12.7 Zinc Smelting

12.7.1 General[1-2]

Zinc is found in the earth's crust primarily as zinc sulfide (ZnS). Primary uses for zinc include galvanizing of all forms of steel, as a constituent of brass, for electrical conductors, vulcanization of rubber and in primers and paints. Most of these applications are highly dependent upon zinc's resistance to corrosion and its light weight characteristics. In 1991, approximately 260,000 megagrams (287,000 tons) of zinc were refined at the 4 U. S. primary zinc smelters. The annual production volume has remained constant since the 1980s. Three of these 4 plants, located in Illinois, Oklahoma, and Tennessee, utilize electrolytic technology, and the 1 plant in Pennsylvania uses an electrothermic process. This annual production level approximately equals production capacity, despite a mined zinc ore recovery level of 520 megagrams (573 tons), a domestic zinc demand of 1190 megagrams (1311 tons), and a secondary smelting production level of only 110 megagrams (121 tons). As a result, the U. S. is a leading exporter of zinc concentrates as well as the world's largest importer of refined zinc.

Zinc ores typically may contain from 3 to 11 percent zinc, along with cadmium, copper, lead, silver, and iron. Beneficiation, or the concentration of the zinc in the recovered ore, is accomplished at or near the mine by crushing, grinding, and flotation process. Once concentrated, the zinc ore is transferred to smelters for the production of zinc or zinc oxide. The primary product of most zinc companies is slab zinc, which is produced in 5 grades: special high grade, high grade, intermediate, brass special, and prime western. The 4 U. S. primary smelters also produce sulfuric acid as a byproduct.

12.7.2 Process Description

Reduction of zinc sulfide concentrates to metallic zinc is accomplished through either electrolytic deposition from a sulfate solution or by distillation in retorts or furnaces. Both of these methods begin with the elimination of most of the sulfur in the concentrate through a roasting process, which is described below. A generalized process diagram depicting primary zinc smelting is presented in Figure 12.7-1.

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. The following reactions occur during roasting:

$$2ZnS + 3O_2 \rightarrow 2ZnO + SO_2 \qquad (1)$$

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (2)$$

In a multiple-hearth roaster, the concentrate drops through a series of 9 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. The reactions are slow and can be sustained only by the addition of fuel. Multiple hearth roasters are unpressurized and operate at about 690°C (1300°F). Operating time depends upon the composition of concentrate and the amount of the sulfur removal required. Multiple hearth roasters have the capability of producing a high-purity calcine.

