ZINC

A. Commodity Summary

The primary source of zinc is the mineral sphalerite (ZnS), which is the source of about 90% of zinc produced today; zinc can also be recovered from six additional minerals, including hemimorphite, smithsonite, zincite, hydrozincite, willemite, and franklinite.[1] The primary uses of zinc are as a protective coating for steel (galvanizing), as alloys in die casting, as an alloying metal with copper to make brass and bronze, and in chemical compounds (e.g., zinc oxide) in rubber and paints.[2]e

Canada and Australia were the world's largest producers of zinc in 1994, accounting for 31% of mine production, followed by China, Peru, the United States, and Mexico.[3] Canada, Australia, and the U.S. also possess 39% of the world's zinc reserves. In the U.S., mines in Alaska, Missouri, New York, and Tennessee produced more than 90% of the nation's total mine output in 1994 of 560,000 metric tons; the four largest U.S. mines (in order of output) in 1992 and their operators and locations were the following:

Mine Name	Operator	Location
Red Dog	Cominco Alaska, Inc.	Northwest Arctic, AK
Elmwood-Gordonsville	Jersey Miniere Zinc Co.	Smith, TN
Greens Creek	Greens Creek Mining Co.	Admiralty Island, AK
Balmat	Zinc Corp. of America (ZCA)	St. Lawrence, NY

All of these mines produce zinc ore. In addition, several mines in the U.S. produce lead-zinc ore or lead ore with secondary zinc values, which can be beneficiated to remove zinc for processing. The larger of these mines include the West Fork and Fletcher mines in Reynolds, MO; the Buick mine in Iron, MO; and the Lucky Friday mine in Shoshone, ID.[4]

Four primary zinc smelters (three using the electrolytic process, the fourth using the electrothermic or pyrometallurgical process) produced 240,000 metric tons of slab zinc in 1994.[5] These plants and their location and process type include the following:

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[1] "Zinc and Zinc Alloys," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. XXIII, 1983, p. 808.

[2] U.S. Bureau of Mines, Mineral Facts and Problems, Bulletin 675, 1985, p. 923.

[3] U.S. Bureau of Mines, "Zinc," from Mineral Commodity Summaries, January 1995, p. 191.

[4] Jolly, J., "Zinc," in Minerals Yearbook Volume 1. Metals and Minerals 1992, U.S. Bureau of Mines, 1992, p. 1477.

[5] U.S. Bureau of Mines, 1995, Op. Cit., p. 190.

Facility Name	Location	Process
Big River Zinc Corp.	Sauget, IL	electrolytic
Jersey Miniere Zinc Co.	Clarksville, TN	electrolytic
Zinc Corp. of America	Bartlesville, OK	electrolytic
Zinc Corp. of America	Monaca, PA	pyrometallurgical

Zinc oxide was produced from zinc metal and scrap by eight companies in 1992. All of these companies produced French-process zinc oxide, except for one company, Eagle Zinc Co., of Hillsboro, IL, which produced American-process zinc oxide (both processes are described below).[6] Total U.S. production of zinc oxide in 1992 was approximately 105,000 metric tons.

In addition, the U.S. also imported 25,000 metric tons of zinc ore and concentrate and 800,000 metric tons of slab zinc, scrap, and compounds in 1994.[7]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Zinc minerals are generally associated with other metals minerals, the most common associations in ores being zinc-lead, lead-zinc, zinc-copper, copper-zinc, or zinc-silver. Zinc also occurs alone in ores. Due to low zinc content, zinc-bearing ores must be concentrated before processing. Beneficiation, which usually occurs at the mine, consists of crushing, grinding, and flotation to produce concentrates of 50% to 60% zinc.[8]

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 produce impure zinc oxide referred to as roasted concentrate or calcine. In electrolytic zinc processing, calcine is digested with sulfuric acid to form a zinc sulfate solution, from which zinc is deposited through electrolytic refining. In pyrometallurgical processing, calcine is sintered and smelted in batch horizontal retorts, externally-heated continuous vertical retorts, or electrothermic furnaces. The sole pyrometallurgical operation in the U.S., Zinc Corp. of America's Monaca smelter, uses an electrothermic furnace. In addition, zinc is 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. The process is used at 12 plants worldwide and accounts for 12% of world capacity. There are no ISF-process plants in the U.S.[9]

