LEAD

A. Commodity Summary

Lead 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 totalled 330,000 mt and 30,000 mt, respectively, in 1994. In addition, domestic secondary production from lead scrap totalled 880,000 mt in 1993, up from 842,000 mt in 1989. United States lead reserves totalled 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. Treatment of lead ores begins with crushing, grinding, and concentrating. Pelletized concentrates are fed with other materials (e.g., smelter 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 (SO_2). The exit gas stream from the sinter 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 other

EXHIBIT 1

SUMMARY OF LEAD MINING, SMELTING, AND REFINING FACILITIES

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
ASARCO	East Helena, MT	Smelting	● Facility is partially located within a 100-yr. floodplain, a wetland, and a fault area ● Approximately 3,500 residents live within one mile of the facility boundary ● The nearest residence is located 100 yards from the facility boundary ● Depth from the bottom of the special waste management units to water in the uppermost usable aquifer is 38 feet ● One aquifer is located between the ground surface and the uppermost usable aquifer; this aquifer is contaminated ● Surface water monitored upstream and downstream of the special waste management units has exceeded national ambient surface water quality criteria for lead ● Ambient air monitored near the special waste management units has exceeded the NAAQS for lead (arithmetic 3-month average, 1.5 µg/m^3)
ASARCO	Glover, MO	Smelting and Refining	● 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 special waste 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 the special waste management units have shown exceedances of the NPDWS for cadmium and the NSDWS for zinc and total dissolved solids

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
ASARCO	Omaha, NE	Refining	● Facility is partially located in a 100-yr. floodplain and a fault area ● Approximately 4,400 residents live within one mile of the facility boundary ● The nearest residence is located approximately three-quarters of a mile outside the facility boundary ● Ambient air monitored near the special waste management units has exceeded the NAAQS for lead (arithmetic 3-month average, 1.5 µg/m^3)
ASARCO Leadville Unit	Leadville, CO	Mining	
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	

EXHIBIT 33-1 (Cont.)

Facility Name	Location	Type of Operations	Potential Factors Related to Sensitive Environments
Montana Tunnels Mine	Jefferson County, MT	Extraction	
Red Dog Mine	Kotzebue, AK	Extraction	
Sunnyside Mine	Silverton, CO	Extraction	
Sweetwater Mine	Bunker, MO	Extraction	
Viburnum Mines (6 mines): Brushy Creek Casteel Fletcher Viburnum 28 Viburnum 29 Buick	Iron, Reynolds, and Washington Counties, MO	Extraction and Beneficiation	
West Fork Mine	Bunker, MO	Extraction	

precious metals. The lead bullion may then be decopperized before being sent to the refining stages. (U.S. EPA, 1990, p. 10-2)

Lead refining operations generally consist of several steps, including (in sequence) softening, desilverizing, dezincing, bismuth removal, and final refining. Various other saleable materials may also 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; the 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 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 Hydrometallurgical Beneficiation.

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, materials 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, although 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-staged 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 also 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 flotation (collectors, frothers, activators, and depressants). Flotation typically occurs in a series of steps, and multiple floats may be required to remove several 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 33-1 (Cont.)

Exhibit 2

Graphic Not Available.

EXHIBIT 33-1 (Cont.)

EXHIBIT 3

MATERIALS FLOW TO AND FROM ASARCO, GLOVER, MISSOURI

Graphic Not Available.

Source:

EXHIBIT 33-1 (Cont.)

EXHIBIT 4

MATERIALS FLOW TO AND FROM ASARCO, HELENA, MONTANA

Graphic Not Available.

Source:

EXHIBIT 33-1 (Cont.)

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 tailing 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 (SO_2). Product sinter is sized for use in the blast furnace, and fine sinter particles are recycled to the 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 may also 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 product (cadmium concentrate), and the residue is recycled to the sinter feed. Blast furnace off-gases also contain small quantities of SO_2 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)

EXHIBIT 33-1 (Cont.)

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 ($NaNO_3$) are added as fluxes. The fluxes react with impurities to form salts such as sodium antimonate ($NaSbO_3$), 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 ($NaSbO_3$), 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 done in two steps. First, a small amount of zinc is added to the molten bullion to generate a skim with high gold content, since 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. One 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 $ZnCl_2$. 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., $CaMg_2Bi_2$) 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) Process(es)

Hydrometallurgical Beneficiation

The U.S. Bureau of Mines has 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 ($PbSiF_6$) leach solution and the sulfur-containing residue, the $PbSiF_6$ 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 (O_2) 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 O_2 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 has 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)

EXHIBIT 33-1 (Cont.)