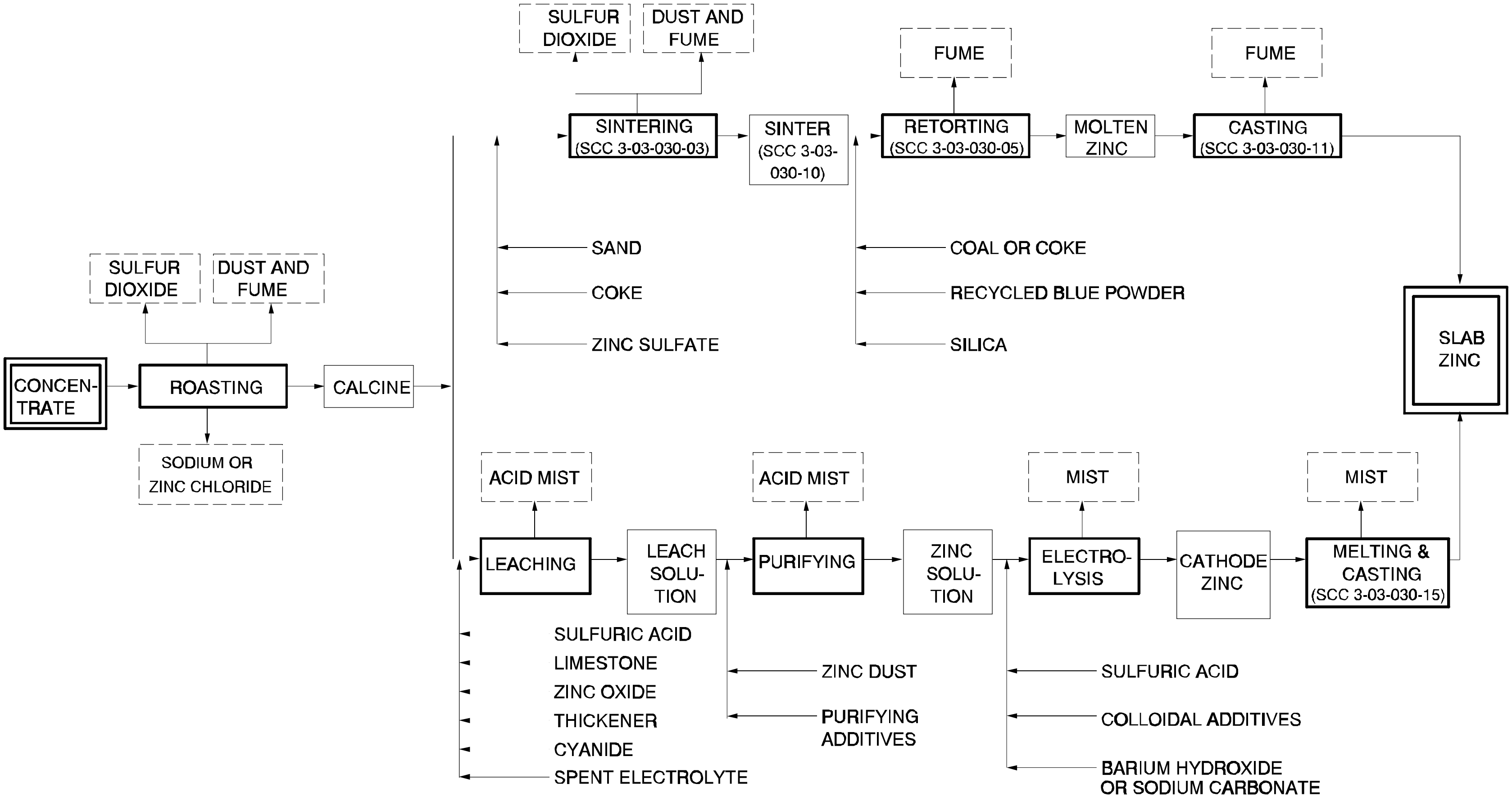

Figure 12.7-1. Generalized process flow for primary zinc smelting. (Source Classification Codes in parentheses.)

In a suspension roaster, the concentrates are blown into a combustion chamber very similar to that of a pulverized coal furnace. The roaster consists of a refractory-lined cylindrical steel shell, with a large combustion space at the top and 2 to 4 hearths in the lower portion, similar to those of a multiple hearth furnace. Additional grinding, beyond that required for a multiple hearth furnace, is normally required to ensure that heat transfer to the material is sufficiently rapid for the desulfurization and oxidation reactions to occur in the furnace chamber. Suspension roasters are unpressurized and operate at about 980°C (1800°F).

In a fluidized-bed roaster, finely ground sulfide concentrates are suspended and oxidized in a feedstock bed supported on an air column. As in the suspension roaster, the reaction 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 at temperatures averaging 1000°C (1800°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.

Electrolytic processing of desulfurized calcine consists of 3 basic steps, leaching, purification, and electrolysis. Leaching occurs in an aqueous solution of sulfuric acid, yielding a zinc sulfate solution as shown in Equation 3 below.

$$ZnO + SO_3 \rightarrow ZnSO_4 \qquad (3)$$

In double leaching, the calcine is first leached in a neutral or slightly alkaline solution, then in an acidic solution, with the liquid passing countercurrent to the flow of calcine. In the neutral leaching solution, sulfates from the calcine dissolve, but only a portion of the zinc oxide enters into solution. The acidic leaching solution dissolves the remainder of the zinc oxide, along with metallic impurities such as arsenic, antimony, cobalt, germanium, nickel, and thallium. Insoluble zinc ferrite, formed during concentrate roasting by the reaction of iron with zinc, remains in the leach residue, along with lead and silver. Lead and silver typically are shipped to a lead smelter for recovery, while the zinc is extracted from the zinc ferrite to increase recovery efficiency.

In the purification process, a number of various reagents are added to the zinc-laden electrolyte in a sequence of steps designed to precipitate the metallic impurities, which otherwise will interfere with deposition of zinc. After purification, concentrations of these impurities are limited to less than 0.05 milligram per liter (4×10^{-7} pounds per gallon). Purification is usually conducted in large agitated tanks. The process takes place at temperatures ranging from 40 to 85°C (104 to 185°F), and pressures ranging from atmospheric to 240 kilopascals (kPa) (2.4 atmospheres).

In electrolysis, metallic zinc is recovered from the purified solution by passing current through an electrolyte solution, causing zinc to deposit on an aluminum cathode. As the electrolyte is slowly circulated through the cells, water in the electrolyte dissociates, releasing oxygen gas at the anode. Zinc metal is deposited at the cathode and sulfuric acid is regenerated for recycle to the leach process. The sulfuric acid acts as a catalyst in the process as a whole.

