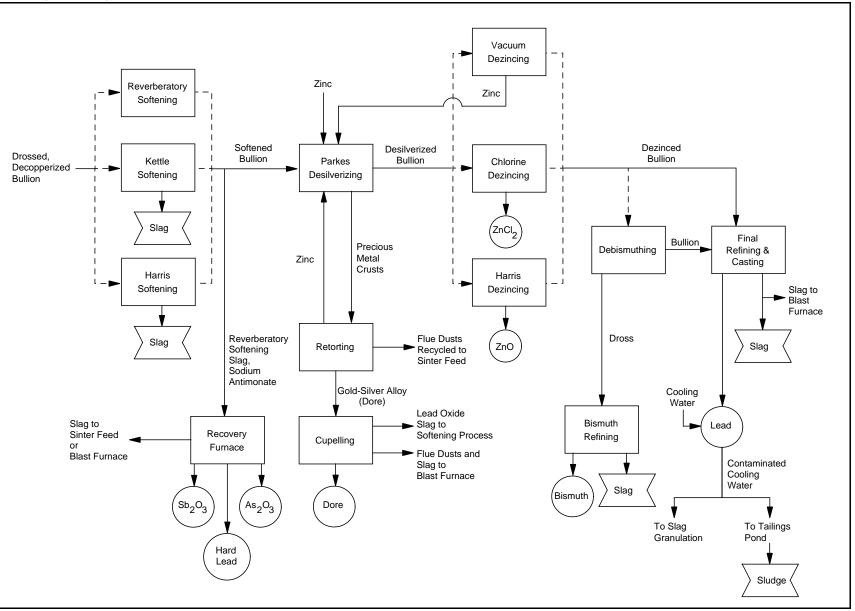


EXHIBIT 3

MATERIALS FLOW TO AND FROM ASARCO, GLOVER, MISSOURI

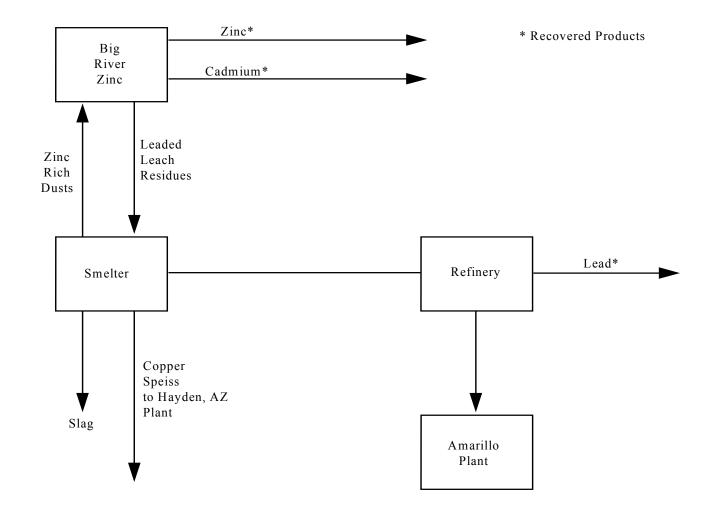
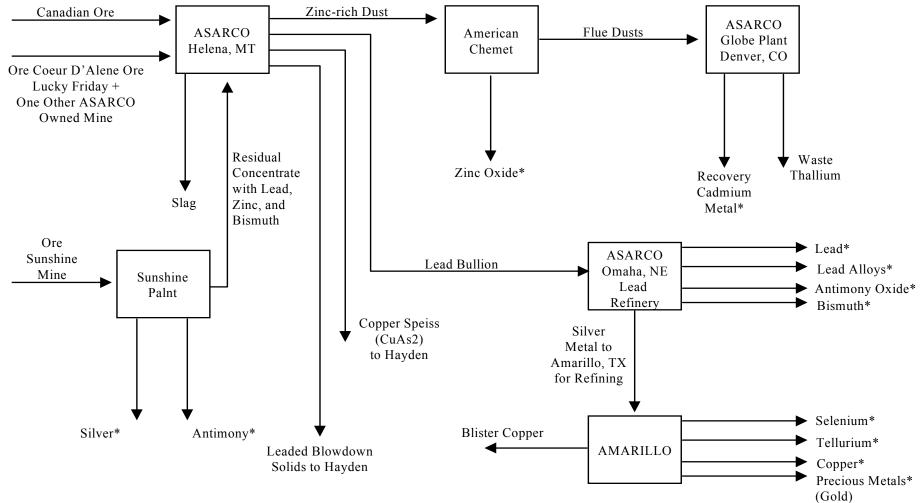


EXHIBIT 4

MATERIALS FLOW TO AND FROM ASARCO, HELENA, MONTANA



* Recovered Products

Liquid overflow from the thickeners, containing wastewater, flotation reagents, and dissolved and suspended mineral products, may be recycled or sent to a tailings pond. Wastes from the rougher, scavenger, and cleaning cells are collected and sent to a tailings thickener. Overflow from the tailings thickener (wastewater containing high solids and some reagent) is often recycled to the flotation cells, and the underflow (containing remaining gangue, unrecovered lead materials, chemical reagents, and wastewater) is pumped to a tailings pond. Clarified water from the tailings pond may be recycled to the mill. (U.S. EPA, 1993b, p. 20)

Sintering

Sintering occurs on a traveling grate furnace known as a "sinter machine." Ore concentrates are mixed with fluxes, recycled sinter, and flue dusts. After moisture is added, the mixture is pelletized and fed to the sinter machine. Inside the furnace, the mixture fuses into a firm porous material, known as sinter. Sintering converts metallic sulfides to oxides, removes volatile metals, and converts most sulfur to sulfur dioxide (SO₂). Product sinter is sized for use in the blast furnace, and fine sinter particles are recycled to the sintering machine feed mixture. (PEI, 1979, pp. 232-234; U.S. EPA, 1993b, p. 23) Sintering is the final beneficiation step in the primary production of lead (U.S. EPA, 1990).

Particulates emitted during sintering are collected using either baghouses or electrostatic precipitators (ESPs) and recycled. (PEI, 1979, p. 234) The sinter plant off-gases are reacted in a contact acid plant to produce concentrated sulfuric acid. Operation of the acid plant may generate wastewaters from scrubbing of the inlet SO_2 stream (acid plant blowdown). These wastewaters may be routed to treatment plants or recycled. Treatment often involves neutralization with lime, followed by thickening, filtering, and recycling of the effluent. (U.S. EPA, 1980, pp. 31-34)

Blast Furnace

Sinter is charged to a blast furnace with coke, limestone, and other fluxing materials and smelted. During smelting, metallic oxides are reduced to metal. The mixture separates into as many as four distinct liquid layers, depending on sinter composition, from the bottom up: lead bullion (94 to 98 percent lead by weight, and other metals); speiss (arsenides and antimonides of iron and other metals); matte (copper sulfides); and slag (flux and metal impurities). The matte and speiss layers are sold to operators of copper smelters for metal recovery, and crude bullion is fed to drossing kettles. Depending on its zinc content, the slag may be either disposed of or sent to a zinc fuming furnace. (PEI, 1979, pp. 235-6; U.S. EPA, 1990, p. 10-2)

Inside a zinc fuming furnace, blast furnace slag and coal are mixed with air and heated. Zinc oxide (ZnO) and lead oxide in the slag are reduced and volatilized, and then oxidized near the top of the furnace, forming particulates. The particulates are recovered in a baghouse and sent to a zinc refinery for zinc recovery. The residual slag is disposed of as described below. (PEI, 1979, pp. 237)

Disposal practices are similar for blast furnace slag and residual slag from zinc fuming operations. The slag may be either dumped while hot onto a slag pile, or granulated with cooling water and then dumped. Some plants dewater the slag; the granulating water may be cleaned in thickeners and recycled to the granulation unit. The granulation water also may be discharged. Particulates emitted from the blast furnace are collected in a baghouse or ESP, and can be recycled to the sinter feed or treated for cadmium recovery. If the cadmium content of the flue dust reaches 12 percent by weight, the dust is roasted to recover cadmium. Fume emissions from the roasting operation are cooled and recovered as a product (cadmium concentrate), and the residue is recycled to the sinter feed. Blast furnace off-gases also contain small quantities of SO₂ that may need chemical scrubbing, possibly generating a waste. (PEI, 1979, pp. 236-253; U.S. EPA, 1980, p. 52; U.S. EPA, 1990, p. 10-3)

Drossing

Lead bullion recovered from the blast furnace is fed to a drossing kettle, agitated with air, and cooled to just above its freezing point. Oxides of lead, copper, and other impurities form a dross on the surface that is skimmed. Sulfur may be added to the drossing kettle to enhance copper removal, forming copper sulfide (Cu_2S) that is skimmed off with the dross. Skimmed dross is sent to the dross reverberatory furnace for additional processing; off

gases and particulates from the drossing kettle are combined with blast furnace off-gases for treatment. The lead product is known as "rough-drossed" lead. (PEI, 1979, pp. 237-8; U.S. EPA, 1980, p. 47; U.S. EPA, 1990, p. 10-2)

Dross is fed into the reverberatory furnace with pig iron, silica sand, and possibly lime rock, and smelted. The products separate into four layers: slag, matte, speiss, and molten lead. The slag and lead are returned to the blast furnace, and the matte and speiss are removed separately, granulated, and shipped to copper smelters for metals recovery. Off gases from the reverberatory furnace are combined with blast furnace off gases. (PEI, 1979, p. 238; U.S. EPA, 1990, p. 10-2)

Decopperizing

Rough-drossed lead bullion is decopperized before refining, occasionally in the same kettle used for the drossing operation. Sulfur is added while the lead is agitated, forming a layer of Cu_2S that is skimmed and recycled either to the dross reverberatory furnace or the drossing kettle (in two-stage drossing). (PEI, 1979, pp. 238-9; U.S. EPA, 1990, p. 10-2)

Softening

Softening removes elements that make lead hard, and is accomplished using one of three techniques: reverberatory softening, kettle softening, or Harris softening. In reverberatory softening, air is blown through molten lead, causing metals such as antimony, arsenic, tin, and copper to form oxides. The oxides form a slag that is skimmed and can be treated for metals recovery. Lead oxide (litharge) may be added to lead with hardness greater than 0.3 to 0.5 weight percent antimony equivalent to increase the oxidation rate. (PEI, 1979, pp. 239-40)

Kettle softening can be used only on bullions with hardness less than or equal to 0.3 percent. The bullion is melted and agitated, and sodium hydroxide (NaOH) and niter (NaNO₃) are added as fluxes. The fluxes react with impurities to form salts such as sodium antimonate (NaSbO₃), resulting in a slag that is skimmed off and discarded. (PEI, 1979, pp. 240)

Harris softening utilizes the same reagents as kettle softening and also requires low levels of impurities. Harris softening occurs in two stages. The first stage is identical to kettle softening and generates a slag for further processing. During the second step, the slag is crushed and leached with hot water to dissolve the sodium salts. The solution is cooled to precipitate sodium antimonate (NaSbO₃), which is filtered from solution and processed to recover antimony. Calcium salts of arsenic and tin are then recovered separately by precipitation and sold. (PEI, 1979, p. 240)

Kettle softening slags and leached slags from Harris softening are discarded with blast furnace or zinc fuming furnace slags. Reverberatory softening slag and sodium antimonate from Harris softening may be treated to recover metal values. To recover antimonial lead ("hard lead"), the softening slag is heated in a furnace with a reducing agent and fluxes, reducing lead and antimony. The antimonial lead is recovered and sold; the slag may be sold if it is rich in tin or recycled to either the sinter feed or the blast furnace. To recover antimonial trioxide (Sb_2O_3) , the sodium antimonate is heated to volatilize antimonial trioxide and arsenic trioxide (As_2O_3) , and these compounds are separated by selective condensation. The antimony trioxide and arsenic trioxide are sent to antimony and arsenic producers, respectively. The furnace residue is recycled to the blast furnace. Arsenic trioxide becomes a waste if it cannot be sold. (PEI, 1979, pp. 240-1)

Parkes Desilverizing

This process is used to recover gold and silver from softened lead bullion. Gold and silver removal are usually performed in two steps. First, a small amount of zinc is added to the molten bullion to generate a skim with high gold content, because zinc alloys preferentially with gold and copper. After this layer is removed, more zinc is added to form a zinc-silver skim, which is also removed. Other metallic impurities, including arsenic, must be removed prior to this operation. The gold and silver-bearing crusts are retorted in furnaces to recover zinc, leaving behind a purified gold-silver alloy (Doré). The zinc can be recycled to the process. Flue dusts from the furnaces can

be cooled and collected with baghouses and recycled to the sinter feed. (PEI, 1979, pp. 241-2; U.S. EPA, 1980, p. 64)

Gold and silver are recovered by melting the alloy in a cupel and introducing air as well as oxidizing agents. Several successive slags are produced, most of which are recycled to the blast furnace. Slag containing lead oxide is recycled to the softening process. The remaining gold-silver alloy is cast and sold. Exhaust gases can be cooled and routed to baghouses; collected dusts are then recycled to the blast furnace. Desilverized lead is sent to the dezincing process. (PEI, 1979, p. 242; U.S. EPA, 1980, p. 65)

Dezincing

Excess zinc added during desilverizing is removed from lead bullion using one of three methods: Vacuum dezincing; chlorine dezincing; or Harris dezincing. During vacuum dezincing, a vacuum is drawn on the molten lead by submerging an inverted bell into the agitated metal. Vaporized zinc condenses on the inner surface of the bell, and solid zinc is scraped from the dome after the vacuum is broken. The zinc is recycled to desilverizing. In chlorine dezincing, molten desilvered lead is reacted with chlorine gas, forming a surface layer of zinc chloride contaminated with small amounts of lead chloride. The layer is skimmed, treated with zinc for lead recovery, and sold as ZnCl₂. In Harris dezincing, caustic soda (NaOH) saturated with lead oxide is mixed with molten lead in a reaction chamber, reducing lead oxide to lead and oxidizing zinc to zinc oxide. The zinc oxide reacts with the caustic to form sodium zincate. The contents of the reaction chamber are fed to a granulator and then reacted with hot water. Sodium zincate hydrolyzes to zinc oxide and sodium hydroxide. Zinc oxide (ZnO) precipitates from solution, and is filtered, dried, and sold. The sodium hydroxide solution is evaporated to anhydrous caustic, which is recycled. Antimony may also be recovered from spent granulated caustic. Dezinced lead is sent to a debismuthing step or to the final refining stage. (PEI, 1979, pp. 242-3; U.S. EPA, 1980, pp. 67-71)

Debismuthing

Desilvered and dezinced lead bullion containing greater than 0.15 percent by weight bismuth must be processed to remove bismuth before casting. Calcium and magnesium are mixed with molten lead, forming ternary compounds (e.g., CaMg₂Bi₂) that rise to the surface when the lead is cooled to just above its melting point, forming a dross, which is then skimmed. The purified lead is sent to a final refining step. Bismuth is recovered by melting the dross in a furnace and then injecting chlorine gas. Magnesium, calcium, and lead contained in the dross form chlorides, which are skimmed from the molten bismuth as a slag. Air and caustic soda are added to the melt to oxidize any remaining impurities, forming a slag which is also removed. The nearly pure bismuth is cast and sold, and the slags are disposed along with blast furnace slag. (PEI, 1979, p. 244; U.S. EPA, 1980, p. 74)

Final Refining and Casting

Lead bullion from dezincing or debismuthing is reacted with caustic soda and niter to remove lead oxide, calcium, and magnesium before final casting. A slag forms, which is removed and recycled to the blast furnace or disposed. The final refined lead is reheated and cast into ingots or pigs, which are cooled by direct contact with water. The cooling water becomes contaminated with particulate lead and lead oxides and can be recycled for use in slag granulation or treated. Treatment may include liming to precipitate solids. (PEI, 1979, pp. 244-5; U.S. EPA, 1980, p. 75; U.S. EPA, 1990, p. 10-2)

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

Hydrometallurgical Beneficiation

The U.S. Bureau of Mines developed a laboratory-scale method that combines oxidative leaching and electrowinning to recover lead metal and elemental sulfur from lead sulfide (PbS) concentrates. Lead sulfide concentrates were leached with fluosilicic acid (H_2SiF_6), using hydrogen peroxide (H_2O_2) and lead dioxide as oxidants. After filtration to separate the lead fluosilicate (PbSiF₆) leach solution and the sulfur-containing residue, the PbSiF₆ was electrowon to produce lead metal and H_2SiF_6 . The H_2SiF_6 was recycled to the leaching step, and sulfur was recovered from the leach residue by solvent extraction. (Lee et al., 1990, p. 2)

Since H_2O_2 proved to be an expensive oxidant, the Bureau of Mines researchers developed and tested a pressure leaching method for lead sulfide concentrates that utilizes oxygen gas (O₂) in place of H_2O_2 . This method also utilizes H_2SiF_6 as the leach solution and electrowinning to recover lead metal. The researchers conducted several experiments, varying O₂ pressure, catalysts, temperature, acid concentration, and time. Lead metal with 99.96 percent purity was recovered by electrowinning from as-leached solution. Lead metal with at least 99.99 percent purity was recovered by electrowinning from leach solutions purified using either of two chemical methods. Finally, elemental sulfur was recovered from the leach residue by solvent extraction, and methods were developed to recover other valuable metals (e.g., Ag, Zn, and Cu) from the final residue. (Lee et al., 1990, pp. 2-3, 6)

The Bureau of Mines also conducted research on the leaching of mixed lead-zinc sulfide concentrates, followed by electrowinning, to produce lead metal. Lead-zinc sulfide concentrates were leached with H_2SiF_6 , using either H_2O_2 or pure oxygen (O_2) as an oxidant. Lead was selectively leached and zinc remained in the solid residue. All experiments were performed on a bench-scale level. (Beyke, 1991, pp. 219-221)

The researchers conducted leaching experiments at both atmospheric pressure and at increased pressures. At atmospheric pressure and at 95 degrees C, 85 percent of the lead was leached from the concentrate, and 87 percent of the zinc remained in the residue. Using pressure leaching, 78 percent of the lead was recovered from the concentrate while 80 percent of the remained in the residue. After filtering the leach residue, the researchers recovered pure lead metal by electrowinning from a purified PbSiF₆ electrolyte produced from the leach solution. The electrowinning step produced H₂SiF₆ that could be recycled to the leaching stage. In addition, once lead was removed, the original leach solution could also be recycled to the leaching stage. (Beyke, 1991, pp. 219, 236) No information was available on whether these hydrometallurgical methods developed by the Bureau of Mines have been expanded to a pilot-scale or demonstration-scale process.

In the early 1980's, another experimental hydrometallurgical process was developed by the Bureau of Mines in cooperation with four U.S. primary lead producers. Galena (PbS) concentrate was leached with ferric chloride solution, and the lead chloride leachate was reduced by a process known as "fused salt electrolysis." The process generated a lead product that required no further refining. The leachate was also processed to yield 99 percent pure sulfur without sulfur dioxide emissions. The Bureau of Mines and the four primary lead producers concluded 18 months of testing in 1981, using a 500-pound-per-day demonstration unit. (BOM, 1985, p. 439) No information was available on whether this method is used today.

4. Beneficiation/Processing Boundary

EPA established the criteria for determining which wastes arising from primary mineral production arise from mineral processing operations and which 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 substantial 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.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between sintering and smelting in a blast furnace. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where the sintered ore is chemically reduced and physically destroyed to lead metal. 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) following the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated downstream of the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

As discussed above (and shown in Exhibit 2), the extraction, beneficiation, and processing of lead generate several solid, liquid, and gaseous wastes, that may be recycled or refined prior to disposal. The generation, treatment, and management of these wastes are discussed below.

Attachment 2 contains a summary of the operational history of and environmental contamination documented at a former lead production site that is now on the Superfund National Priority List.

1. Extraction/Beneficiation Wastes

Wastes generated from the extraction and beneficiation of lead from lead-bearing ores are exempt from RCRA Subtitle C and the scope of BDAT determinations. These wastes are discussed below.

Waste Rock

Lead mining operations generate two types of waste rock, overburden and mine development rock. Overburden results from the development of surface mines, while mine development rock is a material, formerly labeled as a byproduct, of mineral extraction in underground mines. The quantity and composition of waste rock generated at lead mines varies greatly among sites, but these wastes will contain minerals associated with both the ore and host rock. Overburden wastes are usually disposed of in unlined piles, while mine development rock is often used on-site for road or other construction. Mine development rock also may be stored in unlined on-site piles or in underground openings. Waste rock piles may be referred to as mine rock dumps or waste rock dumps. Runoff and leachate from waste rock dumps may contain heavy metals, and these piles may generate acid drainage if sufficient amounts of sulfide minerals and moisture are present. EPA found no information on the quantities of waste rock generated annually. (U.S. EPA, 1993b, pp. 25-26, 28, 105)

Mine Water

Mine water includes all water that collects in surface or underground mines, due to ground water seepage or inflow from surface water or precipitation. While a mine is operational, water may be pumped out to keep the mine dry and allow access to the ore body. The water may be pumped from sumps within the mine or from a system of wells. The recovered water may be used in beneficiation, pumped to tailings or mine water ponds, or discharged to surface water. EPA has no information on the quantities of mine water generated annually at all lead mining/milling locations. One facility, however, the Doe Run mine/mill facility in Fletcher, MO, generates an average of 4.63 million gallons of mine water per day, which is pumped to an on-site mine water pond. (U.S. EPA, 1993b, pp. 26, 109)

The composition and quantity of mine water varies among mining sites, and the chemical composition of mine water depends on the geochemistry of the ore body and the surrounding area. Mine water also may be contaminated with small quantities of oil and grease from mining equipment and nitrates from blasting operations.