Zinc oxide is manufactured by either the French or American processes. In the French process, which is used at ZCA's Monaca smelter, high-grade zinc metal is smelted in horizontal retorts to produce zinc metal vapor, which is burned in a combustion chamber. In the American process, zinc oxide is manufactured by oxidizing zinc vapor in burners; the resulting gases and fume are cooled, and zinc oxide is recovered in baghouses.[10]

2. Generalized Process Flow Diagram

Detailed descriptions of Zinc Corp. of America's Bartlesville, OK (electrolytic) and Monaca, PA (pyrometallurgical) facilities are presented below. These descriptions are based on sampling trips to the facilities in 1989 in support of EPA rulemaking activities.

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[6] Jolly, J., 1992, Op. Cit., p. 1472.

[7] U.S. Bureau of Mines, 1995, Op. Cit., p. 190.

[8] "Zinc and Zinc Alloys," 1983, Op. Cit., pp. 809, 812.

[9] U.S. Bureau of Mines, 1985, Op. Cit., pp. 927-928.

[10] "Zinc and Zinc Alloys," 1983, Op. Cit., pp. 855.

Electrolytic Process

The ZCA electrolytic zinc refinery in Bartlesville, Oklahoma produces several zinc products and associated by-products from zinc ore concentrates. Zinc products include zinc metal, roofing granules, and zinc sulfate solution. By-products include cadmium metal, sulfuric acid, lead/silver residue, copper residue, nickel/cobalt residue, lead scrap, and aluminum scrap. ZCA utilizes zinc sulfide concentrates containing 50-55 percent zinc as feed for its Bartlesville plant.

Production of zinc products from ore concentrates at this facility involves roasting, leaching (digestion), purification, and electrowinning. Roasting takes place at the Zinc Ore Roaster (ZOR), and the remaining three processes take place at the Zinc Refinery (ZRF), as shown in the process flow diagram in Exhibit 1. Both the ZOR and the ZRF are located at the Bartlesville plant.

Zinc ore concentrates are first slurried with water and then roasted, reacting with air to produce a crude zinc oxide calcine and off-gas from the roaster containing 7-10% sulfur dioxide. Calcine dusts are recovered from the off-gas by two cyclone separators and added to the calcine. The off-gas is humidified and passed through a wet electrostatic precipitator in a hot tower to remove remaining solids from the sulfur dioxide gas so that it may be used as feed to produce sulfuric acid in the Zinc Acid Plant (ZAP). Two-thirds of the resulting liquid stream from the precipitator, known as acid plant blowdown, are pumped directly to the facility's wastewater treatment plant, and the remaining third is recycled to the hot tower. Total acid plant blowdown flow is approximately 50 gallons per minute. Process wastewater generated by the ZOR consists of non-contact cooling water used to cool the calcine as it exits the roaster and slurry water that leaks from a pump that directs the slurried ore concentrates to the roaster. These waters collect in a clay-lined sump outside the roaster and are pumped to the wastewater treatment plant. A process wastewater stream generated at the ZAP, consisting of cooling tower blowdown, is pumped directly to the treatment plant.

The leaching (digestion) process dissolves the zinc in the calcine, creating a zinc sulfate solution from which the zinc can be removed through electrowinning. By mixing the calcine from the roaster with 150-170 g/L sulfuric acid in a step called neutral leaching, about 90% of the zinc in the calcine dissolves. The insoluble zinc calcine is separated from the leaching solution in a settling tank. Neutral leach zinc sulfate solution is sent to a purification system, and the solids containing the insoluble zinc are pumped to a residue treatment circuit, where additional sulfuric acid is added to the solids in a series of three hot acid leach tanks to dissolve another 6-7 percent of the zinc from the calcine. Remaining solids in the resulting slurry are separated in a second settling tank and filtered into a cake that is dried and sold for its lead and silver content (20% lead and up to 70 ounces of silver per ton).

When the calcine is leached with sulfuric acid in the hot acid leach tanks, iron in the calcine dissolves along with zinc. Because this solution still contains recoverable zinc, ZCA recycles the solution to the original neutral leach step described above. However, if the dissolved iron in the solution is not removed, it will prevent the eventual recovery of zinc metal. To remove iron from the solution, ZCA

EXHIBIT 1

ELECTROLYTIC ZINC PRODUCTION PROCESS

Graphic Not Available.

