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INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE: CHAPTER 28 PRIMARY ZINC INDUSTRY

by

PEDCo Environmental, Inc.
11499 Chester Road
Cincinnati, Ohio 45246

Contract No. 68-03-2577

Project Officer

John O. Burckle
Energy Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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INDUSTRY DESCRIPTION

The major product of the primary zinc industry is metallic zinc; the industry also produces zinc oxide, sulfuric acid, cadmium, and occasionally other chemicals such as zinc sulfate. For the purpose of this analysis, the zinc industry is considered in segments: pyrometallurgical zinc production, electrolytic zinc production, zinc oxide production, and cadmium recovery. Production of other by-products such as germanium, thallium, gallium, and indium is not considered a part of this industry because it does not take place at primary zinc smelters.

Generally, ore is mined and concentrated at one location and then transferred to smelters for the production of zinc, zinc oxide, or both. Cadmium is normally recovered at smelters from collected dusts and slags with sufficient cadmium content. Direct zinc oxide production uses the same ore concentrate as metallic zinc production.

In 1978, approximately 6,000 people were employed in lead-zinc mining and milling operations. Zinc smelters, including secondary smelters, employed 4,100 people in 1978, including workers involved in by-product processes. Table 1 shows mining, production, and consumption totals for zinc and cadmium in the years 1974 to 1978. These data indicate that zinc and cadmium production have remained fairly constant over the past few years. Consumption has exceeded production; imports and shipments from government stockpiles have made up the difference (1).

The leading states for mine production in 1978 were Tennessee, 29 percent; Missouri, 19 percent; Idaho, 10 percent, and New Jersey, 9 percent. The 25 largest U.S. mines accounted for 97 percent of the zinc ore mined in 1978, and the five largest alone accounted for 41 percent (1). The 25 largest U.S. zinc mines in 1976 are presented in Table 2.

Direct zinc oxide production is considered part of the primary zinc industry since the process involves the reduction of zinc concentrates followed by oxidation. Indirect zinc oxide production is not discussed, since slab zinc is used as the raw material.

All domestic zinc smelters produce cadmium. Collected flue dusts from roasting and sintering operations and cadmium-containing materials from refining and precipitation processes are treated hydrometallurgically for cadmium recovery at the zinc smelter.

TABLE 1. MINING, PRODUCTION, AND CONSUMPTION OF ZINC AND CADMIUM (1)
(thousand metric tons)

	Mine production	Primary slab zinc production	Slab zinc consumption	Cadmium production (includes secondary)[a]	Cadmium consumption
1978	303	441	1051	1.7[b]	5.1[b]
1977	408	408	1000	2.0	4.1
1976	440	453	1029	2.0	5.4
1975	426	397	839	2.0	3.0
1974	453	504	1168	3.0	5.5

[a] There is no significant recycling of cadmium metal. All uses other than nickel-cadmium batteries and alloys are dissipative.

[b] Estimated.

TABLE 2. TWENTY-FIVE LEADING ZINC PRODUCING MINES IN THE UNITED STATES IN 1976, IN ORDER OF OUTPUT (2)

Rank	Mine	County and state	Operator	Source of zinc
1	Balmat	St. Lawrence, N.Y.	St. Joe Minerals Corp.	Zinc ore
2	Buick	Iron, Mo.	AMAX Lead Co. of Missouri	Lead ore
3	Sterling	Sussex, N.J.	New Jersey Zinc Co.	Zinc ore
4	Bunker Hill	Shoshone, Idaho	The Bunker Hill Co.	Lead-zinc ore
5	Friedensville	Lehigh, Pa.	New Jersey Zinc Co.	Zinc ore
6	Elmwood	Smith, Tenn.	New Jersey Zinc Co.	Zinc ore
7	Star Unit	Shoshone, Idaho	The Bunker Hill Co. and Hecla Mining Co.	Lead-zinc ore
8	Young	Jefferson, Tenn.	ASARCO Incorporated	Zinc ore
9	Leadville	Lake, Colo.	ASARCO Incorporated	Lead-zinc ore
10	Eagle	Eagle, Colo.	New Jersey Zinc Co.	Zinc ore
11	New Market	Jefferson, Tenn.	ASARCO Incorporated	Zinc ore
12	Immel	Knox, Tenn.	ASARCO Incorporated	Lead-zinc ore
13	Pend Oreille	Pend Oreille, Wash.	The Bunker Hill Co.	Lead-zinc ore
14	Ontario	Summit, Utah	Park City Ventures	Zinc ore
15	Ground Hog	Grant, N. Mex.	ASARCO Incorporated	Zinc ore
16	Austinville and Ivanhoe	Wythe, Va.	New Jersey Zinc Co.	Zinc ore
17	Zinc Mine Works	Jefferson, Tenn.	United States Steel Corp.	Zinc ore
18	Burgin	Utah, Utah	Kennecott Copper Corp.	Lead-zinc ore
19	Idarado	Ouray, and San Miguel, Colo.	Idarado Mining Co.	Copper-lead-zinc ore
20	Magmont	Iron, Mo.	Cominco American, Inc.	Lead ore
21	Bruce	Yavapai, Ariz.	Cyprus Bruce Copper and Zinc Co.	Copper-zinc ore
22	Jefferson City	Jefferson, Tenn.	New Jersey Zinc Co.	Zinc ore
23	Brushy Creek	Reynolds, Mo.	St. Joe Minerals Corp.	Lead ore
24	Blue Hill	Hancock, Maine	Kerramerican, Inc.	Zinc ore
25	Edwards	St. Lawrence, N.Y.	St. Joe Minerals Corp.	Zinc ore

Other metals recovered as by-products from zinc ore are germanium, thallium, indium, and gallium. This processing, however, is not done at primary zinc smelters in the U.S. Waste materials containing these metals are shipped as intermediate products or are disposed of as waste if the by-product content is not sufficient for recovery.

U.S. primary zinc demand is expected to increase at an annual rate of 2 percent through 1985 (3). Primary domestic smelting capacity, however, has declined 47 percent since 1968, with the closing of eight smelters due to outdated equipment and environmental problems (4).

Jersey Miniere Zinc is constructing a new electrolytic refinery in Clarksville, Tennessee, with start-up scheduled for the second half of 1978; full capacity will be about 90,000 metric tons per year. Most concentrates will come from the company's new Elmwood and Gordonsville mines in Tennessee; a third mine is to be developed near Stonewall. Figure 1 shows the locations of domestic primary zinc producers.

Raw Materials

Zinc is usually found in nature as the sulfide called sphalerite, which has a cubic lattice structure and is commonly referred to as zinc blende, blende, or jack. Zinc content can be 67.1 percent in the pure state. A polymorph of sphalerite, wurtzite, has a hexagonal structure and is more stable at elevated temperatures. Almost all other zinc minerals have been formed as oxidation products of these structures. A list of the most common zinc minerals is presented in Table 3. Most of these oxidized minerals are minor sources of zinc, although franklinite and zincite are mined for their zinc content at the New Jersey Zinc Co. mine (5).

What may prove to be one of the five largest massive zinc-copper sulfide deposits in North America has been discovered near Crandon, Wisconsin. Tests indicate the presence of about 70 million metric tons of ore, analyzed as 5 percent zinc and 1 percent copper (6).

Iron is the most common impurity or associated metal of zinc, owing to the chemical similarities and relative ease of substitution in their respective lattices. A sulfide zinc ore with a ratio of Fe to Zn above 1:8 is known as marmatite.

Cadmium is the second most abundant impurity of zinc. It is always associated with zinc, and is usually present as greenockite (CdS). Complete solid solutions exist between zinc and cadmium sulfides, but the cadmium content rarely exceeds 1 or 2 percent.

In zinc ores, commonly associated nonzinc minerals are calcite ($CaCO_3$) dolomite $(Ca,Mg)CO_3$, pyrite and marcasite (FeS_2), quartz (SiO_2), chalcopyrite ($CuFeS_2$), and barite ($BaSO_4$).

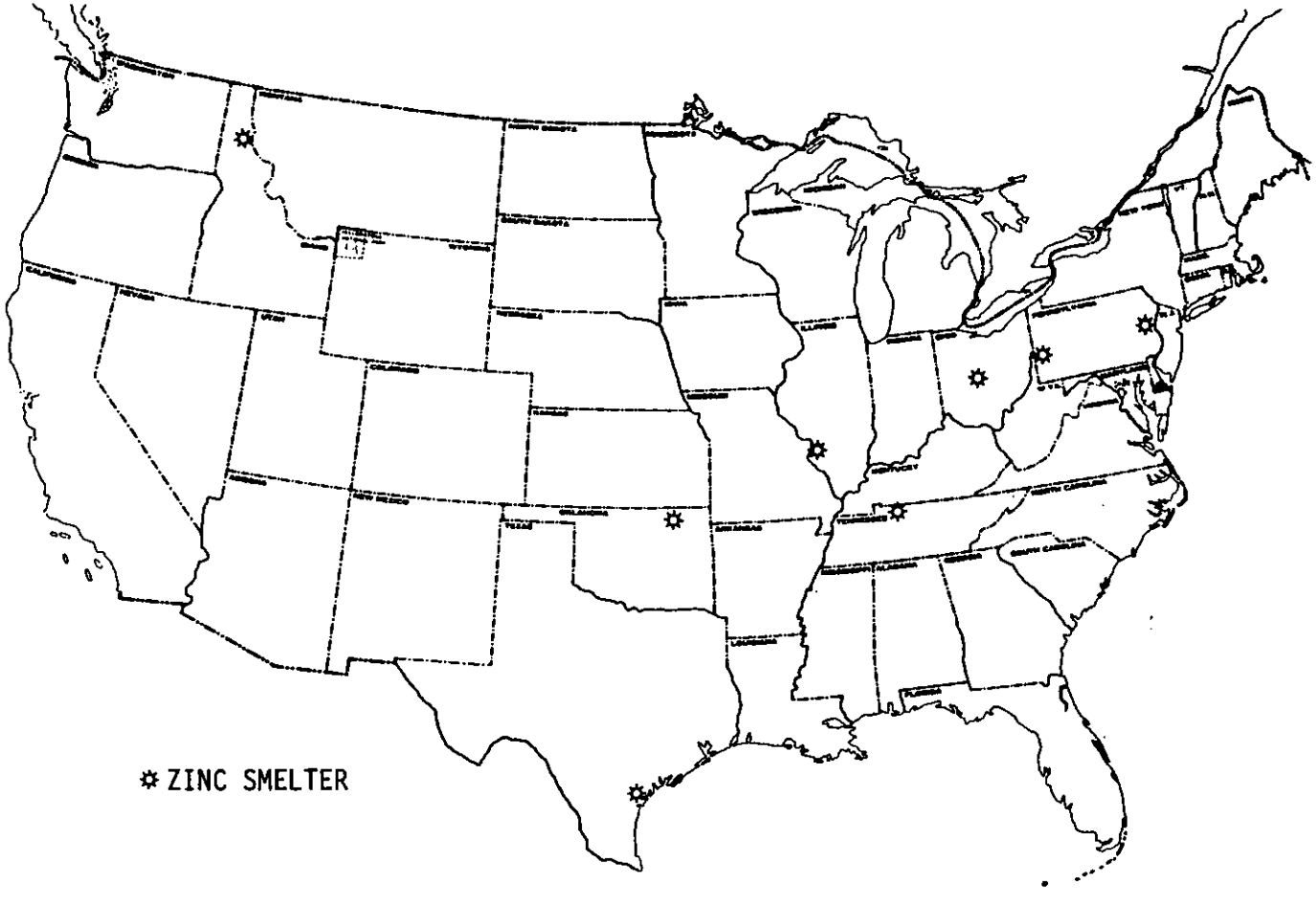

Figure 1. Primary U.S. zinc smelting locations.

TABLE 3. COMMON ORES MINED FOR THEIR ZINC CONTENT (5)

ZnO	Zincite
$ZnSO_4 \cdot 7H_2O$	Goslarite
$ZnCO_3$	Smithsonite (or calamine in Europe)
$Zn_4Si_2O_7(OH)_2 \cdot H_2O$	Hemimorphite (or calamine in America, called electric calamine in Europe)
Zn_2SiO_4	Willemite
$(Zn_2Mn)O \cdot Fe_2O_3$	Franklinite
$2ZnCO_3 \cdot 3Zn(OH)_2$	Hydrozincite
ZnS	Sphalerite, wurtzite
$(Fe,Zn)S$	Marmatite

Zinc ores are processed at the mine to form concentrates containing typically 52 to 60 weight percent zinc, 30 to 33 weight percent sulfur, and 4 to 11 weight percent iron (7). Roasting at the plant lowers the sulfur content to about 2 percent. Other raw materials are required at the smelter for producing metallic zinc. Coke or coal and sand along with inert materials are required during pyrometallurgical sintering, in quantities depending upon the specific concentrate properties and the desired characteristics of the sinter. Coal or coke must also be added during reduction. Exact quantitites are variable, depending on the properties of the feed and type of reduction furnace. In hydrometallurgical processing, sintering or pyrometallurgical reduction is not required but sulfuric acid is required for leaching the calcine.

The energy required for production of one metric ton of slab zinc is 8.8 to 16.4 million kilocalories depending on the process. In 1972, 9.6 billion kilocalories were used in the manufacture of primary zinc slabs, an average of 15.3 million per metric ton (8). This represents a 9 percent increase in efficiency of energy utilization over 1967, primarily due to the closing of inefficient horizontal retorts.