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 $PbSiF_6$ electrolyte produced from the leach solution. The electrowinning step produced H_2SiF_6 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 the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in this section.

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 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) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

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 byproduct of mineral extraction in underground mines. The quantity and composition of waste rock generated at lead mines varies greatly between 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 may also 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. There is 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. There is no information on the quantities of mine water generated annually at all lead mining/milling locations. 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 may also 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 are also 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) There is 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 is classified as a spent material and may be partially recycled based on best engineering judgment.

Surface Impoundment Waste Solids

In past years, surface impoundments at primary lead facilities received various types of wastewaters, including slag granulation water, acid plant blowdown, plant runoff, and plant washdown waters. Solids dredged from these impoundments were typically either recycled to the sinter feed preparation or disposed of at the slag dump. (PEIA, 1984, pp. 3-6 to 3-7, 3-12 to 3-15) However, EPA published a final rule on September 13, 1988 that relisted as hazardous certain wastes generated by metal smelting operations. These wastes include K065 wastes, defined as "surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities." (SAIC, 1991b, p. 1)

The American Mining Congress and other plaintiffs filed suit with the U.S. Court of Appeals challenging the basis for the listings. In July 1990, the court remanded several listings, including K065, to EPA. The Agency is deciding whether to respond to the remand in order to relist the wastes or to manage the wastes as characteristically hazardous. (U.S. EPA, 1994, pp. 8-9) Nonetheless, the relisting of surface impoundment solids resulted in altered waste management practices at primary lead production facilities. For example, at the ASARCO facility in Glover, MO, existing unlined surface impoundments are no longer used and are in the process of clean closure. 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. When sufficient quantities of settled solids have accumulated in the concrete settling tanks, the plant will remove these materials recycle them to the process. (SAIC 1991b, pp. 8-10)

In addition, the Doe Run plant in Herculaneum, MO now continuously treats wastewaters that were formerly routed to unlined surface impoundments. Plant washdown water, blast and dross furnace slag granulation water, and neutralized acid plant blowdown are treated with lime and charged to a clarifier (WWTP-1). The slag granulation waters receive some initial settling treatment in a concrete-lined impoundment, before they are combined with washdown waters and neutralized blowdown. Clarifier underflow is treated in a thickener along with sinter plant scrubber blowdown. The clarifier overflow is sent to gravity filters; backwash from the gravity filters is routed to the clarifier and the filtrate is discharged through an outfall. The thickener underflow is dewatered by a filter press and returned to the sinter plant. The filter press liquids are recycled to the thickener, and the thickener overflow is recycled to the sinter plant. (SAIC, 1991b, pp. 9-12; ICF, 1989, pp. 2-3)

The remaining operational primary lead smelting facility, Asarco, East Helena, MT, is reconstructing its wastewater management system. The reconstructed system will allow the facility to completely recycle wastewater treatment solids from the treatment of acid plant blowdown and other process wastewaters. The modified system will allow the plant to discontinue its use of surface impoundments. When the modified system is complete, wastewater treatment solids will be blended with lead ore concentrates and recycled to the process. (U.S. EPA, 1994, pp. 22-23)

A 1984 study entitled Overview of Solid Waste Generation, Management, and Chemical Characteristics, Primary Lead Smelting and Refining Industry (PEI Associates, November 1984, prepared for the Office of Research and Development) contains results of EP toxicity tests on one sample each of dredged and undredged surface impoundment solids. The plants from which the samples were taken were not identified. The dredged solids came from an impoundment that received blowdown, run-off, and other plant wastewaters; the solids had been stockpiled prior to recycling. This sample exhibited EP toxicity for cadmium (97.5 mg/L) and lead (37.8 mg/L). The undredged solids came from the bottom of an impoundment that received washdown, run-off, scrubber water, and some granulation water. This sample also exhibited EP toxicity for cadmium (92.3 mg/L) and lead (308 mg/L). (PEIA, 1984, pp. 5-16 to 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 characteristic of toxicity for arsenic, cadmium, lead, and mercury.