Source: U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Volume IV: Primary Zinc, Primary Lead, Secondary Lead, and Primary Antimony, EPA 440/1-89-019.9, Office of Water Regulations and Standards, May 1989, p. 479.

utilizes the goethite process.[11] Zinc sulfide concentrates are added to the hot acid leach solution to reduce the dissolved iron to its ferrous or divalent state. Zinc calcine is added to neutralize remnant sulfuric acid from the hot acid leach step. Zinc oxide and air are then added to the solution to oxidize the iron from its divalent to trivalent state and precipitate goethite, a hydrated iron oxide, in a slurry. The slurry settles in a tank; the clarified solution containing recoverable zinc is recycled to the neutral leach step, and the iron oxide slurry (goethite) solids are washed and filtered.

Goethite removed from the filter contains 30-40% iron, but recovery of the iron is currently not economical.[12] Moist goethite cake is stored in an uncovered, unlined waste pile on-site that dates from 1978, when the electrolytic process began at the facility. Runoff from the pile flows to a clay-lined sump pond and then to the wastewater treatment plant.

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 a 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. 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.

Purified, zinc-rich solution is cooled in evaporative cooling towers and stored in tanks before the zinc is electrowon from the solution at the cell house. The cell house consists of 128 electrolytic cells, each with 45 lead anodes and 44 aluminum cathodes. When electric current passes through the zinc sulfate solution, which serves as an electrolyte, positive zinc ions deposit on the negatively-charged aluminum cathodes. Half of the cathodes are removed from their cells each day so that the metallic zinc layer can be scraped off each cathode and so that zinc can continue to be removed from solution with the other cathodes. Spent solution containing dilute sulfuric acid is recycled to the neutral leach step of the leaching process. Because heat builds in the cells, the zinc sulfate solution continuously passes through the cooling towers. Non-contact cooling water along with boiler blowdown, condensate, and brushing water used to wash cathodes make up a process wastewater stream from the ZRF. This stream flows through a feeder ditch to a clay-lined sump pond, then to a large, clay-lined surface impoundment, and is finally pumped to the wastewater treatment plant.

Zinc removed from cathodes is melted in a furnace and cast into 55-pound, 600-pound, or 2,400-pound ingots. Some zinc is converted to dust used in the purification system. Zinc fume collected in the furnace baghouse is recycled.

ZCA also converts scrap zinc from its plant and purchased scrap into usable zinc at its Zinc Secondaries Plant (ZSP), a process that is outside the scope of primary mineral processing and, thus, not described further.

Most process wastewaters at ZCA are made up of small streams from the roasting, purification, electrowinning, and zinc secondaries processes. Acid plant blowdown is generated when sulfur dioxide off-gas from the ZOR passes through a wet electrostatic precipitator in the hot tower to remove solids. Process wastewater from the ZSP consists primarily of water from Venturi scrubbers used to collect dusts from rotary drying of calcine. Process wastewater from the ZRF consists primarily of brushing water used to wash the aluminum cathodes that serve as a depositional surface for zinc ions during electrowinning. The ZAP, which converts sulfur dioxide gas generated in the ZOR to commercial-grade sulfuric acid, generates process wastewater consisting of non-contact cooling tower blowdown. Smaller streams of boiler blowdown, non-contact cooling water from cooling towers, and condensate also make up the wastewater flow.

Process wastewater and plant runoff that collect in the two large, clay-lined surface impoundments are pumped to the wastewater treatment plant. Following a two-stage neutralization process and clarification, sludge is recycled to the roaster and treated water is pumped to two synthetically-lined holding ponds before it is injected in a Class I industrial well.

Pyrometallurgical Process

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[11] Additional methods to precipitate iron include the hematite and jarosite processes.

[12] As of July 1989, ZCA was studying a pilot system to recover iron from goethite; the status of this project is unknown.

