

Lead and Zinc Smelting

Industry Description and Practices

Lead and zinc can be produced pyrometallurgically or hydrometallurgically, depending on the type of ore used as a charge. In the pyrometallurgical process, ore concentrate containing lead, zinc, or both is fed, in some cases after sintering, into a primary smelter. Lead concentrations can be 50–70%, and the sulfur content of sulfidic ores is in the range of 15–20%. Zinc concentration is in the range of 40–60%, with sulfur content in sulfidic ores in the range of 26–34%. Ores with a mixture of lead and zinc concentrate usually have lower respective metal concentrations. During sintering, a blast of hot air or oxygen is used to oxidize the sulfur present in the feed to sulfur dioxide (SO_2). Blast furnaces are used in conventional processes for reduction and refining of lead compounds to produce lead. Modern direct smelting processes include QSL, Kivcet, AUSMELT, and TBRC.

Primary Lead Processing

The conventional pyrometallurgical primary lead production process consists of four steps: sintering, smelting, drossing, and refining. A feedstock made up mainly of lead concentrate is fed into a sintering machine. Other raw materials may be added, including iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and particulates gathered from pollution control devices. The sintering feed, along with coke, is fed into a blast furnace for reducing, where the carbon also acts as a fuel and smelts the lead-containing materials. The molten lead flows to the bottom of the furnace, where four layers form: “speiss” (the lightest material, basically arsenic and antimony), “matte” (copper sulfide and other metal sulfides),

blast furnace slag (primarily silicates), and lead bullion (98% by weight). All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag, which contains zinc, iron, silica, and lime, is stored in piles and is partially recycled. Sulfur oxide emissions are generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed.

Rough lead bullion from the blast furnace usually requires preliminary treatment in kettles before undergoing refining operations. During drossing, the bullion is agitated in a drossing kettle and cooled to just above its freezing point, 370°–425°C (700°–800°F). A dross composed of lead oxide, along with copper, antimony, and other elements, floats to the top and solidifies above the molten lead. The dross is removed and is fed into a dross furnace for recovery of the nonlead mineral values.

The lead bullion is refined using pyrometallurgical methods to remove any remaining nonlead materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as oxides of antimony, arsenic, tin, and copper). The lead is refined in a cast-iron kettle in five stages. First, antimony, tin, and arsenic are removed. Next, gold and silver are removed by adding zinc. The lead is then refined by vacuum removal of zinc. Refining continues with the addition of calcium and magnesium, which combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step, caustic soda, nitrates, or both may be added to remove any remaining traces of metal impurities. The refined lead will have a purity of 99.90–99.99%. It may be mixed with other metals to form alloys, or it may be directly cast into shapes.

Secondary Lead Processing

The secondary production of lead begins with the recovery of old scrap from worn-out, damaged, or obsolete products and with new scrap. The chief source of old scrap is lead-acid batteries; other sources include cable coverings, pipe, sheet, and other lead-bearing metals. Solder, a tin-based alloy, may be recovered from the processing of circuit boards for use as lead charge.

Prior to smelting, batteries are usually broken up and sorted into their constituent products. Fractions of cleaned plastic (such as polypropylene) case are recycled into battery cases or other products. The dilute sulfuric acid is either neutralized for disposal or recycled to the local acid market. One of the three main smelting processes is then used to reduce the lead fractions and produce lead bullion.

Most domestic battery scrap is processed in blast furnaces, rotary furnaces, or reverberatory furnaces. A reverberatory furnace is more suitable for processing fine particles and may be operated in conjunction with a blast furnace.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (about 4.5% of the charge), scrap iron (about 4.5%), limestone (about 3%), and coke (about 5.5%). The remaining 82.5% of the charge is made up of oxides, pot furnace refining drosses, and reverberatory slag. The proportions of rerun slags, limestone, and coke vary but can run as high as 8% for slags, 10% for limestone, and 8% for coke. The processing capacity of the blast furnace ranges from 20 to 80 metric tons per day (tpd).

Newer secondary recovery plants use lead paste desulfurization to reduce sulfur dioxide emissions and generation of waste sludge during smelting. Battery paste containing lead sulfate and lead oxide is desulfurized with soda ash, yielding market-grade sodium sulfate as a by-product. The desulfurized paste is processed in a reverberatory furnace, and the lead carbonate product may then be treated in a short rotary furnace. The battery grids and posts are processed separately in a rotary smelter.

Zinc Manufacturing

In the most common hydrometallurgical process for zinc manufacturing, the ore is leached with

sulfuric acid to extract the lead/zinc. These processes can operate at atmospheric pressure or as pressure leach circuits. Lead/zinc is recovered from solution by electrowinning, a process similar to electrolytic refining. The process most commonly used for low-grade deposits is heap leaching. Imperial smelting is also used for zinc ores.