Products

The principal products of the primary zinc industry are metallic zinc, zinc oxide, and cadmium. Uses for these products are widely varied. Metallic zinc is used for galvanizing, for making pigments and zinc compounds, for alloying, and for grinding into zinc dust. Table 4 shows U.S. consumption of slab zinc for 1978. Usage patterns in the U.S. differ from those in the rest of the world in the heavy emphasis on zinc-base alloy castings, mainly for the automotive industry. The primary product of most zinc companies is slab zinc, which is produced in five grades and classified by its purity. These grades are presented in Table 5.

Zinc oxide is used in rubber, emollients, ceramics, and fluorescent pigments, and in the manufacture of other chemicals. Metallic cadmium is used in production of alloys, in corrosion-resistant plating for hardware, as a counter electrode metal for selenium rectifiers, as neutron shielding rods in nuclear reactors, in nickel-cadmium batteries, and in plastics and cadmium compounds. Cadmium metal accounts for 60 to 70 percent of consumption, and cadmium sulfide used for pigments for another 12 to 15 percent (9).

Companies

Capacities of the eight primary zinc smelters that use primary concentrate feed are listed in Table 6. The three pyrometallurgical plants range in capacity from 57,000 to 227,000 metric tons per year. U.S. primary zinc capacity is about equally divided between pyrometallurgical and electrolytic processes. The single largest plant accounts for 35 percent of the total domestic primary capacity. All of the primary smelters produce sulfuric acid

TABLE 4. U.S. SLAB ZINC CONSUMPTION - (1976) (9)

	Metric tons	Percent
Galvanizing	342,893	38
Brass and bronze products	150,817	15
Zinc-base alloy	387,403	38
Rolled zinc products	27,088	3
Zinc oxide	35,405	3
Other	35,287	3
Total	1,028,893	100

TABLE 5. GRADES OF COMMERCIAL ZINC

	Composition, percent weight			
	Zinc	Lead	Iron	Cadmium
Special high grade	99.990	0.003	0.003	0.003
High grade	99.90	0.07	0.02	0.03
Intermediate	99.5	0.20	0.03	0.40
Brass special	99.0	0.6	0.03	0.50
Prime western	98.0	1.6	0.05	0.50

TABLE 6. PRIMARY ZINC PROCESSING PLANTS IN THE UNITED STATES (10,11,12)

Company	Location	Description	Capacity metric ton/year	Date plant built
AMAX, Inc.	East St. Louis, Illinois	Electrolytic	76,000	1929
ASARCO, Inc.	Corpus Christi, Texas	Electrolytic	98,000	1942
	Columbus, Ohio	Pyrometallurgical	20,000	1967
The Bunker Hill Co.	Silver King, Idaho	Electrolytic	98,000	1928
Jersey Miniere Zinc	Clarksville, Tennessee	Electrolytic	90,000	1978
National Zinc Co.	Bartlesville, Oklahoma	Electrolytic	45,000	1977
New Jersey Zinc Co.	Palmerton, Pennsylvania	Pyrometallurgical	103,000	1899
St. Joe Minerals Corp.[a]	Monaca, Pennsylvania	Pyrometallurgical	227, 000	1930

[a] Scheduled to close at end of 1979.

as a by-product. Four companies were responsible for over 80 percent of primary cadmium production in 1978 (1). Salient statistics for the domestic primary zinc industry in 1978 are presented in Table 7.

Environmental Impact

Uncontrolled atmospheric emissions from the primary zinc industry have decreased in recent years because of the increase in electrolytic zinc recovery operations and the closing of several retort zinc smelters. In 1969, zinc emissions to the atmosphere totalled 65 metric tons from mining and milling, and 45,350 metric tons from metallurgical processing (13). Sulfur dioxide is emitted from roasting and sintering operations, although the roaster SO_2 emissions are normally collected to produce sulfuric acid.

Smelter solid wastes are usually recycled for by-product metal recovery. Some sludges may require several months' storage before recycling, and others may be disposed of as landfill. Sludges and solid wastes generated during mining and concentration processes are disposed of at the mining site in tailings ponds or as mine backfill.

Liquid effluents can be classified as noncontact and contact. Noncontact water is used for cooling in heat exchangers. Contact, or process, wastewater is produced in such operations as scrubbing of roaster gas and reduction furnace gas, cooling of metal castings, cadmium production, and auxiliary air pollution controls. The pollutants of concern are primarily zinc and sulfates, accompanied normally by such elements as cadmium and lead, and small amounts of arsenic and selenium.

Limitations on liquid effluent and atmospheric emissions from new sources have been promulgated (10,11). The solid waste problem is currently under investigation.

Bibliography

1. Commodity Data Summaries, 1979. U.S. Department of Interior. Bureau of Mines. Washington, D.C. 1979.

2. Minerals Yearbook, 1976. U.S. Department of Interior. Bureau of Mines. Washington, D.C. 1978.

3. Mineral Industry Surveys. Zinc Industry in July 1979. U.S. Department of Interior. Bureau of Mines. Washington, D.C. 1979.

4. Deane, G.L., et al. Cadmium: Control Strategy Analysis. GCA Corporation Report No. GCA-TR-75-36-G. U.S. Environmental Protection Agency. Research Traingle Park, North Carolina. April 1976. p. 157.

5. Smelting and Refining of Nonferrous Metals and Alloys. 1972 Census of Manufacturers. Publication MC72(2)-33C Bureau of the Census. U.S. Department of Commerce. 1972.

TABLE 7. PRINCIPAL STATISTICS FOR THE PRIMARY ZINC INDUSTRY IN THE UNITED STATES IN 1976 (9)
(metric tons)

Production:	
Mine, recoverable zinc	302,669
Smelter, slab zinc	441,472
Imports:	
Ores and concentrates (dutiable zinc content)	118,003
Slab zinc	617,840
Consumption:	
Slab zinc	1,050,585
Ores (recoverable zinc content)	89,959
Exports:	
Slab zinc	723

6. U.S. Department of the Interior, Bureau of Mines. Minerals and Materials/A Monthly Survey, 55. July 1977.

7. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

8. Fejer, M.E., and D.H. Larson. Study of Industrial Uses of Energy Relation to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

9. Jones, H.R. Pollution Control in the Nonferrous Metals Industry 1972. Noyes Data Corporation. Park Ridge, New Jersey.

10. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. Office of Air and Waste Management. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. EPA-450/2-74-002a. October 1974.

11. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. U.S. Environmental Protection Agency. Washington, D.C. EPA-440/1-75-032. November 1974.

12. American Bureau of Metal Statistics. Nonferrous Metal Data 1975. New York, New York. 1976.

13. W.E. Davis and Associates. National Inventory of Sources and Emissions, Section V, Zinc. Report No. APTD-1139. National Technical Information Service, U.S. Department of Commerce. Springfield, Virginia. May 1972.

INDUSTRY SEGMENT ANALYSIS

As with the copper and lead segments, the environmental impacts of the zinc mining and smelting industries have received considerable attention in recent years from both private and governmental organizations. This industry segment analysis examines each production operation, to define its industrial purpose and its potential and practice in affecting the quality of the environment. Each process is examined as follows:

1. Function
2. Input Materials
3. Operating Conditions
4. Utilities
5. Waste Streams
6. Control Technology
7. EPA Classification Code
8. References

The only processes included in this section are those that are now operating in the United States. Figure 2 is a flowsheet that shows these processes, their interrelationships, and their major waste streams.

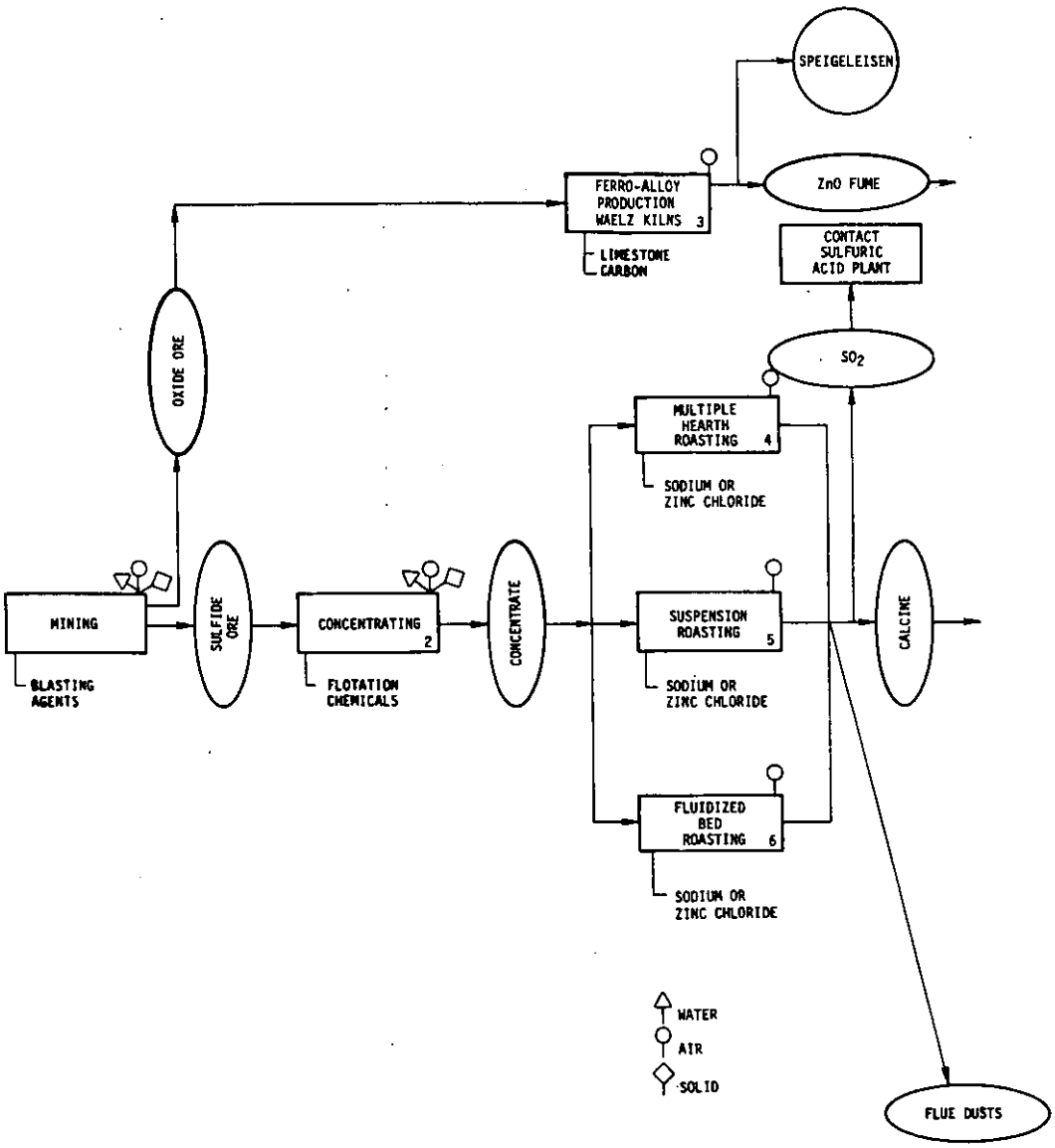

Figure 2. Zinc industry flow sheet.

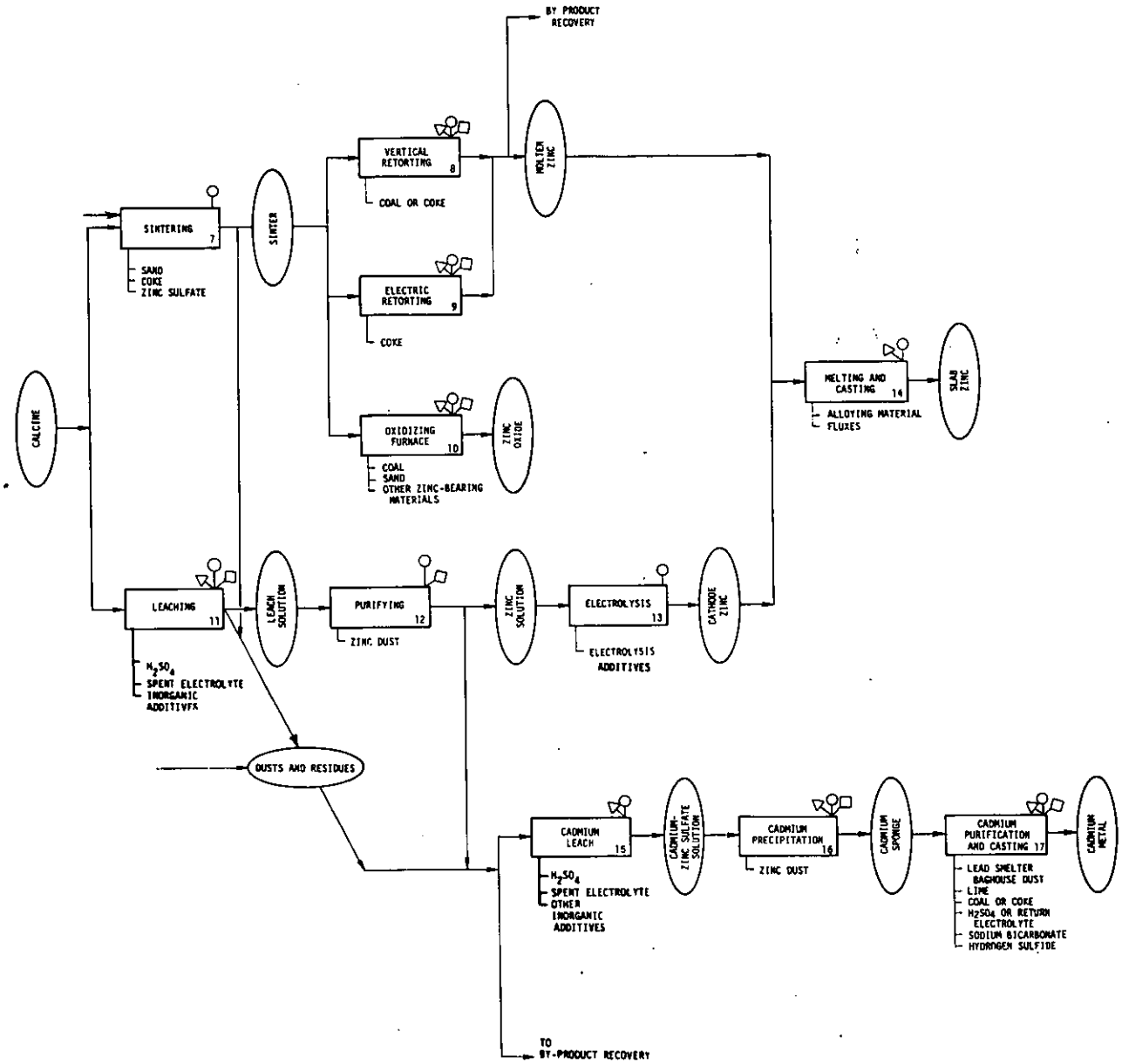

Figure 2 (continued)