The primary mineral processing operations at the Monaca facility produce a variety of zinc and other products from ore concentrate (primarily from a New York State mine) and to a lesser extent secondary materials (e.g., cast off material from galvanizing operations). Zinc products include zinc metal, zinc sulfate solution, zinc dust, and zinc oxide. Other products produced by the facility including sulfuric acid, lead sulfate, cadmium sponge, ferro-silicate, and processed slag. Due to variations in market conditions, some of these materials, especially ferro-silicate and slag, may be stored on-site for several years prior to sale.

Ore concentrate is first dried in an ore dryer and then roasted, as shown in the process flow diagram in Exhibit 2. 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 in a concrete basin (the "Cottrell pond") where 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.

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.[13] 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 from which goes to the facility's wastewater treatment plant. Underflow from the clarifier is centrifuged; liquid removed by the centrifuge is pumped to a concrete basin and then returned to the clarifier and the solids are 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.

Sinter and coke are charged to an electrothermal furnace in which zinc gas is generated and subsequently condensed on molten zinc. Uncondensed zinc is removed from the off-gases by a wet scrubber. Water from the wet scrubber is sent to two concrete basins and then a series of three lined impoundments. 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 of the scrubber water in both the concrete basins and the impoundments. Blue powder is removed from the concrete basins on a weekly basis and placed in adjacent concrete basins to dry prior to being returned to the ore dryer or used to raise the pH of the combined acid plant blowdown and ore dryer scrubber water. Blue powder is removed from the impoundments along with the impoundment liners every two or three years, and both the powder and the liners are charged to the furnace.

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[13] Feed to the zinc sulfate circuit also consists of zinc carbonate that was generated before the zinc sulfate circuit became operational and that is stockpiled onsite.

EXHIBIT 2

PYROMETALLURGICAL ZINC PRODUCTION PROCESS

Graphic Not Available.

Source: U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines and Standards for the Nonferrous Metals Manufacturing Point Source Category. Volume IV: Primary Zinc, Primary Lead, Secondary Lead, and Primary Antimony, EPA 440/1-89-019.9, Office of Water Regulations and Standards, May 1989, p. 480.

Zinc from the furnace is made into a variety of final products including furnace grade 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 generated by the processing operations, to separate the ferrous and non-ferrous fractions. The ferro-silicates are stockpiled onsite and sold to the iron and steel industry when market conditions permit. The non-ferrous slag is graded into four sizes and sold or used as a drainage material in the facility's fly ash landfill.

Wastewaters, which include plant runoff as well as process wastewater from the blue powder impoundments and the zinc sulfate circuit, go to a lined equalization basin and then to a two-stage neutralization process, followed by clarification prior to discharge to the Ohio River through an NPDES-permitted outfall. Solids removed from the clarifier are filtered and then returned to the sintering operation.

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

In addition to the Imperial Smelting Furnace process, which is identified above, 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.[14]

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.[15]

Sulfate roasting of copper-zinc-sulfide concentrate has been examined on a laboratory and 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 D2-EPHA (a solvent extractant), and copper sulfate was crystallized from the purified solution. Recoveries of 95% and 99% were achieved for zinc and copper, respectively.[16]

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% of both zinc (as zinc sulfate) and sulfuric acid in the bleed stream was recovered at concentrations high enough for direct recycle to the process.[17]

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 $CaCl_2$ brine solution at pH 2 for one hour at 90°C. 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. The remaining residue passed the EP toxicity test.[18]

4. Beneficiation/Processing Boundary

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[14] Mishra, B., D. Olson, and W. Averill, "Applications of Molten Salts in Reactive Metals Processing," presented at the Conference for Emerging Separation Technologies for Metals and Fuels, Palm Coast, FL, March 13-18, 1993, sponsored by the Minerals, Metals, & Materials Society, Warrendale, PA.

[15] U.S. Bureau of Mines, 1985, Op. Cit., p. 927

[16] Ferron, C. and J. De Cuyper, "The Recovery of Copper and Zinc from a Sulphide Concentrate Using Sulfate Roasting, Acid Leaching and Solution Purification," International Journal of Mineral Processing, 35, No. 3-4, August 1992, pp. 225-238.

[17] Eyal, A., et. al., 1990, Op. Cit., pp. 209-222.

[18] Beckstead, L., et al., 1993, Op. Cit., pp. 862-875.