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 30 to 35°C (86 to 95°F) and at atmospheric pressure. A portion of the electrolyte is continuously circulated through the cooling towers both to cool and concentrate the electrolyte through evaporation of water. The cooled and concentrated electrolyte is then recycled to the cells. Every 24 to 48 hours, each cell is shut down, the zinc-coated cathodes are removed and rinsed, and the zinc is mechanically stripped from the aluminum plates.

The electrothermic distillation retort process, as it exists at 1 U. S. plant, was developed by the St. Joe Minerals Corporation in 1930. The principal advantage of this pyrometallurgical technique over electrolytic processes is its ability to accommodate a wide variety of zinc-bearing materials, including secondary items such as calcine derived from electric arc furnace (EAF) dust. Electrothermic processing of desulfurized calcine begins with a downdraft sintering operation, in which grate pallets are joined to form a continuous conveyor system. The sinter feed is essentially a mixture of roaster calcine and EAF calcine. Combustion air is drawn down through the conveyor, and impurities such as lead, cadmium, and halides in the sinter feed are driven off and collected in a bag filter. The product sinter typically includes 48 percent zinc, 8 percent iron, 5 percent aluminum, 4 percent silicon, 2.5 percent calcium, and smaller quantities of magnesium, lead, and other metals.

Electric retorting with its greater thermal efficiency than externally heated furnaces, is the only pyrometallurgical technique utilized by the U. S. primary zinc industry, now and in the future. Product sinter and, possibly, secondary zinc materials are charged with coke to an electric retort furnace. The charge moves downward from a rotary feeder in the furnace top into a refractory-lined vertical cylinder. Paired graphite electrodes protrude from the top and bottom of this cylinder, producing a current flow. The coke serves to provide electrical resistance, producing heat and generating the carbon monoxide required for the reduction process. Temperatures of 1400°C (2600°F) are attained, immediately vaporizing zinc oxides according to the following reaction:

$$ZnO + CO \rightarrow Zn\ (vapor) + CO_2 \qquad (4)$$

The zinc vapor and carbon dioxide pass to a vacuum condenser, where zinc is recovered by bubbling through a molten zinc bath. Over 95 percent of the zinc vapor leaving the retort is condensed to liquid zinc. The carbon dioxide is regenerated with carbon, and the carbon monoxide is recycled back to the retort furnace.

12.7.3 Emissions And Controls

Each of the 2 smelting processes generates emissions along the various process steps. The roasting process in a zinc smelter is typically responsible for more than 90 percent of the potential SO_2 emissions. About 93 to 97 percent of the sulfur in the feed is emitted as sulfur oxides. Concentrations of SO_2 in the offgas vary with the type of roaster operation. Typical SO_2 concentrations for multiple hearth, suspension, and fluidized bed roasters are 4.5 to 6.5 percent, 10 to 13 percent, and 7 to 12 percent, respectively. Sulfur dioxide emissions from the roasting processes at all 4 U. S. primary zinc processing facilities are recovered at on-site sulfuric acid plants. Much of the particulate matter emitted from primary zinc processing facilities is also attributable to the concentrate roasters. The amount and composition of particulate varies with operating parameters, such as air flow rate and equipment configuration. Various combinations of control devices such as cyclones, electrostatic precipitators (ESP), and baghouses can be used on roasters and on sintering machines, achieving 94 to 99 percent emission reduction.

Controlled and uncontrolled particulate emission factors for points within a zinc smelting facility are presented in Tables 12.7-1 and 12.7-2. Fugitive emission factors are presented in Tables 12.7-3 and 12.7-4. These emission factors should be applied carefully. Emission factors for sintering operations are derived from data from a single facility no longer operating. Others are estimated based on similar operations in the steel, lead, and copper industries. Testing on 1 electrothermic primary zinc smelting facility indicates that cadmium, chromium, lead, mercury, nickel, and zinc are contained in the offgases from both the sintering machine and the retort furnaces.

Table 12.7-1 (Metric Units). PARTICULATE EMISSION FACTORS FOR ZINC SMELTING[a]

Process	Uncontrolled	EMISSION FACTOR RATING	Controlled	EMISSION FACTOR RATING
Roasting				
Multiple hearth[b] (SCC 3-03-030-02)	113	E	ND	NA
Suspension[c] (SCC 3-03-030-07)	1000	E	4	E
Fluidized bed[d] (SCC 3-03-030-08)	1083	E	ND	NA
Sinter plant (SCC 3-03-030-03)				
Uncontrolled[e]	62.5	E	NA	NA
With cyclone[f]	NA	NA	24.1	E
With cyclone and ESP[f]	NA	NA	8.25	E
Vertical retort[g] (SCC 3-03-030-05)	7.15	D	ND	NA
Electric retort[h] (SCC 3-03-030-29)	10.0	E	ND	NA
Electrolytic process[j] (SCC 3-03-030-06)	3.3	E	ND	NA

[a] Factors are for kg/Mg of zinc ore processed. SCC = Source Classification Code. ESP = Electrostatic precipitator. ND = no data. NA = not applicable.