Mining

1. Function - Mining involves excavation and treatment of zinc ore deposits. Most zinc is mined underground using open shrinkage, cut-and-fill, or square-set stoping methods. In underground mines, walls and pillars are usually left behind to support the overlying rock structure, unless the width of the ore body is such that it can be supported and the entire ore body extracted. A few mines, particularly in early stages of operation, use open pit methods, which closely resemble those used in copper mining.

Mining operations consist of drilling, blasting, and removing the broken rock. After removal from the mine, the ore is loaded onto trucks for transportation to concentrating facilities. Mining operations range in size from those handling several hundred metric tons of ore per day to complexes capable of processing about six thousand metric tons per day. Some large, single-level, open-stage operations utilize "trackless" mining techniques, with equipment mounted on crawler-type tread or pneumatic-tired vehicles. This equipment facilitates movement and increases speed of operations, thus increasing total output and reducing costs; with such equipment it is sometimes feasible to mine ore containing as little as 2 percent zinc.

2. Input Materials - Inputs to the mining process include the ore deposits and the explosives used to remove them.

3. Operating Conditions - Ores are mined at atmospheric conditions. Conditions depend upon type of mining, i.e., open pit or underground.

4. Utilities - Fuels and electricity are used for operating mining equipment and transporting ore to concentrating facilities. One estimate for electrical usage for mining ore in 1973 was 3.1×10^8 kilowatt-hours (1). With the 1973 mine production level of 434,000 metric tons (2), electrical usage was about 720 kilowatt-hours per metric ton of zinc moved. Unspecified amounts of water are pumped into mines for machinery and hydraulic backfill operations.

5. Waste Streams - Zinc ores typically contain 3 to 11 percent zinc (3); thus 10 to 40 tons of ore must be mined for every ton of zinc produced. Most of this ore is mined for other metals as well. Fugitive dust emissions are similar to those of other mining operations, amounting to about 0.1 kg per metric ton of zinc mined (4). Cadmium emissions also occur during the mining of zinc ore. Emissions due to wind loss from mine waste are estimated at 0.1 kilogram per metric ton of ore mined (5). Total emissions of cadmium to the atmosphere were thus 240 metric tons for 1968 (5) and 220 metric tons for 1973 (6).

Mine waste water results from infiltration of ground water, water pumped into the mine for machines and hydraulic backfill operations, and infiltration of surface water. Quantities of pump out water are not necessarily related to the quantity of ore mined. The water required to maintain operations may range from thousands of liters per day to 160 million liters per day. This water contains such impurities as blasting agents, fuel, oil, and

hydraulic fluid. Dissolved solids found in the wastewater are generally lead, zinc, and associated minerals (7).

Conditions compatible with solubilization of certain metals, particularly zinc, are associated with heavily fissured ore bodies. Although the minerals being recovered are sulfides, a fissured ore body allows oxidation of the ore, which increases the solubility of the minerals.

The major solid wastes from mining operations result from removal of rock to get to the ore. The discarded waste is of essentially the same composition as raw ore, with lower metallic content. No quantitative or qualitative estimate was found concerning these wastes.

6. Control Technology - Fugitive dusts from drilling and conveying can be reduced by wetting and control systems (8).

In the zinc industry, mine-water generated from natural drainage is reused in mining and milling operations whenever possible. Discharge may result because of an excess of precipitation, lack of a nearby milling facility, or inability to reuse all of the mine waste water at a particular mill.

Small quantities of water are usually needed in the zinc flotation process; mine water effluent is used at many facilities as mill process makeup water. The mine water may pass through the process first, or it may be conveyed to a tailings pond for later use with recycled process water. The practice of combining mine water with mill water can disturb the overall water balance unless the mill circuit is capable of handling the water volumes generated without a resulting discharge.

Acid mine water is neutralized by the addition of lime and limestone. Acid mine water containing solubilized metals may be effectively treated in the mill tailings pond. The water may be further treated by lime clarification and aeration.

The solid wastes from mining operations are disposed of in a pile or pond. These wastes can be used as mine backfill.

7. EPA Source Classification Code - None

8. References -

1. Dayton, S. The Quiet Revolution in the Wide World of Mineral Processing. Engineering and Mining Journal. June 1975.

2. Commodity Data Summaries 1976. U.S. Department of Interior. Bureau of Mines. Washington, D.C. 1976.

3. McMahon, A.D., et al. In 1973 Bureau of Mines Minerals Yearbook. U.S. Department of the Interior. U.S. Government Printing Office. 1973.

4. National Inventory of Sources and Emissions - Section V, Zinc. W.E. Doris and Associates. Report No. APTD - 1139. National Technical Information Service, U.S. Department of Commerce. Springfield, Virginia. May 1972.

5. W.E. Davis and Associates. National Inventory of Sources and Emissions - Cadmium, Nickel, and Asbestos - 1968. Cadmium, Section I. Report No. APTD - 1968. National Technical Information Service. Springfield, Virginia. February 1970.

6. Deane, G.L., et al. Cadmium: Control Strategy Analysis. GCA Corporation Report No. 6CA-TR-75-36-G. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. April 1976.

7. Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry. Point Source Category Vol. 1. EPA 440/1-75/061. Effluent Guidelines Division Office of Water and Hazardous Materials, U.S. Environmental Protection Agency. Washington, D.C. October 1975.

8. An Investigation of the Best Systems of Emission Reduction for Quarrying and Plant Process Facilities in the Crushed and Broken Stone Industry. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division. Research Triangle Park, North Carolina. Draft. April 1976.

Concentrating

1. Function - Concentrating consists of separating the desirable mineral constituents in the ore from the unwanted impurities by various mechanical processes. The ore from mining must be concentrated because mined sphalerite is seldom pure enough to be reduced directly for zinc smelting.

The zinc-bearing ore is first crushed by standard jaw, gyratory, and cone crushers to a size based on an economic balance between the recoverable metal values and the cost of grinding (1). Size separation is accomplished by vibrating or trommel screens and classifiers. Heavy-medium cones, jigs, and tables separate the zinc minerals from a low specific-gravity gangue. Classification and recycling between stages reduces the material to a particle size appropriate for milling. The final milled product is typically 60 percent smaller than 325 mesh.

After being transported to large bins for blending and storing, the ore is pumped as an aqueous slurry to flotation cells, where it is conditioned by additives and separated by froth flotation to recover the zinc sulfide and sometimes lead or copper sulfides. In some cases, the ore is reconcentrated by mechanical separation based on specific gravity differences prior to froth flotation. Large mixers stir the solution, and the zinc-bearing minerals separate and float to the surface where they are skimmed off. Generally, zinc sulfide flotations are run at a basic pH (usually 8.5 to 11), and the slurry is periodically adjusted with hydrated lime, $Ca(OH)_2$ (1). After flotation, the underflow (tailings or gangue materials) is sent to a tailings pond for treatment.

Once separated, the metal concentrates are thickened in settling tanks and the slurry is fed to vacuum drum filters, which reduce the moisture content. Upon completion of the concentration process, the zinc content is about 55 to 60 percent. Thermal drying in direct-fired rotary dryers may further reduce the moisture content of the concentrates, which are then transported to a storage site. Concentrate enters the dryer with about 11 percent moisture and leaves with about 3 percent moisture (2).

In certain western ores, notably those from Idaho, the lead and zinc are too finely divided for satisfactory separation even by flotation. For such ores, final separation involves sulfuric acid leaching at an electrolytic zinc plant. Some foreign producers use the Imperial furnace to treat these ores, but it is not used at any U.S. zinc smelters. Treatment of such ores was the primary reason for development of electrolytic zinc recovery methods in North America.

The quantity of zinc concentrate produced is about 10 to 15 percent of the zinc ore by weight. A typical analysis would be 52 to 60 percent zinc, 30 to 33 percent sulfur, 4 to 11 percent iron, and lesser quantities of lead, cadmium, copper, and other elements (2). Table 8 lists some of these elements of ore concentrate.

TABLE 8. RANGE OF COMPOSITIONS OF ZINC CONCENTRATES (6,7,8)

Constituent	Percent, weight
Pb	0.85-2.4
Zn	49.0-53.6
Au	not iden.
Ag	not iden.
Cu	0.35
As	0.105-0.15
Sb	not iden.
Fe	5.5-13.0
Insolubles	3.4
CaO	not iden.
S	30.7-32.0
Bi	not iden.
Cd	0.24

2. Input Materials - The quantity of ore required per ton of zinc concentrate produced varies with the zinc content of the ore. A common range is 5 to 10 tons of ore per ton of zinc concentrate (1).

Hydrated lime is used to adjust the pH. Promoters or collectors are added to the zinc sulfide to provide a coating that repels water and encourages absorption of air. Frothers are added to produce a layer of foam on the top of the flotation machine, and depressants are added to stop unwanted minerals from floating. Table 9 lists commonly used reagents.

Additives are an estimated 1.9 kilogram of lime, 0.4 kilogram of copper sulfate, 0.04 kilogram of Z-5 xanthate, and 0.02 kilogram of pine oil per metric ton of concentrate (3).

3. Operating Conditions - Flotation machines are operated at ambient temperatures and pressures. Flotations are generally run at elevated pH values of 8.5 to 11 (1).

4. Utilities - Electrical energy is consumed during milling operations. One estimate for electrical usage in the milling of zinc ores in 1973 is 290 million killowatt-hours (4). At the 1973 mine production level of 434,000 metric tons (5), electrical usage was about 477 killowatt-hours per metric ton of zinc produced.

The water requirement ranges from 330 to 1,100 cubic meters per metric ton of ore processed per day (1). Feed water for the mills is usually taken from available mine waters.

5. Waste Streams - It is estimated that 1 kilogram of particulate is emitted per metric ton of ore processed during crushing and grinding operations. The composition is that of the raw ore fed to the process. After water is added to form an ore-water slurry, particulate emissions are negligible. In plants that incorporate an ore drying operation following concentration, dust emissions occur as the hot air passes over the moving bed of concentrate. Operating factors affecting emissions are the process feed rate and moisture content.

Liquid waste streams from zinc mills vary in volume from 1000 to 16,000 cubic meters per day. In terms of volume of ore processed, liquid waste streams from milling operations range from 330 to 1,100 cubic meters per metric ton (1). Tailings slurry discharge is about 4 cubic meters per metric ton of ore processed.

The raw wastewater from a lead/zinc flotation mill consists principally of the water used in the flotation circuit, along with any housecleaning water. The waste streams consist of the tailings streams (usually the underflow of the zinc rougher flotation cell), the overflow from the concentrate thickeners, and the filtrate from concentrate dewatering.

TABLE 9. TYPICAL FLOTATION REAGENTS USED FOR ZINC CONCENTRATION UNITS (1)

Reagent	Purpose
Methyl isobutyl-carbinol	Frother
Propylene glycol methyl ether	Frother
Long-chain aliphatic alcohols	Frother
Pine oil	Frother
Potassium amyl xanthate	Collector
Sodium isopropol xanthate	Collector
Sodium ethyl xanthate	Collector
Dixanthogen	Collector
Isopropyl ethyl thionocarbonate	Collectors
Sodium diethyl-dithiophosphate	Collectors
Zinc sulfate	Zinc depressant
Sodium cyanide	Zinc depressant
Copper sulfate	Zinc activant
Sodium dichromate	Lead depressant
Sulfur dioxide	Lead depressant
Starch	Lead depressant
Lime	pH adjustment

The principal characteristics of the waste stream from mill operations are as follows:

(1) Solids loadings of 25 to 50 percent (tailings).

(2) Unseparated minerals associated with the tails.

(3) Fine particles of minerals, particularly if the thickener overflow is not recirculated.

(4) Excess flotation reagents not associated with the mineral concentrates.

(5) Any spills of reagents that occur in the mill.