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 prior to the initial roasting step in both the electrolytic and the pyrometallurgical processes. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here, where, as a result of a chemical reaction, sulfur is removed from the zinc sulfate feedstock. 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

1. Extraction/Beneficiation Wastes

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. The primary waste generated by mineral extraction in underground mines is mine development rock, which is typically used in onsite construction for road or other purposes. Surface mines usually generate large volumes of overburden and waste rock that are usually disposed of in waste rock dumps.

After the removal of values in the flotation process, the flotation system discharges tailings composed of liquids and solids. Between 1/4 and 1/2 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.[19]

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[19] Coppa, L., Waste Disposal Activities and Practices in the United States: Copper, Lead, Zinc, Gold, and Silver, U.S. Bureau of Mines, Division of Minerals Availability Open File Report, November, 1984, Washington, DC.

In general, most wastes from beneficiation of lead-zinc ores are disposed of in tailings impoundments from which water is likely to be reclaimed during the mine's life. In addition, other materials typically not considered wastes, such as mine water, may be managed onsite during the active life of the facility and may ultimately become wastes. The chemical composition of mine water generated at mines varies from site to site and is dependent on the geochemistry of the ore body and the surrounding area. Mine water may also contain small quantities of oil and grease from extraction machinery and nitrates (NO_3) from blasting activities. EPA[20] and the Bureau of Mines[21] reported concentration ranges in mine waters of 0.1-1.9 mg/L for lead, 0.12-0.46 mg/L for zinc, 0.02-0.36 mg/L for chromium, 295-1,825 mg/L for sulfate, and pH of 7.9-8.8. After the mine is closed and pumping stops, the potential exists for mines to fill with water. Water exposed to sulfur-bearing minerals in an oxidizing environment, such as open pits or underground workings, may become acidified.

In addition to wastes generated as part of beneficiation, facilities also store and use a variety of chemicals required by the mine and mill operations. A list of chemicals used at lead-zinc mines, compiled from data collected by the National Institute for Occupational Safety and Health (NIOSH), is provided below.[22]

Acetylene
Calcium Oxide
Hexone
Hydrogen Chloride
Methyl Chloroform
Methyl Isobutyl Carbinol
Nitric Acid
Propane
Sodium Cyanide
Sulfur Dioxide
Sulfuric Acid
Diesel Fuel No. 1
Diesel Fuel No. 2
Chromic Acid, Disodium Salt
Copper Solution
Kerosene
Methane, Chlorodifuoro-
Sodium Aerofloat
Sulfuric Acid Copper (2+) Salt (1:1)
Zinc Solution
Zinc Sulfate

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[20] U.S. Environmental Protection Agency, Report To Congress: Wastes From the Extraction and Beneficiation of Metallic Ores, Phosphate Rock, Asbestos, Overburden from Uranium Mining and Oil Shale, EPA/530/SW-85-033, Office of Solid Waste, December, 1985, Washington, DC.

[21] Coppa, L., 1984, Op. Cit..

[22] National Institute for Occupational Safety and Health, 1990.

2. Mineral Processing Wastes

Electrolytic refining operations generate two mineral processing wastes: goethite and leach cake residues, and saleable residues. These are described below.

Spent Goethite and Leach Cake 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 are generated annually by the three electrolytic refineries in the U.S.[23] Site-specific information on management practices for goethite were available for only one facility, ZCA's Bartlesville, OK refinery. Moist goethite cake is stored in an uncovered, unlined waste pile on-site that dates from 1978, when the electrolytic process began at the facility. Runoff from the pile flows to a clay-lined sump pond and then to the facility's wastewater treatment plant. We used best engineering judgment to determine that spent goethite and leach cake residues may exhibit the characteristic of toxicity for arsenic, cadmium, chromium, lead, mercury, selenium, and silver. This waste stream is fully recycled and is classified as a by-product. Data for this wastestream are presented in Attachment 1.

Saleable Residues

Approximately 10,000 metric tons of various saleable residues are recovered annually in the purification of the neutral leach zinc sulfate solution.[24] These include a lead- and silver-bearing filter cake; a copper and cadmium sludge, which is created by adding zinc dust to the solution; and a nickel and cobalt residue, 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. Because these residues are recycled, they are not believed to be solid wastes. No chemical characterization data are available at present for these residues.

