

6

Lead and Zinc

Lead and zinc ores are usually found together with gold and silver. A lead-zinc ore may also contain lead sulfide, zinc sulfide, iron sulfide, iron carbonate, and quartz. When zinc and lead sulfides are present in profitable amounts they are regarded as ore minerals. The remaining rock and minerals are called gangue.

Forms of Lead and Zinc Ore

The two principal minerals containing lead and zinc are galena and sphalerite. These two minerals are frequently found together along with other sulfide minerals, but one or the other may be predominant. Galena may contain small amounts of impurities including the precious metal silver, usually in the form of a sulfide. When silver is present in sufficient quantities, galena is regarded as a silver ore and called argentiferous galena. Sphalerite is zinc sulfide, but may contain iron. Black sphalerite may contain as much as 18 percent iron.

Lead Ore

The lead produced from lead ore is a soft, flexible and ductile metal. It is bluish-white, very dense, and has a low melting point. Lead is found in veins and masses in limestone and dolomite. It is also found with deposits of other metals, such as zinc, silver, copper, and gold. Lead is essentially a co-product of zinc mining or a byproduct of copper and/or gold and silver mining. Complex ores are also the source of byproduct metals such as bismuth, antimony, silver, copper, and gold. The most common lead-ore mineral is galena, or lead sulfide (PbS). Another ore mineral in which lead is found combined with sulfur is anglesite or lead sulfate (PbSO₄). Cerussite (PbCO₃) is a mineral that is a carbonate of lead. All three of these ores are found in the United States, which is one of the chief lead-mining countries. In 2000, lead mines in Missouri

plus lead-producing mines in Alaska, Idaho, and Montana yielded most of the U.S. production. Primary lead was processed at smelter-refineries in Missouri and in Montana.¹

Zinc Ore

Zinc is a shiny, bluish-white metal. Zinc metal is never found pure in nature. Zinc minerals are generally associated with other metal minerals, the most common associations in ores being zinc-lead, lead-zinc, zinc-copper, copper-zinc, zinc-silver, or zinc only. Zinc also occurs in combination with sulfur in a mineral called zinc blende or sphalerite (ZnS). The primary source of zinc is from sphalerite, which provides about 90 percent of zinc produced today. Other zinc-containing minerals include hemimorphite, hydrozincite, calamine, franklinite, smithsonite, willemite, and zincite. Zinc ore is mined in about 50 countries, with approximately one-half the total coming from Australia, Canada, Peru, and the USSR. In 2000, it was produced in six states of which Alaska, Missouri, New York, and Tennessee accounted for 98 percent of domestic mine output. Alaska alone accounted for about three-fourths of U.S. production.²

6.1 Process Overview

6.1.1 Lead and Zinc Ore Mining

Lead and zinc ore is nearly always mined below the surface of the ground. Some veins of ore lie as deep as several thousand feet but most deposits lie close to the surface. Lead and zinc ore is mined 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.

Mining is accomplished using several techniques that involve creating a tunnel or drift along the vein. The ore is removed by drilling and blasting, and removed through the drift to the shaft. The ore is hoisted to the surface for further concentration. In the mine, workers try to separate the ore-bearing minerals from the barren rock as much as possible during the mining process. In some mining districts, the lead or zinc is found in massive deposits and mined similar to coal using room and pillar methods.

6.1.2 Lead and Zinc Ore beneficiation

Due to low zinc content, run-of-mine zinc-bearing ores must be concentrated before smelting and refining. Beneficiation, which usually occurs at the mine, consists of crushing, grinding, and flotation to produce concentrates of 50 to 60 percent zinc. Lead ore also requires processing to remove rock and mineral impurities to achieve a suitable concentration.

¹ U.S. Department of the Interior, U.S. Geological Survey, *Mineral Commodity Summary*, Iron Ores, 2001.

² U.S. Department of the Interior, U.S. Geological Survey, *Mineral Commodity Summary*, Zinc, 2001.

6.1.2.1 Lead and Zinc Ore Milling

Treatment of lead and zinc ores begins with milling. Milling is a multi-stage crushing and grinding operation. It involves coarse crushing followed by wet grinding. 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 slurry. The ore is then ground in rod and ball mills. The slurry may also be ground in autogenous mills (a mill where the ore acts as the grinding medium) or semi-autogenous mills (steel balls are added to the ore). Hydrocyclones are used between each grinding step to separate coarse and fine particles. The coarse particles are returned to the mill for further size reduction. Milling is carefully controlled to produce the required particle size. Grinding the ore too fine will produce slimes or very fine particles, which are difficult to recover in the separation process and are usually lost to tailing.

6.1.2.2 Lead and Zinc Ore Concentration

If the mineral veins separate from the rock cleanly, then processing workers can concentrate the ore by taking advantage of the greater weight mineral compared to the rock. Jigging separates coarse lumps. In this process, the crushed ore is agitated or shaken in water with a vertical motion. This permits the heavy lumps to settle to the bottom and the lighter rock to remain on top. For more finely crushed ore, another concentration method is used. The ore is crushed to sand-size particles. The crushed ore and water mixture flows across a vibrating table that cleanly separates the heavy mineral from the fine ore.

For the most finely crushed ore, processing workers use a method called froth flotation. This method is chiefly used with galena because the mineral is finely dispersed through the rock containing it. Flotation is the usual mineral separation or concentration process of choice.

In flotation, workers use slurry reagents to float the heavy mineral away from the lighter powdered ore. Slurry reagents form frothy bubbles that attach themselves to the mineral and float them to the surface away from the gangue. 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 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. This separation process allows the separate recovery of the galena and sphalerite from the waste materials such as iron pyrite. By using the right kind of frothing agent and with the help of special chemicals, mining companies can make separated concentrates of copper and lead when they are mixed in the same ore. This separation makes the processing of each of the metals more economical.

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 roasting operation.

6.1.2.3 Lead Ore Processing

Lead ore beneficiating includes milling, concentration, and sintering. After sintering, the ore is smelted in a blast furnace to produce rough lead bullion. Rough lead bullion still contains many impurities. Therefore, the rough lead bullion is refined to remove and recover other metals. Primary lead facilities (smelting and refining) in the U.S. employ pyrometallurgical methods to produce lead metal. Some countries have significant electrolytic refinery production associated with cheap coal, hydroelectric power, or subsidized power.

6.1.2.4 Lead Concentrate Sintering and Smelting

Smelting is the process by which rough lead bullion is produced from lead concentrate. After the ore has been concentrated at a mill near the mine, the lead concentrates are shipped to a smelter. Here, in the case of galena, the first step involves removing the sulfur from the mineral. Roasting in air causes the sulfur to be converted to sulfur dioxide gas. This roasting process converts the lead sulfide to lead oxide.

Frequently, processors combine the roasting process with the sintering process. This converts the finely divided concentrates into large lumps more suitable for the blast furnace, which does the next job in smelting.