[b] References 5-7. Averaged from an estimated 10% of feed released as particulate, zinc production rate at 60% of roaster feed rate, and other estimates.

[c] References 5-7. Based on an average 60% of feed released as particulate emission and a zinc production rate at 60% of roaster feed rate. Controlled emissions based on 20% dropout in waste heat boiler and 99.5% dropout in cyclone and ESP.

[d] References 5,13. Based on an average 65% of feed released as particulate emissions and a zinc production rate of 60% of roaster feed rate.

[e] Reference 5. Based on unspecified industrial source data.

[f] Reference 8. Data not necessarily compatible with uncontrolled emissions.

[g] Reference 8.

[h] Reference 14. Based on unspecified industrial source data.

[j] Reference 10.

Table 12.7-2 (English Units). PARTICULATE EMISSION FACTORS FOR ZINC SMELTING[a]

Process	Uncontrolled	EMISSION FACTOR RATING	Controlled	EMISSION FACTOR RATING
Roasting				
Multiple hearth[b] (SCC 3-03-030-02)	227	E	ND	NA
Suspension[c] (SCC 3-03-030-07)	2000	E	8	E
Fluidized bed[d] (SCC 3-03-030-08)	2167	E	ND	NA
Sinter plant (SCC 3-03-030-03)				
Uncontrolled[e]	125	E	NA	NA
With cyclone[f]	NA	NA	48.2	E
With cyclone and ESP[f]	NA	NA	16.5	E
Vertical retort[g] (SCC 3-03-030-05)	14.3	D	ND	NA
Electric retort[h] (SCC 3-03-030-29)	20.0	E	ND	NA
Electrolytic process[j] (SCC 3-03-030-06)	6.6	E	ND	NA

[a] Factors are for lb/ton of zinc ore processed. SCC = Source Classification Code. ESP = Electrostatic precipitator. ND = no data. NA = not applicable.

[b] References 5-7. Averaged from an estimated 10% of feed released as particulate, zinc production rate at 60% of roaster feed rate, and other estimates.

[c] References 5-7. Based on an average 60% of feed released as particulate emission and a zinc production rate at 60% of roaster feed rate. Controlled emissions based on 20% dropout in waste heat boiler and 99.5% dropout in cyclone and ESP.

[d] References 5,13. Based on an average 65% of feed released as particulate emissions and a zinc production rate of 60% of roaster feed rate.

[e] Reference 5. Based on unspecified industrial source data.

[f] Reference 8. Data not necessarily compatible with uncontrolled emissions.

[g] Reference 8.

[h] Reference 14. Based on unspecified industrial source data.

[j] Reference 10.

Table 12.7-3 (Metric Units). UNCONTROLLED FUGITIVE PARTICULATE EMISSION FACTORS FOR SLAB ZINC SMELTING[a]

Process	Emissions	EMISSION FACTOR RATING
Roasting (SCC 3-03-030-24)	Negligible	NA
Sinter plant[b]		
Wind box (SCC 3-03-030-25)	0.12 - 0.55	E
Discharge screens (SCC 3-03-030-26)	0.28 - 1.22	E
Retort building[c] (SCC 3-03-030-27)	1.0 - 2.0	E
Casting[d] (SCC 3-03-030-28)	1.26	E

[a] Reference 9. Factors are in kg/Mg of product. SCC = Source Classification Code. NA = not applicable.

[b] From steel industry operations for which there are emission factors. Based on quantity of sinter produced.

[c] From lead industry operations.

[d] From copper industry operations.

Table 12.7-4 (English Units). UNCONTROLLED FUGITIVE PARTICULATE EMISSION FACTORS FOR SLAB ZINC SMELTING[a]

Process	Emissions	EMISSION FACTOR RATING
Roasting (SCC 3-03-030-24)	Negligible	NA
Sinter plant[b]		
Wind box (SCC 3-03-030-25)	0.24 - 1.10	E
Discharge screens (SCC 3-03-030-26)	0.56 - 2.44	E
Retort building[c] (SCC 3-03-030-27)	2.0 - 4.0	E
Casting[d] (SCC 3-03-030-28)	2.52	E

[a] Reference 9. Factors are in lb/ton of product. SCC = Source Classification Code. NA = not applicable.

[b] From steel industry operations for which there are emission factors. Based on quantity of sinter produced.

[c] From lead industry operations.

[d] From copper industry operations.

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