Oxide retorting, considered a secondary mineral process because it uses primary zinc metal as a feedstock, generates clinker as a secondary mineral processing waste. We used best engineering judgment to determine that this clinker may exhibit the characteristic of toxicity for cadmium.[25]

Production of primary zinc metal at both electrolytic and pyrometallurgical zinc processing plants generate several wastestreams common to both processes, as described below.

Process Wastewater

Process wastewater is generated at all four of the operating zinc processing plants. At ZCA's electrolytic refinery in Bartlesville, OK process wastewaters consist of small streams from the roasting, purification, electrowinning, and zinc secondaries processes, as described above. Process wastewater and plant runoff collect in two large, clay-lined surface impoundments and are pumped to the wastewater treatment plant for neutralization. At ZCA's Monaca, PA smelter, wastewaters include plant runoff as well as process wastewater from the blue powder impoundments and the zinc sulfate circuit. These wastewaters collect in a lined equalization basin and treated in a two-stage neutralization process. Approximately 6.6 million metric tons of process wastewater are generated annually at the four U.S. primary zinc facilities.[26] (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous wastestreams.) We used best engineering judgment to determine that process wastewater may be recycled and may exhibit the characteristic of toxicity for arsenic, cadmium, chromium, lead, selenium, and silver; it may also exhibit the corrosivity characteristic. This waste is classified as a spent material. Data for this wastestream are presented in Attachment 1.

Acid Plant Blowdown

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

[24] Ibid.

[25] Ibid.

[26] Ibid.

Acid plant blowdown is generated when sulfur dioxide off-gas from the roasting operations passes through a wet electrostatic precipitator to remove solids. At ZCA's Bartlesville plant, two-thirds of the acid plant blowdown are pumped directly to the facility's wastewater treatment plant, and the remaining third is recycled to the hot tower. At the Monaca facility, acid plant blowdown is discharged to a concrete basin where 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. Approximately 130,000 metric tons of acid plant blowdown are generated annually at the four U.S. primary zinc facilities.[27] We used best engineering judgment to determine that acid plant blowdown may exhibit the characteristic of toxicity for arsenic, cadmium, chromium, selenium, and silver; it may also exhibit the corrosivity characteristic. Data for this wastestream are presented in Attachment 1. We used best engineering judgment to determine that this waste may also exhibit the characteristic of toxicity for lead and mercury. Although this waste stream is listed as hazardous, it is no longer generated and has been remanded. Therefore, this waste stream was not included in our analysis.

Spent Cloths, Bags, and Filters

Cloths, bags, and filters are utilized in operations at each of the four zinc facilities and may become contaminated with potentially hazardous constituents. Approximately 200 metric tons of these waste materials are generated annually.[28] We used best engineering judgment to determine that spent cloths, bags, and filters may exhibit the characteristic of toxicity for cadmium, lead, mercury, selenium, and silver. This waste stream is recycled and is classified as a spent material.

TCA Tower Blowdown

Approximately 1,000 metric tons of TCA tower blowdown are generated annually.[29] We used best engineering judgment to determine that TCA tower blowdown may exhibit the characteristic of toxicity for cadmium, lead, mercury, and selenium; it may also exhibit the corrosivity characteristic.

Spent Synthetic Gypsum

Synthetic gypsum is generated during the treatment of bleed electrolyte from the electrowinning circuit. Approximately 21,000 metric tons are generated annually.[30] The management practice for this mineral processing waste is unknown, but the gypsum is most likely stockpiled on-site. We used best engineering judgment to determine that spent synthetic gypsum may exhibit the characteristic of toxicity for arsenic, cadmium, and lead. Data for this wastestream are presented in Attachment 1.

Wastewater Treatment Plant Liquid Effluent

Wastewater treatment plant liquid effluent results from the treatment of process wastewaters, including acid plant blowdown, and plant runoff. Approximately 3.5 million metric tons of effluent are generated annually by the four operating U.S. plants.[31] Effluent generated at ZCA's Bartlesville plant is discharged to a Class I industrial injection well on-site, while effluent from the Monaca smelter is discharged through an NPDES-permitted outfall to the Ohio River. We used best engineering judgment to determine that wastewater treatment plant liquid effluent may be partially recycled and may exhibit the characteristic of toxicity for cadmium. This waste stream is classified as a spent material. Data for this wastestream are presented in Attachment 1.