When a mine is closed and pumping stops, the mine may fill with water. Through aeration and contact with sulfide minerals, the accumulated water can acidify and become contaminated with heavy metals. (U.S. EPA, 1993b, pp. 26, 28)

Concentration Wastes

Beneficiation operations used to concentrate mineral ores generate various types of wastes. Flotation systems discharge tailings consisting of liquids and solids. The solids include mostly gangue material and small amounts of unrecovered lead minerals. The liquid component consists of water, dissolved solids, and reagents not consumed during flotation. The reagents may include cyanide, which is used as a depressant in certain flotation operations. Flotation wastes are generally sent to tailings ponds, in which solids settle out. The clarified liquid may be recycled to the mill or discharged, provided it meets water quality standards. The characteristics of flotation tailings vary considerably, depending on the ore, reagents, and processes used. Other types of beneficiation wastes include waste slurries from milling and gravity concentration steps. These wastes also are disposed of in tailings impoundments. Site-specific data on tailings generation were available for one facility, the Doe Run mine/mill facility in Fletcher, MO. This facility generates approximately 1.4 million tons of tailings per year. (U.S. EPA, 1993b, pp. 28-29, 105) EPA has no information on the quantities of tailings generated annually at all lead mining/milling locations.

2. Mineral Processing Wastes

Smelting and Refining operations generate numerous solid, liquid, and gaseous wastes. Slag generated during primary lead smelting and refining is classified as a special waste, and is exempt from RCRA Subtitle C controls and, consequently, BDAT determinations. Descriptions of the other wastes follow.

Process Wastewater

Primary lead production facilities generate various process wastewaters, including slag granulation water, sinter plant scrubber water, plant washdown water, and plant run-off. (PEIA, 1984, p. 3-12; Doe Run Company, 1989b; Asarco, 1989a-c) Approximately 4,965,000 metric tons of process wastewater are generated annually (ICF, 1992). EPA/ORD sampling data, presented as Attachment 1, indicates that this waste stream exhibits the characteristic of toxicity (arsenic, cadmium, lead, and selenium). In addition, the waste stream may be toxic for mercury, based on best engineering judgment.

Site-specific information on process wastewater management practices were available only for one facility. At the Doe Run plant in Herculaneum, MO, a mixture consisting of granulated blast furnace slag and the accompanying slag granulation water are sent to a wastewater treatment plant (WWTP-3) for dewatering. The granulation water is sent to a second wastewater treatment plant (WWTP-1) for additional treatment such as pH adjustment and clarification. Other process wastewaters, including dross reverberatory furnace slag granulation water; sinter plant scrubber water; clothes washing liquids; plant runoff; and washdown from the sinter plant, blast furnace, drossing kettles, dross reverberatory furnace, refinery, baghouses, and pavement are sent directly to WWTP-1 for treatment. (Doe Run Company, 1989b) This waste was formerly classified as a spent material and may be partially recycled, based on best engineering judgment.

Surface Impoundment Waste Solids

Since 1980, the primary lead smelting industry has altered its management of process wastewaters, and the solids that settle from those wastewaters. The three operating primary lead smelters (Asarco in Glover, MO; Asarco in East Helena, MT; and Doe Run in Herculaneum, MO) no longer use surface impoundments and completely

recycle all wastewater treatment solids. The industry now uses tanks to settle solids from lead process wastewater. The collected solids are removed from the tanks for reintroduction to the smelting process.¹

Spent Furnace Brick

Primary lead smelters generate used refractory brick during the reconstruction of blast furnaces. Some plant operators crush and recycle the brick to the blast furnace, while others discard the brick in on-site disposal piles. (PEIA, 1984, p. 3-10) Approximately 1,000 metric tons of spent furnace brick are generated annually (ICF, 1992).

The November 1984 PEI Associates study contains results of EP toxicity tests on two samples of used refractory brick. The plants from which the samples were taken were not identified. Both samples exhibited EP toxicity for lead (1,230 mg/L and 63.3 mg/L). (PEIA, 1984, pp. 5-16 to 5-17) This waste stream is recycled and was formerly classified as a spent material.

WWTP Liquid Effluent

Wastewater treatment plants are utilized in primary lead production for treatment of acid plant blowdown and other wastes, including slag granulation water, plant washdown, and run-on/run-off. These liquids may receive some treatment prior to the WWTP, consisting of settling in lined basins. Treatment in the WWTP often consists of lime neutralization and settling. Treated effluents may be either recycled within the plant or discharged through NPDES outfalls. (PEIA, 1984, pp. 3-6 to 3-7; pp. 3-12 to 3-15; SAIC 1991b, pp. 8-10)

At the Doe Run plant in Herculaneum, MO, a portion of the WWTP-1 liquid effluent is recycled to the sinter plant for use as scrubber water; the rest of the effluent is discharged through an NPDES outfall. Slag granulation water from WWTP-3, as well as neutralized acid plant blowdown from another treatment plant (WWTP-2) are routed to WWTP-1 for further treatment. (Doe Run Company, 1989b)

Approximately 3,500,000 metric tons of WWTP liquid effluent are generated annually (ICF, 1992). The NIMPW Characterization Data Set contains data indicating that this waste stream may exhibit a hazardous characteristic (ICF, 1992). Attachment 1 includes data from EPA/ORD sampling and shows that the waste stream exhibits the characteristic of corrosivity. However, since the effluent is not managed in a land-based unit, and is either recycled within the plant or discharged through a regulated outfall, this waste stream may not meet the definition of a solid waste under RCRA, in which case it would not be subject to Subtitle C regulation. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for lead. This waste stream is fully recycled and was formerly classified as a sludge.

WWTP Sludges/Solids

Wastewater treatment sludges/solids are now completely recycled and reintroduced into the smelting process. Thus, these materials are not considered to be within the definition of solid waste.²

Surface Impoundment Waste Liquids

Unlined surface impoundments are gradually being replaced by lined, engineered impoundments or wastewater treatment systems. At the ASARCO facility in Glover, MO, existing unlined surface impoundments are

¹ National Mining Association. Comment submitted in response to the <u>Supplemental Proposed Rule</u> <u>Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. January 25, 1996. and The Doe Run Company. Comment submitted in response to the <u>Second Supplemental Proposed Rule Applying</u> <u>Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. May 12, 1997.

² National Mining Association. Comment submitted in response to the <u>Supplemental Proposed Rule</u> <u>Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. January 25, 1996.

no longer used. Plant wastewaters (e.g., slag granulation water) are now clarified in two rubber-lined concrete settling tanks. Overflow from the second tank collects in a lined retention pond; overflow from the retention pond is treated with lime in a wastewater treatment plant and discharged through an NPDES outfall. In addition, the Doe Run plant in Herculaneum, MO now continuously treats wastewaters that were formerly routed to unlined surface impoundments. (SAIC 1991b, pp. 9-12) The remaining operational primary lead smelting facility, Asarco, East Helena, MT, is reconstructing its wastewater management system. The modified system will allow the plant to discontinue its use of surface impoundments. (U.S. EPA, 1994, pp. 22-23) The Asarco primary lead refinery in Omaha, NE does not utilize any surface impoundments. (Asarco, 1989c)

The Newly Identified Mineral Processing Waste Characterization Data Set indicated that approximately 5,314,000 metric tons of surface impoundment liquids are generated annually. (ICF, 1992) However, this figure may no longer be accurate, due to changes in management practices for primary lead plant wastewaters and the closure of surface impoundments at several facilities. We used best engineering judgment to determine a waste generation rate of 1,100,000 mt/yr. The waste generation rate is more than one million metric tons per year per facility due to comingling of numerous waste streams.

The November 1984 PEI Associates study contains data on 4 samples of surface impoundment liquids collected at various smelters (the plants were not identified). EP toxicity tests were conducted on one sample of slag granulation water and one sample of granulated slag-pile run-off from separate impoundments at the same site. EP tests were also conducted on two water samples from impoundments at separate facilities that receive miscellaneous plant wastewaters (run-off, washdown, etc.). The samples of slag granulation water and slag pile run-off water did not exhibit EP toxicity. Both samples from impoundments containing miscellaneous plant waters exhibited EP toxicity for lead (69.1 mg/L). The other sample, from an impoundment that collects acid plant cooling water, sintering plant and concentrate storage area washdown, plant run-off, and personnel change-house water exhibited EP toxicity for arsenic (69.8 mg/L). (PEIA, 1984, p. 5-14 to 5-16) The NIMPW Characterization Data Set contains additional data indicating that this waste stream may exhibit a hazardous characteristic (ICF, 1992). We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of toxicity (arsenic, cadmium, and lead). This waste was formerly classified as a sludge.

Acid Plant Blowdown

This acidic liquid waste is generated from wet scrubbing of the sulfur dioxide gas stream that enters the contact acid plant from the sinter plant. The purpose of the scrubbing is to remove particulate matter from the gas before the gas is used to produce sulfuric acid. Some scrubbing solution is continuously purged to prevent a buildup of solids in the recirculating scrubber water. The purged solution is known as acid plant blowdown. (PEIA, 1984, p. 3-6; U.S. EPA, 1994, p. 22)

Typically, acid plant blowdown (APB) is treated through some combination of lime neutralization and settling. Some facilities treat APB with lime at the acid plant and then pump the resulting slurry to an on-site WWTP. Other plants mix APB with other wastewaters, allow settling to occur, and then treat the clarified liquid with lime. Solids derived from blowdown treatment are often recycled to the sinter feed preparation or to the smelter, while the liquids are either discharged through NPDES outfalls or recycled within the plant. The solids may also be sold for metals recovery. (PEIA, 1984, pp. 3-6, 3-7; SAIC, 1991b, pp. 8-12; ICF, 1989, pp. 2-3) Approximately 556,000 metric tons of acid plant blowdown are generated annually (ICF, 1992).

At the Doe Run facility in Herculaneum, MO, acid plant blowdown is neutralized in a wastewater treatment plant (WWTP-2), and the neutralized blowdown is sent to a second wastewater treatment plant (WWTP-1) for additional neutralization and clarification. (Doe Run Company, 1989b)

The November 1984 PEI Associates study contains results of EP toxicity tests on two samples of limeneutralized acid plant blowdown collected at different smelters (the plants were not identified). Each sample exhibited the characteristic of EP toxicity, one for lead (22 mg/L) and the other for arsenic (24.4 mg/L) and cadmium (2.61 mg/L). The study also contains the results of an EP toxicity test on one sample of blowdown treatment material formerly labeled as sludge. The material sample exhibited EP toxicity for arsenic (304 mg/L) and cadmium (155 mg/L). (PEIA, 1984, pp. 5-14, 5-16, 5-17) The NIMPW Characterization Data Set contains additional data indicating that this waste stream may exhibit a hazardous characteristic (ICF, 1992). Attachment 1 includes EPA/ORD sampling data which shows that this waste stream exhibits the characteristics of toxicity (arsenic, cadmium, lead, and selenium) and corrosivity. We used best engineering judgment to determine that this waste stream may exhibit the characteristic of toxicity for mercury. This waste is recycled and was formerly classified as a spent material.

Slurried APC Dust

At one integrated smelter/refinery, ESP dust and scrubber underflow from the cleaning of sinter plant offgases destined for the acid plant were slurried into a thickener. The thickened solids were placed on the slag dump along with other solids for air drying, and eventually recycled to the sinter feed preparation step. The facility at which this practice occurred was not identified. (PEIA, 1984, p. 3-5) Approximately 7,000 metric tons of slurried APC dust are generated annually. (ICF, 1992)

The 1989 RTI Survey for the Doe Run facility in Herculaneum, MO, suggests another source of this waste stream. The flow diagram included with the survey shows that baghouses are used to collect particulates in off-gases generated by the sinter plant, blast furnace, and the dross reverberatory furnace. The diagram also shows that a liquid waste (process wastewater) known as "department washdown" flows from the baghouses to an on-site wastewater treatment plant (WWTP-1), for treatment that includes pH adjustment and clarification. (Doe Run Company, 1989b) However, the survey does not specify whether or not the department washdown contains entrained baghouse dust.

The November 1984 PEI Associates study contains results of EP toxicity tests on one sample of solids from sumps that collect slurried ESP dust, "cyclone underflow," and plant washdown. The study adds that the solids are stockpiled on-site before they are recycled. The sample exhibited the characteristic of EP toxicity for lead (959 mg/L) and cadmium (22 mg/L). (PEIA, 1984, pp. 5-16, 5-17) This waste stream is fully recycled and was formerly classified as a sludge.

Solids in Plant Washdown

At some plants, washdown liquids from storage and blending areas (sinter feed preparation) are typically sent to concrete sumps and allowed to settle. The water is recycled, and the solids are stored to allow dewatering and drying. The collected solids are returned to sinter feed piles or blending bins. (PEIA, 1984, p. 3-2)

Alternatively, plant washdown may be sent to on-site wastewater treatment plants. At the Doe Run facility in Herculaneum, MO, washdown from the sinter plant, blast furnace, drossing kettles, dross reverberatory furnace, refinery, and baghouses is sent along with other wastewaters, to a single treatment plant (WWTP-1) for neutralization, clarification, and other treatment. Dewatered material formerly labeled as sludge from this treatment plant is returned to the sinter feed. (Doe Run Company, 1989b) This washdown may contain entrained solids and particulates.

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 Plant Sludge

This waste stream was identified in a 1987 draft of an EPA Report to Congress on mineral processing operations. The report provided an estimated annual generation rate of 14,600 metric tons per year, but did not include any specific information on how the waste was generated or its composition. (ICF, 1987, pp. 3-41 to 3-44) According to a process flow chart provided in the 1989 RTI survey, this waste stream was recycled to the sintering machine. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity. This waste was formerly classified as a sludge.

Solid Residues

This waste stream was identified in the 1989 RTI Survey for the Doe Run facility in Boss, MO. The waste consisted of two types of material, "rice paddy" and "filter cake," and the facility reported generating the waste as a residue from its sinter plant. (Doe Run Company, 1989a) According to the RTI Survey, this waste was recycled to the sintering process. The Boss primary lead facility is no longer operational, and it is not known whether this waste is generated by any other primary lead production facilities. This waste stream has a reported annual waste generation rate of 400 metric tons/yr. The NIMPW Characterization Data Set contains data indicating that this waste stream may exhibit a hazardous characteristic. (ICF, 1992) We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristic of toxicity for lead. This waste was formerly classified as a by-product.

Baghouse Dust

Several components of the primary lead production process generate off-gases that contain dusts or particulates. Particulates in off-gases from sintering operations are collected by baghouses and ESPs. These dusts are returned to the sinter feed preparation. Particulates in off-gases from the blast furnace, dross kettle, the dross reverberatory furnace, and silver/gold recovery operations are also collected using baghouses and ESPs and are recycled to the sinter feed. (PEI, 1979) Approximately 46,000 metric tons of baghouse dust are generated annually (ICF, 1992).

At the Doe Run facility in Herculaneum, MO, baghouses are used to collect particulates in off-gases generated by the sinter plant, blast furnace, and the dross reverberatory furnace. However, ultimate destination of the dust is unclear from the survey. The facility flow diagram indicates that a liquid waste (process wastewater) known as "department washdown" flows from the baghouses to an on-site wastewater treatment plant (WWTP-1). However, the survey does not specify whether or not the department washdown contains entrained baghouse dust. (Doe Run Company, 1989b)

Dust collected in baghouses at one of ASARCO's facilities (a smelter) accumulates in cellars beneath the baghouse. The baghouse is taken off-line every two to four weeks so that the dust can be removed from the cellar. This material is then stored in a containment area to await further processing.³

The November 1984 PEI Associates study contains results of EP toxicity tests on one sample of baghouse dust. The plant from which the sample was taken, the source of gas entering the baghouse, and the sample location were not identified. This sample exhibited EP toxicity for cadmium (3,580 mg/L) and lead (61.7 mg/L). (PEIA, 1984, pp. 5-16 to 5-17) This waste stream is fully recycled and was formerly classified as a sludge.

Cooling Tower Blowdown

The 1989 RTI Survey for the Doe Run facility in Herculaneum, MO indicated that an on-site surface impoundment received Acid Plant, Dross Furnace, and Blast Furnace cooling tower blowdown. (Doe Run Company, 1989b) However, the Herculaneum facility no longer uses surface impoundments as part of its wastewater management system. It is not known whether any of these wastes are still generated at the Herculaneum facility.

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 Nickel Matte

³ ASARCO Incorporated. Comment submitted in response to the <u>Second Supplemental Proposed Rule</u> <u>Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. May 12, 1997.

The 1989 RTI Survey for the Doe Run facility in Herculaneum, MO indicated that the dross plant reverberatory generates a product known as nickel matte. (Doe Run Company, 1989b) It is not known whether this material is still generated at the Herculaneum facility. 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.

SVG Backwash

The 1989 RTI Survey for the Doe Run facility in Herculaneum, MO indicated that an on-site wastewater treatment plant (WWTP-1) received a liquid inflow known as "SVG Backwash." (Doe Run Company, 1989b) It is not known whether this material is still generated at the Herculaneum facility. 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.

Baghouse Fume

The 1989 RTI Survey for the Doe Run facility in Herculaneum, MO indicated that in 1988, the sinter plant received approximately 30,000 short tons of "baghouse fume" as a material input, but does not describe the composition of this material or identify its source. (Doe Run Company, 1989b) No information is available on whether this material is a waste stream, or its current annual generation rate. In addition, it is not known whether this material is still generated at the Herculaneum facility.

Baghouse Incinerator Ash

At most primary lead production facilities, used bags from baghouses are fed to the blast furnace. At one integrated smelter/refinery, however, the bags are washed and then incinerated in a small, on-site industrial incinerator. The incinerator ash is landfilled on-site, and the bag washwater is sent to an on-site wastewater treatment plant. (PEIA, 1984, pp. 3-5 to 3-6) The facility was not identified.

The November 1984 PEI Associates study contains results of EP toxicity tests on one sample of ash from an incinerator that burned baghouse bags and other plant waste. The plant from which the sample was taken was not identified. This sample exhibited EP toxicity for cadmium (5.76 mg/L) and lead (19.2 mg/L). (PEIA, 1984, pp. 5-16, 5-17) Although no published information regarding waste generation rate was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 300 metric tons/yr, 3,000 metric tons/yr, and 30,000 metric tons/yr, respectively.

Stockpiled Miscellaneous Plant Waste

This waste stream consists of a mixture of consolidated refractory brick, slag, matte, sweepings, and other cleanup wastes. The November 1984 PEI Associates study contains results of EP toxicity tests on one sample of this materials, which includes refractory brick, slag, matte, "cleanups," and plant "sweepings." The sample exhibited the characteristic of EP toxicity for lead (1,380 mg/L) and cadmium (29.4 mg/L). (PEIA, 1984, pp. 5-16, 5-17) The plant from which the sample was obtained was not identified. Although EPA found no published information regarding waste generation rate, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 400 metric tons/yr, 88,000 metric tons/yr, and 180,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may be partially recycled and was formerly classified as a spent material.

D. Non-uniquely Associated Wastes

Non-uniquely associated 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), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and waste oil and other lubricants. (U.S. EPA, 1993b, p. 110)

The Asarco facilities in East Helena, MT, Glover, MO, and Omaha, NE each generate less than 100 kg of solvents per month. These facilities hold RCRA identification numbers and are classified as conditionally exempt small quantity generators. At the Glover and Omaha facilities, used solvents are collected by Safety-Kleen for disposal. (ASARCO, 1989a-c) The Doe Run facility in Herculaneum, MO also holds a RCRA I.D. number, but no information was available on the types of hazardous wastes that are generated. (Doe Run, 1989b)

E. Summary of Comments Received by EPA

New Factual Information

Two commenters indicated that the three operating primary lead smelters (Asarco in Glover, MO; Asarco in East Helena, MT; and Doe Run in Herculaneum, MO) no longer use surface impoundments and completely recycle all wastewater treatment solids (COMM 58, 1019). This new information was used to update the Surface Impoundment Waste Solids section in the discussion of mineral processing wastes. One commenter mentioned that baghouse dust accumulates in cellars beneath the baghouse and is removed every two to four weeks (COMM 1034). This new information has been included in the Baghouse Dust section.

Sector-specific Issues

One commenter stated that certain operations downstream of sintering should be considered beneficiation, not processing (COMM 36). EPA disagrees with this conclusion because it maintains that smelting is a processing operation, while sintering (or other defined beneficiation operation preceding smelting) is a beneficiation activity. Another commenter indicated that it no longer uses surface impoundments and completely recycles wastewater treatment solids (COMM 58). Thus, the commenter believed that these wastes should not be considered as solid and hazardous wastes. EPA agrees that wastewater treatment solids may not be considered hazardous wastes if they are not stored on land and are reclaimed for their metal, acid, water, or cyanide values. The Agency has removed the WWTP sludges/solids waste stream from the RIA.