A 1991 study entitled Characterization Report for Surface Impoundment Solids Contained in and Dredged from Surface Impoundments at Primary Lead Smelting Facilities (K065) for ASARCO, Glover, Missouri, and Doe Run Company, Herculaneum, Missouri (SAIC, April 25, 1991, prepared for the Office of Research and Development) contains results of TC tests on one sample of settled K065 material collected from a lined retention pond at the Asarco plant. The sample exhibited the toxicity characteristic for lead (395 mg/L) and cadmium (69.9 mg/L). The sample contained no volatile organics, semivolatile organics, organochlorine pesticides, or PCBs, but some phenoxyacetic acid herbicides and organophosphorus insecticides were detected. The authors suggested that the detected compounds could be the result of a mixing of plant wastewater streams with facility run-off. When the sample was analyzed using the SPLP, it exhibited leachable levels of lead (28.7 mg/L) and cadmium (23.2 mg/L) above the levels specified in 40 CFR 261.24. Dioxins and furans were also detected in the ASARCO K065 sample, but all homologs were present at levels below existing EPA treatment standards. A 2,3,7,8-TCDD equivalent of 0.0885 ppb was calculated. (SAIC, 1991b, pp. 13-23)

As described above, the three remaining active primary lead smelting facilities (Asarco's Omaha, NE facility is a refinery only) are moving away from the use of surface impoundments for managing plant wastewaters. All three plants have replaced, or are in the process of replacing their on-site surface impoundments with engineered settling/retention basins or wastewater treatment systems. As a result, surface impoundment solids may no longer be generated.

This waste stream is listed as hazardous but has been remanded. Therefore, the waste stream was not included in our analysis.

Spent Furnace Brick

Primary lead smelters generate used refractory brick during the reconstruction of blast furnaces. Some plants crush and recycle the brick to the blast furnace, while other plants 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 is 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 is classified as a sludge.

WWTP Sludges/Solids

Wastewater treatment sludges and solids consist of solid materials that settle following lime neutralization of influent wastewaters. The sludges and solids are typically recycled to the sinter feed preparation operation. For example, at the Doe Run Herculaneum facility, a thickener serves as the final collection point for solids in the WWTP. Thickener solids are dewatered using a filter press and then shipped by rail car to the sinter plant. (PEIA, 1984, pp. 3-12 to 3-15; SAIC 1991b, pp. 9-12) Approximately 380,000 metric tons of WWTP sludges and solids are generated annually (ICF, 1992). The waste generation rate per facility is greater than 45,000 metric tons/yr due to comingling of numerous waste streams. The NIMPW Waste 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. We used best engineering to determine that this waste stream may exhibit the characteristic of toxicity (cadmium and lead). This waste stream is fully recycled and is classified as a sludge.

The April 25, 1991 SAIC study contains data on samples of clarifier underflow and filter press solids collected from the wastewater treatment system (WWTP-1) at Doe Run's Herculaneum, MO facility. The clarifier underflow sample, which is derived from plant washdown and acid plant blowdown, exhibited the toxicity characteristic for cadmium (8.51 mg/L). The filter press solids, which are derived from thickened clarifier underflow and sinter plant blowdown, exhibited the toxicity characteristic for lead (185 mg/L) and cadmium (98.8 mg/L). The Doe Run samples were not analyzed for any organic compounds. (SAIC, 1991b, pp. 13, 15)

Surface Impoundment Waste Liquids

As noted above, 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 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. A sample from an impoundment that receives plant washdown and run-off (but not blowdown) 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 is 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 lime-neutralized 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 sludge. The sludge 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 is classified as a spent material.

Slurried APC Dust

At one integrated smelter/refinery, ESP dust and scrubber underflow from the cleaning of sinter plant off-gases 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 is 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 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 is 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 is 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, it is unclear from the survey what the dust's ultimate destination is. 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)

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 is 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. In addition, it is not known whether, or how, acid plant cooling tower blowdown differs from acid plant blowdown.

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

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 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 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 is classified as a spent material.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum 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)

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EXHIBIT 33-1 (Cont.)

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).

Originally, all liquid and solid residues from the milling operations were discharged directly into the South Fork of the Coeur d'Alene River and its tributaries. Periodic floods deposited contaminated wastes onto the valley floor. In the 1920's, mill tailings were discharged to a small impoundment, and lead smelter slag was placed in what became the slag pile. In 1928, the first impoundment at the Central Impoundment Area (CIA) began operation. After 1961, the coarse fraction of mill tailings were used as sand 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 µg/L), iron (1,146 µg/L), manganese (1,507 µg/L), and zinc (3,270 µg/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 µg/m^3 (on a quarterly basis) and ambient levels of total suspended particulates have ranged from 30 to 70 µm/m^3 (on an annual basis) with daily values ranging to 900 µg/m^3. The NAAQS for lead is 1.5 µg/m^3 (on a quarterly basis) and the primary NAAQS for particulate matter is 150 µg/m^3 (on a 24-hour basis, for particles <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.

Media	Lead (in ppm)		Cadmium (in ppm)		Zinc (in ppm)	
	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.