Wastewater Treatment Plant Sludge

Wastewater treatment plant sludge also results from the treatment of process wastewaters, acid plant blowdown, and plant runoff. Approximately 45,000 metric tons of sludge are generated annually by the four

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[27] Ibid.

[28] Ibid.

[29] Ibid.

[30] Ibid.

[31] Ibid.

operating U.S. plants.[32] Wastewater treatment plant sludge from primary zinc processing is a RCRA-listed hazardous waste and must be managed and disposed accordingly. At ZCA's Bartlesville and Monaca plant, these solids are recycled to the zinc ore roaster. We used best engineering judgment to determine that wastewater treatment plant sludge may exhibit the characteristic of toxicity for cadmium. Data for this wastestream are presented in Attachment 1.

Spent Surface Impoundment Liquids

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. Approximately 2.5 million metric tons of liquid are generated annually by the four operating plants.[33] (The excessive generation rate for this wastewater [i.e., greater than one million metric tons/yr] is due to commingling of numerous wastestreams.) We used best engineering judgment to determine that spent surface impoundment liquid may exhibit the characteristics of corrosivity and toxicity (cadmium). This waste stream may be partially recycled and is classified as a spent material. Data for this wastestream are presented in Attachment 1.

Spent Surface Impoundment Solids

Surface impoundment solids consists 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 the four operating plants.[34] We used best engineering judgment to determine that surface impoundment solids may exhibit the characteristic of toxicity for arsenic, cadmium, lead, mercury, selenium, and silver. Data for this wastestream are presented in Attachment 1.

Smelting of zinc ore concentrate generates four mineral processing wastes: zinc-rich slag, zinc-lean slag, ferrosilicon, and refractory brick.

Zinc-rich Slag

Zinc-rich slag results from the distillation of purified zinc vapor in the electrothermic furnace. Approximately 157,000 metric tons are generated annually at the Monaca facility.[35] EP leach test concentrations of all eight inorganic constituents with EP toxicity regulatory levels are available for one sample of zinc slag from the Monaca facility. Of these constituents, only lead was found to exceed the EP toxicity regulatory level, by a factor of 12. The zinc slag sample that failed the EP toxic level was also analyzed using the SPLP leach test, and the lead concentration measured using the SPLP leach test was three orders of magnitude below the EP toxic level.[36] However, zinc-rich slag is considered to be a RCRA special waste because of the volume generated; consequently, it is exempt under the Bevill Exclusion from regulation as a hazardous waste. The slag is treated to recover coke and zinc fines, which are recycled to the process, and zinc-lean slag and ferrosilicon.

Zinc-lean Slag

Zinc-lean slag, or processed slag, is stored in slag waste piles, disposed in a flyash landfill, or sold for such uses as road gravel or construction aggregate. Approximately 17,000 metric tons are generated annually at the Monaca facility.[37] We used best engineering judgment to determine that zinc-lean slag may be recycled and may exhibit the characteristic of toxicity for lead. This waste is classified as a by-product. Data for this wastestream are presented in Attachment 1.

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[32] Ibid.

[33] Ibid.

[34] Ibid.

[35] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-8.

[36] U.S. Environmental Protection Agency, "Primary Zinc Processing," from Report to Congress on Special Wastes from Mineral Processing, Vol. II, Office of Solid Waste, July 1990, p. 14-3.

[37] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-8.

Waste Ferrosilicon

Ferrosilicon is accumulated in a stockpile until it can be sold. Approximately 17,000 metric tons are generated annually at the Monaca facility.[38] We used best engineering judgment to determine that waste ferrosilicon may be recycled and may exhibit the characteristic of toxicity for lead. This waste is classified as a by-product. Data for this wastestream are presented in Attachment 1.

Discarded Refractory Brick

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, most likely in a landfill on-site. Approximately 1,000 metric tons of refractory brick are removed from furnaces annually.[39] We used best engineering judgment to determine that refractory brick may exhibit the characteristic of toxicity for arsenic, cadmium, chromium, and lead.

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.

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[38] Ibid.

[39] U.S. Environmental Protection Agency, 1992, Op. Cit., p. I-8.

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