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ATTACHMENT 1

	Total Cor	nstituent Anal	ysis - PPM		EP Toxic	ity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.043	3.75	17.90	8/8	0.050	4.85	18.80	4/4	-	-
Antimony	0.005	2.97	21.90	9/9	0.050	7.82	30.20	4/4	-	-
Arsenic	0.029	765.04	3,800.00	9/9	0.002	530.41	3,160.00	6/6	5.0	2
Barium	0.001	0.18	0.50	7/7	0.050	0.25	0.50	5/5	100.0	0
Beryllium	0.0003	0.01	0.05	6/6	0.005	0.03	0.05	4/4	-	-
Boron	-	-	· -	0/0	-		· -	0/0	-	-
Cadmium	0.002	8.76	31.30	13/13	0.001	2.78	8.96	6/6	1.0	2
Chromium	0.001	0.13	0.50	7/7	0.001	0.19	0.50	6/6	5.0	0
Cobalt	0.006	0.49	2.10	9/9	0.050	0.28	0.50	4/4	-	-
Copper	0.009	30.20	250	10/10	0.138	0.72	1.75	4/4	-	-
Iron	0.035	26.51	77.80	9/9	0.050	1.38	5.69	5/5	-	-
Lead	0.002	1,820.30	21000	13/13	0.220	15.54	84.00	6/6	5.0	2
Magnesium	0.008	17.91	61.30	9/9	0.500	22.43	54.00	4/4	-	-
Manganese	0.010	4.97	33.60	8/8	0.030	0.93	2.86	5/5	-	-
Mercury	0.0001	12.86	90.00	7/7	0.0001	0.0032	0.0180	6/6	0.2	0
Molybdenum	0.020	1.07	4.62	6/6	0.050	1.66	4.67	4/4	-	-
Nickel	0.002	0.55	1.90	9/9	0.050	0.28	0.50	4/4	-	-
Selenium	0.004	0.23	1.66	9/9	0.001	0.94	4.96	6/6	1.0	1
Silver	0.001	0.16	0.50	9/9	0.005	0.19	0.50	6/6	5.0	0
Thallium	0.220	1.04	2.50	7/7	0.250	1.47	2.50	4/4	-	-
Vanadium	0.001	0.11	0.50	9/9	0.050	0.28	0.50	4/4	-	-
Zinc	0.010	99.61	690.00	11/11	0.500	20.18	83.20	5/5	-	-
Sulfide	25.00	136.33	207.00	3/3					-	-
Sulfate	270.00	1,785.88	5300	8/8					-	-
Fluoride	0.010	6.34	19.00	3/3					-	-
Chloride	5.00	1,158.09	7000	9/9					-	-
TSS	1.31	10,325.34	73700	8/8					-	-
pH *	2.22	8.41	13.30	17/17					2 <ph>12</ph>	3
Organics (TOC)	4.56	16.47	39.20	5/5					-	-

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

	Total Co	nstituent Anal	ysis - PPM		EP Toxic	ty Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	0.05	1.82	7.68	5/6	0.05	0.58	1.18	3/3	-	-
Antimony	0.05	29.57	148	6/6	0.05	30.72	91.60	3/3	-	-
Arsenic	0.05	785.14	2370	6/6	0.05	840.18	2,520.00	3/3	5.0	1
Barium	0.05	0.14	0.50	6/6	0.05	0.35	0.50	3/3	100.0	0
Beryllium	0.0005	0.02	0.05	5/5	0.005	0.035	0.050	3/3	-	-
Boron	-		-	0/0	-			- 0/0	-	-
Cadmium	0.41	77.21	362.00	7/7	3.67	126.78	368.00	3/3	1.0	3
Chromium	0.00	0.20	0.50	5/5	0.05	0.35	0.50	3/3	5.0	0
Cobalt	0.05	0.55	2.32	6/6	0.05	0.35	0.50	3/3	-	-
Copper	0.01	2.85	17.80	7/7	0.05	0.35	0.50	3/3	-	-
Iron	0.63	29.19	94.80	6/6	0.50	14.21	39.20	3/3	-	-
Lead	1.63	115.30	674.00	7/7	1.79	4.14	7.29	3/3	5.0	1
Magnesium	2.90	23.92	78.20	6/6	7.94	25.88	54.00	3/3	-	-
Manganese	0.53	1.71	3.81	6/6	0.78	0.99	1.17	3/3	-	-
Mercury	0.0010	1.23	4.80	5/5	0.0001	0.0001	0.0002	3/3	0.2	0
Molybdenum	0.05	0.22	0.50	3/3	0.05	0.35	0.50	3/3	-	-
Nickel	0.05	0.61	2.81	6/6	0.05	0.35	0.50	3/3	-	-
Selenium	0.05	1.91	5.59	3/3	0.05	1.36	3.54	3/3	1.0	1
Silver	0.01	0.18	0.50	5/5	0.05	0.35	0.50	3/3	5.0	0
Thallium	0.25	47.77	142.00	3/3	0.25	36.58	107.00	3/3	-	-
Vanadium	0.00	0.21	0.50	5/5	0.05	0.35	0.50	3/3	-	-
Zinc	0.32	47.43	160	7/7	0.29	59.50	113.00	3/3	-	-
Sulfate	536	1,126.83	3150	6/6					-	-
Fluoride	57	364.50	672	2/2					-	-
Chloride	3	1,250.56	4300	9/9					-	-
TSS	21.30	7,965.06	24730	8/8					-	-
pH *	0.62	3.91	9.04	7/7					2 <ph>12</ph>	2
Organics (TOC)	8.81	125.90	350.00	3/3					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - ACID PLANT BLOWDOWN - LEAD

	Total Co	nstituent Anal	ysis - PPM		EP Toxi	city Analysis	- PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	· -	-	0/0		-	-	- 0/0	-	-
Antimony			· -	0/0		-	-	- 0/0	-	-
Arsenic			· -	0/0		-	-	- 0/0	5.0	0
Barium			· -	0/0		-	-	- 0/0	100.0	0
Beryllium				0/0		-	-	- 0/0	-	-
Boron			· -	0/0		-	-	- 0/0	-	-
Cadmium			· -	0/0		-	-	- 0/0	1.0	0
Chromium			· -	0/0		-	-	- 0/0	5.0	0
Cobalt			· -	0/0		-	-	- 0/0	-	-
Copper	10,000	10,000	10,000	1/1		-	-	- 0/0	-	-
Iron	100,000	100,000	100,000	1/1		-	-	- 0/0	-	-
Lead	500,000	500,000	500,000	1/1		-	-	- 0/0	5.0	0
Magnesium			· -	0/0		-	-	- 0/0	-	-
Manganese		· -	· -	0/0		-	-	- 0/0	-	-
Mercury		· -	· -	0/0		-	-	- 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	50,000	50,000	50,000	1/1		-	-	- 0/0	-	-
Sulfate			· -	0/0					-	-
Fluoride			· -	0/0					-	-
Chloride	· · ·		· -	0/0					-	-
TSS	· · ·		· -	0/0					-	-
pH *	· · ·		· -	0/0					2 <ph>12</ph>	0
Organics (TOC)			. <u> </u>	0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - MISCELLANEOUS SOLIDS - LEAD

	Total Co	nstituent Anal	ysis - PPM		EP Toxi	city Analysis	- PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum			· -	0/0		-	-	- 0/0	-	-
Antimony			· -	0/0		-	-	- 0/0	-	-
Arsenic	18.00	18.00	18.00	1/1		-	-	- 0/0	5.0	0
Barium			· -	0/0		-	-	- 0/0	100.0	0
Beryllium			· -	0/0		-	-	- 0/0	-	-
Boron			· -	0/0		-	-	- 0/0	-	-
Cadmium	0.05	5.53	20.70	4/4		-	-	- 0/0	1.0	0
Chromium			· -	0/0		-	-	- 0/0	5.0	0
Cobalt			· -	0/0		-	-	- 0/0	-	-
Copper	0.01	0.23	0.50	4/4		-	-	- 0/0	-	-
Iron	0.25	0.52	1.00	3/3		-	-	- 0/0	-	-
Lead	0.95	2.28	3.18	4/4		-	-	- 0/0	5.0	0
Magnesium	18.00	18.00	18.00	1/1		-	-	- 0/0	-	-
Manganese	3.00	3.00	3.00	1/1		-	-	- 0/0	-	-
Mercury			· -	0/0		-	-	- 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	2.00	15.10	43.20	4/4		-	-	- 0/0	-	-
Sulfate			· -	0/0					-	-
Fluoride			· -	0/0					-	-
Chloride	· ·		· -	0/0					-	-
TSS	· ·		· -	0/0					-	-
pH *	7.00	7.60	8.00	3/3					2 <ph>12</ph>	0
Organics (TOC)			· <u> </u>	0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SURFACE IMPOUNDMENT LIQUIDS - LEAD

	Total Cor	stituent Anal	ysis - PPM		EP Toxic	ity Analysis	- PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-	· -	· 0/0	-		-	- 0/0	-	-
Antimony	-	-		· 0/0			-	- 0/0	-	-
Arsenic	-	-		0/0	-		-	- 0/0	5.0	0
Barium	-	-		· 0/0			-	- 0/0	100.0	0
Beryllium	-	-		· 0/0			-	- 0/0	-	-
Boron	-	-		· 0/0			-	- 0/0	-	-
Cadmium	19.00	19.00	19.00	1/1			-	- 0/0	1.0	0
Chromium	-	-		· 0/0			-	- 0/0	5.0	0
Cobalt	-	-		· 0/0			-	- 0/0	-	-
Copper	2,500	2,500	2,500	2/2			-	- 0/0	-	-
Iron	-	-		· 0/0			-	- 0/0	-	-
Lead	1,290	27,430	59,000	3/3			-	- 0/0	5.0	0
Magnesium	-	-		· 0/0			-	- 0/0	-	-
Manganese	-	-		· 0/0			-	- 0/0	-	-
Mercury	-	-		· 0/0			-	- 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	68	64,689	98,000	3/3			-	- 0/0	-	-
Sulfate	-	-		· 0/0					-	-
Fluoride	-	-		· 0/0					-	-
Chloride	-	-		· 0/0					-	-
TSS	-	-		· 0/0					-	-
pH *	0.00	7.55	13.00	5/5					2 <ph>12</ph>	1
Organics (TOC)		-		· 0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER TREATMENT PLANT SLUDGE/SOLIDS - LEAD

	Total Co	nstituent Anal	ysis - PPM		EP Toxi	city Analysis	s - PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum		- ·		- 0/0		-	-	- 0/0	-	-
Antimony				- 0/0		-	-	- 0/0	-	-
Arsenic				- 0/0		-	-	- 0/0	5.0	0
Barium				- 0/0		-	-	- 0/0	100.0	0
Beryllium				- 0/0		-	-	- 0/0	-	-
Boron				- 0/0		-	-	- 0/0		
Cadmium	0.08	0.08	0.08	1/1		-	-	- 0/0	1.0	0
Chromium				- 0/0		-	-	- 0/0	5.0	0
Cobalt				- 0/0		-	-	- 0/0	-	-
Copper				- 0/0		-	-	- 0/0	-	-
Iron				- 0/0		-	-	- 0/0	-	-
Lead	15.00	17.50	20.00	2/2		-	-	- 0/0	5.0	0
Magnesium				- 0/0		-	-	- 0/0	-	-
Manganese				- 0/0		-	-	- 0/0	-	-
Mercury				- 0/0		-	-	- 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	35.00	35.00	35.00	1/1		-	-	- 0/0	-	-
Sulfate				- 0/0					-	-
Fluoride				- 0/0					-	-
Chloride				- 0/0					-	-
TSS				- 0/0					-	-
pH *	7.00	9.08	13.00	4/4					2 <ph>12</ph>	1
Organics (TOC)			·	- 0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER TREATMENT PLANT LIQUID EFFLUENT - LEAD

	Total Cor	stituent Anal	ysis - PPM		EP Toxic	ity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-		· 0/0				- 0/0	-	-
Antimony	-	-		· 0/0				- 0/0	-	-
Arsenic	-	-		· 0/0	0.00	46.95	304.00	7/7	5.0	2
Barium	-	-		· 0/0	0.15	1.08	2.60	6/6	100.0	0
Beryllium	-	-		· 0/0				- 0/0	-	-
Boron	-	-		· 0/0				- 0/0		
Cadmium	640.00	670.00	700.00	2/2	0.01	54.34	155.00	7/7	1.0	6
Chromium	28.00	44.00	60.00	2/2	0.00	0.02	0.07	3/7	5.0	0
Cobalt	-	-		· 0/0				- 0/0	-	-
Copper	-	-		· 0/0				- 0/0	-	-
Iron	-	-		· 0/0	0.05	30.25	178.00	6/6	-	-
Lead	115000	127500	140000	2/2	0.22	188.01	959.00	7/7	5.0	3
Magnesium	-	-		· 0/0				- 0/0	-	-
Manganese	-	-		· 0/0	0.03	513.63	3,560.00	7/7	-	-
Mercury	-	-		· 0/0	0.0001	1.1313	7.9000	7/7	0.2	1
Molybdenum	-	-		· 0/0				- 0/0	-	-
Nickel	-	-		· 0/0				- 0/0	-	-
Selenium	-	-		· 0/0	0.001	0.077	0.420	7/7	1.0	0
Silver	-	-		· 0/0	0.015	0.018	0.030	5/5	5.0	0
Thallium	-	-		· 0/0	0.02	0.02	0.02	1/1	-	-
Vanadium	-	-		· 0/0				- 0/0	-	-
Zinc	80000	106000	132000	2/2	0.02	65.66	184.00	7/7	-	-
Sulfate	-	-		· 0/0					-	-
Fluoride	-	-		· 0/0					-	-
Chloride	-	-		· 0/0					-	-
TSS	-	-		· 0/0					-	-
pH *	4.80	6.29	11.20	6/6					2 <ph>12</ph>	0
Organics (TOC)	-	-		· 0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SURFACE IMPOUNDMENT SOLIDS - LEAD

ATTACHMENT 2

Mining Sites on the National Priority List

Name of Site:	Bunker Hill Mining and Metallurgical Complex
Owner of Site:	Bunker Limited Partnership
Location of Site:	Kellogg, Idaho
Climate Data:	To be determined
Commodity Mined:	Lead and Zinc
Facility History:	The Bunker Hill Superfund Site is located in the Silver Valley of the South Fork of the Coeur d'Alene River in Northern Idaho. It is approximately 60 miles east of Spokane, Washington. The site is 3 miles wide and 7 miles long and bisected by Interstate 90. The site includes the cities of Wardner, Kellogg, Smelterville, and Pinehurst, with a total population of 5000. Lead and zinc mining began on the Bunker Hill site with the location of the Bunker Hill and Sullivan claims in 1885 by Noah Kellogg. The first mill began operations in 1886 and a larger mill was constructed in 1891. The lead smelter began operation in 1917. An electrolytic zinc plant, capable of producing 99.99% zinc, began operation in 1928. An electrolytic antimony plant was constructed in 1939, but it operated only for a few years. In 1943, a slag fuming plant was constructed to recover zinc from the blast furnace slag of the lead smelter. A cadmium recovery plant was added in 1945. A sink-float plant operated from 1941 to 1953. A phosphoric acid plant began operations in 1961. The plant used sulfuric acid from the zinc plant and phosphate rock from southern Idaho or Wyoming to produce phosphoric acid and gypsum. Sulfuric acid plants were added to the zinc facilities in 1954 and 1966. The lead smelting process was changed in 1970 from a downdraft ore-roasting operation to a Lurgi updraft sintering process with a sulfuric acid recovery plant. In 1976, a 715-foot stack was added to the lead smelter, and a 610-foot stack was added to the zinc plant in 1977. In December 1981, the smelter complex was shut down.
Waste(s) at Issue:	The major environmental problems at the Bunker Hill site were caused by smelter operations and mining and milling. Contaminants of concern are lead, zinc, cadmium, antimony, arsenic, beryllium, copper, mercury, PCBs, selenium, silver, cobalt, and asbestos. During smelter operations (1917-1981) wastes and feed stock were stored onsite. In addition, the smelter discharged heavy metal particulates and sulphur dioxide gas to the atmosphere. In order to capture the heavy metal particulates, baghouse filtration systems were installed at the lead and zinc plants. However, a 1973 fire severely damaged the baghouses. Two of the seven baghouses were destroyed and the remaining five were shut down for 6 months to be repaired. During this time, 20 to over 100 tons/month of particulates containing 50 to 70 percent lead were emitted from the stacks (compared to the normal 10 to 20 tons/month).

	backfill in the Bunker Hill Mine. The CIA also received mine drainage beginning in 1965, gypsum from the phosphoric acid and fertilizer plant after 1970, and wastes from the zinc plant and smelter after 1974. Decant from the CIA was discharged directly into the river until 1974, when the Central Treatment Plant began operation. After 1974, decant gypsum discharge was returned to the phosphate plant.
Disposal Site:	The Bunker Hill Mining Complex includes the Bunker Hill Mine (lead and zinc), a milling and concentrating operation, a lead smelter, a silver refinery, an electrolytic zinc plant, a phosphoric acid and phosphate fertilizer plant, sulfuric acid plants, and a cadmium plant. Also included within the site boundary are the Page Mine (inactive), the Page tailings disposal area known as the "Page Ponds" (currently the site of Silver Valley water treatment facility), and numerous old mines, mill sites, and prospects.
Soil Pathway:	Residual soil contamination with metals is a major concern at this site. During smelter operation, metal-laden particulates were discharged from the smelter. In 1974 the top 0.5 inch of hillside soil had lead concentrations ranging from 1,000 to 24,000 ppm and cadmium concentrations ranging from 50 to 236 ppm. On undisturbed areas, most of the metals were found in the top 3 inches, while in severely eroded areas, airborne contamination penetrated at least the top 10 inches. Soil near the smelting complex has also been severely impacted by metals deposition. Around the smelter complex, extremely high concentrations of lead (1,000 to 40,000 ppm) and cadmium (80 to 240 ppm) were detected. The upper 10 to 20 feet of soils on the valley floor were combined with mine and mill tailings generated by the mineral processing industry in the early part of the 20th century. These early milling practices resulted in the deposition of metals-rich tailings in low-lying areas. Lead and cadmium levels in the valley area are similar to those in the hillside soils. The Smelterville Flats encompass an area of approximately 2 square miles northwest of the City of Smelterville, where significant amounts of unconfined tailings have accumulated over time. Surface metal concentrations ranged from 6,000 to 25,000 ppm lead and 30 to 70 ppm cadmium. The Page Ponds and the CIA cover 240 acres and contain several million cubic yards of tailings. These areas are located close to major residential areas and have lead concentrations ranging from 2,000 to 20,000 ppm (1974 and 1977 studies). In 1986 and 1987, a soil survey was conducted in the communities of Smelterville, Kellogg, Wardner, and Page. Samples of the top 1 inch of mineral soil and litter were analyzed from 1,020 of 1547 homes (64%). Five percent of all homes sampled had lead levels below 500 ppm; 11 percent had lead levels between 500 and 1,000 ppm; and 84 percent had lead levels above 1,000 ppm.
Ground Water Pathway:	Primary sources of ground water contamination include: seepage from the CIA (estimated to be 1 ft ³ /sec), infiltration and ground water flow through valley-wide deposits of tailings, and ground water inflow upgradient of the site. Other sources of ground water contamination include discharges from Magnet Gulch, Pine Creek, and Milo Gulch; infiltration of incident precipitation through the CIA; and seepage from Sweeney Pond, McKinley Pond, and other surface impoundments. Contaminants of primary concern include: arsenic, cadmium, lead, cobalt, and zinc. Maximum zinc and cadmium levels have been detected in wells adjacent to the CIA at 50 and 0.1 mg/L, respectively (1974). These values appear to have reflected partly diluted direct seepage from the CIA. While studies have been done to evaluate the seepage and metal transport to ground water from the CIA, they have not specifically targeted the extent and degree of ground water contamination, and thus, have not determined the spread of contaminants into the confined lower aquifer. Ground water in the Smelterville Flats area contain high levels of heavy metals, but the concentrations generally decrease with depth and linear distance from the South Fork. The ground water appears to be in hydraulic connection with surface ponds in the flats. In 1979, it was estimated that the flats discharge about 5.3 kg/day of zinc to the ground water. The Page Ponds discharged 8 kg/day of zinc to the ground water in 1975. The ponds have subsequently been converted for sewage

	treatment. Information on the potential of heavy-metal contamination of ground water from these ponds remains unavailable.
Surface Water Pathway:	The Bunker Hill site is situated in the Coeur d'Alene River basin. The main surface water features at the Bunker Hill Complex include: the Coeur d'Alene River, the CIA, which includes the central impoundment pond, the gypsum pond, and the slag pile. Other smaller impoundments areas are located near the lead and zinc smelter, including Sweeney Pond and the main reservoir in the lead smelter complex, and the main reservoir and settling ponds in the zinc plant area. Major streams on the complex include Government Creek, Bunker Creek, and Mile Creek. The streams in the vicinity of past mining activities at this site have received a heavy sediment load of mine and mill tailings. The South Fork of the Coeur d'Alene River has been receiving mine and mill wastes for approximately 90 years. Even though the site was closed in 1981, discharges to the South Fork still continue; including, for example, those from the operating wastewater treatment plant. As of 1984, concentrations of several contaminants were still significant in the South Fork: cadmium (28.6 μ g/L), iron (1,146 μ g/L), manganese (1,507 μ g/L), and zinc (3,270 μ g/L).
Air Pathway:	Lead, cadmium, zinc, mercury, and arsenic emissions from the lead smelter main stack were calculated for the period of 1965 to 1981. In excess of 6 million lbs of lead; 560,000 lbs of cadmium; 860,000 lbs of zinc; 29,000 lbs of mercury; and 70,000 lbs of arsenic were emitted during this period. These figures do not include vent or fugitive emissions, which were believed to total more than stack emissions. Since smelter closure, ambient lead levels and total suspended particulates have generally been within primary National Ambient Air Quality Standards (NAAQS). Ambient lead levels have ranged from 0.1 to 0.5 μ g/m ³ (on a quarterly basis) and ambient levels of total suspended particulates have ranged from 30 to 70 μ m/m ³ (on an annual basis) with daily values ranging to 900 μ g/m ³ . The NAAQS for lead is 1.5 μ g/m ³ (on a 24-hour basis, for particulate <10 microns).
Environmental Issues:	The pathways for human exposure include household dusts, soils, and locally grown vegetables. EPA has (through a health intervention program) recommended against eating the vegetables since 1985. Shown below are concentrations of lead, cadmium, and zinc from studies performed in 1974 and 1983.

	Lead (in ppm)		Cadmium	ı (in ppm)	Zinc (in ppm)		
Media	1974	1983	1974	1983	1974	1983	
Household Dust	11,920	3,994	NA	67	NA	2,840	
Soils	7,224	3,504	63	54	2,340	126	
Garden Vegetables	231	48	28	5	NA	73	

NA - not analyzed

Environmental and ecological damage has also occurred. The Bunker Hill Company, as part of a revegetation effort beginning in the early 1970's, identified about 14,000 acres that had been damaged. Studies conducted as part of the Remedial Investigation concluded that site vegetation has been damaged by logging, fires, and emissions from the lead smelter, zinc plant, and phosphoric acid/fertilizer plant.

LIGHTWEIGHT AGGREGATE

A. Commodity Summary

Lightweight aggregates are minerals, natural rock materials, rock-like products, and byproducts of manufacturing processes that are used as bulk fillers in lightweight structural concrete, concrete building blocks, precast structural units, road surfacing materials, plaster aggregates, and insulating fill. Lightweight aggregates are also used in architectural wall covers, suspended ceilings, soil conditioners, and other agricultural uses. Lightweight aggregates may be classified into four groups:

- *Natural lightweight aggregate materials* which are prepared by crushing and sizing natural rock materials, such as pumice, scoria, tuff, breccia, and volcanic cinders.
- *Manufactured structural lightweight aggregates* which are prepared by pyroprocessing shale, clay, or slate in rotary kilns or on traveling grate sintering machines.
- *Manufactured insulating ultralightweight aggregates* which are prepared by pyroprocessing ground vermiculite, perlite, and diatomite.
- *Byproduct lightweight aggregates* which are prepared by crushing and sizing foamed and granulated slag, cinders, and coke breeze.