Sintering occurs on a traveling grate furnace known as a "sinter machine." The lead concentrates are mixed with fluxes, recycled sinter, and flue dusts and other recycled materials. After moisture is added, the mixture is pelletized and fed to the sinter machine. A thin layer of the feed is directed onto the grates, and ignited with natural gas burners. Additional feed is then placed on top of the ignited layer, and air is blown through the grates for the bottom of the sinter machine. The air combines with the heated lead sulfide in the feed, producing lead oxide and sulfur dioxide. The process progresses from the bottom of the layer to the top, fusing the feed into a firm, porous material called sinter. Sintering converts metallic sulfides to oxides, removes volatile metals, and converts most sulfurs into sulfur dioxide (SO₂). The product sinter is sized for use in the blast furnace, and fine sinter particles are recycled to the feed mixture. Sintering is the first step in the primary production of lead.

The smelting process reduces metallic oxides to metal in a blast furnace. The lead blast furnace is constructed in the shape of a vertical shaft. The sides of the blast furnace consist of water-cooled steel jackets, while the bottom of the furnace is a refractory crucible. Air pipes (called tuyeres) are installed in the lower jackets, allowing air to be blown into the furnace. The sintered ore (lead oxide) is fed (charged) to the top of the blast furnace, along with coke, fluxes, and recycled materials. The feed gradually sinks down the shaft while air passes up the column from the bottom. The air causes the coke to burn intensely, producing heat and carbon monoxide. The carbon monoxide reacts with the lead oxide in the feed, producing lead metal. The heat from the burning coke melts the lead and the other compounds present in the feed. The lead metal (bullion) flows out the bottom of the furnace, along with other molten oxides present in the

feed. These oxides (primarily the oxides of iron, silicon, calcium, and zinc) are called slag, and are much less dense than the molten lead. This difference in density allows the lead to be separated from the slag in a settler or forehearth, which is installed adjacent to the blast furnace.

The hot lead bullion from the furnace is an excellent solvent for many other elements, including gold, silver, copper, antimony, arsenic, and sulfur. Depending on the feed to the furnace, these impurities may amount to several percent of the overall total. The high impurity content often results in the lead bullion being called “rough” or “crude” lead bullion.

If the forehearth is of sufficient size, settling (and cooling) will cause lead bullion to separate into phases. The rough lead bullion may be separated into as many as four distinct liquid layers, depending on the sinter composition. The lead bullion (94 to 98 percent lead by weight) will collect at the bottom of the forehearth, with speiss (a mixture of the arsenides and antimonides of copper) above the bullion. Matte (primarily copper sulfide) collects above the speiss, and the slag (consisting of the oxides which were not reduced to the metallic state in the blast furnace) floats above the matte.

Matte and speiss are sold to the operators of copper smelters for metal recovery. Depending on the zinc content, the slag may be sent to a zinc fuming furnace or stored. The two Missouri smelters recover slag and rough lead bullion from the furnace settlers. Neither smelter operates a fuming furnace to recover zinc from slag. The slag is stored on-site in state permitted storage areas. Both of the Missouri smelters transfer the rough lead bullion to drossing kettles for further processing.

In a conventional zinc fuming furnace, air and powdered coal are injected into molten blast furnace slag. The zinc oxide (ZnO) and lead oxide in the slag are reduced, and the metallic zinc and lead are volatilized. As the metallic vapor exits the furnace, it is oxidized, forming particles of zinc oxide and lead oxide. The particulate is recovered in a baghouse and sent to a zinc refinery for zinc recovery.

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 particulate. The particulate is recovered in a baghouse and sent to a zinc refinery for zinc recovery.

6.1.2.5 Lead Ore Drossing and Decopperizing

Rough lead bullion produced from the blast furnace is transferred to a drossing kettle. Here, it is allowed to cool to less than 1,000 degrees Fahrenheit. As the temperature decreases, the metals that were dissolved at blast furnace temperatures begin to precipitate as solid dross. This dross contains a wide variety of metals (copper, nickel, arsenic, antimony, and lead) present in the form of sulfides, arsenides, and antimonides. The bullion may be stirred during cooling to decrease the particle size of the dross. The solid dross is skimmed from the kettle and either sold or processed in a dross reverberatory furnace. The term “rough-drossed bullion” is used for the lead bullion that remains in the kettle. Off-gases from the reverberatory furnace are combined with blast furnace off-gases for filtration.

If a dross reverberatory furnace is used, the dross is added to the furnace along with fluxes, which include sodium carbonate, sulfur, and coke breeze. Upon melting, the dross separates into four layers or phases: metallic lead, speiss, matte, and slag. The lead is returned to the dross kettle for further treatment, while the matte and speiss are granulated and shipped to a copper smelter for metals recovery. Off-gases from the reverberatory furnace are combined with blast furnace off-gases for filtration.

After drossing, the rough-drossed bullion will contain low levels of copper. The residual copper is removed in a step called “decopperizing”. The bullion is decopperized by cooling, and then stirring in sulfur, or a mixture of sulfur and pyrite. The decopperizing dross is skimmed from the kettle, and returned to either the dross kettle or the blast furnace.

6.1.2.6 Lead Ore Refining

The lead that comes from the blast furnace, called base bullion, usually contains many impurities that require additional refining. 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 silver, oxides of antimony, arsenic, tin, and copper. Refiners remove silver and gold by adding zinc to the hot lead, cooling it to the melting point, and skimming off the zinc crust that forms. The crust contains all the gold and silver. Bismuth is removed in a similar way using calcium, magnesium or potassium instead of zinc. 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, and the purified bullion is then cast into ingots.

6.1.2.7 Lead Bullion 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, and tin to form oxides. The oxides form a slag (dross) that is skimmed and returned to the blast furnace 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.

Kettle softening can be used only on bullion with hardness less than or equal to 0.3 percent. The bullion is melted and agitated. 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.

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.

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). 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.

6.1.2.8 Lead Bullion Desilverizing

Silver, gold, and copper may be removed from softened lead by the addition of metallic zinc. This procedure, known as the Parkes Process, is the standard pyrometallurgical approach to recover precious metals. The Parkes Process consists of two stages. In the first, zinc is added to the softened bullion to produce dross, which contains appreciable levels of silver. If gold is present, a small amount of zinc may be added at the beginning of the first stage to produce enriched gold dross.

After the dross is removed by skimming, the lead is cooled. During cooling, additional zinc dross is precipitated, and this dross is skimmed to the first stage of the process. The bullion is cooled as near as practical to freezing. At this point, it is transferred (by bailing or pumping) to the dezincing kettle. The cold bullion will typically contain less than five parts per million of silver, and 0.55 percent zinc.

The dross from desilverizing is processed to recover gold, silver, zinc, and lead. In some cases, the dross is liquated (melted) in a "coffee-pot" or "teapot" kettle. When the dross melts, the lead is recovered and returned to the desilverizing kettle. The enriched silver/zinc alloy (also containing gold and copper) is subjected to a distillation process for zinc removal. In this procedure, also known as "retorting", the zinc is volatilized and then recovered in a condenser. The zinc metal is collected and returned to the desilverizing kettle. The retort metal (containing silver, gold, copper, and lead) is sent to a cupel furnace for additional refining. In the cupel, the molten metal is oxidized to remove impurities. Metallic lead may be added to the cupel to assist in the formation of a litharge (lead oxide) slag to remove the residual copper and zinc from the retort metal. This litharge slag contains appreciable levels of silver, and is returned to either the softening process or the blast furnace.