It is very difficult analytically to detect the presence of excess flotation reagents, particularly those that are organic. The surfactant parameters may give some indication of the presence of organic reagents, but provide no definitive information.

A typical quantity of solid wastes is 0.9 to 1 metric ton per metric ton of ore milled. Based on a 25 to 50 percent solids loading in the liquid waste stream, solid wastes from flotation could range from 80 to 550 cubic meters per metric ton (1). The main component of the waste is dolomite.

Table 10 gives raw and treated waste characteristics of five mills. This summary does not include information for a mill using total recycle and one at which mill wastes are mixed with metal refining wastes in the tailings pond. Feed water for the mills is usually drawn from available mine waters; however, one mill uses water from a nearby lake. These data illustrate the wide variations caused by ore mineralogy, grinding practices, and reagents.

6. Control Technology - Particulate abatement equipment at the dryer can capture dust and recirculate it into a storage bin for further use. This can be accomplished with low-energy scrubbers and multicyclones. Cyclones, operating on a dry principle, could remove many of the large particles for reuse directly in the roaster without further processing. Particulates caught in the scrubbers must be dried before reuse in roasters or sintering plants.

Lime precipitation is often used for the removal of heavy metals from wastewater. This treatment yields reductions for several heavy metals including copper, zinc, iron, manganese, and cadmium.

Various techniques are employed to augment lime neutralization. Among these are the secondary settling ponds, clarifier tanks, or the addition of flocculating agents (such as polyelectrolytes) to enhance removal of solids and sludge before discharge. Readjustment of the pH after lime treatment can be accomplished either by addition of sulfuric acid or by recarbonation. Sulfide precipitation may be necessary for further removal of metals such as cadmium and mercury.

TABLE 10. RANGES OF CONSTITUENTS OF WASTEWATERS AND RAW WASTE LOADS FOR FIVE SELECTED MILLS (1)

Parameter	Range of concentration in wastewater mg/l		Range of raw waste load			
			Per unit ore milled, kg/1000 metric tons		Per unit concentrate produced, kg/1000 metric tons	
	lower limit	upper limit	lower limit	upper limit	lower limit	upper limit
pH[a]	7.9	8.8				
Alkalinity	26	609	410	1,600	1,450	10,200
Hardness	310	1,760	460	4,700	2,290	32,500
TSS	<2	108	7	285	30	2,000
TDS	670	2,834	940	8,500	4,800	50,900
COD	71.4	1,535	6	4,800	30	50,000
TOC	11	35	6.35	130	30	580
Oil and grease	0	8	5	21	30	130
MBAS surfactants	0.18	3.7	0.236	13	2.05	60.7
P	0.042	0.150	0.108	0.876	0.54	2.54
Ammonia	<0.05	14	0.064	26.4	0.32	185
Hg	<0.0001	0.1	<0.00013	0.0026	<0.00168	0.130
Pb	<0.1	1.9	<0.127	6.9	<0.900	32.2
Zn	0.12	0.46	0.089	17.2	0.62	86.0
Cu	<0.02	0.36	<0.026	0.158	<0.18	1.96
Cd	0.005	0.011	0.008	0.018	<0.18	8.85
Cr	<0.02	0.67	<0.026	1.77	<0.18	1.36
Mn	<0.02	0.08	<0.026	0.290	<0.45	10.0
Fe	0.05	0.53	0.064	1.16	0.012	0.198
Cyanide	<0.01	0.03	<0.013	0.109	0.091	0.509
Sulfate	295	1,825	130	4,800	1,260	33,700
Chloride	21	395	20	870	210	4,070
Fluoride	0.13	0.26	0.370	0.944	203	5.45

[a] Value in pH units.

Water separated from the concentrates is often recycled in the mill, but it may be pumped to the tailings pond, where primary separation of solids occurs. Usually, surface drainage from the area around the mill is also collected and sent to the tailings pond for treatment, as is process water from froth flotation.

Tailings pond water may be decanted after sufficient retention time. One alternative to discharge, which reduces the output of effluent, is reuse of the water in other facilities as either makeup water or process water. Usually, some treatment is required before reuse of this decanted water. Treatments include secondary settling, phosphate or lime addition, pH adjustment, flocculation, clarification, and filtration.

The most frequently used control technology is the use of a settling or sedimentation pond system consisting of primary tailings pond and secondary settling or "polishing" pond, with pH adjustment prior to discharge. Six lead and zinc ore processing facilities now use this technology. Effluent concentrations are limited to the following average values (in milligrams per liter): copper - 0.05, mercury - 0.001, lead - 0.02, and zinc - 0.5 (1).

Tailings from mine concentrator operations may present a serious water pollution problem if adequate precautions are not taken. Coarse tailings may be removed with a cyclone separator and pumped to the mine for backfilling (1). The most effective means of control is impoundment with isolation of disposal sites from surface flows. Techniques include the following (1):

(1) Construction of a clay or other type of liner beneath the planned waste disposal area to prevent infiltration of surface water (precipitation) or water contained in the waste into the groundwater system.

(2) Compaction of waste material to reduce infiltration.

(3) Maintenance of uniformly sized refuse to enhance good compaction (which may require additional crushing).

(4) Construction of a clay liner over the material to minimize infiltration. This is usually followed by placement of top soil and seeding to establish a vegetative cover for control of erosion and runoff.

(5) Excavation of diversion ditches surrounding the refuse disposal site to exclude surface runoff. These ditches can also be used to collect seepage from refuse piles, with subsequent treatment if necessary.

No data were found on the extent of application of these methods.

7. EPA Source Classification Code - None

8. References -

1. Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry. Point Source Category Vol. 1. Publication EPA-440/1-75/061. Effluent Guidelines Division Office of Water and Hazardous Materials, U.S. Environmental Protection Agency. Washington, D.C. October 1975.

2. Field Surveillance and Enforcement Guide for Primary Metallurgical Industries. EPA-450/3-73-002. Office of Air and Water Programs, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973. pp. 269-309.

3. Denver Equipment Company. Mineral Processing Flowsheets. Denver, Colorado. 1962.

4. Dayton, S. The Quiet Revolution in the Wide World of Mineral Processing. Engineering and Mining Journal. June 1975.

5. Commodity Data Summaries 1976. U.S. Department of the Interior, Bureau of Mines. Washington, D.C. 1976.

6. Water Pollution Control in the Primary Nonferrous - Metals Industries. Volume 1, Copper, Zinc, and Lead Industries. EPA-R2-73-247a. Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. September 1973.

7. Burgess, Robert P., Jr., and Donald H. Sargent. Technical and Microeconomic Analysis of Arsenic and Its Compounds. EPA-560/5-76-016. Office of Toxic Substances. U.S. Environmental Protection Agency. Washington, D.C. April 12, 1976.

8. Katari, V., et al. Trace Pollutant Emissions from the Processing of Metallic Ores. EPA-650/2-74-115. U.S. Environmental Protection Agency, Office of Research and Development. Research Triangle Park, North Carolina. October 1974.

Ferroalloy Production

1. Function - One U.S. zinc smelter recovers a ferro-manganese by-product from zinc oxide ore by means of reduction, vaporization, and oxidation in Waelz kilns. The ore, from a New Jersey mine, is not amenable to flotation. The zinc oxide fume produced in the kilns is collected and sintered in the same manner as roasted sulfide concentrates.

The Waelz kilns in use are rotary kilns similar to those used in the cement industry. Their sizes range from 3.0 meters in diameter by 42.7 meters long to 3.7 meters in diameter by 48.8 meters long. Gas flow is countercurrent to the solids flow, with the zinc oxide fume and kiln gases withdrawn at the feed end. Automatic 10-compartment dust tube collectors remove zinc oxide from the gas streams, which have been previously cooled by dilution and radiation loss. Solid residues from the kiln contain 20 to 24 percent iron and approximately 10 percent manganese; they are processed in open-arc electric furnaces to produce a nominal 20 percent manganese iron (Spiegeleisen) (1).

2. Input Materials - The charge to the Waelz kilns consists of the oxide ores which are mixed with anthracite coal to raise the carbon content and limestone to stiffen the charge. Feed to the kilns ranges between 9 and 15 metric tons per hour (1). Various furnace residues and slags may also be added.

3. Operating Conditions - Waelz kilns operate at atmospheric pressures (2). Operating temperatures are about 1300°C in the kiln, with about 80 percent of the kiln length kept above the boiling point of zinc.

4. Utilities - Heat generated by the oxidation reactions is usually sufficient to sustain reduction. Additional heat if required for reduction of the zinc can be supplied by the combustion of coal, oil, natural gas, or electric furnace gas. No information is available as to the quantities of additional heat that may be supplied by combustion of fuel.

5. Waste Streams - Unknown quantities of combustion products are emitted from the kilns and vented to the atmosphere.

There are no liquid or solid wastes from the process.

6. Control Technology - There are no known environmental controls on the Waelz kilns used for ferroalloy production.

7. EPA Source Classification Code - None

8. References -

1. The New Jersey Zinc Company. Manufacturing Operations. Palmerton, Pennsylvania.

2. Schlecten, A.W. and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

Multiple-Hearth Roasting

1. Function - Multiple-hearth roasting is a high-temperature process that removes sulfur from the concentrate and converts zinc to an impure zinc oxide called calcine. Roasting may also be accomplished by suspension (process No. 5) or fluidized-bed (Process No. 6) units. In a multiple-hearth roaster, the concentrates drop from hearth to hearth. As much as 20 percent of the cadmium present in the zinc concentrate may be vaporized (1). Any mercury present is volatilized and enters the gas stream. Multiple-hearth roasters are the oldest type of roaster in use in the United States.

At present, only two domestic primary zinc smelters use multiple-hearth roasters. At one of these plants, the multiple-hearth roaster is used in conjunction with fluidized-bed roasters. The deleaded product, termed "partially desulfurized concentrate," typically contains about 22 percent sulfur and is used as feed to the fluidized-bed roasters. Mercury is recovered from the flue dusts captured in the electrostatic precipitators used to clean the gas stream from these roasters.

In roasting, if enough sulfur is originally present as sulfide, the operation becomes autogenous. For pyrometallurgical refining, zinc sulfate must be removed. The following reactions occur during roasting:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$ZnO + SO_3 \rightarrow ZnSO_4$$

In pyrometallurgical reduction only the oxide state is desired, whereas in electrolytic reduction, small amounts of the sulfate state are acceptable (3).

Elimination of the remaining small percentages of sulfur requires a long residence time. Hence a multiple-hearth-type roaster that eliminates all but 6 to 8 percent sulfur from up to 350 tons of copper concentrates per day can roast only about 50 to 60 tons of zinc concentrate per day to about 2 percent sulfur.

The roaster consists of a brick-lined cylindrical steel column with 9 or more hearths. A motor-driven central shaft has two rabble arms attached

for each hearth, as well as cooling pipes. The concentrates enter at the top of the roaster and are first dried in an upper hearth. The central shaft rotates slowly, raking the concentrates over the hearth with the rabble arms, gradually moving them to the center and a drop hole to the next hearth. They move across this second hearth to a slot near the outer edge, where they drop to the next hearth. The concentrates continue down through the roaster in this spiral fashion and are discharged at the bottom. Additional fuel must be added to maintain combustion.

The low production rates are a major disadvantage of multiple-hearth roasting. However, since less dust is carried away in the gas stream, more volatile sulfides such as cadmium are removed preferentially. This is helpful when cadmium is to be recovered from the flue dust, since there is less zinc dust contamination (4).

Total residual sulfur in the calcine produced in multiple-hearth roasters is 2.4 percent; 0.5 to 1.0 percent is present as sulfide and the balance as sulfate (3).

Feed capacities for multiple-hearth roasters average 180 metric tons per day.

2. Input Materials - Zinc concentrate is the input material for multiple-hearth roasters. Approximately 2.4 tons of pure ZnS is required to produce 1 ton of pure ZnO. In practice, the quantity of raw materials required to produce one unit of calcine varies depending on impurities in the concentrate, efficiency of the dust-collecting devices on the roaster, and the type of roaster used.

Sodium or zinc chloride may be added to combine with cadmium dust in the roaster and facilitate removal of cadmium as a by-product after sintering. Specific quantities have not been reported.

3. Operating Conditions - Multiple-hearth roasters are unpressurized. Average operating temperature is about 690°C (3); the lower hearths (sixth through tenth from the top) are maintained at 950° to 980°C (2). Operating time depends upon the type of roaster, composition of concentrate, and amount of sulfur removal required.

4. Utilities - The reaction converting ZnS to ZnO is exothermic and is self-sustaining after ignition. Gas, coal, or oil must be added initially to bring the charge up to reaction temperature. About 280,000 kilocalories per metric ton of ore are required for ignition. The primary fuel is natural gas. In some multiple-hearth furnaces, when concentrations of less than 1.0 percent of sulfide sulfur are required, about 1.1 million kilocalories are required per metric ton of feed (5). Some additional fuel is added to the lower hearths to reduce the zinc sulfide content to as low as 0.5 to 1.0 percent.

Cooling water and air are also used to cool the furnace shaft. Electricity powers the rabble arms.

5. Waste Streams - In a zinc smelter the roasting process is typically responsible for more than 90 percent of the potential SO_2 emissions; 93 to 97 percent of the sulfur in the feed is emitted as sulfur oxides. Concentrations of SO_2 in the off-gas vary with the type of roaster operation. Off-gases contain up to 6 to 7 percent sulfur, depending on the sulfur content of the feed. The volume of off-gases ranges from 140 to 170 cubic meters per minute (6) for furnaces currently in use (approximately 180 metric tons per day). Typical SO_2 concentrations range from 4.5 to 6.5 percent (3). Oxygen, nitrogen, carbon dioxide, and water vapor are other components of the gas.