The first three groups of lightweight aggregates are produced from naturally occurring materials, while the fourth is produced as a byproduct of iron and steel production. Lightweight aggregates are distinguished from other mineral aggregate materials by their lighter unit weights. Exhibit 1 presents the names and locations of facilities involved in the production of lightweight aggregates from naturally occurring raw materials. Exhibit 2 presents the names of facilities involved in the production of lightweight aggregates from naturally occurring raw materials.

B. Generalized Process Description

Lightweight aggregate materials are produced mainly by two methods. The first method of lightweight aggregate production is from naturally occurring raw materials. The second method is byproduct production from iron and steel production. These processes are quite different and are described separately below. Section 1 describes lightweight aggregate production from naturally occurring raw materials. Section 2 describes byproduct lightweight aggregate production.

SECTION 1: Production From Naturally Occurring Raw Materials

1. Discussion of Typical Production Processes

While natural lightweight aggregates are prepared through basic operations including steps such as mining, grinding, and sizing, manufactured lightweight aggregate and manufactured ultralightweight aggregate products are produced by heating certain types of clay, shale, slate, and other materials in a rotary kiln which forces the materials to expand or "bloat;" resulting in a porous product. The product will retain its physical strength despite its lighter unit weight when cooled.¹ The process is described in more detail below.

¹ Bruce Mason, "Lightweight Aggregates," from <u>Industrial Minerals and Rocks</u>, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 343-350.

FACILITIES PRODUCING LIGHTWEIGHT AGGREGATES FROM NATURALLY OCCURRING RAW MATERIALS

Facility Name	Location
Arkansas Lightweight Aggregate	West Memphis, AR
Big River	Livingstone, AL
Big River	Erwinville, LA
Buildex	Dearborn, MO
Buildex	Ottawa, KS
Buildex	Marquette, KS
Chandler Materials Co.	Tulsa, OK
Chandler Materials Co.	Choctaw, OK
Dakota Block Co.	Rapid City, SD
Featherlite	Strawn (Ranger), TX
HP Brick Co.	Brooklyn, IN
HP Brick Co.	Independence, OH
Jackson Concrete	Jackson, MS
Kanta	Three Forks, MT
Lehigh Portland Cement Co.	Woodsboro, MD
Lorusso Corp.	Plainville, MA
Norlite	Cohoes, NY
Parkwood Lightweight Plant	Bessemer, AL
Porta Costa	Porta Costa, CA
Ridgelite	Frazier Park, CA
Solite	Cascade, VA
Solite	Arvonia, VA
Northeast Solite	Mount Marion, NY
Carolina Solite	Norwood, NC
Kentucky Solite	Brooks, KY
Florida Solite	Green Cove Springs, FL
Strawn	Strawn, TX
Texas Industries	Streetman, TX
Utelite	Coalville, UT
Weblite	Blue Ridge, VA

Source: Determination of Waste Volume for Twenty Conditionally Retained Bevill Mineral Processing Wastes, 1990, pp. 5-9, A10.

Facilities that burn hazardous waste fuels are shaded.

Facilities	Location
Waylite Corporation	Bethlehem, PA
Standard LaFarge Corporation	Cleveland, OH
Edward C. Levy Company	Detroit, MI
Koch Minerals	Gary, IN

Byproduct Lightweight Aggregate Producers

2. Generalized Process Flow Diagram

Naturally occurring lightweight aggregate raw materials, such as pumice and volcanic cinders, are normally mined by open pit or quarry methods, depending on the degree of consolidation of the raw materials. Shale, clay, and slate mined by open pit and quarry methods are dried in large sheds or open stockpiles to control water content in the raw feed prior to high temperature pyroprocessing in either rotary kilns or sintering machines. The resulting clinker may then be crushed before screening to yield proper gradation mixes for final use. Most lightweight aggregate plants use coal as a primary source of fuel. Waste-derived fuels and solvents from various industrial processes are also used as alternate fuel sources at a few locations (e.g., those operated by Solite and Norlite). Exhibit 3 presents a typical process flow diagram for lightweight aggregate production for facilities using a wet scrubber air pollution control technology or a dry collection method. All facilities currently use dry collection systems.

3. Identification of Novel (or otherwise distinct) Processes

None identified.

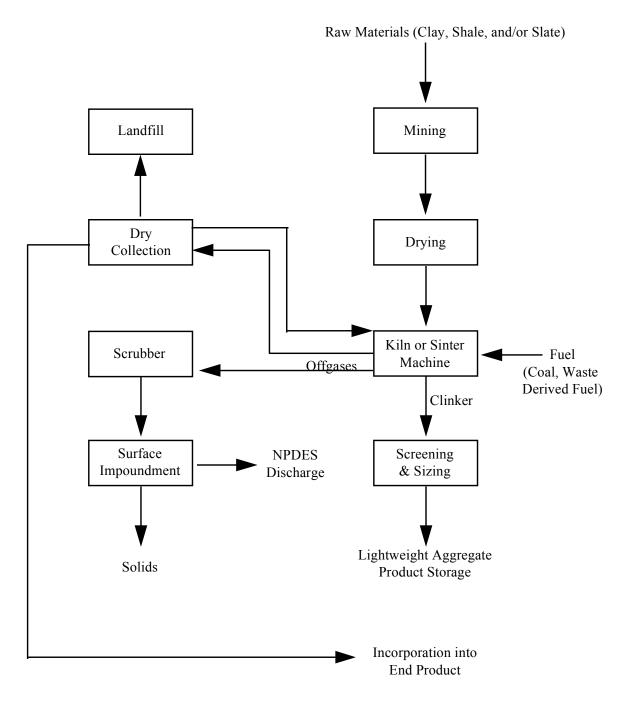
4. Beneficiation/Processing Boundaries

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.

LIGHTWEIGHT AGGREGATE PROCESS FLOW DIAGRAM



EPA determined that for the production of lightweight aggregates from naturally ocurring raw materials, the beneficiation/processing line occurs after drying at the kiln/sinter machine because the elevated temperatures destroy the physical structure of the raw material. 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/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

SECTION 2: By-product Production

1. Discussion of Typical Production Processes

Both expanded slag and air-cooled slag are lightweight aggregate products produced as by-products from iron and steel production. The process is described below.

2. Generalized Process Flow Diagram

Expanded slag and air-cooled slag are byproducts of iron and steel production. Expanded slag is manufactured by spraying a stream of water through molten blast furnace slag as it is drawn from the furnace. The resulting foamed slag is crushed and screened for use in concrete block or structural concrete. Air-cooled slag is manufactured by pouring molten blast furnace slag into pits where it is cooled by water. It is then excavated, crushed, and screened.² Iron and steel slags are considered special wastes, and were addressed in the 1990 Report to Congress on Special Wastes from Mineral Processing. Exhibits 4 and 5 present flow diagrams for expanded slag and air-cooled slag, respectively.

3. Identification of Novel (or otherwise distinct) Processes

None identified.

4. Extraction/Beneficiation Boundaries

Because lightweight aggregates are recovered as by-products of mineral processing activities in the iron and steel sector, all of the wastes generated during lightweight aggregate recovery also are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral commodity, see the sector report for iron and steel presented elsewhere in this document.

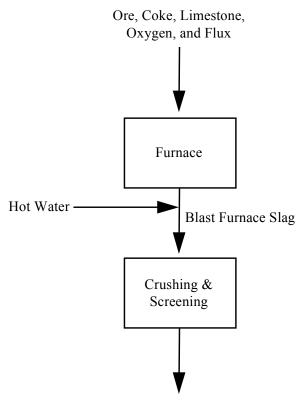
C. Process Waste Streams

1. Extraction/Beneficiation Wastes

The preparation of natural lightweight aggregate materials only generates extraction/beneficiation wastes because no thermal processes are involved. However, production of manufactured lightweight aggregates generates both extraction/beneficiation and mineral processing wastes. **Overburden**, **waste rock**, **raw fines from primary crushing operations**, and **sludge from rock washing operations** are generated from the mining and extraction of lightweight aggregate minerals. These materials likely are left in place at the original mining site.

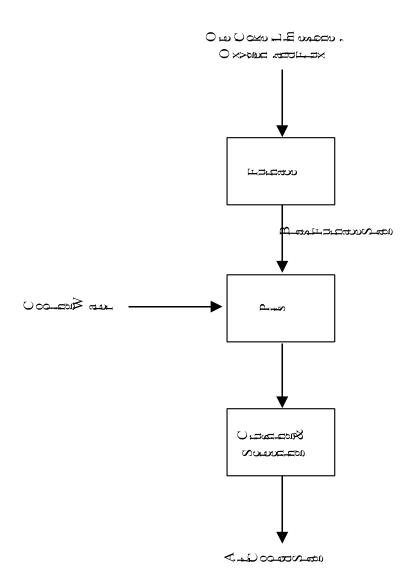
² Bruce Mason, 1994, <u>Op. Cit.</u>, pp. 343-350.

EXPANDED SLAG PROCESS FLOW DIAGRAM



Expanded Slag Product

AT MOOTED WIGH TROMETOS UTARKE



2. Mineral Processing Wastes

Hazardous waste fuels may be burned for use as a heat source in the production of lightweight aggregates. Therefore, some of the waste streams discussed below would be considered hazardous through application of the derived-from rule. Likely waste-derived fuels are high in Btu values and oily substances. Waste generated from this process may contain metals, semivolatiles, and dioxins/furans. Six facilities burn listed hazardous waste as fuel in their kilns. These facilities are Carolina Solite, Florida Solite, Kentucky Solite, Norlite, and the two Solite facilities in Virginia.³ However, the Solite facility in Cascade, VA generates no solid waste because all the APC dust that is generated is returned to the operation and the Florida Solite facility currently is inactive.⁴

Air pollution control scrubber water and solids. Most facilities now use dry collection systems and no longer generate this waste. However, two wet scrubbers continue to be operated as kiln air pollution control devices at Solites' North Carolina Plant.⁵ Kilns equipped with wet scrubbers generate scrubber wastewater which contained particles from the kiln. In 1989, 18 of the active facilities used wet scrubbers for air pollution control. Lightweight aggregate production for these 18 facilities ranged from 23,123 to 907,185 mt/y, and the volume of scrubber solids generated ranged from 104 to 61,235 mt/y. Generally, the scrubber solids were managed in settling ponds, surface impoundments, or landfills where dewatering occurred and the particulate matter settled out in the form of sludge.⁶ In 1989, this waste was generated at a rate of 2,420,000 mt/y.⁷ Attachment 1 presents waste characterization data for this waste stream. Exhibit 6 presents facility specific management information as well as generation rates and waste characteristics for the facilities that do not burn hazardous waste fuels in their kilns.

Because of the derived-from rule, scrubber water and solids are considered a hazardous waste at facilities that use wet scrubbers and burn hazardous waste fuels in their kilns. Although this waste currently is generated at only one facility, Exhibit 7 presents waste generation rates for five facilities that, in the past, have generated hazardous scrubber water and solids.

Air pollution control dust/sludge. Lightweight aggregate facilities that use baghouses and other dry collection systems generate APC dust that is collected in dry form. Some facilities using dry collection systems recycle the dust to the process or use it in products (e.g., block mix). At Arkansas Lightweight Aggregate Corporation, particulate matter that is too fine to continue on in the kilning process is exhausted in the mechanical dust collector. After filtering, the waste dust drops into conical piles beneath the collector. Three piles collect beneath the collector, one consisting of heavier particles and two consisting of lighter particles. This waste is collected by a shovel loader and placed in a waste water impoundment onsite. The wet scrubber at the Arkansas facility operates for particulate removal only; no chemical treatment of water occurs.⁸

⁵ Ibid.

⁶ U.S. Environmental Protection Agency, 1990, Op. Cit., pp. 5-9, A10.

⁷ U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Office of Solid Waste, 1992, Vol. I, pp. I-2 - I-8.

⁸ U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, pp. 5-9, A10.

³ U.S. Environmental Protection Agency, <u>Addendum to the Technical Background Document</u>, <u>Development of the Cost and Economic Impacts of Implementing the Bevill Mineral Processing Wastes Criteria</u>, Office of Solid Waste, 1990.

⁴ Solite Corporation. <u>Op. Cit.</u>

APC SCRUBBERWATER AND SOLIDS AT FACILITIES NOT USING WASTE-DERIVED FUELS

Facility	RTI ID#	1988 Generation	рН	Management Practices
Buildex, Dearborn, MO	100685	Wastewater: 8,784,000 gallons	5.8	Sent to bedrock lined surface impoundment for settling
Chandler Materials, Tulsa, OK	101725	Wastewater: 17,900,000 gallons Solids: 177 cubic yards	5.5	Sent to bedrock lined surface impoundment for solids precipitation
Chandler, Choctaw, OK	101766	Wastewater: 14,100,000 gallons	5.6	Sent to in-situ clay lined surface impoundment for solids precipitation
Featherlite, Strawn, TX	101659	Wastewater: 4,535 mtons	NA	Sent to in-situ clay lined surface impoundment for solids precipitation
HP Brick, Brooklyn, IN	100263	Wastewater: 9,071 mtons	5.5	Sent to in-situ shale lined surface impoundment for dewatering
Texas Industries, Streetman, TX	101808	Wastewater: 250,000,000 gallons	9.94	Sent to in-situ clay lined surface impoundment for solids precipitation
Porta Costa, Porta Costa, CA	100792	Wastewater: 600 gallons	7.2	Sent to in-situ clay lined surface impoundment for water evaporation and solids recycling
Parkwood, Bessemer, AL	100180	Wastewater: 8,981 mtons	NA	Sent to bedrock lined surface impoundment for solids precipitation and pH adjustment with caustic soda
Jackson Ready Mix Concrete, Jackson, MS	100438	Wastewater: 104 mtons	NA Sent to recompacted loc clay lined surface impoundment for solids precipitation	
Big River, Livingston, AL	NA	NA	NA	NA
Big River, Erwinville, LA	NA	NA	NA	NA
Arkansas Lightweight Aggregate, West Memphis, AR	NA	NA	NA	NA
NE Solite, Mt. Marion, NY	NA	NA	NA	NA

SOURCE: 1988 RTI Surveys.

Facility	Location	cation APC Scrubberwater and Solids (mt/y)		APC Dust/Sludge (mt/y)
Carolina Solite	Norwood, NC	61,235	6.63	4,060
Florida Solite	Green Cove, FL	31,248	6.53	2,040
Kentucky Solite	Brooks, KY	43,293	19.28	8,347
Norlite	Cohoes, NY	NA	NA	NA
Solite	Arvonia, VA	NA	NA	NA

1988 APC SCRUBBERWATER AND SOLIDS AT FACILITIES USING WASTE-DERIVED FUELS

Source: Results of EPA's Final Analysis (Exhibit 4), Lightweight Aggregate Production and Air Pollution Control Wastes. Technical Background Document Supporting the Supplemental Proposed Rule Applying Phase IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. EPA, Office of Solid Wasts. December 1995.

At Solite's facilities that burn hazardous wastes, the lightweight aggregate APC dust/sludge (baghouse dust) is collected in baghouses and conveyed to the finish end of Solite's lightweight aggregate plants where it is added to crushed and sized clinker. In some cases, it is returned to the beginning of the manufacturing process and reinserted into the kiln in extruded form, but the more usual practice is to incorporate the baghouse dust directly into a product referred to as "block mix."

Block mix is comprised of lightweight aggregate ranging in size from 3/16 of an inch in diameter to very fine material. The very fine material typically comprises no more than 12 to 16 percent of the block mix, and the percentage of bag house dust in the very fine material varies. Usually, about 75 percent of Solite's total lightweight aggregate output consists of block mix. However, this percentage can vary from plant to plant and in response to customer demand. The fine material is a necessary component of block mix, and if it is not introduced in the form of baghouse dust it must be produced by crushing the kiln clinker.

The finished block mix product is usually stored in an on-site pile prior to sale. It is kept damp during storage and transportation to control fugitive dust emissions and because substantial moisture is needed to mix the block mix with cement and other ingredients to make concrete. Block mix is transported by truck or rail car to concrete block manufacturing plants where it is used as a primary ingredient in the manufacture of lightweight concrete masonry units. The block mix confirms to ASTM Standard Number C 331 and individual customer specifications.

Although Solite is not currently selling LAKD as a separate product, the company believes that LAKD could be marketed as a mineral filler for asphalt and/or an ingredient in some concrete products. It may be necessary to pursue this market if the demand for block mix is insufficient to absorb all of the baghouse dust.⁹

This waste would be considered a hazardous waste at facilities that burn hazardous waste fuels because of the derived-from rule. These facilities are identified in Exhibit 1. The Solite facility in Cascade, VA does not generate this waste because all APC dust is returned to the process at this facility. Exhibit 7 presents waste generation rates for the remaining five facilities.

⁹ Solite Corporation. Comment submitted in response to the <u>Supplemental Proposed Rule Applying Phase IV</u> Land Disposal Restrictions to Newly Identified Mineral Processing Wastes. January 25, 1996.

Wastewater treatment plant (WWTP) liquid effluent. Attachment 1 presents waste characterization data for this waste stream. In 1991, the waste generation rate for this waste stream was 1,094,000 metric tons per year.¹⁰ At the Carolina Solite facility in Norwood, NC, WWTP liquid effluent is discharged under an NPDES permit.¹¹ This waste is not expected to be hazardous.

Surface impoundment waste liquids. Attachment 1 presents characterization data for this waste stream. The generation rate for this waste stream is 2,571,00 metric tons per year¹² (adjusted from a reported value to reflect recent changes in the sector). This waste is discharged under an NPDES permit at the Carolina Solite in Norwood, NC and the Norlite Corporation in Cohoes, NY.¹³ This waste is not expected to be hazardous.

Byproduct Production

Waste streams from byproduct production of lightweight aggregate products from iron and steel production include **cooling water** and **slag**. These wastes are not expected to be hazardous.

D. Non-uniquely Associated Wastes

Non-uniquely associated wastes 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 (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

One commenter addressed the lightweight aggregates sector report and provided new information about its facilities that burn hazardous waste. This information has been included in the sector report, as appropriate.

Sector-specific Issues

None.

¹⁰ U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, pp. 5-9, A10.

¹¹ U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Office of Solid Waste, 1992, Vol. II, pp. 22-1 - 22-19.

¹² U.S. Environmental Protection Agency, 1990, <u>Op. Cit.</u>, pp. 5-9, A10.

¹³ U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, Vol. II, pp. 22-1 - 22-19.

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US EPA ARCHIVE DOCUMENT

ATTACHMENT 1

	Total Co	onstituent Ar	alysis - PPI	N	EP Toxic	ity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	11.50	171	330	2/2	18.90	18.90	18.90	1/1	-	-
Antimony	0.030	0.14	0.25	0/3	0.050	0.050	0.050	0/1	-	-
Arsenic	0.0040	0.28	0.81	2/3	0.050	0.050	0.050	0/1	5.0	0
Barium	0.21	1.92	3.62	2/2	0.21	0.21	0.21	1/1	100.0	0
Beryllium	0.0050	0.016	0.025	1/3	0.0050	0.0050	0.0050	0/1	-	-
Boron	-	· -	-	- 0/0	-	· -		- 0/0	-	-
Cadmium	0.025	0.39	1.08	2/3	0.0050	0.0050	0.0050	0/1	1.0	0
Chromium	0.0025	0.44	1.08	1/3	0.050	0.050	0.050	0/1	5.0	0
Cobalt	0.25	0.31	0.36	1/2	0.050	0.050	0.050	0/1	-	-
Copper	0.025	0.21	0.34	1/3	0.050	0.050	0.050	0/1	-	-
Iron	1.16	145	289	2/2	2.07	2.07	2.07	1/1	-	-
Lead	0.013	0.13	0.35	3/3	0.025	0.025	0.025	0/1	5.0	0
Magnesium	90.60	212	334	2/2	21.60	21.60	21.60	1/1	-	-
Manganese	13.50	30.20	46.90	2/2	4.55	4.55	4.55	1/1	-	-
Mercury	0.0017	0.0018	0.0020	2/3	0.00010	0.00010	0.00010	0/1	0.2	0
Molybdenum	0.250	0.250	0.250	0/1	0.050	0.050	0.050	0/1	-	-
Nickel	0.050	0.30	0.53	3/3	0.050	0.050	0.050	0/1	-	-
Selenium	0.001	0.092	0.25	0/3	0.050	0.050	0.050	0/1	1.0	0
Silver	0.01	0.090	0.25	1/3	0.050	0.050	0.050	0/1	5.0	0
Thallium	0.074	0.52	1.25	1/3	0.25	0.25	0.25	0/1	-	-
Vanadium	0.050	0.31	0.56	2/2	0.050	0.050	0.050	0/1	-	-
Zinc	0.23	1.33	2.51	3/3	0.34	0.34	0.34	1/1	-	-
Cyanide	-	· -	-	0/0	-			- 0/0	-	-
Sulfide	-	· -	-	. 0/0	-			- 0/0	-	-
Sulfate	653	653	653	1/1	-			- 0/0	-	-
Fluoride	-		· -	- 0/0	-			- 0/0	-	-
Phosphate	-	. <u>-</u>	· -	- 0/0	-			- 0/0	-	-
Silica		· -	-	0/0	-	· -		- 0/0	-	-
Chloride	23.70	25.35	27.00	2/2	-	· -		- 0/0	-	-
TSS	1,650	4,525	7,400	2/2	-			- 0/0	-	-
рН *	5.50	5.50	5.50	1/1					2 <ph>12</ph>	0
Organics (TOC)	-		· -	. 0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - APC SCRUBBER WATER AND SOLIDS - LIGHTWEIGHT AGGREGATE