Waste Characteristics

The principal air pollutants emitted from the processes are particulate matter and sulfur dioxide (SO₂). Fugitive emissions occur at furnace openings and from launders, casting molds, and ladles carrying molten materials, which release sulfur dioxide and volatile substances into the working environment. Additional fugitive particulate emissions occur from materials handling and transport of ores and concentrates. Some vapors are produced in hydrometallurgy and in various refining processes. The principal constituents of the particulate matter are lead/zinc and iron oxides, but oxides of metals such as arsenic, antimony, cadmium, copper, and mercury are also present, along with metallic sulfates. Dust from raw materials handling contains metals, mainly in sulfidic form, although chlorides, fluorides, and metals in other chemical forms may be present. Off-gases contain fine dust particles and volatile impurities such as arsenic, fluorine, and mercury. Air emissions for processes with few controls may be of the order of 30 kilograms lead or zinc per metric ton (kg/t) of lead or zinc produced. The presence of metals in vapor form is dependent on temperature. Leaching processes will generate acid vapors, while refining processes result in products of incomplete combustion (PICs). Emissions of arsine, chlorine, and hydrogen chloride vapors and acid mists are associated with electrolytic refining.

Wastewaters are generated by wet air scrubbers and cooling water. Scrubber effluents may contain lead/zinc, arsenic, and other metals. In the electrolytic refining process, by-products such as gold and silver are collected as slimes and are subsequently recovered. Sources of wastewater include spent electrolytic baths, slimes recovery, spent acid from hydrometallurgy processes, cooling water, air scrubbers, washdowns, and stormwater. Pollutants include dissolved

and suspended solids, metals, and oil and grease.

The larger proportion of the solid waste is discarded slag from the smelter. Discard slag may contain 0.5–0.7% lead/zinc and is frequently used as fill or for sandblasting. Slags with higher lead/zinc content—say, 15% zinc—can be sent for metals recovery. Leaching processes produce residues, while effluent treatment results in sludges that require appropriate disposal. The smelting process typically produces less than 3 tons of solid waste per ton of lead/zinc produced.

Pollution Prevention and Control

The most effective pollution prevention option is to choose a process that entails lower energy usage and lower emissions. Modern flash-smelting processes save energy, compared with the conventional sintering and blast furnace process. Process gas streams containing over 5% sulfur dioxide are usually used to manufacture sulfuric acid. The smelting furnace will generate gas streams with SO₂ concentrations ranging from 0.5% to 10%, depending on the method used. It is important, therefore, to select a process that uses oxygen-enriched air or pure oxygen. The aim is to save energy and raise the SO₂ content of the process gas stream by reducing the total volume of the stream, thus permitting efficient fixation of sulfur dioxide. Processes should be operated to maximize the concentration of the sulfur dioxide. An added benefit is the reduction (or elimination) of nitrogen oxides (NO_x).

- Use doghouse enclosures where appropriate; use hoods to collect fugitive emissions.
- Mix strong acidic gases with weak ones to facilitate production of sulfuric acid from sulfur oxides, thereby avoiding the release of weak acidic gases.
- Maximize the recovery of sulfur by operating the furnaces to increase the SO₂ content of the flue gas and by providing efficient sulfur conversion. Use a double-contact, double-absorption process.
- Desulfurize paste with caustic soda or soda ash to reduce SO₂ emissions.
- Use energy-efficient measures such as waste heat recovery from process gases to reduce fuel usage and associated emissions.

- Recover acid, plastics, and other materials when handling battery scrap in secondary lead production.
- Recycle condensates, rainwater, and excess process water for washing, for dust control, for gas scrubbing, and for other process applications where water quality is not of particular concern.
- Give preference to natural gas over heavy fuel oil for use as fuel and to coke with lower sulfur content.
- Use low-NO_x burners.
- Use suspension or fluidized bed roasters, where appropriate, to achieve high SO₂ concentrations when roasting zinc sulfides.
- Recover and reuse iron-bearing residues from zinc production for use in the steel or construction industries.
- Give preference to fabric filters over wet scrubbers or wet electrostatic precipitators (ESPs) for dust control.

Good housekeeping practices are key to minimizing losses and preventing fugitive emissions. Losses and emissions are minimized by enclosed buildings, covered conveyors and transfer points, and dust collection equipment. Yards should be paved and runoff water routed to settling ponds.

Pollution Reduction Targets

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The following production-related targets can be achieved by measures such as those described above. The figures relate to the production processes before the addition of pollution control measures.

The target pollutant load for lead and zinc smelting operations for particulate matter is 0.5 kg/t of concentrated ore processed. ESPs are used to recover dust. Pollutant load factors for lead in air emissions are 0.08 kg/t from roasting, 0.08 kg/t from smelting, and 0.13 kg/t from refining.