Particulate matter is also emitted. The amount and composition vary depending on such operating conditions as air flow rate, particle size distribution, and equipment configuration. Particulate emissions consist of fumes and dusts composed of the zinc concentrate elements in various combinations. One plant has reported the following compositions of flue dusts from multiple-hearth, suspension, and fluid bed roasters: zinc, 54.0 percent; lead, 1.4 percent; sulfur, 7.0 percent; cadmium, 0.41 percent; iron, 7.0 percent; copper, 0.40 percent; manganese, 0.21 percent; tin, 0.01 percent; and mercury, 0.03 percent (2). Typical particulate emissions in the off-gas range from 5 to 15 percent of the feed (5). Composition of the distilled metal fumes, which constitute an appreciable portion of the waste gas particulate carryover, depends primarily on the concentrate composition and operating conditions. The single zinc smelter using multiple-hearth roasters, which also uses suspension and fluidized-bed roasters, recovers mercury eliminated during roasting from the gas purification stream (2). At that smelter, the roasted material is treated by flotation to separate a fraction of waste rock prior to further processing.

Information on liquid and solid wastes is not available at this time.

6. Control Technology - Gases leaving the roaster are routed directly to "hot" Cottrells, operating at 200° to 220°C, and then to the acid plant (2).

7. EPA Source Classification Code - Roasting/multiple-hearth 3-03-030-02.

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75/032. Effluent Guidelines Division Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

2. Lund, R.E., et al. Josephtown Electrothermic Zinc Smelter of St. Joe Minerals Corporation. AIME Symposium on Lead and Zinc, Vol. II. 1970.

3. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. EPA-450/2-74-002a. Office of Air and Waste Management. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

4. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

5. Fejer, M.E., and D.H. Larson. Study of Industrial Uses of Energy Relative to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

6. Field Surveillance and Enforcement Guide for Primary Metallurgical Industries. EPA-450/3-73-002. Office of Air and Water Programs, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973.

Suspension Roasting

1. Function - Suspension, or flash, roasting is a process for rapid removal of sulfur and conversion of zinc to calcine by allowing the concentrates to fall through a heated oxidizing atmosphere or blowing them into a combustion chamber. Roasting in suspension promotes better heat transfer than multiple-hearth roasting and thereby increases reaction rates for desulfurization. The chemical reactions occurring in the two processes are the same, and the SO_2 stream produced during conversion of the zinc sulfides to calcine is strong enough for sulfuric acid production. Removal of mercury and cadmium is also similar.

Suspension roasting is similar to the burning of pulverized coal, in that finely ground concentrates are suspended in a stream of air and sprayed into a hot combustion chamber where they undergo instantaneous desulfurization. In practice, a stream of hot air passes through the finely ground concentrate to temporarily suspend the particles. The reaction usually proceeds without the addition of fuel unless the sulfide content of the ore is too low.

The roaster consists of a refractory-lined cylindrical steel shell with a large combustion space at the top and two to four hearths in the lower portion, similar to those of a multiple hearth furnace. Because the feed must be carefully sized, additional grinding may be needed for proper preparation. In more recent models of flash furnaces, concentrate is introduced into the lower one or two hearths to dry before final grinding in an auxiliary ball mill and introduction into the combustion chamber.

About 40 percent of the roasted product settles out on a collecting hearth at the bottom of the combustion chamber. This coarser material is likely to contain the most sulfur, so it is further desulfurized by being rabbled across this hearth and another hearth immediately below before being discharged from the roaster. Particulate collected in ducts and control devices can be fed to these hearths to achieve further oxidation and sulfate decomposition or to obtain a more homogeneous product (1).

The remaining 60 percent of the product leaves the furnace with the gas stream, passing first through a waste heat boiler and then to cyclones and an electrostatic precipitator, where it is recovered. About 20 percent of the suspended dust drops out in the boiler; the cyclones and precipitator remove about 99.5 percent of the remainder (1).

Total residual sulfur in the calcine is 2.6 percent, with 0.1 to 5.0 percent as sulfide and the balance as sulfate (2).

Feed capacities of older suspension roasters are about 90 metric tons per day, whereas newer roasters can handle about 320 metric tons of concentrate per day (1).

2. Input Materials - Zinc concentrate is the input material for suspension roasters. Sodium or zinc chloride may be added to facilitate later removal of cadmium and lead. Specific quantities for these inputs are not available.

3. Operating Conditions - Suspension roasters are unpressurized and operate at an average temperature of 980°C (1). Off-gases exit the roaster at about 1000°C (3). Operating times vary, depending upon the same factors as in multiple-hearth roasting.

4. Utilities - Natural gas, oil, or coal is used to bring the roaster feed to ignition, after which exothermic oxidation of the sulfur maintains operating temperatures. About 280,000 kilocalories per metric ton of ore are required for ignition (4). Air is also added to the suspension roaster. Water is supplied to the waste heat boiler system, and relatively small amounts of electricity are required for fans, pumps, and rabble arms.

5. Waste Streams - The SO_2 concentration in the off-gas from suspension roasting is higher than that in multiple-hearth processes, averaging 10 to 13 percent (5). It also contains oxygen, nitrogen, carbon dioxide, and water vapor. The higher SO_2 content increases the efficiency of sulfuric acid production. Emission of particulates depends on operating conditions, averaging about 6 percent of the feed. These emissions consist of dust and metal fumes, depending on the concentrate composition and operating conditions. The volume of off-gases ranges from 280 to 420 cubic meters per minute (5).

There are no process water or solid wastes. There is a boiler blowdown from the waste heat boiler. Solids are recycled to recover by-product metals.

6. Control Technology - The SO_2 stream is concentrated enough to allow sulfuric acid production. The roaster off-gases are cooled to about 400°C by heat transfer with waste heat boilers (3). The gas is then typically diluted with air and humidified with water sprays before cleaning in an ESP. After conditioning, gas volume is 475 to 700 cubic meters per minute, and the SO_2 concentration is 6 to 8 percent (6).

7. EPA Source Classification Code - None

8. References -

1. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

2. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. EPA-450/2-74-002a. Office of Air and Waste Management, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75/032. Effluent Guidelines Division Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

4. Study of Industrial Uses of Energy Relative to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

5. Field Surveillance and Enforcement Guide for Primary Metallurgical Industries. EPA-450/3-73-002. Office of Air and Water Programs, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973.

6. Jones, H.R. Pollution Control in The Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

Fluidized-Bed Roasting

1. Function - The fluidized-bed roaster is the newest method for removing sulfur and converting zinc to calcine. In this roaster, finely ground sulfide concentrates are suspended and oxidized in a 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. The chemistry of this process is the same as that in other roasters. This process also produces enough SO_2 for manufacture of sulfuric acid. Removal of mercury and cadmium is similar to removal of other wastes.

The fluidized-bed roaster was originally designed for calcining arsenopyrite gold ores; several North American zinc smelters have adopted it in different forms for use in pyrometallurgical and electrolytic processes. Designs differ primarily in whether the roasters are charged with a wet slurry or a dry charge. One variation is fluid column roasting, which was developed in this country by the New Jersey Zinc Company after being used abroad. In this process, feed to the roasters is pelletized. The calcined product is also pelletized, eliminating the need for further agglomeration by sintering. Fluid column roasting operates at slightly higher temperatures than fluidized bed.

In the fluidized-bed process, no additional fuel is required after ignition has been achieved. Operation of the system is continuous. The feed enters the furnace and becomes fluidized, or suspended, in a bed supported on an air column. Temperature control is achieved manually or automatically, via water injection. Relatively low, uniform operating temperatures appear to lessen the formation of ferrite. The temperatures in the roaster are high enough to warrant the use of waste heat boilers to cool the off-gases.

The sulfur content of the charge is reduced from about 32 to 0.3 percent. Efficiency of the operation is maximum when 20 to 30 percent excess air is supplied over stoichiometric requirements for oxidation of both sulfur and metals of the charge (1).

Dust carryover into the dust collecting system is somewhat less than in flash roasting. Particulates emitted average 50 to 85 percent for fluidized bed and only 17 to 18 percent for fluid column (2). Amounts vary with the feed rate (and consequently with the air rate), and with the size of the material being roasted.

The SO_2 content of roaster gas is reported to be 7 to 12 percent. If higher, it is diluted to about 7 percent before reaching the contact acid plant. The theoretical maximum SO_2 concentration achievable is 14.6 percent when roasting 100 percent zinc sulfide concentrates to completion, unless the air supply is enriched with oxygen (1).

Although the preferred method of regulating temperature within the bed is by water injection with automatic thermocouple-operated control, water

injection and slurry feeding can be eliminated when it is desirable to minimize the water content of the gas.

The major advantage of the fluidization roaster is its ability to process higher tonnages per furnace per unit time, because of the increased reaction rates for desulfurization. Fewer man-hours are required. Also, like the suspension roaster, the fluidized-bed roaster can produce a calcine with lower total sulfur content than the multiple-hearth processes; the exact percentage elimination of sulfur during roasting is a function of the initial sulfur content of the concentrate.

Total residual sulfur is 2.6 percent, with 0.1 percent as sulfide and the balance as sulfate (3).

Feed capacities can range up to 320 metric tons of concentrate per day (3).

2. Input Materials - Zinc concentrate is the primary input material for fluidized-bed roasting. As with other processes, sodium or zinc chloride may be added to combine with cadmium dust, facilitating the later removal of cadmium as a by-product. The feed is usually finely ground at one plant to 90 percent minus 0.044 millimeter (4). However, in some modifications, the feed is pelletized to provide longer retention time in the roaster (5).

3. Operating Conditions - Fluidized-bed roasters operate under a pressure slightly lower than atmospheric through as much of the system as possible. Operating temperatures average 1000°C. The temperature in fluid column roasters is 1050°C. Operating times are variable, depending upon the same factors as in other roasting processes.

4. Utilities - Natural gas, oil, or coal is used to bring the roaster feed up to reaction temperatures, after which exothermic oxidation of the sulfur maintains the temperature and operation is continuous. About 280,000 kilocalories per metric ton of ore is required for ignition (6). Cooling water is added, as well as low-pressure air (19 to 21 kg/cm^2) which is introduced into the windbox for combustion and fluidization of the mix.

5. Waste Streams - Typical SO_2 concentrations in the off-gas from fluidized-bed roasters range from 7 to 12 percent, although the higher figure is more common. Fluid column roasters average 11 to 12 percent. Exit gases also contain oxygen, nitrogen, carbon dioxide, and water vapor. The volume of off-gas produced ranges from 170 to 280 cubic meters per minute (5). Temperatures are approximately 950°C.

As with the other processes, the amount and composition of particulates and metal fumes depend on the concentrate composition and operating conditions.

As with other roasting processes, solids are recycled to recover by-product metals and there are no solid or process-water wastes.

6. Control Technology - Emission controls are the same as for the flash roasting process. The SO_2 stream is used for sulfuric acid production. Since SO_2 control systems normally require clean gas streams, particulates are captured by cyclones and ESP's before the gas stream enters the acid plant and thus present no air pollution problems. Waste heat boilers cool the gases to 400°C.

In one operation, roasting 127 metric tons of dry concentrates per day, 30 percent of the calcine left the roaster via the overflow pipe, 23 percent was deposited in the waste heat boiler, 44 percent was captured by the cyclones, and 3 percent entered the hot Cottrell electrostatic precipitator with the flue gases (1). Flue dusts are not recirculated to the reactor, being sufficiently low in sulfide sulfur. Roasters with pelletized feed yield about 80 percent to the overflow and 20 percent carry-over as dust.

7. EPA Source Classification Code - None

8. References -

1. Schlechten, A. W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encylcopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

2. Field Surveillance and Enforcement Guide for Primary Metallurgical Industries. EPA-450/3-73-002. Office of Air and Water Programs, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973.

3. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. EPA-450/2-74-002a. Office of Air and Waste Management, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

4. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. Battelle Columbus Laboratories. EPA Contract Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973.

5. Van Den Neste, E. Metallurgie-Hoboken-Overpelt's Zinc Electrowinning Plant. CIM Bulletin. Sixth Annual Hydrometallurgical Meeting. 1977.

6. Study of Industrial Uses of Energy Relative to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

Contact Sulfuric Acid Plant

1. Function - An acid plant catalytically oxidizes SO_2 gas to sulfur trioxide, and absorbs it in water to form sulfuric acid.

Contact sulfuric acid plants are continuous steady-state processing units that are operated in other industries using SO_2 made by burning elemental sulfur. They may be used with waste SO_2 streams if the gas is sufficiently concentrated, is supplied at a reasonably uniform rate, and is free from impurities.

The heart of a sulfuric acid plant is a fixed bed of vanadium pentoxide or other special catalyst which oxidizes the SO_2. All other components of the plant are auxiliary to this catalytic converter. The other components clean and dry the stream of gas, mix the proper amount of oxygen with it (unless sufficient oxygen is present), preheat the gas to reaction temperature, and remove the heat produced by the oxidation.

The plant incorporates one or two absorbers to contact the gas with water to form the acid. If only one absorber is provided, this is described as a single-contact sulfuric acid plant. If two are provided, the second is placed between stages of the converter, and this is a double-contact plant. The second absorber allows a larger proportion of the SO_2 to be converted into acid, and thus removes more SO_2 from the gas stream if the initial concentration is high.