After cupellation, the silver/gold alloy commonly known as doré is cast and sold. Exhaust gases from the refining steps are cooled and routed to baghouses. The particulate that is recovered there is returned to the blast furnace.

6.1.2.9 Lead Bullion Dezincing

The desilverized lead from the Parkes Process contains approximately 0.55 percent zinc, which is the saturation level of zinc in lead at the finishing temperature. The zinc may be removed using one of three dezincing methods: vacuum, chlorine, or Harris. Of these methods, vacuum dezincing is preferred, as it recovers zinc in the metallic state. The zinc metal (commonly called vacuum zinc) is returned to the desilverizing process, where it reduces the overall zinc cost.

6.1.2.10 Lead Bullion Debismuthizing

Prior to debismuthizing, the bullion from the dezincing process is commonly stirred with caustic soda and niter to remove the trace amounts of zinc and antimony. After the dross is skimmed, bullion is transferred to debismuthizing.

The first step in dross treatment consists of removing the calcium and magnesium by oxidation or chlorination. In oxidation, the dross is melted in a kettle and then agitated. In chlorination, the dross is mixed with molten lead chloride. Both processes produce lead/bismuth alloy containing between 5 and 10 percent bismuth. The oxide dross is returned to the blast furnace, but the chloride dross is typically discarded.

Bismuth is recovered from the high-bismuth alloy by melting in a cast iron kettle and then injecting chlorine gas. Lead, calcium, and magnesium are collected in molten lead chloride slag, which is skimmed. The bismuth metal from this process is stirred with caustic soda and niter to remove remaining impurities. Metallic bismuth is cast and sold. Lead chloride is either marketed or discarded. The drosses are returned to the blast furnace.

6.1.2.11 Final Lead Bullion Refining and Casting

Lead bullion from dezincing or debismuthizing reacts 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, as well as lead oxides, and can be recycled for use in slag granulation or treated. Treatment may include liming to precipitate solids.

6.1.2.12 Hydrometallurgical Beneficiation of Lead Ore

Researchers at the former U.S. Bureau of Mines developed bench-scale alternative processes for producing lead. These techniques consist of hydrometallurgical methods. 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 are 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 are electrowon to produce lead metal and H_2SiF_6 . The H_2SiF_6 are recycled to the leaching step and sulfur was recovered from the leach residue by solvent extraction.

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 such as 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.

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.

The researchers conducted leaching experiments at both atmospheric pressure and increased pressures. At atmospheric pressure and at 95°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 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. 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, the Bureau of Mines developed another experimental hydrometallurgical process 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. No information was available on whether this method is used today.

6.1.2.13 Zinc Ore Processing

Zinc is processed through either of two primary processing methods, electrolytic or pyrometallurgical. However, before either method, zinc concentrate is roasted to remove the sulfur from the concentrate and produces impure zinc oxide referred to as roasted concentrate or calcine. Valuable elements are recovered during zinc ore processing. Most common byproducts include cadmium, germanium, lead, silver, and sulfur. Indium, gallium, copper, and gold may also be recovered.

Zinc oxide is manufactured by either the French or American processes. In the French process, metallic zinc is fed into either a horizontal retort or distillation column. The produced zinc metal vapor is burned in a combustion chamber. In the American process, zinc oxide is manufactured by oxidizing zinc vapor in burners. The resulting gases and fumes are cooled, and zinc oxide is recovered in baghouses.

6.1.2.14 Zinc Ore Electrolytic Processing

In electrolytic zinc processing, calcine is digested with sulfuric acid to form a zinc sulfate solution from which zinc is deposited through electrolytic refining. Zinc ore electrolytic processing usually involves roasting, leaching (digestion), purification, and electrowinning.

6.1.2.15 Zinc Concentrate Calcining or Roasting

Calcining or roasting is common to both pyrometallic and electrolytic (a form of hydrometallurgy) zinc refining. Calcining is performed to eliminate sulfur and form leachable zinc oxide. Roasting is a high-temperature process that converts zinc sulfide concentrate to an impure zinc oxide called calcine. Roaster types include multiple-hearth, suspension or fluidized-bed. Sometimes, zinc ore concentrates are first slurried with water prior to roasting.

In a multiple-hearth roaster, the concentrate drops through a series of nine or more hearths stacked inside a brick-lined cylindrical column. As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine. Multiple hearth roasters are unpressurized and operate at approximately 1,300° F.

In a suspension roaster, the concentrates are blown into a combustion chamber. The roaster consists of a refractory-lined cylindrical shell with a large combustion space at the top and two to four hearths in the lower portion. Additional grinding, beyond that required for a multiple hearth furnace, is normally required to assure that heat transfer to the material is sufficiently rapid for desulfurization and oxidation reaction to occur in the furnace chamber. Suspension roasters are also unpressurized and operate at about 1,800° F.

Fluidized bed roasters require that the sulfide concentrates be finely ground. The concentrates are then suspended and oxidized on a feedstock bed supported on an air column. As in the suspension bed roaster, the reduction rates for desulfurization are more rapid than in the older multiple-hearth processes. Fluidized-bed roasters operate under a pressure slightly lower than atmospheric and temperatures averaging 1,800° F. In the fluidized-bed process, no additional fuel is required after ignition has been achieved. The major advantages of this roaster are greater throughput capacities and greater sulfur removal capabilities. All of the above calcining processes generate sulfur dioxide, which is controlled and converted to sulfuric acid as a marketable process byproduct.

6.1.2.16 Zinc Calcine Leaching

Leaching refers to the dissolving of the captured calcine in a solution of sulfuric acid to form a zinc sulfate solution. The calcine may be leached once or twice. In the double-leach method, the calcine is dissolved in a slightly acidic solution to remove the sulfates. The calcine is then leached a second time in a stronger solution that dissolves the zinc. This second leaching step is actually the beginning of the third step of purification because many of the iron impurities (such as goethite and hematite) drop out of the solution as well as the zinc.

6.1.2.17 Zinc Calcine Purification

In the purification step, trace impurities from the zinc oxide calcine that dissolved in the leaching steps are removed from the neutral leach solution. Like iron, these impurities must be removed so that zinc can be converted to metal. Zinc dust is added to the solution to chemically replace copper and cadmium, which precipitate out of solution as sludge. Cadmium metal and copper residue are recovered for sale. Zinc dust is again added along with antimony as a catalyst to replace nickel and cobalt, which are also recovered for sale. After purification, the solution is ready for the final step of electrowinning.

6.1.2.18 Zinc Calcine Electrowinning

Zinc electrowinning takes place in an electrolytic cell and involves running an electric current from a lead-silver alloy anode through the aqueous zinc solution. This process charges the suspended zinc and forces it to deposit onto an aluminum cathode (a plate with an opposite charge) which is immersed in the solution. Every 24 to 48 hours each cell is shut down, the zinc-coated cathodes are removed and rinsed and the zinc mechanically stripped from the aluminum plates. The zinc concentrate is then melted and cast into ingots and is often as much as 99.995 percent pure.