	Total Co	onstituent Ar	nalysis - PPI	N	EP Toxic	ity Analysis -	PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	16,900	20,050	23,200	2/2	-	-		- 0/0	-	-
Antimony	0.70	0.75	0.79	1/2	-	-		0/0	-	-
Arsenic	17.00	26.50	36.00	2/2	0.00050	0.038	0.25	8/13	5.0	0
Barium	193	470	746	2/2	0.10	1.12	8.10	7/13	100.0	0
Beryllium	0.81	1.26	1.70	2/2	-	-		- 0/0	-	-
Boron	-	· -		- 0/0	-	-		0/0	-	-
Cadmium	9.40	9.40	9.40	1/1	0.0025	0.18	0.78	9/13	1.0	0
Chromium	9.90	74.95	140	2/2	0.0050	0.071	0.12	3/13	5.0	0
Cobalt	-			- 0/0	-	-		0/0	-	-
Copper	29.70	84.85	140	2/2	-	-		0/0	-	-
Iron	28,200	34,050	39,900	2/2	-	-		0/0	-	-
Lead	8.91	274	539	2/2	0.05	0.46	2.55	7/13	5.0	0
Magnesium	10,900	11,550	12,200	2/2	-	-		0/0	-	-
Manganese	611	816	1,020	2/2	-	-		0/0	-	-
Mercury	0.40	0.67	0.93	2/2	0.00020	0.0012	0.0050	3/12	0.2	0
Molybdenum	-			0/0	-	-		0/0	-	-
Nickel	14.70	26.85	39.00	2/2	-	-		0/0	-	-
Selenium	0.49	2.85	5.20	2/2	0.00050	0.031	0.15	6/13	1.0	0
Silver	1.70	1.70	1.70	1/1	0.0050	0.029	0.25	1/13	5.0	0
Thallium	0.55	5.08	9.60	1/2	-	-		0/0	-	-
Vanadium	31.00	41.50	52.00	2/2	-	-		- 0/0	-	-
Zinc	9.90	240	470	2/2	-	-		0/0	-	-
Cyanide	0.105	0.15	0.19	0/2	0.50	0.50	0.50	0/2	-	-
Sulfide	-	· -			0.50	4.75	9.00	1/2	-	-
Sulfate	-	· -		0/0	-	-		0/0	-	-
Fluoride	-			- 0/0	-	-		- 0/0	-	-
Phosphate	-			- 0/0	-	-		- 0/0	-	-
Silica		-		0.10	-	-		0/0	-	-
Chloride	-			0/0	-	-		0/0	-	-
TSS	710,000	767,667	830,000	3/3	550,000	673,440	756,400	5/5	-	-
рН *	-	· · ·		0/0	·				2 <ph>12</ph>	0
Organics (TOC)				0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - AIR POLLUTION CONTROL DUST/SLUDGE - LIGHTWEIGHT AGGREGATE

	Total Co	onstituent Ar	nalysis - PPN	Л	EP Tox	icity Analysis	- PPM		TC	# Values
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	· -	· -	0/0		-	-	- 0/0	-	-
Antimony	-	· -	· -	0/0		-	-	- 0/0	-	-
Arsenic	10.00	10.00	10.00	2/2		-	-	- 0/0	5.0	0
Barium	57.00	57.00	57.00	2/2		-	-	- 0/0	100.0	0
Beryllium	-	· -	· -	0/0		-	-	- 0/0	-	-
Boron	-	· -		0/0		-	-	- 0/0	-	-
Cadmium	8.00	-	· -	0/0		-	-	- 0/0	1.0	0
Chromium	12.00	12.00	12.00	2/2		-	-	- 0/0	5.0	0
Cobalt	-	-	· -	0/0		-	-	- 0/0	-	-
Copper	-	-	· -	0/0		-	-	- 0/0	-	-
Iron	-	-		0/0		-	-	- 0/0	-	-
Lead	11.00	11.00	11.00	2/2		-	-	- 0/0	5.0	0
Magnesium	-	· -		0/0		-	-	- 0/0	-	-
Manganese	-	-		0/0		-	-	- 0/0	-	-
Mercury	0.100	0.100	0.100	2/2		-	-	- 0/0	0.2	0
Molybdenum	-	-	· -	0/0		-	-	- 0/0	-	-
Nickel	-	-	· -	0/0		-	-	- 0/0	-	-
Selenium	0.700	0.700	0.700	2/2		-	-	- 0/0	1.0	0
Silver	0.400	0.400	0.400	2/2		-	-	- 0/0	5.0	0
Thallium	-	-	· -	0/0		-	-	- 0/0	-	-
Vanadium	-	-		0/0		-	-	- 0/0	-	-
Zinc	-	-	· -	0/0		-	-	- 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	-	-		o /o		-	-	- 0/0	-	-
Chloride	-			0/0		-	-	- 0/0	-	-
TSS	-	· -		0.10		-	-	- 0/0	-	-
рН *				0.10					2 <ph>12</ph>	0
Organics (TOC)				- · · -						-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - WASTEWATER TREATMENT PLANT LIQUID EFFLUENT - LIGHTWEIGHT AGGREGATE

	Total Co	onstituent Ar	nalysis - PPI	Μ	EP Tox	EP Toxicity Analysis - PPM				
Constituents	Minimum	Average	Maximum	# Detects	Minimum	Average	Maximum	# Detects	Level	In Excess
Aluminum	-	-		- 0/0		-	-	- 0/0	-	-
Antimony	-	-		- 0/0		-	-	- 0/0	-	-
Arsenic	-	-		- 0/0		-	-	- 0/0	5.0	0
Barium	-	-		- 0/0		-	-	- 0/0	100.0	0
Beryllium	-	-		- 0/0		-	-	- 0/0	-	-
Boron	-	-		- 0/0		-	-	- 0/0	-	-
Cadmium	-	-		- 0/0		-	-	- 0/0	1.0	0
Chromium	-	-		- 0/0		-	-	- 0/0	5.0	0
Cobalt	-	-		- 0/0		-	-	- 0/0	-	-
Copper	-	-		- 0/0		-	-	- 0/0	-	-
Iron	-	-		- 0/0		-	-	- 0/0	-	-
Lead	-	-		0.0		-	-	- 0/0	5.0	0
Magnesium	-	-		- 0/0		-	-	- 0/0	-	-
Manganese	-	-		- 0/0		-	-	- 0/0	-	-
Mercury	-	-		- 0/0		-	-	- 0/0	0.2	0
Molybdenum	-	-		0.0		-	-	- 0/0	-	-
Nickel	-	-		0.0		-	-	- 0/0	-	-
Selenium	-	-		- 0/0		-	-	- 0/0	1.0	0
Silver	-	-		0.10		-	-	- 0/0	5.0	0
Thallium	-	-		- 0/0		-	-	- 0/0	-	-
Vanadium	_	-		- 0/0		-	_	- 0/0	-	-
Zinc	-	-		0.0		-	-	- 0/0	-	-
Cyanide	-	-		- 0/0		-	_	- 0/0	-	-
Sulfide	-	-		- 0/0		-	-	- 0/0	-	-
Sulfate	500	500	500	2/2		-	-	- 0/0	-	-
Fluoride	_			- 0/0		-	_	- 0/0	-	-
Phosphate	-	-		- 0/0		-	_	- 0/0	-	-
Silica	-	-		- 0/0		-	-	- 0/0	-	-
Chloride	100	100	100			-	_	- 0/0	-	-
TSS	400	400	400	2/2		-	_	- 0/0	-	-
рН *	6	6.00	6.00	2/2				5,0	2 <ph>12</ph>	0
Organics (TOC)	-			0.10						-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SURFACE IMPOUNDMENT LIQUIDS - LIGHTWEIGHT AGGREGATE

LITHIUM AND LITHIUM CARBONATE

A. Commodity Summary

Primarily, lithium is produced in the United States by two companies: Cyprus-Foote Mineral Company and FMC Corp. Cyprus-Foote produces lithium carbonate from its brine deposit in Silver Peak, Nevada and spodumene concentrate at its mine in Kings Mountain, North Carolina. Cyprus-Foote also produces lithium chemicals and metals at plants in Virginia and Tennessee. FMC purchased the Lithium Corporation of America assets and mines and processes spodumene ores at the Bessemer City site.¹ Exhibit 1 presents the names and locations of all the facilities involved in the production of lithium and lithium carbonate.

EXHIBIT 1

SUMMARY OF LITHIUM AND LITHIUM CARBONATE FACILITIES

Facility Name	Location
Cyprus-Foote	New Johnsonville, TN
Cyprus-Foote	Sunbright, VA
Cyprus-Foote	Kings Mountain, NC
FMC Corp	Bessemer City, NC

Lithium is found primarily in the mineral spodumene in pegmatites containing mineral assemblages which are derived from the crystallization of post magnetic fluids or from metasomatic action by residual pegmatitic fluids.²

Lithium compounds are used primarily in ceramics, glass, and primary aluminum production. Lithium is also used in the manufacture of lubricants and greases as well as in the production of synthetic rubbers.³ Specifically, lithium hydroxide is used in the production of lubricating greases and lithium carbonate is used as an additive in aluminum refining. Lithium chloride and bromide are used in absorption refrigeration systems and dehumidification systems.⁴ The consumption rate of lithium was estimated at 2,300 metric tons in 1994.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Lithium is obtained either from spodumene concentrates or from lithium-containing brines. It is chiefly produced as lithium carbonate or as hydroxide salts. Each of these processes is described in detail below.

¹ Joyce A. Ober, "Lithium," from <u>Minerals Yearbook Volume 1. Metals and Minerals</u>, 1992, U.S. Bureau of Mines, p. 754.

² U.S. Environmental Protection Agency, "Lithium," from <u>1988 Final Draft Summary Report of Mineral Industry</u> <u>Processing Wastes</u>, Office of Solid Waste, 1988, pp. 2-11-2-15.

³ Joyce A. Ober, "Lithium." from Mineral Commodity Summaries, 1995, pp. 98-99.

⁴ U.S. Environmental Protection Agency, 1988, <u>Op. Cit.</u>, p. 2-11.

2. Generalized Process Flow Diagram

Spodumene Concentrates

Exhibit 2 presents the process flow diagram for recovery from spodumene concentrates. After mining, the spodumene is crushed and ground. Following this, the spodumene undergoes a flotation process (e.g., froth flotation) to yield a spodumene concentrate. This concentrate is then heated to 1,075°C to 1,100°C (changing the molecular structure of the mineral) to make it more reactive with sulfuric acid.⁵ Following the roasting and cooling, the spodumene is treated with sulfuric acid and reroasted to yield lithium oxide. This calcine is then leached, neutralized with limestone, and filtered to remove gangue constituents. The resulting lithium-containing filtrate is treated with lime and soda ash to remove the soluble calcium and magnesium compounds. Following this, the remaining solution is concentrated by evaporation to yield a lithium sulfate solution. Insoluble portions of ore are removed by filtration and the purified solution is treated with soda ash to precipitate lithium carbonate. The carbonate is separated, washed and dried for sale.⁶ The lithium can also be used as the feedstock in the production of other lithium compounds.⁷

Lithium-containing Brines

Exhibit 3 presents the process flow diagram for the recovery of lithium from brines. In Nevada, brines enriched in lithium chloride (300 ppm) are pumped from the ground into solar evaporation ponds, where in a year to 18 months, the concentration of the brines increases to 6,000 ppm.⁸ During the evaporation, halite and sylvite crystallize and magnesium is precipitated as hydroxide by the addition of lime.⁹ When the proper concentration has been reached, the liquid is pumped to a recovery plant and treated with soda ash to precipitate the lithium carbonate. The carbonate can then be removed through filtration and dried for shipment.¹⁰

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

None Identified.

4. Beneficiation/Processing Boundary

EPA determined that this mineral commodity sector does not generate any mineral processing wastes. **Process Waste Streams**

1. Extraction/Beneficiation Wastes

From Spodumene Concentrates

Although generation rates are available for the wastes generated during the recovery of lithium carbonate from spodumene, characterization and management data are not available for all of the wastes.

⁶ Ibid.

C.

7 Ibid.

⁸ Ibid.

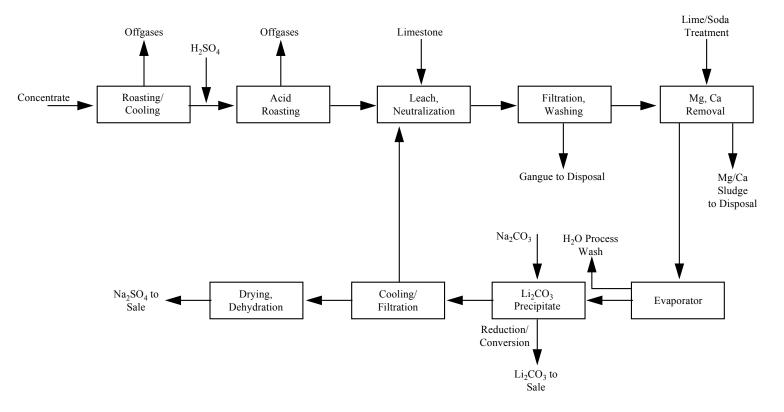
⁹ U.S. Environmental Protection Agency, 1988, <u>Op. Cit.</u>, p. 2-11.

⁵ Joyce A. Ober, 1992, <u>Op. Cit.</u>, p. 753.

¹⁰ Joyce A. Ober, 1992, <u>Op. Cit.</u>, p. 754.

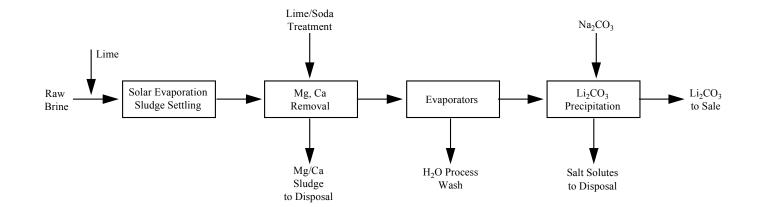
LITHIUM CARBONATE FROM SPODUMENE

(Adapted from: Technical Background Document, 1989.)



LITHIUM CARBONATE FROM BRINES

(Adapted from: Technical Background Document, 1989.)



Roaster Off-gases. Sources indicate the following generation rates: 600 ACF/lb, containing 0.01 lb dust/ lb. The generated dusts are concentrate fines.¹¹

Acid roaster gases. Sources indicate the following generation rates: 60 ACF/lb, containing 0.001 lb dust/ lb. The off-gases contain trace amounts of sulfuric acid and sulfur dioxide.¹²

Gangue. Sources indicate the following generation rates for gangue: 35 lb/lb, aluminosilicate residues of concentrate gangue. The solids generated contain 25 lb/lb water with trace amounts of lithium and other salts.¹³

Magnesium/Calcium sludge. Sources indicate the following generation rates for Mg/Ca sludge: 0.1 lb/lb hydrous oxides/carbonates. The sludge contains trace amounts of lithium and other salts.¹⁴

Flotation Tailings. Solid residues are generated as a result of the froth flotation process. The solid residues may be directly recovered and landfilled on-site. Characterization data are not available for either the content or the generation rate for this waste.

Wastewater from Wet Scrubber. Wastewater generated as a result of wet scrubbing emissions may be used for process make-up water. Wastewater from the wet scrubbing acid roaster emissions can be used for process water after it has been neutralized. Alternatively, some plants may recycle the wastewater.¹⁵

From Brines

Magnesium/Calcium sludge. Sludge generated during recovery from brines, containing trace amounts of lithium and other salts in addition to magnesium and calcium, is sent to disposal. Some magnesium hydroxide sludge may be stored on-site.¹⁶ Generation rates are not available.

Salt Solutions. Spent brines containing sodium and potassium chlorides and trace amounts of other brines are generated. These wastes may be sent to on-site evaporation ponds or reprocessed to recover potassium chloride.¹⁷

2. Mineral Processing Wastes

None Identified.

¹² Ibid.

¹³ <u>Ibid</u>.

¹⁴ <u>Ibid</u>.

¹⁷ <u>Ibid</u>.

¹¹ U.S. Environmental Protection Agency, "Lithium: Mineral Processing Waste Generation Profile," <u>Technical</u> <u>Background Document: Development of the Cost, Economic, and Small Business Impacts Arising from</u> <u>Reinterpretation of the Bevill Exclusion for Mineral Processing Wastes</u>, 1989.

¹⁵ Versar, Inc., "Lithium Derivatives," <u>Multi-media Assessment of the Inorganics Chemical Industry</u>, 1980, p. 25-7.

¹⁶ Versar, Inc., 1980, <u>Op. Cit.</u>, p. 25-8.

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 and other lubricants.

E. Summary of Commented Received by EPA

EPA received no comments that address this specific sector.

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MAGNESIUM AND MAGNESIA FROM BRINES

A. Commodity Summary

There are ten magnesium compound producers in the United States. Each of the facilities obtains its raw source material from either magnetite, lake brines, well brines, or seawater. In addition, there are three facilities that produce magnesium metal. Magnesia, the primary magnesium compound, is produced at three facilities. Exhibits 1 through 3 present the names and locations of facilities involved in the production of magnesium, magnesium metal, and magnesia from brines, respectively.

Magnetite and dolomite, which have a theoretical magnesium content of 47.6% and 22%, respectively, comprise the largest mineral sources of magnesium and magnesium compounds. Other sources of magnesium and its compounds include seawater, brines, and bitterns.¹

Magnesium and its alloys are used in the manufacture of structural components for automobiles, trucks, aircraft, computers, and power tools. Because of its light weight and ease of machinability, magnesium is used by the iron and steel industry for external hot-metal desulfurization and in the production of nodular iron. Producers of several nonferrous metals often use magnesium as a reducing agent. Magnesium anodes are used for cathodic protection of underground pipe and water tanks. Small quantities of magnesium are used as a catalyst in the synthesis of organic compounds, as photoengraving plates, and in alloys (other than aluminum). Caustic magnesia can be used as a cement if combined with magnesium chloride.

Refractory magnesia represents the largest use of magnesium in compounds. It is used principally for linings in furnaces and auxiliary equipment used to produce iron and steel. Caustic-calcined magnesia (partially calcined magnesite) is used in the agricultural, chemical, construction, and manufacturing industries.²

The most commonly used source for magnesia is magnesium carbonate, with the largest source being magnesia-rich brines and seawater. Magnesite is one of the minerals directly and widely exploited for its magnesia content. When pure, it contains 47.8% magnesia and 52.2% carbon dioxide. Sintered magnesia is used for refractory manufacturing while lighter fired caustic magnesia is used in fluxes, fillers, insulation, cements, decolorants, fertilizers, chemicals, in the treatment of wastewater including pH control, and in the removal of sulfur compounds from gas exhaust stacks. In addition to naturally occurring magnesia, refractory grade magnesia can also be produced synthetically. This involves the calcination of either magnesium hydroxide or magnesium chloride.³

B. Generalized Process Description

1. Discussion of Typical Production Processes

The two main operation types for recovery of magnesium are (1) electrolytic production, and (2) thermal production. Each of these processes is described in more detail below.

² <u>Ibid</u>.

³ L.R. Duncan and W.H. McCracken, "Magnesite and Magnesia," from <u>Industrial Minerals and Rocks</u>, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 643-654.

¹ Deborah A. Kramer, "Magnesite and Magnesia," from <u>Minerals Yearbook Volume 1. Metals and Minerals</u>, U.S. Bureau of Mines, 1992, pp. 163-173.

SUMMARY OF MAGNESIUM PROCESSING FACILITIES

Facility Name	Location	Type of Operations
Barcroft Co.	Lewes, DE	MgO from seawater
Dow Chemical Co.	Freeport, TX	MgCl from seawater
Great Salt Lake	Ogden, UT	MgCl from lake brine
Marine Magnesium Co.	South San Francisco, CA	MgO from seawater
Martin Marietta Chemicals	Manistee, MI	MgCl from brine
Morton Chemical Co.	Manistee, MI	MgCl from brine
National Refractories & Minerals Corp.	Moss Landing, CA	MgO from seawater
Premier Services Inc.	Port St. Joe, FL	MgO from seawater
Premier Services Inc.	Gabbs, NV	Mine magnesium carbonate and calcine to MgO
Reilly Ind.	Wendover, UT	Brine Extraction

EXHIBIT 2

SUMMARY OF MAGNESIUM METAL PROCESSING FACILITIES

Facility	Location
Dow Chemical Co.	Freeport, TX
Magnesium Corp. of America	Rowley, UT
Northwest Alloys Inc.	Addy, WA

EXHIBIT 3

SUMMARY OF MAGNESIA (MGO) PROCESSING FACILITIES

Facility Name	Location	Type of Operations
Basic Incorporated	Gabbs, NV	Uncertain
Dow Chemical Co.	Freeport, TX	Brine Extraction
Magnesia Operations	San Francisco, CA	Uncertain

2. Generalized Process Flow Diagram

Electrolytic Production

Hydrous Magnesium Chloride Feed. The Dow Chemical Company is the only magnesium producer using hydrous magnesium chloride as feed for the electrolytic cells. A flow sheet of the Dow process is presented in Exhibit 4. In this process, magnesium is precipitated from seawater as magnesium hydroxide by addition of lime or caustic in large agitated flocculators. The magnesium hydroxide is then settled in Dorr thickeners. The overflow enters the plant wastewater system where it is neutralized and returned to the ocean. The thickened underflow is pumped to rotary filters where it is dewatered, washed, and reslurried with wash water from the magnesium chloride purification step. It is then pumped to the neutralizers where it is treated with hydrochloric acid and enough sulfuric acid to precipitate excess calcium as calcium sulfate. The brine is filtered to remove calcium sulfate and other solids such as clavs and silica and is further purified to reduce sulfate and boron and forwarded to the dryer. The purified brine is dried by direct contact with combustion gases in a fluid-bed dryer to produce granules of magnesium chloride. The granules are stored in large tanks from which they are fed to the electrolytic cells. The cells are fed semicontinuously and produce both magnesium and chlorine. The dilute, wet chlorine gas is drawn into refractory regenerative furnaces and converted to HCl which is recycled to neutralize magnesium hydroxide. The magnesium collects in compartments in the front of the cell from which it is periodically pumped into a computer-controlled crucible car operating at ground level. The crucible is conveyed to the casting house where it is emptied into a holding furnace or into alloying pots from which the metal is pumped into molds on continuous mold conveyors.⁴

Surface Brine Feed. A second process for magnesium production, shown in Exhibit 5, utilizes surface brine from the Great Salt Lake as feed to a series of solar evaporation ponds. This brine is further concentrated and treated with CaCl₂. Solids such as calcium sulfate and potassium and sodium chlorides are removed in a thickener. Further concentration provides feed for the spray dryer whose waste gases provide heat for the concentration process. The spray dryers convert the brine into a dry MgCl₂ powder containing about 4% magnesia, 4% water, and other salts which comprise the cell bath. The dryers are heated with exhaust gases from gas-fired turbines that generated some of the power used to operate the cells. The spray-dried MgCl₂ powder is melted in large reactors and further purified with chlorine and other reactants to remove magnesium oxide, water, bromine, residual sulfate, and heavy metals. The molten MgCl₂ is then fed to the electrolytic cells. Only a part of the chlorine produced is required for chlorination, leaving up to 1kg/kg magnesium produced available for sale as byproduct chlorine.⁵

Underground Brine Feed. A third process for magnesium recovery uses underground brines as its source of raw material. Brine is pumped from below the ground into a large system of plastic-lined solar evaporation ponds, where the magnesium chloride concentration is increased to 25% which reduces the solubility of sodium chloride to 1%. The brine is then moved by pipeline to the plant where it is further concentrated, purified, and spray dried. The spray-dried feed is further purified by chlorination. The magnesium chloride is electrolyzed in diaphragmless cells and the molten magnesium is removed by vacuum ladle. It is then transported to a refining furnace where it is cast into ingots. The chlorine is collected, cleaned, and liquefied.⁶ Exhibit 5 presents a flow diagram of the process for recovering magnesium from underground brines and surface brines.