A double-contact, double-absorption plant should emit no more than 2 kg of sulfur dioxide per ton of sulfuric acid produced, based on a conversion efficiency of 99.7%. Sulfur dioxide should be recovered to produce sulfuric acid, thus yielding a marketable product and reducing SO₂ emis-

sions. Fugitive emissions are controlled by using enclosed conveyors.

Treatment Technologies

ESPs and baghouses are used for product recovery and for the control of particulate emissions. Dust that is captured but not recycled will need to be disposed of in a secure landfill or in another acceptable manner.

Arsenic trioxide or pentoxide is in vapor form because of the high gas temperatures and must be condensed by gas cooling so that it can be removed in fabric filters.

Collection and treatment of vent gases by alkali scrubbing may be required when sulfur dioxide is not being recovered in an acid plant.

Effluent treatment of process bleed streams, filter backwash waters, boiler blowdown, and other streams is required to reduce suspended and dissolved solids and heavy metals and to adjust pH. Residues that result from treatment are recycled to other industries such as the construction industry, sent to settling ponds (provided that groundwater and surface water contamination is not a concern), or disposed of in a secure landfill.

Slag should be either landfilled or granulated and sold for use in building materials.

Emissions Guidelines

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process on the basis of country legislation and the *Pollution Prevention and Abatement Handbook*, as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The guidelines given below present emissions levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. The emissions levels given here can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unac-

ceptable. All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

Air Emissions

The air emissions levels presented in Table 1 should be achieved.

The environmental assessment should address the buildup of heavy metals from particulate fallout in the vicinity of the plant over its projected life.

Liquid Effluents

The effluent emissions levels presented in Table 2 should be achieved.

Table 1. Emissions from Lead/Zinc Smelting
(milligrams per normal cubic meter)

Parameter	Maximum value
Sulfur dioxide	400
Arsenic	0.1
Cadmium	0.05
Copper	0.5
Lead	0.5
Mercury	0.05
Zinc	1.0
Particulates	20

Table 2. Effluents from Lead/Zinc Smelting
(milligrams per liter, except for pH and temperature)

Parameter	Maximum value
pH	6–9
TSS	20
Arsenic	0.1
Cadmium	0.1
Copper	0.5
Iron	3.5
Lead	0.1
Mercury	0.01
Zinc	2.0
Total metals ^a	5
Temperature increase	≤ 3°C ^b

a. Includes arsenic, beryllium, cadmium chromium, gold, lead, mercury, nickel, selenium, silver, thallium, and vanadium.

b. The effluent should result in a temperature increase of no more than 3° C at the edge of the zone where initial mixing and dilution take place. Where the zone is not defined, use 100 meters from the point of discharge.

Ambient Noise

Noise abatement measures should achieve either the levels given below or a maximum increase in background levels of 3 decibels (measured on the A scale) [dB(A)]. Measurements are to be taken at noise receptors located outside the project property boundary.

Receptor	Maximum allowable log equivalent (hourly measurements), in dB(A)	
	Day (07:00–22:00)	Night (22:00–07:00)
Residential, institutional, educational	55	45
Industrial, commercial	70	70

Monitoring and Reporting

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for the parameters listed in this document should be as described below.

Air emissions should be monitored continuously for sulfur dioxide and particulate matter. Other air emissions parameters should be monitored monthly. Fugitive emissions should be monitored annually.

Liquid effluents should be monitored daily for pH and total suspended solids and at least weekly for all other parameters.

All solid waste, tailings, and leachates should be monitored for toxic metals. Contamination of groundwater and surface waters should be avoided.

Monitoring data should be analyzed and reviewed at regular intervals and compared with

the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

Key Issues

The key production and control practices that will lead to compliance with emissions requirements can be summarized as follows:

- Give preference to the flash-smelting process where appropriate.
- Choose oxygen enrichment processes that allow higher SO₂ concentrations in smelter gases to assist in sulfur recovery; use the double-contact, double-absorption process.
- Improve energy efficiency to reduce fuel usage and associated emissions; use low-NO_x burners; give preference to natural gas as fuel.
- Reduce air emissions of toxic metals to acceptable levels.
- Maximize the recovery of dust and minimize fugitive emissions; use hoods and doghouse enclosures.
- Reduce effluent discharge by maximizing wastewater recycling.
- Avoid contamination of groundwater and surface waters by leaching of toxic metals from tailings, process residues, slag, and other wastes.

Sources

- Bounicore, Anthony J., and Wayne T. Davis, eds. 1992. *Air Pollution Engineering Manual*. New York: Van Nostrand Reinhold.
- Environment Canada. 1980. "A Study of Sulphur Containment Technology in the Non-Ferrous Metallurgical Industries." Report EPS 3-AP-79-8. Ottawa.