Electrolytic zinc smelters contain as many as several hundred cells. A portion of the electrical energy is converted into heat, which increases the temperature of the electrolyte. Electrolytic cells operate at temperature ranges from 86° to 95° F at atmospheric temperature. During electrowinning a portion of the electrolyte passes through cooling towers to decrease its temperature and to evaporate the water it collects during the process.

6.1.2.19 Zinc Pyrometallurgical Processing

In pyrometallurgical processing, calcine is sintered and smelted in batch horizontal retorts, externally-heated continuous vertical retorts or electrothermic furnaces. The processing stages generally used in pyrometallurgical refining are drying and roasting, sintering, electrothermal furnacing and scrubbing. Only about 20 percent of the total zinc refining is done pyrometallurgically.

6.1.2.20 Zinc Calcine Drying and Roasting

Ore concentrate is first dried in an ore dryer and then roasted. Off-gas from the ore dryer is scrubbed prior to discharge to the atmosphere and off-gases from roasting are cleaned prior to being used as the feedstock for sulfuric acid production. Ore dryer scrubber water and acid plant blowdown (from roaster gas cleaning operations) are mixed and the pH is raised to prevent corrosion of plant piping prior to being returned to the scrubber or being used as feed in the sintering process.

6.1.2.21 Zinc Calcine Sintering

The sintering process, which follows roasting, agglomerates the oxidized ore concentrate in preparation for furnacing. Dust, which is removed from sintering off-gases in baghouses, is returned to the sintering operation or used as a feed to the zinc sulfate circuit. The zinc sulfate circuit consists of a series of steps in which the baghouse dust is first slurried with water and soda ash. The solids (metal carbonates) are then removed from this slurry in a clarifier. The overflow of slurry goes to the facility's wastewater treatment plant. Underflow from the clarifier is centrifuged. Liquid removed by the centrifuge is then returned to the clarifier. Next, the solids are then leached with sulfuric acid, which solubilizes zinc and cadmium sulfates. Solids are separated using a filter press and sold for lead recovery. Zinc dust is added to the remaining sulfate solution to precipitate cadmium sponge, which is sold to a cadmium metal producer, leaving a zinc sulfate solution, which also is sold as a product.

6.1.2.22 Zinc Sinter Electrothermal Furnacing and Scrubbing

Sinter and coke are charged to an electrothermal furnace in which zinc gas is generated and subsequently condensed on molten zinc. A wet scrubber removes uncondensed zinc from the off-gases. Water from the wet scrubber is sent to clarifiers. About half of the water is then returned to the scrubber while the other half is sent to the wastewater treatment plant. Blue powder, a mixture of primarily zinc oxides and elemental zinc, settles out and is placed in concrete basins to dry prior to being returned to the sinter plant. It may also be used to raise the pH of the combined acid plant blowdown and dryer scrubber water.

Zinc from the furnace is made into a variety of final products, including Prime Western and high purity zinc metal, zinc dust and zinc oxide. Furnace residues are processed to recover coke, which is returned to the furnace as fines, and zinc, which is sent to the sinter plant. The slag is used as a drainage material in a permitted fly ash landfill.

6.1.2.23 Zinc Ore Novel Processing Methods

Zinc can be smelted in blast furnaces through the Imperial Smelting Furnace (ISF) process, which is capable of recovering both zinc and lead from mixed zinc-lead concentrates. This process is used at 12 plants worldwide and accounts for 12 percent of world capacity. There are no ISF-process plants in the U.S. In addition to the Imperial Smelting Furnace process, several other novel processes for zinc recovery are being (or have been) investigated or utilized.

A research program is being conducted at the Colorado School of Mines for developing a pyrochemical process using molten salts for recovering reactive metals including zinc from beneficiated ore. The process takes place in a hybrid reactor combining electrolytic production of a calcium reductant and in situ utilization of the reductant to reduce metal compounds. The reactor operates at a temperature less than 1,000 °C. The technology reportedly generates little waste.

Two companies in Canada (Cominco and Kidd Creek) utilize pressure leaching to digest zinc ore concentrates, eliminating both the roasting step and the need for a sulfuric acid plant in the electrolytic process. Zinc concentrate is reacted with oxygen and electrolyte recovered from the electrowinning step in a pressure autoclave. Zinc dissolves and forms zinc sulfate, which is sent to the electrowinning step. Sulfur in the zinc concentrate is converted to elemental sulfur as part of the residue and is extracted or wasted with the residue. The process reportedly has lower capital costs than a traditional electrolytic plant.

Sulfate roasting of copper-zinc-sulfide concentrate has been examined in a laboratory and on a pilot-plant scale in open-hearth and fluidized bed furnaces. The resulting calcine was leached with mild sulfuric acid. Zinc and iron were co-extracted from the leach solution with a solvent extractant and copper sulfate was crystallized from the purified solution. Recoveries of 95 percent and 99 percent were achieved for zinc and copper, respectively.

A solvent extraction process for treating waste streams from electrowinning was developed using acid-base couple extractants composed of amines and organic acids. Approximately 95 percent of both zinc (as zinc sulfate) and sulfuric acid in the bleed stream were recovered at concentrations high enough for direct recycle to the process.

AMAX created a process to recover zinc and other metals from RCRA-hazardous zinc leach residue through brine leaching. The process involves leaching the residue with a CaCl₂ brine solution at pH 2 for one hour at 90 degrees Celsius. Silver, lead, copper, cadmium, zinc and iron were extracted at percentages of 95, 80, 50, 50, 30 and less than 0.5 percent, respectively. Zinc was recovered through sulfide precipitation.

6.2 Summary of Inputs/Outputs

The following lists the inputs and outputs for lead and zinc mining and processing. Figure 6-1 illustrates the lead and zinc mining process with its major inputs and outputs.