Thermal Reduction

In the thermal reduction process, magnesium oxide, as a component of calcined dolomite, reacts with a metal such as silicon to produce magnesium. The silicon is usually alloyed with iron. There are two principle methods: (1) carbothermic, and (2) silicothermic.

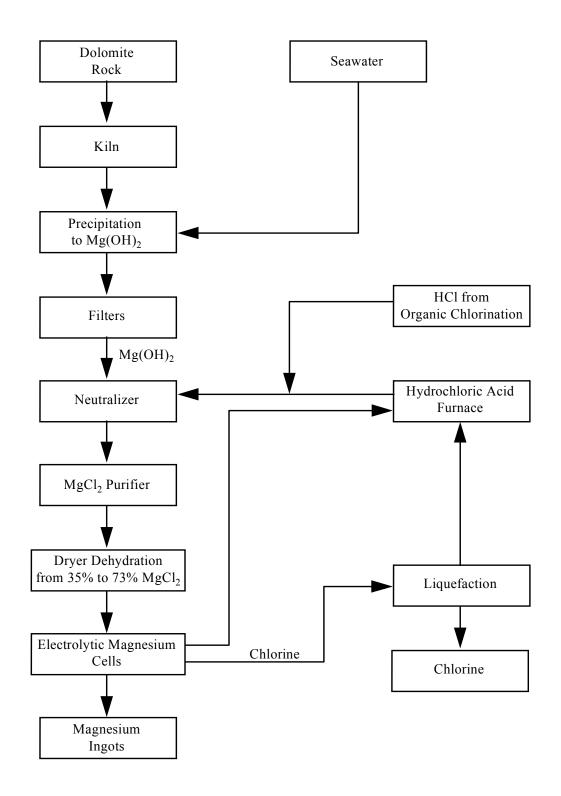
⁶ <u>Ibid</u>.

⁴ Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XIV, 1981, pp. 576-586, 631-635.

⁵ <u>Ibid</u>.

ELECTROLYTIC PRODUCTION USING HYDROUS MAGNESIUM CHLORIDE FEED

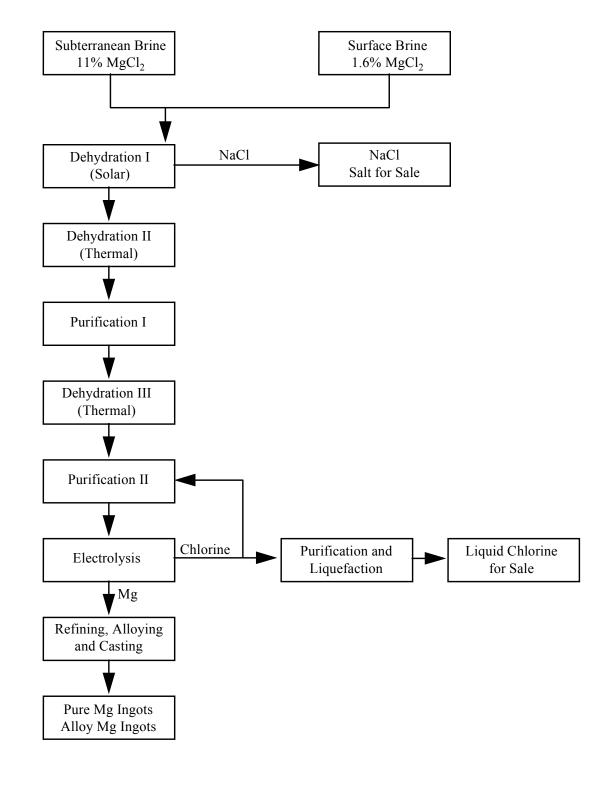
(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 578.)



Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 578.

ELECTROLYTIC PRODUCTION USING SURFACE AND UNDERGROUND BRINES AS FEED

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 582.)



Source: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 582.

In the *carbothermic process*, magnesium oxide is reduced with carbon using modified shock cooling to produce magnesium and carbon monoxide. Both products are in the vapor phase. In order to recover the magnesium, the temperature must be dropped rapidly to prevent reversion. Shock cooling produces very finely divided magnesium dust which is pyrophoric.⁷

The *silicothermic process* is based on the reaction of silica with carbon to give silicon metal which is subsequently used to produce magnesium by reaction with calcined dolomite. The Pidgeon and Magnetherm processes employ this procedure.

The Pidgeon process is a batch process in which dolime and silicon are sized, briquetted, and charged into gas-fired or electrically heated retorts of nickel-chrome-steel alloy. The retort is equipped with removable baffles and a condensing section that extends from the furnace and is water-cooled. High purity crowns are remelted and cast into ingots.⁸ Exhibit 6 presents a flow diagram of the Pidgeon process.

In the Magnetherm process, sufficient alumina is added to melt the dicalcium silicate slag that forms at around 1500° C. This permits the reactor to be heated by the electrical resistance of the slag and further allows the reaction products to be removed in the molten state. About 0.45 kg calcined bauxite or alumina, 2.7 kg dolime, and 0.45 kg ferrosilicon are required to produce 0.45 kg metallic magnesium. As the reactants are fed to the furnace, magnesium is evolved and passes through a large tuyere into the condensation chamber. Magnesium collects as a liquid and runs down into a collection pot where it solidifies. The slag is tapped twice a day by introducing argon into the furnace to break the vacuum. The slag outlet is electrically lanced and the molten calcium aluminum silicate is quenched in water to stabilize the slag (which can be used as cement). About 5.9 kg slag are produced per kg magnesium. The residual ferrosilicon containing 20% silicon is removed and can be used as low grade silicon alloy. The magnesium collection crucible is removed once a day and the magnesium is remelted, alloyed if required, and then cast into ingots.⁹

Magnesia from Brines

Magnesia, magnesium oxide, is usually produced by calcining the mineral magnesite or magnesium hydroxide obtained from seawater or brine by liming. It is also produced by the thermal decomposition of magnesium chloride, magnesium sulfate, magnesium sulfite, nesquehonite, and the basic carbonate.¹⁰ A flow diagram of magnesia recovery from seawater is presented in Exhibit 7.

Magnesite ores contain varying amounts of silica, iron oxide, alumina, and lime as silicates, carbonates, and oxides. The deposits are mined selectively and the ores are often beneficiated to reduce lime and silica concentrations prior to calcining. Beneficiation methods include crushing and size separation, heavy-media separation, and froth flotation. Magnetic separation reduces iron concentration, but is effective only when the iron is present in the form of discrete ferromagnetic minerals rather than as ferrous carbonate.¹¹

In chemical beneficiation processes, the magnesium is dissolved as a salt, the insoluble impurities are removed by filtration or sedimentation, and purified magnesia is recovered by thermally decomposing the clean salt solution. Special processes are needed to separate out calcium due to its similarity to magnesium. Three of these processes are discussed below.

⁷ Ibid.

⁸ <u>Ibid</u>.

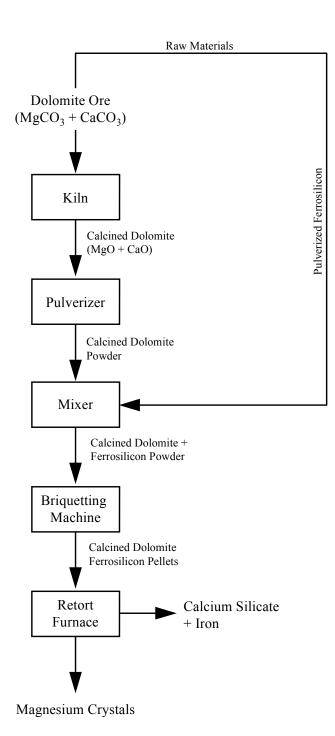
⁹ <u>Ibid</u>.

¹⁰ Ibid.

¹¹ <u>Ibid</u>.

THE PIDGEON PROCESS

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 584.)

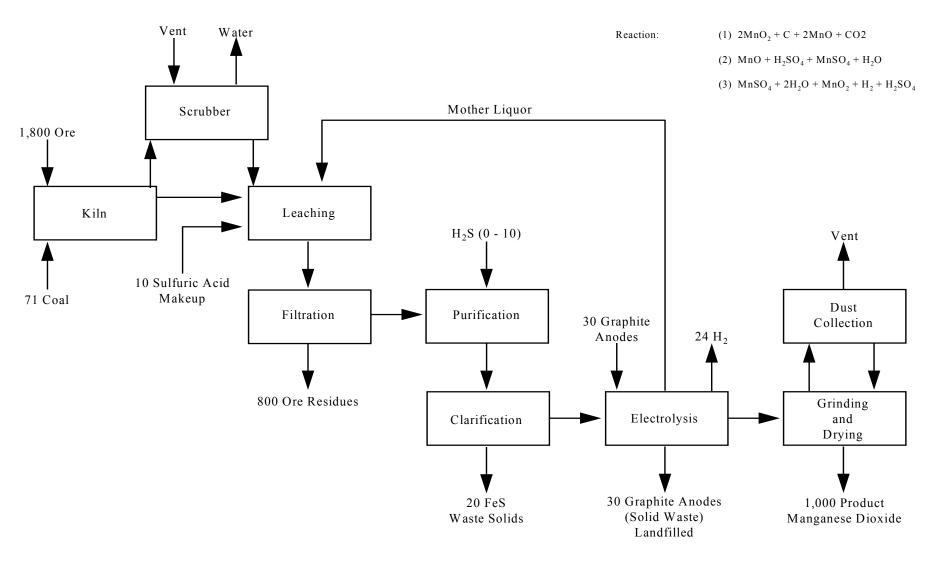


Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 584

Source:

PRODUCTION OF ELECTROLYTIC MANGANESE DIOXIDE

(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, pp. 6-14.)





The first process to separate out calcium is the Pattinson process. In this process, a suspension of magnesium hydroxide is carbonated to form a solution of magnesium bicarbonate. After the insoluble impurities are separated, the solution is decarbonated by heating or aeration and the magnesium carbonate precipitates as the trihydrate, the pentahydrate or the basic carbonate. The precipitate is recovered from the solution by filtration or sedimentation and converted to the oxide by thermal decomposition. The highly reactive grades of caustic-calcined magnesia are usually produced using a modified form of this process.¹²

In a second process for the separation of calcium impurities, magnesium is dissolved with the aid of sulfur dioxide or a mixture of sulfur dioxide and carbon. One variation of this method can be employed to remove SO_2 from flue gas. The flue gas is treated with a magnesium hydroxide slurry in a venturi scrubber to form MgSO₃ and some MgSO₄, which is subsequently calcined to recover the magnesium oxide and sulfur dioxide. The magnesium oxide is recycled and the sulfur dioxide may be used to manufacture sulfuric acid.¹³

In a third process, magnesia is dissolved in hydrochloric acid. After the insoluble impurities are removed, the magnesium chloride solution is thermally decomposed to recover the magnesia.¹⁴

There are several operations used to recover magnesium oxide from dolomite. Because calcite and magnesite decompose at different temperatures, a stepwise decomposition permits a selective calcination in which the magnesium carbonate is completely decomposed without decomposing the calcium carbonate. The magnesium oxide is then separated mechanically from the half-calcined dolomite by screening or air separation. Another scheme employs a modification of the Pattinson process in which the dolomite is calcined, slaked, and then carbonated in steps to precipitate calcium carbonate and magnesium carbonate trihydrate. This is further carbonated to dissolve the trihydrate as magnesium bicarbonate and the calcium carbonate is removed by filtration. The clean solution is finally decarbonated to precipitate magnesium carbonate trihydrate which is thermally decomposed to produce magnesia.¹⁵

Highly reactive grades of caustic-calcined magnesia are produced by calcining basic magnesium carbonate or magnesium carbonate trihydrate in small batches under carefully controlled conditions. They generally have magnesia contents above 99% and contain small quantities of carbon dioxide and moisture. The carbonates for these grades are prepared by a variation of the Pattinson process described above. The less reactive grades are obtained by calcining magnesium hydroxide or magnesite in multiple-hearth furnaces or rotary kilns.¹⁶

Dead-burned magnesia is used almost exclusively for refractory applications in the form of basic granular refractories and brick. It is produced in a number of grades.¹⁷

Fused magnesia is produced by melting calcined magnesia in an electric arc furnace. The furnaces have water-cooled shells and no refractory linings. The material serves as its own refractory because only a small pool of material in the center is actually melted. When magnesia is fused for the purpose of making grain, it is allowed to

¹² Ibid.

¹³ <u>Ibid</u>.

¹⁴ Ibid.

¹⁵ <u>Ibid</u>.

¹⁶ <u>Ibid</u>.

¹⁷ <u>Ibid</u>.

4. 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.

Electrolytic Production of Magnesium

EPA determined that for the production of magnesium through this process, the beneficiation/processing line occurs when the dried MgCl, undergoes electrolytic refining at the electrolytic magnesium cells and chlorine is chemically removed to yield pure magnesium. 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.

Production of Magnesium Through Thermal Reduction

EPA determined that in the production of magnesium through thermal reduction, the beneficiation/processing line is crossed when calcined dolomite ferrosilicon (CDF) pellets are introduced to the furnace for retorting when magnesium crystals are produced through the thermal destruction of the CDF pellets. 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

¹⁸ Ibi<u>d</u>.

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

None identified.

Beneficiation/Processing Boundaries

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.

Magnesia from Brines

EPA determined that for the production of magnesia from brines, the beneficiation/processing line occurs between filtration or sedimentation and when trihydrates are converted to the oxide through thermal decomposition. 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.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Ore Extraction and Beneficiation

Possible waste streams from ore extraction processes include tailings and offgases from calcining.

Brine Extraction and Beneficiation

Extraction waste streams from brines include calcium sludge, spent seawater, and offgases.

2. Mineral Processing Wastes

Electrolytic Production

Casting plant slag. This waste stream was generated at a rate of 3,000 metric tons per year in 1991.¹⁹ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Smut (sludge and dross). This waste, generated at a rate of 26,000 metric tons per year, may be toxic for barium.²⁰ Management for this waste includes disposal in an unlined surface impoundment.²¹ Waste characterization data are presented Attachment 1. This waste may be recycled and is classified as a byproduct.

Process wastewater is a possible waste stream from magnesium production. This waste was generated at a rate of 2,465,000 metric tons per year in 1991.²² Process wastewater may contain calcium sulfate and boron and

²⁰ Ibid.

²² U.S. Environmental Protection Agency, <u>Op. Cit.</u>, Vol. I, August, 1992, pp. I-2 - I-8.

¹⁹ U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data</u> <u>Set</u>, Office of Solid Waste, Vol. I, August, 1992, pp. I-2 - I-8.

²¹ U.S. Environmental Protection Agency, <u>Technical Background Document</u>, <u>Development of Cost</u>, <u>Economic</u>, <u>and Small Business Impacts Arising from the Reinterpretation of the Bevill Exclusion for Mineral Processing</u> Wastes, August 1989, pp. 3-4--3-6.

have a low pH. This waste is may be discharged to a waste pond.²³ EPA determined in 1994 that the great majority of process wastewater is comprised of two special wastes -- scrubber underflow process wastewater and scrubber liquor process wastewater.²⁴

Thermal Reduction

Cathode scrubber liquor. Dissociation of magnesium chloride molten salt from magnesium produces chlorine gas which is passed through a scrubber system. This produces a cathode scrubber liquor, which is discharged to surface impoundments with other wastewaters.²⁵ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

APC Dust/Sludge is a possible waste stream from magnesium production.²⁶ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Slag is a possible waste stream from magnesium production. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Casthouse dust. During the refining of magnesium metal, casthouse dust is produced. 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 76 metric tons/yr, 760 metric tons/yr, and 7,600 metric tons, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for barium. This waste may be recycled and is classified as a sludge.

Magnesia from Brines

Possible waste streams from magnesia production from brines include **calciner offgases**, **calcium sludge**, and **spent brines** (which may be sold). Existing data and engineering judgement suggest that these materials do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

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 and other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

²³ U.S. Environmental Protection Agency. <u>Mineral Processing Waste Sampling Survey Trip Reports</u>. AMAX Magnesium Company, Rowley, Utah. August 30, 1989.

²⁵ <u>Ibid</u>.

²⁶ U.S. Environmental Protection Agency, 1992, <u>Op. Cit.</u>, pp. I-2 - I-8.

²⁴ U.S. Environmental Protection Agency, Memorandum

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- U.S. Environmental Protection Agency. <u>Newly Identified Mineral Processing Waste Characterization Data</u> <u>Set</u>. Office of Solid Waste. Vol. I. August 1992. pp. I-2 - I-8.
- U.S. Environmental Protection Agency. "Magnesium Production." From <u>Report to Congress on Special Wastes</u> from Mineral Processing. 1990. pp. 11-1 - 11-15.

ATTACHMENT 1

	Total C	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		-		- 0/0	-	-	-	- 0/0	-	-
Arsenic		-		- 0/0	0.1	0.375	0.65	2/2	5.0	0
Barium		-		- 0/0	14.9	81.95	149	2/2	100.0	1
Beryllium		-		- 0/0	-	-	· -	- 0/0	-	-
Boron		-		- 0/0	-	-	· -	- 0/0	-	-
Cadmium		-		- 0/0	0.01	0.0185	0.027	2/2	1.0	0
Chromium		-		- 0/0	0.023	0.0385	0.054	2/2	5.0	0
Cobalt		-		- 0/0	-	-	· -	- 0/0	-	-
Copper		-		- 0/0	0.025	1.2325	2.44	1/2	-	-
Iron		-		- 0/0	0.22	0.29	0.36	2/2	-	-
Lead		-		- 0/0	0.043	1.8415	3.64	2/2	5.0	0
Magnesium		-		- 0/0	-	-	-	- 0/0	-	-
Manganese		-		- 0/0	0.03	0.1	0.17	1/2	-	-
Mercury		-		- 0/0	0.0008	0.0009	0.001	2/2	0.2	0
Molybdenum		-		- 0/0	-	-	-	- 0/0	-	-
Nickel		-		- 0/0	-	-	-	- 0/0	-	-
Selenium		-		- 0/0	0.013	0.0145	0.016	2/2	1.0	0
Silver		-		- 0/0	0.05	0.095	0.14	2/2	5.0	0
Thallium		-		- 0/0	-	-	-	- 0/0	-	-
Vanadium		-		- 0/0	-	-	-	- 0/0	-	-
Zinc		-		- 0/0	0.02	0.355	0.69	1/2	-	-
Cyanide		-		- 0/0	-	-	-	- 0/0	-	-
Sulfide		-		- 0/0	-		-	- 0/0	-	-
Sulfate		-		- 0/0	4	4	4	0/2	-	-
Fluoride		-		- 0/0	0.2	1.3	2.4	2/2	-	-
Phosphate		-		- 0/0	-	-	-	- 0/0	-	-
Silica		-		- 0/0	-	-	-	- 0/0	-	-
Chloride		-		- 0/0	25600	27150	28700	2/2	-	-
TSS		-		- 0/0	-	-	-	- 0/0	-	-
pH *		-		- 0/0					2 <ph>12</ph>	0
Organics (TOC)		-		- 0/0					-	-

SUMMARY OF EPA/ORD, 3007, AND RTI SAMPLING DATA - SMUT (SLUDGE AND DROSS) - MAGNESIUM

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

MANGANESE, MANGANESE DIOXIDE, FERROMANGANESE, AND SILICOMANGANESE

A. Commodity Summary

Approximately 95 percent of all manganese ore is consumed in the manufacture of steel, primarily as ferromanganese and silicomanganese, and other minor alloy-related industries. The other five percent is used by the non-alloying industries, including the chemical, paint, fertilizer, and battery industries, and in the production of manganese metal.¹ Manganese ore was consumed mainly by about 20 firms with plants principally in the Eastern and Midwestern United States. Metallic manganese is often too brittle and unworkable to be widely used.² However, leading identifiable end uses of manganese were construction, machinery, and transportation, which were estimated to be 14 percent, 9 percent, and 9 percent of total manganese demand, respectively. The other end uses include a variety of iron and steel applications.³

Manganese ore containing 35 percent or more manganese was not produced domestically in 1993.⁴ The manganese industry in the United States relies almost entirely on foreign ores containing 35 to 55 percent manganese. The small amount of manganese ore produced in the United States is generally used as a pigment in the manufacture of brick.⁵

As of 1992, there were four companies that produced manganese, manganese oxide, ferromanganese or silicon manganese in six plants in the United States. Exhibit 1 presents the names, locations, products and types of processes used by the facilities involved in the production of manganese, manganese oxide, ferromanganese, and silicomanganese.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Almost all of the ore processed in the United States is imported as a concentrate. Nonetheless, typical operations used to produce concentrates include crushing, screening, washing, jigging, and tabling, as well as flotation, heavy-media, and high-intensity magnetic separation.⁶ Ferromanganese is made by smelting ore (which contains both iron and manganese) with coke and limestone, and silicomanganese is produced by smelting the slag from standard ferromanganese with additional ore and coke. Manganese metal is frequently produced by preparing a solution of manganous sulfate from ore that has been reduction roasted, and electrolyzing this solution. Manganese dioxide is prepared either chemically or electrolytically. Each of these processes is described in greater detail below.