2. Input Materials - Most contact sulfuric acid plants operate most efficiently with a constant gas stream that contains 12 to 15 percent SO_2. Performance almost as good can be achieved in plants that are designed for 7 to 10 percent SO_2 content. The ability of a plant to convert most of the SO_2 to sulfuric acid declines either as gas streams become weaker in SO_2 or as the flow rate or concentration becomes less consistent. A concentration lower than 4 percent SO_2 is extremely inefficient, since sufficient catalyst temperature cannot be maintained (1). Certain modifications of the process, which add heat by combustion of fuel, can provide better conversion at low SO_2 concentrations.

The gas that enters the catalyst bed must be cleaned of all particulate matter, be almost completely dried, and contain no gases or fumes that act as poisons to the catalyst. The acid plant is always supplied with special scrubbers to remove final traces of objectionable materials.

Clean water is required to react with the SO_3 to form sulfuric acid. It may be necessary to deionize the water in a special ion exchange system in order to avoid excessive corrosion or to meet acid quality specifications. Steam condensate may also be used.

3. Operating Conditions - The catalyst bed operates properly only if temperatures are maintained between 450° and 475°C. Pressures do not usually exceed 2 kilograms per square centimeter. The plants are usually not enclosed in a building.

4. Utilities - Noncontact cooling water is required. At one plant producing 1500 metric tons of acid per day, about 12 million liters of water is required each day (2).

A small amount of electricity is required for pumps and blowers. This may be generated on-site in some cases, where recovery of waste heat is maximized.

In certain patented modifications, heat from combustion of natural gas is used to provide better efficiency at low SO_2 concentrations. Natural gas or oil is also required to heat any acid plant to operating temperature following a shutdown.

5. Waste Streams - Single-contact sulfuric acid plants using weak gas streams can at best absorb only 96 to 98 percent of the SO_2 fed to them. The remaining quantity passes through to the atmosphere. Efficiencies as low as 60 percent have been reported (3).

Double-contact acid plants provide a higher percentage of SO_2 removal if they are fed gas with a higher SO_2 content. Efficiencies higher than 99 percent have been reported. Exit gas SO_2 concentration is still usually within the same range as shown above, although one recently developed process claims stack emissions of less than 0.005 percent SO_2 (4).

In sulfuric acid plants, it is difficult to prevent some loss of SO_3, in the form of a fine mist of sulfuric acid, with the absorber exit gases. This is usually 0.02 to 0.04 kilogram of SO_3 per metric ton of 100 percent acid produced.

The scrubbing columns that clean the waste gas stream create off-grade weak acid that cannot be sold. The amount is estimated as 4 to 8 liters for each 10 cubic meters of gas treated (5).

In this industry, most particulate matter from gas cleaning equipment is recycled to the metallurgical processes. The small quantities of particulate removed by the acid scrubbing operations, however, are mixed with a stream of weak sulfuric acid and cannot readily be recycled. They are discharged with the acid plant blowdown.

In some sections of the country it is difficult to sell the product acid, even for less than the cost of manufacture. Therefore, it may be less expensive to neutralize and discard the acid than to absorb the costs of shipment to a distant user. Thus, the product acid can itself become a waste stream.

An acid plant does not produce solid wastes directly, but the gypsum formed in neutralization of acid can constitute a significant solid waste.

6. Control Technology - In this country the SO_2 in the tail gas from the sulfuric acid plant is not controlled. When SO_2 emissions are large, the best control may be to increase operating efficiency by adding additional catalyst stages or by adding heating equipment to maintain proper catalyst temperature. Changes in the metallurgical operations to produce a stream of higher SO_2 concentration at a more uniform rate are also good controls, if this is possible. Scrubbing of the weak SO_2 stream for final SO_2 absorption may also be necessary.

Mist eliminators in the form of packed columns or impingement metal screens can minimize acid mist emissions. Manufacturers claim elimination of all but 35 to 70 milligrams of mist per cubic meter of gas, and the units at times perform better. To prevent formation of plumes of mist during periods of abnormal operations, however, electrostatic precipitators are often used. Better regulation of feed rate and quality also minimizes acid loss.

If volumes of strong acid must be neutralized, treatment with limestone followed by more precise pH adjustment with lime, and discharge to a pond for in-perpetuity storage of the resulting gypsum is the only tested and economical method of disposal.

7. EPA Source Classification Code - None

8. References -

1. Jones, H.R. Pollution Control in the Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

3. Hallowell, J.B., et al. Water Pollution Control in the Primary Nonferrous Metals Industry - Volume I. Copper, Zinc, and Lead Industries. EPA-R2-73-274a. U.S. Environmental Protection Agency. Washington, D.C. September 1973.

3. Confidential information from EPA.

4. Browder, T.J. Advancements and Improvements in the Sulfuric Acid Industry. Tim J. Browder Co. San Marino, California.

5. Vandergrift, A.E., L.J. Shannon, P.G. Gormena, E.W. Lawless, E.E. Sallee, and M. Reichel. Particulate Pollutant System Study - Mass Emissions, Volumes 1, 2, and 3. PB-203 128, PB-203 522, and PB-203 521. U.S. Environmental Protection Agency. Durham, North Carolina. May 1971.

Sintering

1. Function - Sintering has two purposes: first, to volatilize lead and cadmium impurities and discharge them into the off-gas stream where they can be captured; and second, to agglomerate the charge into a hard, permeable mass suitable for feed to a pyrometallurgical reduction system.

Dwight-Lloyd-type sinter machines are typically used in the zinc industry. These are downdraft units in which grated pallets are joined to form a continuous conveyor system. The feed is normally a mixture of calcine or concentrates, recycled ground sinter, and the required amount of carbonaceous fuel, which is pelletized and sized to assure a uniform, permeable bed for sintering before it is fed to the machines and ignited. Different smelting methods demand different properties of the sintered feed. Purity of the final zinc product dictates the type of sinter needed.

The feed is dumped on one end of a moving conveyor and is ignited as it enters the natural gas-fired ignition box. Combustion is sustained by supplying air to the pellets. Temperature control is achieved by limiting the coke and coal content and sulfur content of the sinter mix. Once oxidation is started, it becomes self-sustaining. Air flow regulation provides additional temperature control. A rotating scalper shaves off the top layer of the sinter bed just before the discharge end of the machine. This top layer is the sinter product, with composition at one plant as shown in Table 11. Estimates are that 80 to 90 percent of the cadmium and 70 to 80 percent of the lead are removed from the sinter feed (2). Dust collected from this circuit is greatly enriched in these impurities, and by recycling, levels are built up high enough in the flue dust to permit economic recovery of cadmium. The lower portion of the bed, which was not removed by the scalper, is discharged to a set of crushers. Coarser material may be separated on a vibrating screen. Oversized particles are returned to the sinter machine, while undersized material is incorporated with the feed mix. Usually 5 to 10 percent of the total feed appears as dust in the gas that is discharged (2). These dusts become the input material to the cadmium recovery process.

Structural strength of the sinter must be considered, especially in vertical reduction furnaces, since it must be able to support a great amount of confining pressure from the overburdening charge. Mechanical collapse is prevented by close chemical control of the nonvolatile ingredients and addition of silica to increase hardness and strength of the sinter mass. In horizontal-reduction-type retorts, no longer in use in this county, a soft, friable sinter was usually desirable. Structural strength was not needed because of the lack of heavy overburdening pressures. Cadmium content of the dust is usually 1 percent, allowing profitable cadmium recovery.

A process known as "sinter slicing" may be utilized in Dwight-Lloyd machines where higher grades of zinc are sought or recovery of impurities is profitable. The process is based on the fact that sintering or ignition is not homogenous throughout the charge, but migrates downward, eventually resulting in concentration of lead and cadmium sulfides at the bottom of the

TABLE 11. PRODUCT SINTER COMPOSITION (3)
(percent weight)

	Zn	Pb	Fe	Cd	SiO_2	S	Other dusts
Prime western	55.5	0.33	7.9	0.017	9.4	0.15	5-10
Intermediate	57.1	0.037	8.9	0.015	8.8	0.15	5-10
High-grade soft	63.6	0.005	6.8	0.012	5.2	0.36	5-10
High-grade hard	58.6	0.006	7.9	0.006	8.9	0.10	5-10

sinter cake. The finished sinter is sliced off for further refining in zinc-reduction retorts. The lower section of the sinter cake, with its high cadmium content, passes on to the discharge end of the machine. After crushing it is returned to the charge.

Dust collected in a baghouse still contains incompletely oxidized materials such as submicron-sized particles of cadmium metal. Temperatures are controlled by CO gas burners and tempering air. The burned dust usually contains 10 to 20 percent cadmium, 12 to 15 percent zinc, and 35 to 45 percent or more lead (4). The dust is sent to a lead smelter for further cadmium concentration and then to an electrolytic plant for recovery of pure cadmium.

In sintering preroasted charges, it is reported that substitution of fluosolid calcines for those made by older types of roasters has meant handling a more finely divided charge. Such a charge consists of about 2.8 percent sulfur, of which about 2.4 percent is sulfate. These calcines are reported to sinter very rapidly when mixed with 4 to 5 percent fine coal. The product averages approximately 0.3 percent sulfur and 0.05 percent cadmium (5).

In one pyrometallurgical zinc plant, a briquetting step is added in preparing the charge for reduction. The sinter is ground, then mixed with pulverized coal, clay, moisture, and a binder. The mixture is pressed into small briquettes (about 0.7 kg) which are fed into a step-grade autogenous coking furnace. The briquettes attain a strong structure which resists disintegration as well as keeping the reductant and zinc oxide in close contact. Heat is generated by burning volatile constituents of the charge produced inside the furnace (6).

2. Input Materials - Specific quantities of input materials to a sinter machine are dependent on properties of the concentrate and the type of reduction (i.e. retort or electric). The sinter mix typically contains calcine, recycled sinter, coke or oil, and sand or other inert ingredients. One plant has reported using 22 kilograms of sand and 80 kilograms of coke breeze (not including carbon in furnace residue and bag filter dust) per metric ton of sinter produced (6). Moisture is added when the constituents are mixed, although where available, zinc sulfate solutions from in-plant leaching operations are used to moisten the feed for pelletizing, since this conserves water and enhances zinc recovery.

In typical zinc sintering operations, charging capacities range from 220 to 550 metric tons per day; from 35 to 80 percent of the new feed is recycled (7).

3. Operating Conditions - Typical operating parameters for zinc sintering are 1040°C temperature and atmospheric pressure. The wind box fan operates at a high negative pressure required to pull combustion air through the bed.

4. Utilities - The sinter mix usually contains 4 to 5 percent coke or coal to supply enough heat for sintering (3). Natural gas is used to ignite the mix. Electrical energy is required for operating the sinter machine. Fuel consumption has been estimated to be about 280,000 kilocalories per metric

ton of concentrate processed (8), although one plant reported use of 51,000 kilocalories per metric ton of sinter produced. Water (or zinc sulfate solution, if available) is added to facilitate pelletizing. Air is supplied to maintain combustion (6).

5. Waste Streams - The sintering operation is a source of air pollutants in the form of particulates and SO_2. The SO_2 concentration in off-gas from the sinter machine is very low, 0.1 to 2.4 percent by volume, which represents only 1 to 5 percent of the sulfur originally present in the feed (3). When zinc calcines are sintered, sulfur emissions from a sinter machine are primarily determined by the sulfur content of the input calcine, although some emissions result from the zinc sulfate liquor added to the sinter mix. Typically, the resulting weak off-gas stream contains approximately 1000 ppm SO_2; the concentration, however, can range from 400 to 3000 ppm SO_2, depending upon the total sulfur content of the feed stock (7).

All of the particulate matter is less than 10 microns. Solids loadings range from 9 to 100 grams per cubic meter (9). Emissions consist of dusts and metallic fumes of a composition similar to that of the calcine. Typical chemical composition of particulates is 5 to 25 percent zinc, 30 to 55 percent lead, 2 to 15 percent cadmium, and 8 to 13 percent sulfur (9). Other constituents include copper, arsenic, antimony, bismuth, selenium, tellurium, and tin. Cadmium and lead contents are especially high because about 90 percent of the cadmium and 70 to 80 percent of the lead is eliminated in the sinter machine. The fumes condense and are collected with the dust. An analysis of particulate emissions from a sinter machine is presented in Table 12.

In the briquetting step used at one plant, the coker combustion products are released through an uncontrolled stack and contain sizable quantities of metallic fume (10). Data on particulate emissions from this process are presented in Table 13.

Gas rates vary widely. With a calcined feed, exhaust gas rates vary from 42 to 72 cubic meters per square meter of grate. The gas rate with a concentrate feed is 5.4 to 6.5 cubic meters per square meter (9). Temperature of combined exit sinter gases varies from 160°C to 380°C in different plants (9). In addition to sulfur oxides, the gases contain air, water vapor, carbon dioxide, and traces of other gases.

The sinter process includes no sources of process liquid or solid wastes. Water that is added to the mix is vaporized and emitted through the stack, while all solids left unsintered are recycled.

6. Control Technology - Currently no control methods are applied to the weak SO_2 stream from the sintering operation. Best available control technology is application of chemical scrubbing techniques. Exit gases may be cooled by air dilution and water sprays in preparation for gas cleaning.