Inputs

Electricity
Diesel Fuel
Coal
Coke
Limestone
Sulfur

Outputs

Mine Water
Dust
Fines
Tailings
Metals
Minerals
Sulfur Dioxide

Figure 6-1. Lead and Zinc Ore Mining Flow Diagram

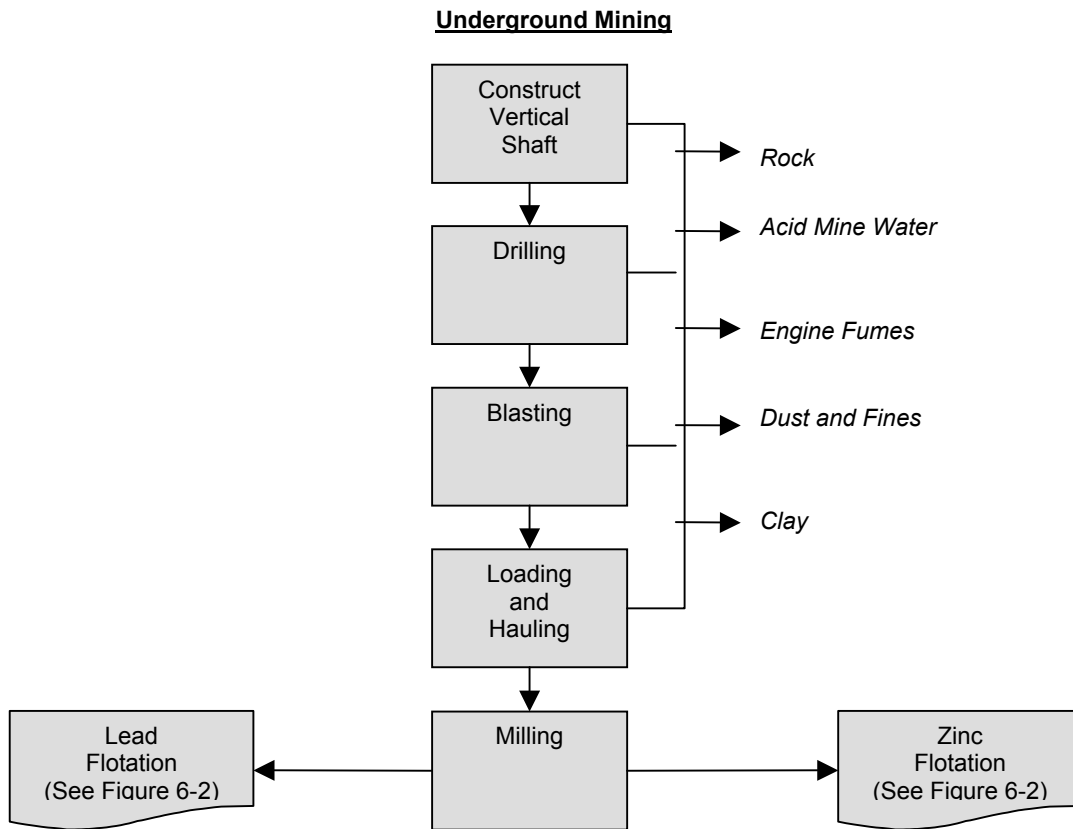
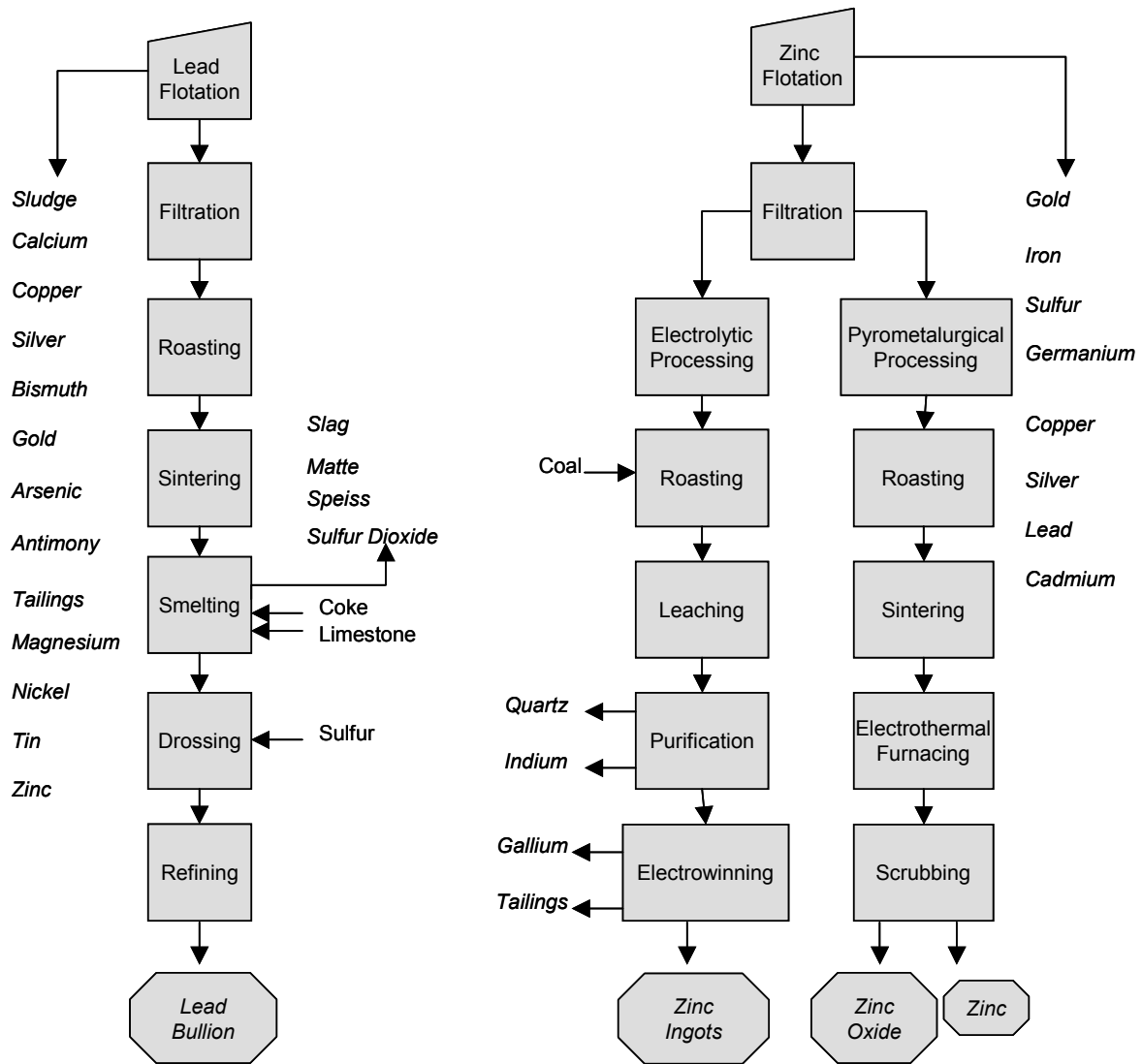


Figure 6-2. Lead and Zinc Beneficiation and Processing Flow Diagram



6.3 Energy Requirements

6.3.1 Materials Handled

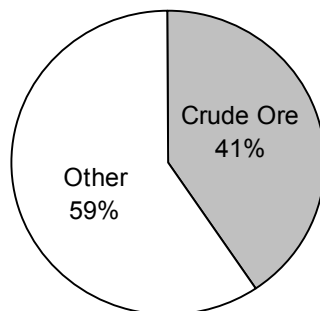
Materials handled refers to the amount of ore and other material that must be handled in mining. Figure 6-3 shows the amount of lead and zinc mined in relation to the amount of waste materials produced. When looking at energy requirements in mining and processing the tonnage of materials which must be handled drives energy consumption mining operations. For example, in 2000 the amount of lead and zinc produced was almost 6.8 million tons and the amount of other material produced was 9.6 million tons. The average crude ore ratio was 41 percent.