⁴ <u>Ibid</u>.

¹ R.A. Holmes, "Manganese Minerals," from <u>Industrial Minerals and Rocks</u>, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, p. 657.

² T.S. Jones, "Manganese," from <u>Minerals Yearbook. Volume 1. Metals and Minerals</u>, U.S. Bureau of Mines, 1992, p. 790.

³ T. S. Jones, "Manganese," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 104.

⁵ R. A. Holmes, <u>Op. Cit.</u>, p. 656.

⁶ T. S. Jones, 1992, <u>Op. Cit.</u>, p. 791.

Facility Name	Location	Products	Type of Process	
Chemetals Inc.	Baltimore, MD	MnO ₂	Chemical	
Chemetals Inc.	New Johnsonville, TN	MnO ₂	Electrolytic	
Elkem Metals Co.	Marietta, OH	FeMn, SiMn, Mn	Electric Furnace and Electrolytic	
Kerr McGee Chemical Corp.	Hamilton, MS	Mn	Electrolytic	
Kerr McGee Chemical Corp.	Henderson, NV	MnO ₂	Electrolytic	
Everready Battery Co.	Marietta, OH	MnO ₂	Electrolytic	

SUMMARY OF MANGANESE, MANGANESE DIOXIDE, FERROMANGANESE, AND SILICOMANGANESE PRODUCERS^a

^a - Jones, T. S., "Manganese." Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. p. 802.

2. Generalized Process Flow Diagram

Ferromanganese and Silicomanganese

In the United States, electrothermy is the predominant method of manufacturing manganese ferroalloys, using the submerged-arc furnace process. Standard or high-grade ferromanganese is the principal intermediate form into which manganese concentrates and other ore products are processed. Exhibit 2 shows a typical ferromanganese production process. Typically, a charge of ore, coke, and limestone is smelted in a submerged-arc furnace. In the manufacture of silicomanganese, an ore with a relatively high silica content, such as quartz or slag from standard ferromanganese is included in the charge introduced into the submerged-arc furnace. Smelting economics favor an integrated standard ferromanganese-silicomanganese electric-furnace operation, in which the high manganese slag from ferromanganese production is used as part of the charge to the silicomanganese furnace, along with ore and coke.⁷ If silicomanganese is not co-produced, ore containing lower concentrations of manganese or higher concentrations of base oxides may be used, and the resulting slag is discarded.

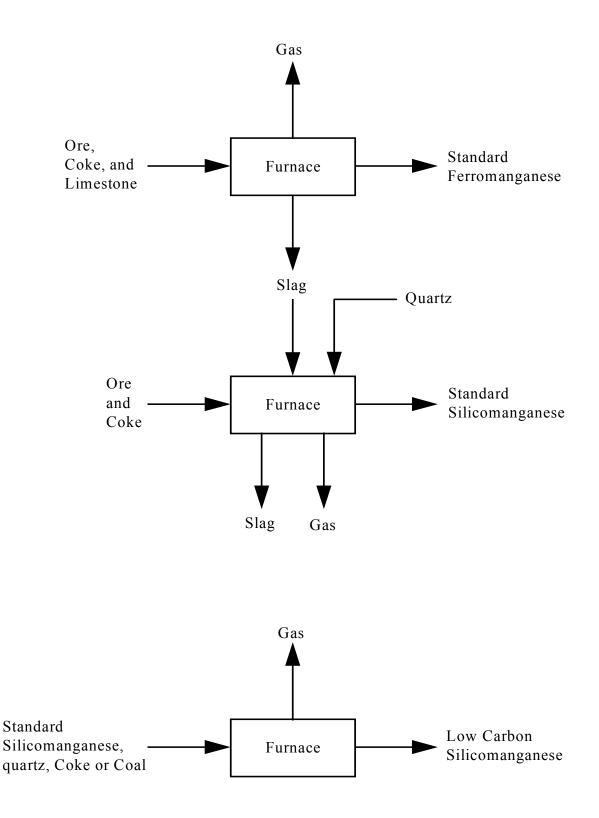
Low carbon silicomanganese (or ferromanganese-silicon) is produced in a manner similar to standard silicomanganese, using standard silicomanganese, quartz, and coke or coal as the charge. Both standard ferromanganese and silicomanganese produce a slag and an off-gas containing CO_2 . Low carbon silicomanganese manufacture is a slagless process, where the quartz is reduced to silicon and displaces the carbon in the remelted silicomanganese.⁸ The gases are filtered through either wet scrubbers or baghouses. Ore fines are often sintered into bulkier particles before charging them to the furnace to lower the CO_2 concentration in the off-gas, and reduce energy consumption.⁹

⁹ <u>Ibid</u>, p. 832.

⁷ T.S Jones, "Manganese," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, pp. 487-88.

⁸ "Manganese and Manganese Alloys," <u>Kirk-Othmer Encyclopedia of Chemical Technology</u>, 3rd. ed., Volume XIV, 1981, p. 833.

FERROMANGANESE AND SILICOMANGANESE PRODUCTION



Medium and low carbon ferromanganese are called refined ferromanganese. Silicon in silicomanganese or low carbon silicomanganese reacts with manganese ore and lime to produce refined ferromanganese.¹⁰ Exhibits 3 through 5 illustrate three variations of this process.

Manganese Metal

Manganese metal is frequently produced by preparing a solution of manganous sulfate from ore that has been reduction roasted, and electrolyzing this solution. Exhibit 6 depicts a typical production process of manganese metal from ore. Manganese ore is roasted to reduce the higher oxides to manganese (II) oxide. Slag from the production of high carbon ferromanganese may also supply manganese (II) oxide. The reduced ore or slag is leached with sulfuric acid to produce manganese (II) sulfate. Impurities, such as iron and aluminum, are precipitated and filtered. Other metal impurities are removed as sulfides, by introducing hydrogen sulfide gas. Either ferrous or ammonium sulfide and air are added to remove colloidal sulfur, colloidal metallic sulfides, and organic matter. The purified liquid is put into a diaphragm cell, and electrolyzed. The manganese metal deposits on the cathode in a thin layer, which is brittle and extremely pure.¹¹ Manganese metal can also be made electrolytically by fused-salt electrolysis (not shown.) Manganese ore that has been reduced to the manganese(II) level is charged to an electrolytic cell which contains molten calcium fluoride and lime. Fused electrolyte is periodically removed, as the volume of fused electrolyte increases.¹²

Manganese Dioxide

Manganese dioxide is prepared either chemically or electrolytically. Exhibit 7 illustrates the electrolytic production of manganese dioxide, which is similar to the electrolytic production of manganese metal. Manganese ore and coke are reacted in kilns at 600°C. The mixture is cooled and leached with a solution containing 50 grams per liter of manganese sulfate and 67 grams per liter of sulfuric acid at 90°C. After leaching, the solutions are filtered to remove the insoluble ore residues, which are discarded as a waste. The filtered solution are treated with hydrogen sulfide to precipitate iron salts and sulfides. These solids are removed by filtration and the purified solutions are fed to electrolytic cells. The cells used are generally lead lined with graphite cathodes and anodes. During electrolysis, manganese dioxide builds up a costing on the anodes as thick as 6 mm before it is removed. The manganese dioxide is periodically stripped from the electrodes, recovered from the cells, crushed, washed, first with dilute soda ash solutions and then with pure water, dried, pulverized and packaged. The hydrogen co-product from the electrolysis is flared, and the spent process liquor containing mostly sulfuric acid is recycled to the ore leaching step.

Manganese dioxide also may be prepared chemically, either by chemical reduction of permanganate (Type I) or by thermally decomposing manganese salts, such as $MnCO_3$ or $Mn(NO_3)_2$ under oxidizing conditions (Type II).¹³ To produce Type I chemical manganese dioxide (not shown), the byproduct manganese dioxide from the oxidation of organics using potassium permanganate, is treated with hydrochloric or sulfuric acid, followed by $MnSO_4$. This treatment removes the excessive quantities of adherent and bound alkali. $KMnO_4$ is added to convert the ion exchanged divalent Mn into MnO_2 . The product is washed and dried at low temperature, so as to avoid the undesirable loss of water of hydration.¹⁴

¹⁴ Ibid.

¹⁰ <u>Ibid.</u>, pp. 834-837.

¹¹ Ibid., pp. 835-836.

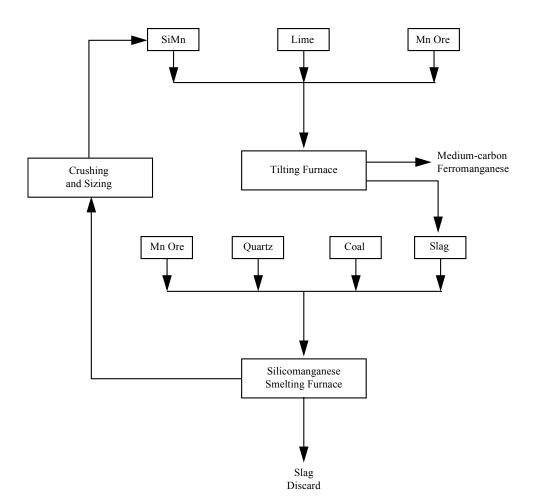
¹² <u>Ibid.</u>, p. 837.

¹³ <u>Ibid.</u>, p. 863.

REFINED FERROMANGANESE PRODUCTION

MEDIUM-CARBON FERROMANGANESE RAW ORE PRACTICE

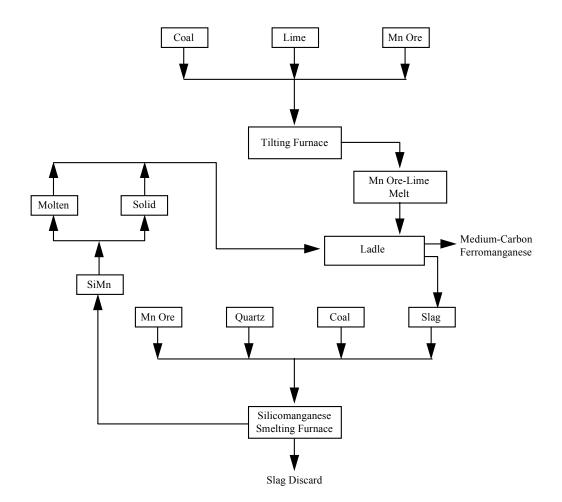
(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 835 - 837.)



REFINED FERROMANGANESE PRODUCTION

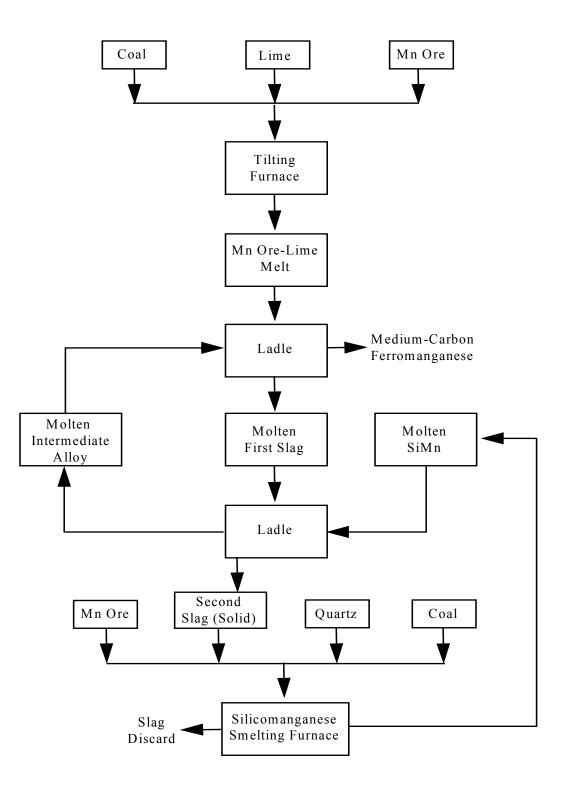
MEDIUM-CARBON FERROMANGANESE FUSED ORE

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 835 - 837.)

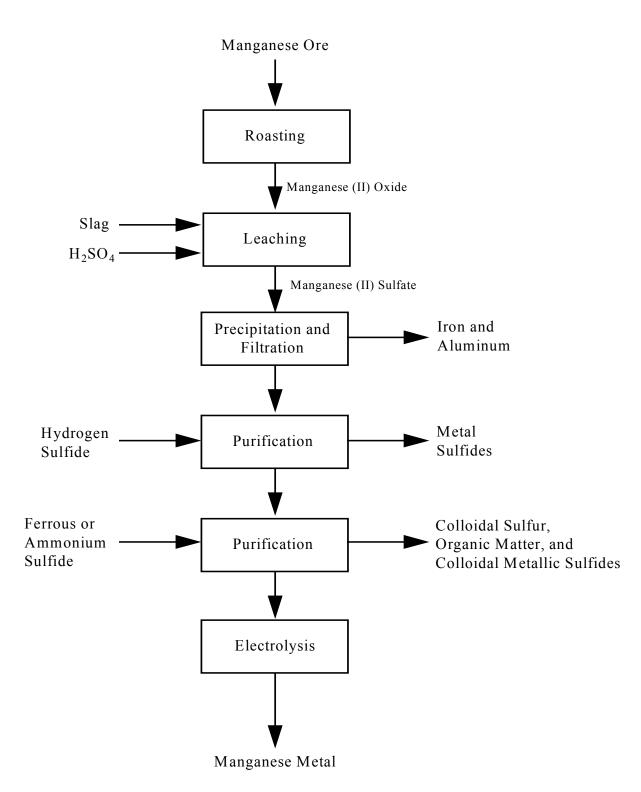


REFINED FERROMANGANESE PRODUCTION MEDIUM-CARBON FERROMANGANESE FUSED ORE

(Adapted from: Kirk-Othmer Encyclopedia of Chemical Technology, 1981, pp. 835 - 837.)

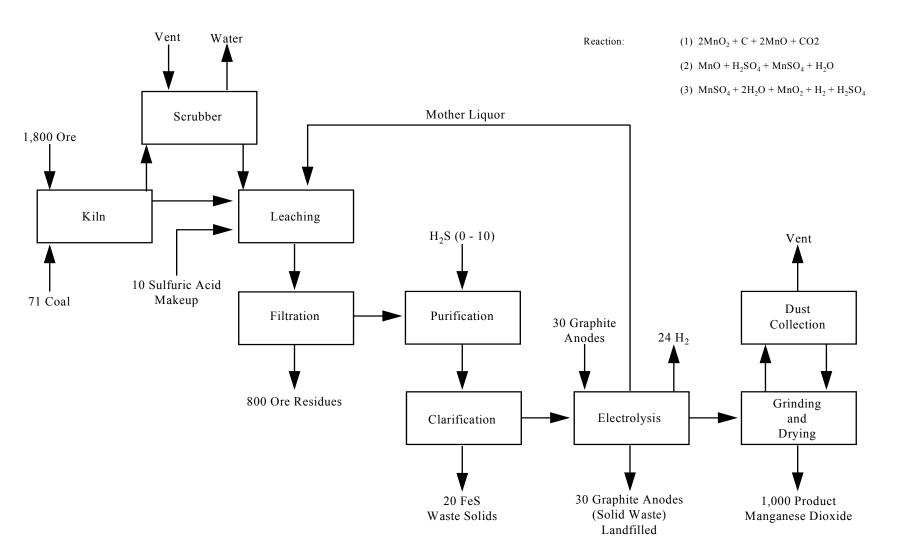


MANGANESE METAL PRODUCTION



PRODUCTION OF ELECTROLYTIC MANGANESE DIOXIDE

(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, pp. 6-14.)



To make Type II chemical manganese dioxide, as shown in Exhibit 8, manganese ore is reacted with coke in kilns at 600°C, then cooled and leached with 10 percent nitric acid at 85°C to generate a neutral manganese nitrate solution. This solution is filtered to remove insoluble materials, treated with sulfides to precipitate iron impurities and refiltered. The ore residues and iron sulfides are discarded as waste. The purified manganese nitrate solution is evaporated to about half the original volume. Manganese nitrate crystals separate at this point and are recovered by centrifugation. The mother liquor is recycled to the evaporators and the recovered crystals are heated to 200°C to produce manganese dioxide and nitrogen dioxide, which is absorbed as nitric acid for reuse. The manganese dioxide is recovered and packaged.

Type II chemical manganese dioxide can also be made from finely ground manganese dioxide ore that has been reduced with H_2 —CO to manganese (II) oxide (not shown). This substance is leached with sulfuric acid and the manganese sulfate solution neutralized to pH 4-6 to precipitate iron, aluminum, nickel, cobalt, and other impurities. The solution is filtered to remove the precipitates, and (NH₄)₂CO₃ is added to precipitate manganese carbonate. The MnCO₃ is filtered, dried, and roasted in air to produce manganese dioxide (MnO₂) and carbon dioxide (CO₂).¹⁵

Other Manganese Products

Both manganese sulfate and manganese carbonate can also be prepared from ore. Manganese sulfate is used primarily as an agricultural chemical, while manganese carbonate is used to prepare other manganese compounds for specialty purposes. Both the sulfate and the carbonate production use less than five percent of total manganese ore demand. Manganese sulfate can be prepared by either the hydroquinone process or the ore-coke process.¹⁶

In the hydroquinone process, as shown in Exhibit 9, manganese ore, aniline, and sulfuric acid are reacted to produce manganese sulfate, quinone and ammonium sulfate. The reacted mixture is steam distilled to separate quinone, which is collected and processed on-site to hydroquinone. The remaining materials are filtered, and gangue solids are removed as a waste material. The filtrate is partially evaporated and manganese sulfate crystallized from solution is recovered as a solid. The spent liquor containing ammonium sulfate is sent to waste treatment and the recovered manganese sulfate is dried and packaged. The ore-coke process for manufacturing manganese sulfate is shown in Exhibit 10. Manganese ore and coke are reacted in a kiln and the product is leached with sulfuric acid. The resulting slurry is evaporated to dryness to recover a 30 percent product for agricultural purposes. The insoluble residues are left with the product.¹⁷

To produce manganese carbonate, as shown in Exhibit 11, manganese sulfate and soda ash are reacted in solution to form the carbonate, which precipitates from solution and is recovered by filtration, dried and packaged. The spent solutions containing by-product sodium sulfate are normally wasted.¹⁸

¹⁵ <u>Ibid</u>.

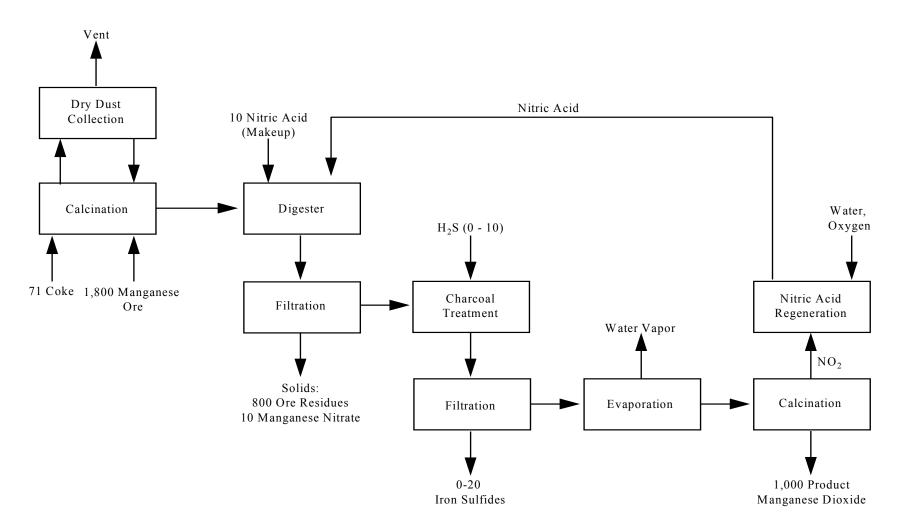
¹⁷ <u>Ibid.</u>, pp. 6-2 - 6-8.

¹⁸ <u>Ibid.</u>, pp. 6-8 - 6-9.

¹⁶ U.S. Environmental Protection Agency, <u>Multi-Media Assessment of the Inorganic Chemicals Industry</u>, Vol. II, August 1980, p. 6-1.

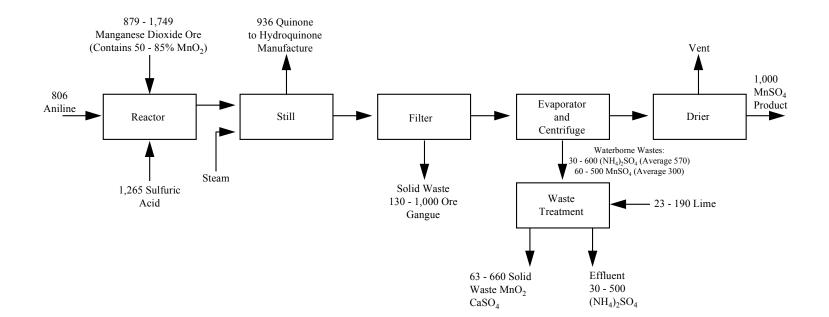
PRODUCTION OF CHEMICAL MANGANESE DIOXIDE (TYPE II)

(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, pp. 6-16.)



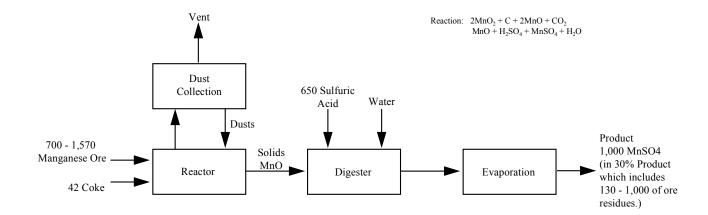
PRODUCTION OF MANGANESE SULFATE (HYDROQUINONE PROCESS)

(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, pp. 6-5.)