TABLE 12. PARTICULATE EMISSIONS FROM A ZINC SINTERING PROCESS (10)

		Size	Cd	Pb	Zn	Cu	Total particulates
Cyclone and ESP control	Emission factors (kg/metric ton zinc)	>2 μm	0.432	0.310	0.846	0.002	4.97
		<2 μm	0.648	0.435	0.794	0.001	3.28
		Total	1.08	0.745	1.64	0.003	8.25
	Emission rates (kg/hr)	>2 μm	3.43	2.45	6.71	0.017	39.4
		<2 μm	5.14	3.45	6.29	0.011	25.9
		Total	8.57	5.90	13.0	0.027	65.3
Cyclone control only	Emission factors (kg/metric ton zinc)	Total	3.16	2.18	4.80	0.010	24.1
	Emission rates (kg/hr)	Total	17.1	6.43	38.8	0.118	191

TABLE 13. PARTICULATE EMISSIONS FROM A ZINC COKING FURNACE (10)

	Size	Cd	Pb	Zn	Cu	Total particulates
Emission factors (kg/metric ton zinc)	>2 μm	0.421	0.250	10.3	0.005	12.2
	<2 μm	0.749	0.375	2.48	0.004	11.7
	Total	1.17	0.625	12.8	0.010	23.9
Emission rates (kg/hr)	>2 μm	0.670	0.400	16.5	0.009	19.6
	<2 μm	1.20	0.600	3.98	0.007	18.7
	Total	1.87	1.00	20.5	0.016	38.3

Ideal control for SO_2 emissions from sintering would be to eliminate as much sulfur as technically possible during roasting. Based on the capability of fluid bed and suspension roasters, a calcine averaging 1.5 percent total sulfur could be produced, rather than the current typical calcine with approximately 3 percent total sulfur. Roasting operations that reduce the residual sulfur content in the calcine produce a corresponding decrease in sulfur emissions to the atmosphere by sintering. Since additional coke or coal is then needed to accomplish sintering, elimination of sulfur in the calcine could increase costs.

Various combinations of settling flues, cyclones, ESP's, and baghouses are used on sintering machines. Efficiencies range from 94 to 99 percent. Table 12 includes comparative data for different control devices.

Sinter crushing and screening operations have enormous potential for particulate emissions. These operations are hooded and ducted to control devices. The exhaust gas is further cooled by dilution air and water sprays to condition it for cleaning in dust collectors.

7. EPA Source Classification Code - 3-03-030-03

8. References -

1. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75/032. Effluent Guidelines Division Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

2. Field Surveillance and Enforcement Guide for Primary Metallurgical Industries. EPA-450/3-73-002. Office of Air and Water Programs, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973.

3. Lund, R.E., et al. Josephtown Electrothermic Zinc Smelter of St. Joe Minerals Corp. AIME Symopsium on Lead and Zinc, Vol. II. 1970.

4. Howe, H.E. Cadmium and Cadmium Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

5. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

6. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. Battelle Columbus Laboratories. EPA Contract No. 68-01-1518. Draft data.

7. McMahon, A.D., et al. The U.S. Zinc Industry: A Historical Perspective. Bureau of Mines Information Circular 8629. U.S. Department of Interior. 1974.

8. Fejer, M.E., and D.H. Larson. Study of Industrial Uses of Energy Relative to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

9. Jones, H.R. Pollution Control in The Nonferrous Metals Industry. Noyes Data Corporation. Park Ridge, New Jersey. 1972.

10. Jacko, Robert B., and David W. Nevendorf. Trace Metal Emission Test Results from a Number of Industrial and Muncipial Point Sources. Journal of the Air Pollution Control Association. 27(10):989-994. October 1977.

Vertical Retorting

1. Function - The vertical retort process is a continuous reduction/volatilization method for producing high-purity zinc from zinc oxide by reduction with carbon at elevated temperatures in vertical silicon-carbide retorts. An alternate retorting process is the electric retort (Process No. 10). The older horizontal retorting process is no longer in use in the United States.

Because of the relatively low boiling point of zinc (906°C), reduction and purification of zinc-bearing minerals can be accomplished to a greater extent than with most minerals. Immediate separation from nonvolatile impurities is possible. In fact, if the material is treated pyrometallurgically, there is virtually no alternative. Even at 857°C (the lowest temperature at which the oxide can be continuously reduced), the vapor pressure of zinc is high enough to cause it to vaporize immediately upon reduction. Balanced against the easy separation from nonvolatiles, however, are the difficulties of condensing the vapor and the high volatility of several of the most common impurities, especially cadmium and lead.

The substance most responsible for direct reduction of zinc commercially is carbon monoxide. The zinc-reduction cycle consists of the following reactions:

$ZnO + CO \rightarrow Zn(vapor) + CO_2$ (actual reduction step)

$CO_2 + C \rightarrow 2\ CO$ (regeneration of CO)

Both reactions are reversible, and since the second is the slower of the two at temperatures below about 1100°C, it controls the rate of reduction in most commercial situations. Above 1100°C the rates of diffusion and heat transfer predominate as rate-controlling factors. Both of the above reactions are highly endothermic (1). The following additional reactions occur during retorting:

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

$Fe_2O_3 + C \rightarrow 2FeO + CO$

$ZnS + Fe \rightarrow Zn + FeS$

$Zn + CO_2 \rightarrow ZnO + CO$ (blue powder formation)

$Zn_2SiO_4 + 2C \rightarrow 2Zn + 2CO + SiO_2$

$FeO + SiO_2 \rightarrow xFeO{\cdot}SiO_2$ (slag formation).

Carbon for reduction is normally provided by coal or coke, the choice determined by the need for structural strength within the smelting column or, if zinc oxide is the product, by the danger of contaminating the product with soot. Carbon in excess of stoichiometric reduction requirements is normally

provided to furnish extra reaction surface; this compensates for the slowness of reduction of carbon dioxide by carbon.

The charge to a vertical retort must be in the form of a hard sinter or briquette. The reduction fuel is mixed with ore and a temporary binder. The briquettes are then coked in an autogeneous coking furnace in an operation that also drives off volatiles which serve as fuel. Each unit has a capacity of 90 to 108 metric tons of briquettes averaging about 40 percent zinc (1).

Although briquetting is an expensive operation, the ability to use briquetted sinter feed could be turned into an advantage since it permits the use of a soft sinter produced either by coke-sintering or roast-sintering. Such a process is being used in England by the Imperial Smelting Corporation, Limited, but, with one exception, has not been adopted by domestic producers.

Vertical retorts are large, refractory-lined vessels with external gas chambers. The furnaces consist of three major sections - the charge column, the reflux section, and the combustion-heating chambers. The retort is rectangular in general cross-section, about 0.3 meter wide, 1.8 to 2.4 meters long, and 10.6 meters high, giving a capacity of about 7.25 metric tons of zinc per retort per day. Walls are of silicon carbide to facilitate heat transfer and minimize penetration by zinc vapor. Joints in the end walls are packed with silicon carbide and graphite to permit differential expansion upon heating. Production rates are reported at an average 195 to 215 kilograms of metallic zinc per day for each square meter of long wall surface when heated to 1300°C. Reported life of retorts is about 3 years (1).

Without intermediate cooling, coked briquettes are fed to the charging extension at the top of each vertical retort. The charge is heated by gas in chambers surrounding the retort sidewalls. Gases from the combustion chambers are used to preheat incoming air for combustion by means of recuperators. The briquettes maintain their shape throughout the reduction operation. The furnace has a vertical retort shaft which allows the charge, with the aid of gravity, to pass downward through the combustion or heating zone of the column; heat produced in the combustion chamber is transferred through the refractory walls of the column to the charge. As the charge moves down through the retort, the zinc oxide decomposes to form zinc vapors and carbon monoxide. Approximately 95 percent of the zinc vapor leaving the retort is condensed to liquid zinc (2). The residue, containing approximately 10 percent zinc (3), is removed at the bottom through an automatically controlled roll discharge mechanism into a quenching compartment, from which it is removed for further treatment.

During the passage of the briquettes through the retort, sufficient air or exhaust combustion products are introduced at the base of the charge to ensure that no zinc vapor moves concurrently with the charge and eventually condenses on spent residue. The gaseous-reaction products formed in the retort, which rise up through the charge column, are approximately 40 percent zinc vapor, 45 percent carbon monoxide, 8 percent hydrogen, 7 percent nitrogen, and some carbon dioxide (4). These gases exit near the top of the charge column, pass through a zinc condenser, and then to a venturi scrubber.

By means of a splash system, whereby a mechanically driven device fills the condenser chamber with a rain of zinc droplets that fall back into a batch of molten zinc, the zinc vapor from the retorts is condensed and collected with excellent efficiency. Over 95 percent of the zinc vapor leaving the retort is condensed to liquid zinc (5). The carbon monoxide is recycled to the combustion zone.

When the zinc vapor is not cooled quickly enough from reduction temperatures to condensation temperatures, some of the carbon monoxide present in the mixture forms carbon dioxide. This carbon dioxide, and the small amount already present in the vapor mixture oxidizes a portion of the vaporized zinc at temperatures below 1100°C. The resulting zinc oxide adheres to fine globules of condensed zinc forming an undesirable by-product called "blue powder" (1). The blue powder floats on top of the zinc bath and is periodically skimmed off. Scrubbers may be used to remove the entrained blue powder from the flue gases, and the cleaned gas may be either used as supplementary fuel or flared.

About one-half of the zinc produced in vertical retorts is refined to 99.99 percent purity by means of continuous fractional distillation. The condensed vapors from this process are typically high in cadmium content and can be used for cadmium recovery. The boiling point of lead is about 1620°C and of cadmium, 767°C. The boiling point of zinc lies between the two. Since none of these elements forms stable compounds with each other that vaporize without dissociation, they are amenable to separation by fractional distillation. The most common method entails dual fractionating columns of silicon carbide, heated externally. Cadmium and zinc are largely volatilized from the first column, leaving lead, iron, and other high-boiling-point constituents that can be removed from the base. The condensate passes to a second, or cadmium, column where cadmium and low-boiling-point impurities are removed by reflux condensation. Purified zinc flows out the bottom of the column. The cadmium is collected as cadmium-zinc metal or as cadmium dust depending on how the process is operated.

2. Input Materials - Feed consists of sinter, coal or coke, and recycled material in the blue powder charge. In addition, since the charge must be either a hard sinter or briquette, temporary binder such as sulfite waste liquor, tar, or pitch is added. A typical composition is approximately 60 percent sinter, 25 percent bituminous coal, 5 percent anthracite fines, 10 percent plastic refractory clay, and 1 percent sulfite liquor (4). With zinc recovery typically 90 percent, about 2.8 metric tons of feed is required per metric ton of zinc collected in the condenser for a feed containing 40 percent by weight zinc. Quantities of coal or coke required range from 0.5 to 0.8 metric ton per metric ton of slab zinc produced (3).

3. Operating Conditions - Vertical reduction furnaces generally operate from 1300°to 1400°C (1). Internal pressures are slightly below ambient. Exact operating temperatures for fractional distillation or other purification steps vary, since separation is based on differences in boiling points.

4. Utilities - Heating is done in vertical retort furnaces by combustion of gas surrounding the retort side walls. One source estimates that 4,000 to 5,000 kilocalories per kilogram of zinc are required (6). Another source reports energy efficiency to be about 10 percent, with typical energy consumption 5.0 million kilocalories per metric ton of zinc produced. One company using vertical retorts finds that 9.1 million kilocalories of coal and coke per metric ton of zinc produced is required for the briquetting process. However, this company claims an energy consumption by retorts of only 2.8 million kilocalories per metric ton of distilled zinc, for a total energy consumption of 12.8 million kilocalories per metric ton (7). Energy requirements for refining are about 834,000 kilocalories per metric ton of zinc produced (8).

5. Waste Streams - Emissions are minor when compared with other steps in the smelting process such as roasting and sintering. SO_2 emissions average less than 50 ppm (9). Flow rate for the carrier gas is 23,000 cubic meters per metric ton of product, with 2.5 to 3.0 percent carbon dioxide (3).

Particulate emissions are evident only during charging for approximately one minute. High-efficiency metal recovery is possible from these metal and metal oxide fumes. Information on particulate emissions, including size distribution data is presented in Table 14. Blue powder is the principal constituent of these emissions along with cadmium, copper, chromium, lead, and iron.

The zinc and coke content of the feed and the air flow rates are the important process variables. Temperature is the most important process parameter.

The gas washing water contains zinc and metal oxides, possibly hydrocarbons, various particulates (as suspended solids), and the corresponding products of hydrolysis.

Residues are also generated in vertical retorting operations. Amounts produced are around 1050 kilograms per metric ton of zinc produced (3). The residues contain a variety of metals such as lead, copper, silver, gold, nickel, germanium, gallium, arsenic, antimony, cadmium, zinc, indium, silicon, iron, calcium, aluminum, magnesium, and manganese.

The germanium and gallium contents originally found in the blends are, in general, concentrated in the residues from the retorts. These residues can be treated by dissolution in caustic soda, followed by treatment by various methods, most important probably being the extraction of gallium chloride with an organic solvent. There are many variations on these methods to circumvent various impurity problems. This processing is not done at any of the primary zinc smelters. Two companies, one in Arkansas and one in Oklahoma, account for the total domestic production of gallium, using residues from zinc and aluminum production. One refinery in Oklahoma produced all the primary domestic germanium from zinc smelter residues in 1978 (11).