6.3.2 Energy Requirements for Lead and Zinc Ore Mining and Processing

A 1985 study by the U.S. Department of the Interior estimated that approximately 29.5 million Btu is required to produce 1.10 tons of refined lead, which is about 25 percent of that required for copper, and less than 50 percent that required for zinc. About one-third of the energy consumed for lead is in mining and beneficiation.³

An energy-use-pattern study of zinc refining processes in the early 1970's showed that the electrolytic process used the least energy at 66 million Btu per ton of zinc produced, followed by the vertical retort process at 72 million Btu and the electrothermic process at 80,000,000 Btu. The weighted average for energy used in zinc refining for the industry was 72×10^6 Btu. Natural gas or fuel oil is used for heating the vertical retorts, coal is used as the reducing agent in retorts and electricity is used in electrolytic zinc plants and in the electrothermic process.⁴

Figure 6-3. Materials Handled for Lead and Zinc Mining



Source: U.S. Department of the Interior, U.S. Geological Survey, *Minerals Year Book*, Statistical Summary 1996, 1998, 2000
U.S. Department of the Interior, U.S. Geological Survey, *Minerals Year Book*, Mining and Quarrying Trends, 1994, 1995, 1996, 1997, 1998, 1999, 2000

³ U.S. Department of Interior, Bureau of Mines, *Mineral Facts and Problems*, p. 433-452, 1985

⁴ U.S. Department of Interior, Bureau of Mines, *Mineral Facts and Problems*, p. 923-940, 1985

Table 6-1. Lead and Zinc Production and Energy Consumed by Type ^a				
	Units	1987	1992	1997
Lead and Zinc Production	Million tons		1.0	1.1
Energy Consumption				
Coal	Thousand tons	Withheld	Withheld	Withheld
Fuel oil ^b	Thousand bbl.	Withheld	88.3	Withheld
Gas	Billion Cubic Feet	Withheld	Withheld	Withheld
Gasoline	Million Gallons	0.2	0.2	0.1
Electricity Purchased	Million kWh	414.9	552.8	461.7
Electricity Generated Less Sold	Million kWh	0.0	Withheld	Withheld

a Lead and Zinc are SIC Code 1031 (1997 NAICS Code 212231)

b Summation of distillate and residual fuel oil

Sources: U.S. Department of Commerce, Economics and Statistics Administration, Bureau of the Census, Census of Mineral Industries, *Industry Series*, Lead and Zinc Ores.

US Department of the Interior, US Geological Survey, *Minerals Year Book*, Statistical Summary, 1997 & 1994

In 1992, lead and zinc mining consumed 7.2 trillion Btu.⁵ Table 6-1 shows the fuels consumed by lead and zinc mining as reported by the U.S. Census of Mineral Industries.

Due to a lack of current information on energy use in mining and processing, the *SHERPA Mine Cost Estimating Model* along with the *Mine and Mill Equipment Cost, An Estimators Guide* from Western Mine Engineering, Inc. was selected to calculate the energy requirements of mining and processing lead and zinc. A hypothetical mine was created in order to fit the model's requirements. This lead and zinc mine operates over a 20-year lifetime with a 26,936,000-ton output at the end of its life. The mine runs 365 days a year with three 8.00 hour shifts per day. This gives it a daily production rate of 3,690 tons per day. The deposit is 1,240 feet below the surface and extends for nine miles. The mine's width is 700 feet with an average height of 40 feet. Using the results of the mine model and Equipment Cost Guide, reasonable energy consumption estimates were developed for mining. These provide a frame-of-reference in identifying energy-intense operations.

Table 6-2 shows model outputs for energy requirements for an underground lead and zinc mine in the U.S. The main fans require the most energy in the mine and are also the most energy

⁵ U.S. Department of Commerce, Bureau of Census, Census of Mineral Industries, *Subject Series*, Fuels and Electricity Consumed, 1992

intensive pieces of equipment. The fans run on electric energy and account for 51 percent of the total energy consumed per ton. Another large energy consumer is the rear-dump truck. These trucks run on diesel fuel and accounts for 40 percent of the total energy consumed per ton. Both types of equipment are energy intensive but it is simply because of the large number of equipment required that consumes the majority of the energy in the mine. Both types of equipment are energy intensive, but it is the number of units required that makes them large-

Table 6-2. Energy Requirements for a 3,690 ton/day Underground Lead Mine					
Equipment (number of units)	Daily hours/ unit	Energy Consumption			
		Single Unit (Btu/ton)	All Units (Btu/hour)	All Units (Btu/day)	All Units (Btu/ton)
Main Fan ^b (44)	24.00	14,400	97,200,000	2,330,000,000	632,000
Rear Dump Truck ^c (40)	24.00	12,200	75,100,000	1,800,000,000	488,000
Two Boom Jumbo ^{a b} (18)	18.00	1,560	5,770,000	104,000,000	28,100
Front Loader ^c (19)	13.68	1,170	5,970,000	81,700,000	22,100
Hoist ^b (1)	24.00	14,100	2,160,000	52,000,000	14,100
Drain Pumps ^b (5)	24.00	2,160	1,660,000	39,800,000	10,800
Service Trucks ^c (23)	16.93	1,560	7,810,000	132,000,000	35,800
ANFO Loaders ^c (5)	13.92	1,280	1,700,000	23,600,000	6,400
Raise Borers ^b (1)	24.00	5,630	866,000	20,800,000	5,630
Drills ^b (3)	24.00	802	370,000	8,880,000	2,410
Roof Bolter ^c (1)	24.00	1,540	237,000	5,690,000	1,540
Diamond Drill ^b (2)	24.00	385	118,000	2,840,000	770
Water Pumps ^b (2)	24.00	72	22,300	535,000	145
Total			199,000,000	4,610,000,000	1,250,000

a Drills not included

b Calculated at \$0.049 per kWh: average for Rocky Mountain Region, 1999

c Calculated at \$0.535 per gallon: average prices for sales to end-users in U.S. Petroleum Administration for Defense District No. IV, 1999

Note: Mine operates over a 20-year lifetime with a 26,936,000-ton output at the end of its life. Assumes 364 days a year with three 8.00 hour shifts. Assumes daily production rate of 3,690 tons per day. Deposit is 1,240 feet below the surface and extends for 9 miles. Mine's width is 700 feet with an average height of 40 feet.

Sources: BCS, Incorporated estimates (September 2002)) using the Western Mining Engineering, Inc. *SHERPA Mine Cost Software* and *Mine and Mill Cost, An Estimators Guide* Conversations with Industry Experts

energy consumers.

Table 6-3 shows the energy requirements for the processing of lead and zinc. The primary energy consumption is for the grinding of ore. Combined, the ball and rod mills account for 50 percent

Table 6-3. Energy Requirements for Lead Processing					
Equipment (number of units)	Daily hours/ unit	Energy Consumption			
		Single Unit (Btu/ton)	All Units (Btu/hour)	All Units (Btu/day)	All Units (Btu/ton)
Rod Mill ^b (1)	24.00	11,500	1,770,000	42,400,000	11,500
Ball Mill ^b (1)	24.00	10,100	1,550,000	37,100,000	10,100
Flotation ^b (20)	24.00	430	1,330,000	31,800,000	8,610
Furnace (1)	24.00	13,300	2,040,000	49,000,000	13,300
Filters ^b (2)	24.00	140	43,200	1,040,000	281
Total			6,720,000	161,000,000	43,700

a Drills not included

b Calculated at \$0.049 per kWh: average for Rocky Mountain Region, 1999

c Calculated at \$0.535 per gallon: average prices for sales to end-users in U.S. Petroleum Administration for Defense District No. IV, 1999

Note: Mine operates over a 20-year lifetime with a 26,936,000-ton output at the end of its life. Assumes 365 days a year with three 8.00 hour shifts per day. Assumes daily production rate of 3,690 tons per day. Deposit is 1,240 feet below the surface and extends for 9 miles. Mine's width is 700 feet with an average height of 40 feet.