PRODUCTION OF MANGANESE SULFATE (ORE-COKE PROCESS)

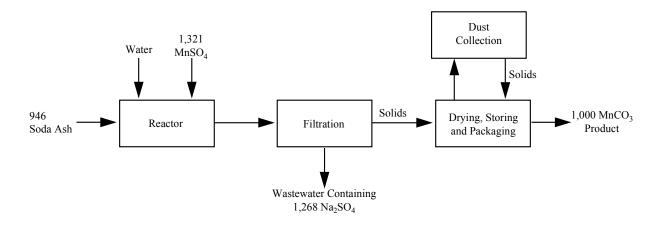
(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, pp. 6-7.)



PRODUCTION OF MANGANESE CARBONATE

(Adapted from: Multi-Media Assessment of the Inorganic Chemicals Industry, 1980, pp. 6-9.)

Reaction: $MnSO_4 + Na_3CO_3 \rightarrow MnCO_3 + Na_2SO_4$



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

Researchers are investigating how to increase recovery of manganese from refractory ores and steel slag.^{19,20,21}

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.

Ferromanganese and Silicomanganese

EPA determined that for ferromanganese and silicomanganese, processing begins with smelting in a submerged arc furnace because the ore undergoes physical/chemical reactions which significantly alter the physical/chemical structure. 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.

²¹ P.A. Rusin, J.E. Sharp, R.G. Arnold, and N.A. Sinclair, "Enhanced Recovery of Manganese and Silver from Refractory Ores," <u>Mineral Bioprocessing</u>, The Minerals, Metals, and Materials Society, 1991.

¹⁹ P. Comba, K.P.V. Lei, and T.G. Carnahan, "CaF₂-Enhanced Leaching of a Manganese-Bearing Silicate Ore," U.S. Bureau of Mines, Report of Investigations 9372, 1991.

²⁰ S.N. McIntosh, and E.G. Baglin, "Recovery of Manganese from Steel Plant Slag by Carbamate Leaching," U.S. Bureau of Mines, Report of Investigations 9400, 1992.

Since production of low carbon silicomanganese uses standard silicomanganese, all of the wastes generated during silicomanganese production are mineral processing wastes.

Manganese Metal

EPA determined that for this specific mineral commodity, the beneficiation/processing line occurs between reduction roasting and leaching because the ore (manganese (II) oxide) is converted to manganese (II) sulfate. 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.

Manganese Dioxide

Electrolytic Production

EPA determined that for manganese dioxide, mineral processing begins in the kiln because the ore reacts with coal to produce manganese dioxide. 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.

Chemical (Type I) Production

Since this process begins with byproduct manganese dioxide, all of the wastes generated during the process are mineral processing wastes.

Chemical (Type II) Production

EPA determined that for this specific process, mineral processing begins with the reaction of manganese ore with coke in kilns because the reaction alters the chemical structure of the ore. 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 Manganese Products

Hydroquinone Process

EPA determined that for other manganese products produced via the hydroquinone process, mineral processing begins with reacting the ore, aniline, and sulfuric acid because the resulting chemical reaction alters the chemical structure of the ore. 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.

Ore-Coke Process

EPA determined that for other manganese products produced via the ore-coke process, mineral processing begins with the reaction of the ore and coke in kilns because the reaction alters the chemical structure of the ore. 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.

Manganese Carbonate

Since manganese carbonate is produced from manganese sulfate, all of the wastes generated during manganese carbonate production are mineral processing wastes.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

The following wastes may be generated by extraction and beneficiation operations: gangue, flotation tailings, spent flotation reagents, and wastewater.

2. Mineral Processing Wastes

Ferromanganese Production

Both **Slag** and **APC Dust/Sludge** are recycled where possible. Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Electrolytic Manganese Dioxide and Metal

Waste Electrolyte. Available data do not indicate that waste electrolyte exhibits hazardous characteristics.²² Therefore, the Agency did not evaluate this material further.

Spent Graphite Anodes. The spent anodes are directly recovered from the process and landfilled.²³ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

²² U.S. Environmental Protection Agency, "Manganese," from <u>1988 Final Draft Summary Report of Mineral</u> <u>Industrial Processing Wastes</u>, 1988, p. 3-149.

²³ U.S. Environmental Protection Agency, 1980, <u>Op. Cit.</u>, pp. 6-13 - 6-15.

Iron Sulfide Sludge. This waste is generated by solution purification prior to electrolysis and is landfilled.²⁴ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

APC Water. Particulates generated during the calcination and product drying steps are collected by wet scrubbers. The scrubber waters are used as process make-up waters.²⁵ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater. This waste is generated during product washing and in slurring ore residues to disposal lagoons, and may contain suspended ore residue and minor amounts of soda ash. Wastewater is treated with lime to precipitate manganese salts and then discharges to lined evaporation ponds.²⁶ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Chemical Manganese Dioxide

APC Dust. Dry particulate collection methods are used to reduce ore calcination and product handling particulate emissions. Collected materials are recycled.²⁷ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Ore residues. These wastes are generated in the leaching operations, which are acid insoluble material such as aluminates and silicates, and in the purification of the intermediate manganese nitrate. There is also some unrecovered manganese nitrate entrained in these wastes, which are slurried to treatment lagoons. Lime is added to the lagoons to precipitate any soluble manganese present.²⁸ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater. This waste is generated by slurrying the ore residues to the treatment lagoons. After treatment the slurry water is discharged.²⁹ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

²⁴ Ibid.

²⁶ Ibid.

²⁸ <u>Ibid.</u>, p. 6-17.

²⁹ <u>Ibid.</u>, p. 6-17.

²⁵ <u>Ibid.</u>, p. 6-13.

²⁷ <u>Ibid.</u>, p. 6-17.

Other Manganese Products - Manganese Sulfate (Hydroquinone Process)

APC Dust. This dust consists of particulates generated in the calcination and drying operations, which are captured and recycled.³⁰ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Spent Process Liquor. This waste contains ammonium sulfate and unrecovered manganese sulfate. This waste, along with washings from the ore residues are lime treated to precipitate residual manganese, settled, and discharged.³¹ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater Treatment Solids. These solids formed by wastewater treatment (i.e., manganese oxides and calcium sulfate) are left in ponds. Solid ore residues wastes are washed free of soluble manganese and land disposed.³² Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Other Manganese Products - Manganese Sulfate (Ore-Coke Process)

APC Dust. This dust consists of particulates generated in the calcination and drying operations, which are captured and recycled.³³ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Other Manganese Products - Manganese Carbonate

APC Dust. This dust consists of particulates generated in the drying operation, which are captured and recycled.³⁴ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Spent Process Liquor. This waste contains sodium sulfate and small amounts of unrecovered product. This waste is lime treated to precipitate residual manganese salts, settled, neutralized, and discharged.³⁵ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Wastewater Treatment Solids. The solids formed by wastewater treatment (i.e., manganese oxides and calcium sulfate) are left in ponds.³⁶ Existing data and engineering judgement suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

³¹ Ibid.

³² <u>Ibid.</u>, p. 6-6.

³³ Ibid., p. 6-8.

³⁴ <u>Ibid.</u>, pp. 6-8 - 6-10.

³⁵ <u>Ibid.</u>, p. 6-10.

³⁶ Ibid.

³⁰ <u>Ibid.</u>, pp. 6-2 - 6-6.

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 and other lubricants.

E. Summary of Comments Received by EPA

EPA received no comments that address this specific sector.

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MERCURY

A. Commodity Summary

Mercury, also known as quicksilver, is a liquid metal at room temperature. It is used in batteries, lighting, thermometers, manometers, and switching devices. Mercury compounds are used in agriculture as bactericides and disinfectants, in pharmaceutical applications in diuretics, antiseptics, skin preparations, and preservatives, and in the production of caustics, such as sodium and potassium hydroxide. Mercury also is used as a catalyst for production of anthraquinone derivatives, vinyl chloride monomers, and urethane foams. Mercury can be found in nature in more than a dozen minerals, including cinnabar, which is the most common. No mercury is mined in the United States, although mercury is recovered in small quantities as a coproduct of gold mining.^{1,2} Seven gold mining operations in California, Nevada, and Utah recovered mercury as a result of gold retorting in 1994, as shown in Exhibit 1.³

EXHIBIT 1

Summary of Mines Producing Mercury as a Coproduct in 1994^{a,b}

Company Name	Mine	Location	
Barrick Mercur Gold Mines Inc.	Mercur	Toole, UT	
FMC Gold Co.	Getchell	Humboldt, NV	
FMC Gold Co.	Paradise Peak	Nye, NV	
Homestake Mining Co.	McLaughlin	Napa, CA	
Independence Mining Co. Inc.	Enfield Bell	Elko, NV	
Newmont Gold Co.	Carlin Mines Complex	Eureka, NV	
Placer Dome U.S.	Alligator Ridge	White Pine, NV	

^a "Mercury," Minerals Yearbook. Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1991. p. 989.

^b Personal Communication between ICF Incorporated and Steven M. Jasinski, U.S. Bureau of Mines, November 1994.

B. Generalized Process Description

1. Typical Production Processes

Mercury can be produced from mercury ores and gold-bearing ores by reduction roasting or calcining. The primary mercury production process is described below.

¹ U.S. Environmental Protection Agency, "Mercury, Hg," from <u>1988 Final Draft Summary Report of Mineral</u> <u>Industrial Processing Wastes</u>, 1988, pp. 1-2.

² Newmont Gold Company. Comment submitted in response to the <u>Supplemental Proposed Rule Applying Phase</u> <u>IV Land Disposal Restrictions to Newly Identified Mineral Processing Wastes</u>. January 25, 1996.

³ Jasinski, S.M., "Mercury," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, p. 108.

2. Generalized Process Flow Diagram

Exhibit 2 is a typical production flow diagram, illustrating the primary production of mercury. Although currently not in use domestically, mercury is recovered from primary mining operations by crushing the ore, and concentrating the mercury by flotation (not shown). The flotation operation produces a tailings stream. The concentrate is heated in a furnace to vaporize the mercury, and the resulting vapor is condensed.^{4,5} The sulfur in the ore is oxidized to sulfur dioxide (SO₂). Some water may condense with the mercury and is discharged as a waste stream (labeled stream No. 4 in Exhibit 2). The mercury is recovered from the condenser and may be washed before being sold (creating wastewater stream No. 5). The sulfur dioxide and other gaseous emissions from the mercury roasting furnace are controlled with a multistage scrubber (creating stream No. 1). After SO₂ removal, the clean stack gases are cooled with contact cooling water and discharged to the atmosphere (stream No. 3). Waste streams may also result from the quenching of calciner wastes to reduce the temperature prior to disposal (stream No. 5).

The process for recovering mercury from gold ore is shown in Exhibit 3, and it is similar to recovery from cinnabar ore. If the gold ore is a sulfide ore, it typically is sent to a roasting step prior to leaching. This roasting operation is similar to primary mercury ore roasting in that the mercury and sulfide are both volatilized. The exhaust gases are passed through wet electrostatic precipitators (ESPs), and if necessary, through carbon condensers. The sulfur dioxide is removed by lime prior to venting. If the treated sulfide ore has a high mercury content, the primary mercury recovery process occurs from the wet ESPs. However, if the concentration is sufficiently low, no attempt is made to recover mercury for sale.⁷

If the gold ore is an oxide-based ore, the crushed ore is mixed with water and sent to a classifier, followed by a concentrator, which reduces the water content. The concentrate is sent to an agitator containing cyanide leach solution. The slurry from the agitators is filtered, the filter cake is disposed, and the filtrate, which contains the gold and mercury, is transferred to the electrowinning process. If the carbon-in-pulp process is used, the cyanide pulp in the agitators is treated with activated carbon to adsorb the gold and mercury. The carbon is filtered from the agitator tanks and treated with an alkaline cyanide alcohol solution to desorb the metals. This liquid is then transferred to the electrowinning process, the gold and mercury are electrodeposited onto a stainless steel wool cathode, which is sent to a retort to remove mercury and other volatile impurities. The stainless steel wool containing the gold is transferred from the retort to a separate smelting furnace where the gold is melted and recovered as crude bullion.⁸ The exhaust gas from the retort, containing mercury, SO₂, particulates, water vapor, and other volatile components, passes through condenser tubes where the mercury condenses as a liquid and is collected under water in the launders. Slag quenchwater is stored prior to being recycled to the carbon-in-leach circuit (CIL). From the launders, the mercury is purified and sent to storage.⁹

⁴ Personal communication between ICF Incorporated and Steve Jasinski, U.S. Bureau of Mines, March 1994.

⁵ Carrico, L.C., "Mercury," from Mineral Facts and Problems, U.S. Bureau of Mines, 1985, p. 501.

⁶ U.S. Environmental Protection Agency, <u>Development Document for Effluent Limitations Guidelines and</u> <u>Standards for the Nonferrous Metals Manufacturing Point Source Category</u>, Volume V, Office of Water Regulations and Standards, May 1989, pp. 2167-68, 2178.

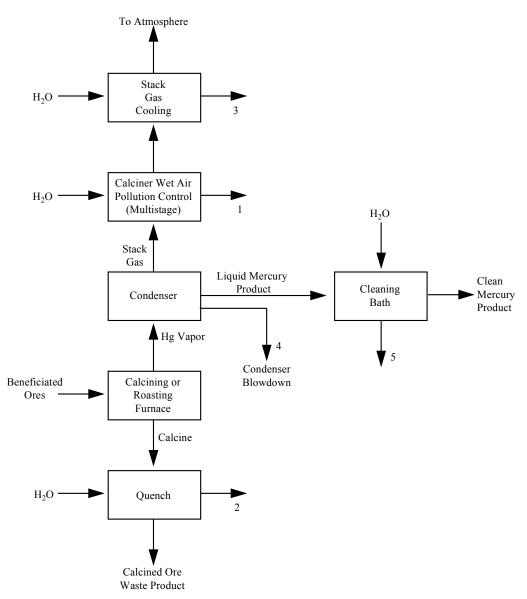
⁷ Personal Communication between ICF Incorporated and Steven M. Jasinski, November 1994.

⁸ U.S. Environmental Protection Agency, <u>Technical Resources Document:</u> Extraction and Beneficiation of Ores and Minerals, Volume 2: Gold, Office of Solid Waste, July 1994, p. 1-31.

⁹ Personal Communication between ICF Incorporated and Steven M. Jasinski, November 1994.

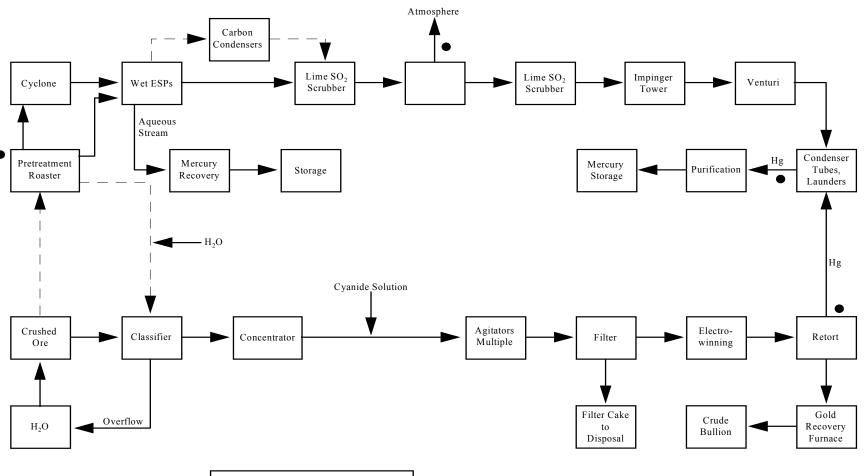
PRODUCTION OF METALLIC MERCURY FROM PRIMARY MERCURY ORES

(Adapted from: Development Document for Effluent Limitations Guidelines, 1989, p. 2175.) (No primary mercury mining is now conducted in the U.S.)



PRODUCTION OF METALLIC MERCURY FROM GOLD ORES

(Source: Personal Communication Between ICF Incorporated and Steven M. Jasinski, November 1994.)



• Potential Mercury Emission Sources

Mercury is also recovered from industrial scrap and waste materials, such as discarded dental amalgams, batteries, lamps, switches, measuring devices, control instruments, and wastes and sludges generated in laboratories and electrolytic refining plants. Scrap products are broken down to liberate metallic mercury or its compounds, heated in retorts to vaporize the mercury, and cooled to condense the mercury.¹⁰ This secondary recovery of mercury is outside primary mineral processing and is, therefore, outside the scope of the this report.

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

There are several alternative processing options, including leaching with sodium sulfide and sodium hydroxide, followed by precipitation with aluminum or electrolysis. Alternatively, mercury can be dissolved in sodium hypochlorite solution, then passed through activated carbon to adsorb the mercury. The mercury is recovered from the carbon by heating, producing elemental mercury. Neither of these processes are in use today. A third option, also not in use, is electrooxidation.¹¹ Research is continuing on the best way to recover mercury from gold and silver solutions for coproduct mercury production.^{12,13,14}

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.

¹⁰ "Mercury," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. XV, 1981, pp. 147-48.

¹¹ Carrico, L.C., 1985, <u>Op. Cit.</u>, p. 501.

¹² "Mercury," 1981, Op. Cit., p. 148.

¹³ Simpson, W.W., W.L. Staker, and R.G. Sandberg, "Calcium Sulfide Precipitation of Mercury From Gold-Silver Cyanide Leach Slurries," from <u>Report of Investigations 9042</u>, U.S. Bureau of Mines, 1986. p. 1.

¹⁴ Sandberg, R.G., W.W. Simpson, and W.L. Staker, "Calcium Sulfide Precipitation of Mercury During Cyanide Leaching of Gold Ores," from <u>Report of Investigations 8907</u>, U.S. Bureau of Mines, 1984. p. 1.

Production of Metallic Mercury from Primary Mercury Ore

EPA determined that for the production of metallic mercury from primary mercury ore, the beneficiation/processing line occurs between calcining/roasting and condensing since there is no leaching directly after the roasting step and the resulting product undergoes further beneficiation (i.e., cleaning). 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.

Production of Metallic Mercury from Gold Ores

Because mercury is being recovered as a co-product of other metals obtained during mineral processing operations, all of the wastes generated during mercury recovery also are mineral processing wastes. For a description of where the beneficiation/processing boundary occurs for this mineral, see the gold and silver sector reports.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

The following wastes may be generated by extraction and beneficiation operations: gangue, flotation tailings, spent flotation reagents, and wastewater.¹⁵

2. Mineral Processing Wastes

Primary Retorting is not currently used in the United States, due to the economics of mining primary mercury ores. Therefore, the wastes associated with primary retorting are not included in the tables summarizing waste stream generation rates and waste characteristics. The following three primary retorting waste streams are included in this report for completeness.

Furnace Calcines. Approximately 10 metric tons of furnace calcines were produced annually in the United States in 1992. Available data do not indicate the waste exhibits hazardous characteristics.¹⁶ No other information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

SO₂ Scrubber Effluent. Approximately 3,000 metric tons of SO₂ scrubber effluent were produced annually in the United States in 1992. Available data do not indicate the waste exhibits hazardous characteristics.¹⁷ No other information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

Particulate Control Effluent. Approximately 2,000 metric tons of particulate control effluent were produced annually in the United States in 1992. Available data do not indicate the waste exhibits hazardous

¹⁵ Harty, D.M., and P.M. Terlecky, <u>Characterization of Wastewater and Solid Wastes generated in Selected Ore</u> <u>Mining Subcategories</u>, (Sb, Hg, Al, V, W, Ni, Ti), U.S. Environmental Protection Agency, August 21, 1981, pp. II-36 - II-40.

¹⁶ U.S. Environmental Protection Agency, <u>Newly Identified Mineral Processing Waste Characterization Data Set</u>, Volume I, Office of Solid Waste, August 1992, p. I-6.

characteristics.¹⁸ No other information on waste characteristics, waste generation, or waste management was available in the sources listed in the bibliography.

Co-product Retorting. The wastes produced in coproduct retorting will vary greatly depending on the input materials. The wastes also may contain other metals.

Dust. Approximately 7 metric tons of dust are produced annually from the mercury sector in the U.S.¹⁹ Although no published information regarding waste characteristics was found, we used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity for mercury. We also used best engineering judgment to determine that this waste stream is not believed to be recycled. This waste stream was formerly classified as a sludge.

Furnace Residues. Approximately 77 metric tons of furnace residues are produced annually from the mercury sector in the United States.²⁰ Although no published information regarding waste characteristics was found, we used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity for mercury. This waste stream is not recycled.

Quenchwater. During the retorting process, mercury gas is vaporized from the gold filter cake. The mercury gas is quenched with a direct contact water spray and condensed to form liquid mercury, which is collected for sale. Waste mercury quenchwater is generated at a rate of 20 to 30 gallons per minute at the facility, and is recycled to the CIL circuit. This waste generation rate corresponds to low, medium, and high sector-wide generation rates of 63,000 mt/y, 77,000 mt/y, and 420,000 mt/y, respectively. This waste may be toxic for lead and mercury. This waste stream is believed to be fully recycled and was formerly classified as a spent material.

D. Non-uniquely Associated Wastes

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

E. Summary of Comments Received By EPA

New Factual Information

Newmont Gold Company was the sole commenter on the mercury sector report. This commenter (COMM57) provided new factual information to be added to the mercury sector report, stating that the flow diagram depicting the mercury production process for recovery of mercury from gold ores and the accompanying narrative did not resemble the process used at Newmont Gold nor at other gold producers. The commenter did not provide any suggested changes and, therefore, the flow diagram was not revised.

¹⁸ <u>Ibid</u>.

¹⁹ <u>Ibid</u>.

²⁰ <u>Ibid</u>.

Sector-specific Issues

The commenter also provided several suggestions related to sector-specific issues. The commenter stated that mercury is a "co-product," not a "by-product" because the mercury in question is not a secondary stream that is discarded or recycled for further mercury recovery. Therefore, it is not a RCRA Subtitle C byproduct. The same commenter stated that they were unaware of any statutory/regulatory language or EPA interpretive guidance that would lead to the conclusion that all wastes generated during mercury recovery as a coproduct of other metals are mineral processing wastes. In addition, this commenter stated that retort quenchwater can be a by-product or a spent material, depending on the circumstances. EPA has revised the report to indicate that mercury is recovery from gold ores are mineral processing wastes because the mercury recovery process occurs during mineral processing operations for recovery of other metals. The report was not modified with respect to retort quenchwater because the distinction between by-product and spent material is made irrelevant by today's Rule.

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