Sources: BCS, Incorporated estimates (September 2002) using the Western Mining Engineering, Inc. *SHERPA Mine Cost Software* and *Mine and Mill Cost, An Estimators Guide*
Conversations with Industry Experts

of the total energy required per ton of lead and zinc mined. One of the factors making the rod and ball mills so energy intensive is the fact that during the crushing and grinding process, the rods and balls often miss the ore and instead strike the mill wall. Looking at both mining and processing, lead requires 1,293,700 Btu per ton of lead produced.

6.4 Emissions

Lead Ore Processing Emissions

The primary air emissions from lead processing are substantial quantities of SO₂ and/or particulate. Nearly 85 percent of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. The off-gas containing a strong stream of SO₂ (five to seven percent SO₂) is sent to a sulfuric acid plant, while the weak stream (less than 0.5 percent SO₂) is vented to the atmosphere after removal of particulate. Particulate generated by the sinter plant, blast furnace, and the dross reverberatory furnace are collected using either baghouses or electrostatic

precipitators (ESPs) and then recycled. The sinter plant off-gases are reacted in a contact acid plant to produce concentrated sulfuric acid.⁶

Particulate emissions from sinter machines range from five to twenty percent of the concentrated ore feed. Approximately 15 percent of the sulfur in the ore concentrate fed to the sinter machine are eliminated in the blast furnace. However, only half of this amount, about seven percent of the total sulfur in the ore, is emitted as SO₂. Particulate emissions from blast furnaces contain many different kinds of material, including a range of lead oxides, quartz, limestone, iron pyrites, iron-limestone-silicate slag, arsenic and other metallic compounds associated with lead ores. The emission controls most commonly employed are fabric filters and ESPs.

Zinc Ore Processing Emissions

Primary zinc processing generates air emissions during roasting. Roasting is responsible for more than 90 percent of the potential SO₂ emissions. Approximately 93 to 97 percent of the sulfur in the feed is emitted as sulfur oxides. Sulfur dioxide emissions from the roasting process at primary zinc processing facilities are recovered at on-site sulfuric acid plants. Much of the particulate matter emitted from primary zinc facilities is also attributable to roasters. Though the amount and composition of particulate varies with operating parameters, the particulate is likely to contain zinc and lead.

6.5 Effluents

Lead and Zinc Ore Extraction Effluents

Lead and zinc ore mining activities can alter the topography and vegetative land cover effecting the volume and rate of surface water run-off. The run-off increases the variability in stream flows and can dramatically affect aquatic life. In most cases, however, the water is maintained and managed in ponds pursuant to mining permits, thereby improving aquatic life by not introducing variability in stream flows. Underground mining generally has less impact on soil and vegetation than surface mining, but can cause greater quantities of acid or alkaline drainage from mine water. The zinc ore black sphalerite may contain as much as 18 percent iron. Manganese and the rare element cadmium are usually present in small amounts.

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 typically is used in beneficiation or pumped to mine water ponds.

The composition and quantity of mine water varies among mining sites. 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

⁶ U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 371-408, April 1998

mine may fill with water. Through aeration and contact with sulfide minerals, the accumulated water can acidify and become contaminated with heavy metals, although the potential for such acidification is relatively low as fewer sulfides are available than before mining.

Lead and Zinc Ore Beneficiation Effluents

Lead and zinc ore beneficiation also generates effluents. During lead or zinc flotation, 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 then 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.

After the removal of values in the flotation process, the flotation system discharges tailings composed of liquids and solids. Between 25 and 50 percent of the tailings generated are made up of solids, mostly gangue material and small quantities of unrecovered lead-zinc minerals. The liquid component of the flotation waste is usually water and dissolved solids, along with any remaining reagents not consumed in the flotation process. These reagents may include cyanide, which is used as a sphalerite depressant during galena flotation. Most operations send these wastes to tailings ponds where solids settle out of the suspension. The liquid component either is recycled back to the mill or discharged if it meets water quality standards. The characteristics of tailings from the flotation process vary greatly, depending on the ore, reagents and processes used. Lead, zinc, chromium, iron and sulfate were all found in the wastewater of the selected facilities. Other types of beneficiation wastes include waste slurries from milling and gravity concentration steps. These wastes are disposed of in tailings impoundments.

Lead Ore Processing Effluents

The smelting of primary lead produces a number of wastewaters and slurries including sinter plant scrubber water, acid plant blowdown, slag granulation water, plant run-off and plant washdown water. Plant washdown water results from plant housekeeping and normally contains a substantial amount of lead and other process materials. Wastewater is usually treated and recycled. The lead ore processing effluents are listed with quantities in Table 6-4.

Effluent	Quantity (metric tons/year)
Acid Plant Blowdown	556,000
WWTP Effluents	3,500,000

Source: U.S. Environmental Protection Agency, Office of Solid Waste, Identification and Description of Mineral Processing Sectors and Waste Streams, lead and zinc, April 1998

Lead Ore Acid Plant Blowdown

Acid plant blowdown (APB) 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 (acidic liquid waste) is known as APB. This wastewater may be routed to treatment plants or recycled. Treatment often involves neutralization with lime, followed by thickening, filtering and recycling of the effluent.

Some facilities treat APB with lime at the acid plant and then pump the resulting slurry to an on-site waste water treatment plant. Other plants mix APB with other wastewaters. They 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 or recycled within the plant. The solids may also be sold for metals recovery. Approximately 556,000 metric tons of APB is generated annually.⁷

Lead Slag Granulation Water

Slag granulation water is generated with hot slag. Approximately 70 percent of the granulated slag is recycled to the sinter plant for use as a flux. The remaining slag is sent to storage. Both Missouri facilities use dewatering systems that separate the slag from the slag granulation water. The separated slag granulation water is recycled back to the granulation process for reuse.

Waste Water Treatment Plant - Lead Production

Waste water treatment plants (WWTP) are utilized in primary lead production for treatment of acid plant blowdown and other wastewaters, including slag granulation water, plant washdown and run-off. These liquids may receive treatment prior to the WWTP such as settling. Treatment in the WWTP often consists of lime neutralization and additional settling. Approximately 3,500,000 metric tons of WWTP liquid effluents are generated annually and are completely recycled and reintroduced into the smelting process.⁸

Zinc Processing Effluents

Production of primary zinc metal at both electrolytic and pyrometallurgical zinc processing plants generates several wastestreams common to both processes. Wastewaters may be generated during the leaching, purification and electrowinning stages of primary zinc processing when electrolyte and acid solutions become too contaminated to be reused again. This wastewater needs to be treated before discharge. Wastewater from zinc processing is also generated from acid plant blowdown and wastewater treatment plant liquid. Surface impoundment liquid consists of process wastewaters, acid plant blowdown, and plant runoff, the majority of which is sent on to the wastewater treatment plant. Although acid plant blowdown is listed as hazardous, it is no longer generated. Wastewaters are partially recycled into the process.

⁷ U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 371-408, April 1998

⁸ U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 371-408, April 1998

Lead and Zinc Ore Miscellaneous Effluents

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 naphtha), acidic tank cleaning wastes and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include sanitary sewage, waste oil and other lubricants.

6.6 Byproducts and Solid Waste

The following describes solid wastes and by-products from each of the major activities in lead and zinc mining and processing.

Extraction

Solid wastes generated by lead-zinc mining operations include materials such as waste rock, tailings and refuse. Many of these materials may be disposed of onsite or offsite, while others may be used or recycled during the active life of the operation. Waste constituents may include base metals, sulfides, or other elements found in the ore and any additives used in beneficiation operations.

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.

Processing

Table 6-5 lists the solid wastes and quantities from lead ore processing.

Lead ore solid residues collected include, "rice paddies" and "filter cakes." This byproduct waste is recycled to the sintering process. Primary lead processing activities usually result in other solid wastes that include blast furnace slag, spent furnace brick, wastewater solids, slurried APC dust, and baghouse incinerator ash.

Effluent	Quantity (metric tons/year)
Spent Furnace Brick	1,000
Slurried APC Dust	7,000

Source: U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, lead and zinc, April 1998.

Lead Blast Furnace Slag

The blast furnace slag captures the remaining sulfur present, and is composed primarily of iron and silicon oxides, as well as aluminum and calcium oxides. Other metals may also be present in smaller amounts, including antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, silver, and zinc. This blast furnace slag is either recycled back into the process or stored in state permitted areas on site.

Spent Lead 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. Approximately 1,000 metric tons of spent furnace brick are generated annually.⁹

Lead Wastewater

Surface impoundment solids consist of solids that settle out of process wastewaters. Surface impoundments at some primary lead facilities receive various types of wastewaters, including slag granulation water, acid plant blowdown, plant runoff, and plant washdown waters. Wastewater treatment sludges and solids consist of solid materials that settle following lime neutralization of influent wastewaters. Solids dredged from these impoundments are either recycled to the sinter feed preparation or disposed of at the slag dump and are typically recycled to the sinter feed preparation operation.

In some methods, 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 for neutralization, clarification, and other treatment. Dewatered sludge from this treatment plant is returned to the sinter feed. This washdown may contain entrained solids and particulate. 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.

Lead Slurried APC Dust

At one refinery, ESP dust and scrubber underflow from the cleaning of sinter plant off-gases destined for the acid plant was slurried into a thickener. The thickened solids can be placed on the slag dump along with other solids for air drying, and eventually recycled to the sinter feed preparation step. The refinery generates approximately 7,000 metric tons of slurried APC dust annually.¹⁰

⁹ U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 371-408, April 1998

¹⁰ U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 371-408, April 1998

Lead Ore 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.

Zinc Ore Beneficiation and Processing

Table 6-6 lists the by-products from zinc beneficiation and processing activities.

Solid wastes, some of which are hazardous, are generated at various stages in primary zinc processing. Solid wastes include ferrosilicon, tower blowdown, mineral residue, spent cloths, bags and filters, gypsum, impoundment solids, slag, and refractory brick.

Zinc Ferrosilicon and Tower Blowdown

Ferrosilicon is accumulated in a stockpile until it can be sold. Approximately 1,000 metric tons of tower blowdown are generated annually in the U.S. Tower blowdown may exhibit the characteristics of corrosivity and toxicity for cadmium, lead, mercury and selenium.

Effluent	Quantity (metric tons/year)
Ferrosilicon	17,000
Tower Blowdown	1,000
Goethite	15,000
Saleable Residues	10,000
Spent cloths, Bags, and Filters	200
Synthetic Gypsum	21,000
Surface Impoundment Solids	1,000
Zinc-Rich Slag	157,000
Zinc-lean Slag	17,000
Refractory Brick	1,000

Source: U.S. Environmental Protection Agency, Office of Solid Waste, Identification and Description of Mineral Processing Sectors and Waste Streams, lead and zinc, April 1998.

Zinc Ore Residuals

Electrolytic refining operations generate mineral processing residues such as goethite and leach cake residues and saleable residues. Goethite is generated to remove iron from the zinc sulfate solution generated by leaching calcine with sulfuric acid. Approximately 15,000 metric tons of goethite is generated annually by the three electrolytic refineries in the U.S. Runoff flows to a clay-lined sump pond and then to the facility's wastewater treatment plant. Spent goethite and leach cake residues are fully recycled and classified as a byproduct.

Saleable residues are recovered in the purification of the neutral leach zinc sulfate solution. These include a lead- and silver-bearing filter cake, a copper and cadmium sludge, which is created by adding zinc dust to the solution. Nickel and cobalt residue is also created by adding zinc dust along with antimony as a catalyst. These residues are stockpiled along with others, such as sump and tank cleanings, on an unlined pad until they are sold or recycled. Runoff from the pad collects in a sump and is pumped to a large surface impoundment and eventually to the

wastewater treatment plant. Due to the fact these residues are recycled, they are not considered solid wastes. Approximately 10,000 metric tons of various saleable residues are recovered.

Spent Cloths, Bags, and Filter By-product - Zinc Production

Cloths, bags and filters are utilized in zinc processing operations which may become contaminated with potentially hazardous constituents. Approximately 200 metric tons of these waste materials are generated annually. Spent cloths, bags and filters are recycled and classified as a spent material.

Zinc Ore Spent Synthetic Gypsum

Synthetic gypsum can be generated during the treatment of bleed electrolyte from the electrowinning circuit. Approximately 21,000 metric tons are generated annually.

Spent Surface Impoundment - Zinc Production

Surface impoundment solids consist of solids that settle out of process wastewaters, acid plant blowdown and plant runoff discharged to the surface impoundment. Approximately 1,000 metric tons of solids are generated annually by four operating plants. Smelting of zinc concentrate generates two mineral processing secondary materials: zinc slag and refractory brick.

Zinc Smelting

Zinc-rich slag results from the distillation of purified zinc vapor in the electrothermic furnace. The slag is treated to recover coke and zinc fines, which are recycled to the smelting process, and zinc slag. Zinc-lean slag is used as drainage material in a permitted flyash landfill.

Refractory brick is used to line the furnaces in which primary zinc smelting occurs. As furnaces are periodically relined, spent brick is removed from the furnaces and disposed or recycled. Approximately 1,000 metric tons of refractory brick are removed from furnaces annually.

Zinc Ore Fuming

Disposal practices are similar for blast furnace slag and residual slag from zinc fuming operations. The slag may be first 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. They can also 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). 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.

Lead and Zinc Ore Miscellaneous

This waste stream consists of a mixture of consolidated refractory brick, slag, matte, sweepings and other cleanup wastes. This waste may be partially recycled and is classified as a spent material. Non-hazardous wastes may include tires from trucks and large machinery.

6.7 Hazardous Waste

The commodities lead and zinc have been evaluated from extraction to the first saleable product. There are no RCRA-listed (Resource Conservation and Recovery Act) hazardous wastes associated with lead and zinc ore mining, beneficiation, and processing. The material generated from lead and zinc ore mining, beneficiation, and processing is managed through recycling.