An analysis of some constituents in the residue from one vertical retort furnace is given in Table 15.

TABLE 14. UNCONTROLLED PARTICULATE EMISSIONS FROM A ZINC VERTICAL RETORTING FURNACE (10)

	Size	Cd	Pb	Zn	Cu	Total particulates
Emission factors (kg/metric ton zinc)	>2 μm	0.006	0.038	0.920	0.0006	2.11
	<2 μm	0.027	0.131	2.28	0.0004	5.04
	Total	0.033	0.169	3.20	0.001	7.15
Emission rates (kg/hr)	>2 μm	0.002	0.016	0.393	0.0002	0.890
	<2 μm	0.012	0.057	0.967	0.0002	2.14
	Total	0.014	0.073	1.36	0.0004	3.03

TABLE 15. ANALYSIS OF VERTICAL RETORT FURNACE RESIDUES (3)

Constituent	Concentration, ppm
Cadmium	850
Chromium	46
Copper	4,600
Lead	2,400
Zinc	107,000

Blue powder production amounts to only about 3 percent of the zinc charged, considerably less than in horizontal retorting (12). The residue also contains less zinc.

In the redistillation system, no zinc vapors can escape since it is a closed circuit. Solid residues can be reprocessed to recover zinc and other metals. Waste gases are produced by the combustion; their composition depends on the type of fuel used.

6. Control Technology - Wet scrubbers are the available control method for particulate emissions. All gases are exhausted from the furnace by means of a venturi scrubber. The carbon monoxide from the zinc condensation chamber is scrubbed with water sprays to remove entrained solids. The gas is then used as part of the fuel for heating the retorts. Metallic zinc and zinc oxide is recovered as blue powder residue from the scrubbing system and from the condenser during periodic cleaning. The blue powder is recycled.

Residues are either disposed of in open slag dumps or processed to recover their metal values. The best control technology for the slag dump is sealing the soil and routing runoff to a waste treatment lagoon.

7. EPA Source Classification Code - 3-03-030-05

8. References -

1. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

2. McMahon, A.D., et al. The U.S. Zinc Industry: A Historical Perspective. Bureau of Mines Information Circular 9629. United States Department of the Interior. 1974.

3. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II, Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

4. Field Surveillance and Enforcement Guide for Primary Metallurgical Industries. EPA-450/3-73-002. Office of Air and Water Programs, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1973.

5. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75/032. Effluent Guidelines Division Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

6. Restricting Emission of Dust and Sulfur Dioxide in Zinc Smelters. Association of the Metal Smelting and Refining Trade and Committee on Zinc of the German Ore Smelting and Mining Society VDI No. 2284. September 1961.

7. Battelle Columbus Laboratories. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-68-01-1518. Draft data.

8. Fejer, M.E., and D.H. Larson. Study of Industrial Uses of Energy Relative to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

9. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. EPA-450/2-74-002a. Office of Air and Waste Management. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

10. Jacko, Robert B., and David W. Neuendorf. Trace Metal Particulate Emission Test Results from a Number of Industrial and Municipal Point Sources. Journal of the Air Pollution Control Association. 27(10):989-994. October 1977.

11. Commodity Data Summaries 1979. U.S. Department of the Interior, Bureau of Mines. Washington, D.C. 1979.

12. Water Pollution Control in the Primary Nonferrous Metals Industry - Vol. 1, Copper, Zinc, and Lead Industries. EPA-R2-73-247a. Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. September 1973.

Electric Retorting

1. Function - Electric retorting is a continuous reduction/volatilization process in which electricity supplies the energy needed to produce high-purity zinc from zinc oxide by reduction with carbon at elevated temperatures in a vertical cylindrical retort. Vertical retorting (Process No. 9) is the other reduction method in use at zinc smelters. This newest zinc-smelting furnace was designed to overcome the difficulties involved in heating the charge externally. As in the other retorting process, carbon monoxide is used for direct reduction, producing zinc vapor. The carbon dioxide also produced in this reaction is regenerated with carbon. The carbon for reduction is provided by coke.

There are several variations on the resistance-type electric furnace available, including the electrothermic arc furnace (Sterling Process) and the Imperial Smelting Furnace. However, the only electric retorts in use in the United States are the electrothermic furnaces developed by St. Joe Minerals Corporation, which began commercial operation in 1930 (1).

The St. Joe electrothermic furnaces are basically vertical, refractory-lined cylinders. The largest furnaces now in use have an inside diameter of 1.5 meters and are 15 meters high, with a production capacity of about 90 metric tons per day (2). Graphite electrodes protrude into the shaft, and the reaction heat is generated from the resistance of the furnace charges to the current flow between the electrodes. Eight pairs of electrodes introduce power into the furnace. Each top electrode has a mate near the bottom.

Preheated coke and sinter, along with miscellaneous minor zinc-bearing products such as blue powder, are fed continuously into the top of the furnace from a rotary feeder. As in a vertical retort, gravity moves the charge downward through the shaft. Unlike other retorting processes, an unusually hard sinter is required to maintain strength and porosity in the tall columns, even after most of the zinc content has been removed. Silica is usually added to the sinter mix to increase its structural strength. The coke serves as the principal electrical conductor, carrying the alternating current between each top electrode and the bottom electrode on the opposite side. The heat developed provides the energy required for smelting. The zinc vapor and carbon monoxide produced pass from the main furnace to a vapor ring, which provides a free space around the periphery of the charge for removal of the gaseous mixture. The gas then goes to a condenser, where zinc is recovered by bubbling through a molten zinc bath. It was the development of this Weaton-Najarian vacuum condenser that first made possible the production of over 90 metric tons per day from a single unit. If necessary, further refining, such as the liquation and redistillation steps described for the other retorting processes, may be used.

The electrothermic furnace has a number of advantages over other processes. First, the increased thermal efficiency (compared with external heating methods) results in cost savings in fuel consumption. Larger quantities of charge can be treated, and the continuous operation is amenable to

automation. The furnace can readily process secondary zinc scrap and zinc residues. Because of special deleading by heat treatment in multiple-hearth roasters followed by desulfurization in fluidized-bed roasters, electrothermic furnaces emit practically no SO_2 or particulates.

2. Input Materials - The feed consists of sinter, coke, and recycled zinc-bearing products, such as blue powder. In addition, silica is usually added to increase structural strength. Particle size is controlled so as to provide coke particles larger than sinter, thereby concentrating larger coke at the axis of the furnace. In this way the maximum fraction of electric current is directed along the axis, which becomes the region of maximum temperature, minimizing both damage to the refractory walls by slagging and heat loss through the walls. Quantities of coke required range from 0.5 to 0.8 ton per ton of slab zinc produced (3).

3. Operating Conditions - The St. Joe electrothermic furnaces operate at atmospheric pressure. Internal temperatures are 1400°C and higher at the axis of the furnace, 1200°C in the main body of the charge, and 900°C near the wall. A vacuum of 15 to 25 centimeters mercury is applied to the outlet of the condenser, causing the vapor/gas mixture to be drawn through it in large bubbles (4). Water-cooled hairpin loops at the condenser cooling well maintain a constant batch temperature of 480° to 500°C (2). Temperatures for purification steps vary, since separation is based on differences in boiling points.

4. Utilities - Electrothermic furnaces use electricity to supply the energy for reduction. Current through each of the 30-centimeter diameter graphite electrodes may range as high as 800 amperes. A furnace contains eight individual single-phase circuits, each typically carrying 770 to 1190 kilowatts. The working range for such a circuit is 100 to 250 volts. The overall power factor of transformers, bus system, and furnaces is from 90 to slightly over 95 percent. One plant using electrothermic furnaces reported energy consumption averaging 2800 kilowatt-hours per metric ton of metal. Power input per electrode circuit ranging up to 1255 kilowatts, corresponding to a maximum of 10,000 kilowatts per furnace has been reported (5). Energy consumption for subsequent refining steps is the same as that used in other retorting processes.

Another source reports 25 to 30 percent energy efficiency for electrothermic retorting, with the process consuming about 2.8 million kilocalories per metric ton of zinc. With an additional 5.8 million kilocalories per metric ton of zinc consumed as coke, a total of 8.6 million kilocalories per metric ton of zinc is used. If the energy for electric generation is also considered (assuming 33 percent efficiency), total energy consumption increases to 14.2 million kilocalories per metric ton (6).

5. Waste Streams - As with other types of retorting, emissions are minor relative to those from roasting or sintering.

Particulate emissions consist primarily of metal and metal oxide fumes. Particulate emission levels for electrothermic retorting average about 10 kilograms per metric ton of zinc produced. As in the other retorting processes, blue powder is the principal constituent of these emissions, along with cadmium, copper, chromium, lead, and iron. Also as with the other processes, the important process variables are the zinc and coke content of the feed and the air flow rates. Temperature, which is controlled by regulating current flow to the electrodes, is the most important process parameter.

Temperature of the gases vented from the furnace vapor ring averages 850°C. Gas composition is approximately 45 percent zinc vapor and 45 percent carbon monoxide; the balance is nitrogen, carbon dioxide, and hydrogen (5).

The gas washing water contains the same impurities as in vertical retorting.

The residues generated during electrothermic reduction are similar in composition and quantity to those from the other retorting processes. Germanium and gallium are extracted from the residues by various methods at other facilities.

Waste streams from further purification steps such as liquation and redistillation are the same as described for vertical retorting.

6. Control Technology - High-velocity-impingment-type scrubbers are used to clean gases from the condenser. The clean gas, containing 80 percent carbon monoxide and having a heating value of 2200 kilocalories per cubic meter, furnishes fuel for smelter use (5). Some blue powder or uncondensed zinc and zinc oxide is later recovered by settling the scrubber slurry in ponds. The solids (75 to 80 percent zinc) are dried and briquetted for furnace feed.

Residue is removed from the furnace, preferably as discrete solid particles. It goes to a reclamation plant, where residual coke and some unreacted zinc are recovered and recycled. Besides permitting recovery of residue containing enough zinc and carbon to make retreatment worthwhile, a minimum of power is consumed in unproductive melting of residue. At the reclamation plant, where sand may be added to make a hard sinter, sufficient ferrosilicon is present in some residues to warrant recovery as a by-product.

7. EPA Source Classification Code - None

8. References -

1. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. EPA-450/2-74-002a. Office of Air and Waste Management, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

2. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75/032. Effluent Guidelines Division Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

3. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II, Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

4. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Volume 22. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

5. Lund, R.E., et al. Josephtown Electrothermic Zinc Smelter of St. Joe Minerals Corporation. AIME Symposium on Lead and Zinc, Vol. II. 1970.

6. Fejer, M.E., and Larson, D.H. Study of Industrial Uses of Energy Relative to Environmental Effects. EPA-450/3-74-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. July 1974.

Oxidizing Furnace

1. Function - In the direct, or American, process for zinc oxide production, zinc vapor from sintering is immediately oxidized without being condensed. As with zinc metal production, zinc must first be produced in vapor form. Only the direct method of producing zinc oxide is discussed because other production methods, such as the French process, start with slab zinc, the major product of the primary zinc industry.

The three types of furnaces used for this purpose in the U.S. are the grate-type furnace, the rotary or Waelz kiln, and the electrothermic furnace. In all three, the feed is reduced to form zinc vapor and subsequently the vapor is oxidized and the product collected. Two of the main difficulties in producing zinc metal, dilution of the zinc vapor and reoxidation by carbon dioxide, are desirable in the production of zinc oxide.

In grate-type furnaces, the coal-sinter feed (usually as briquettes) is spread over grates (traveling or stationary). Coal is spread first and ignited, then the sinter is deposited on top of the fuel layer. Air is forced through the bed to support combustion and furnish a reducing atmosphere to liberate the zinc vapors. The zinc vapors are then ducted to a combustion chamber, where oxidation occurs and the zinc oxide product is formed.

The Waelz kiln is a large diameter, long rotary kiln that can be used for production of pure zinc oxide, although it is more commonly used for pyrometallurgical concentration of residues of a rather mixed character. Zinc-bearing material and solid fuel are continuously fed to the kiln, which typically rotates 1 to 1.5 rpm (1). The additional heat for reduction of the zinc is supplied by the flow of gaseous fuel through the kiln. The vaporized zinc then is ducted to a combustion chamber, where air is admitted and the vapor burned to form zinc oxide. Temperature control is very important, since intimate contact must be maintained between the solid, zinc-bearing part of the charge, the solid fuel in the charge, and the reducing atmosphere.

The St. Joe vertical electrothermic furnace may be modified for use as either a metal or an oxide producer (2). Instead of a large "vapor ring" or bulge in the furnace barrel midway between the upper and lower electrodes, the oxide furnace has openings at four levels between the electrodes, through which evolved zinc vapor and carbon monoxide exit the charge. Preheated coke and zinc-bearing sinter are continously fed to the furnace. Coke serves as the principal electrical conductor. Electricity introduced through the electrodes develops the heat energy required for smelting. Further details on the electrothermic furnace are given in Process No. 9.

Analysis of an American process zinc oxide from one plant is presented in Table 16.

TABLE 16. ZINC OXIDE IMPURITIES AND BRIGHTNESS (2)

Lead as PbO	0.009%
Cadmium as CdO	0.010%
Iron as Fe_2O_3	0.015%
Manganese as MnO	0.002%
+325 mesh screen residue	<0.03%
Brightness; Hunter D-40	93.0 for large sizes 91.0 for fine sizes

The zinc oxide is filtered from the carrier gases in bag collectors. Soft zinc oxide pellets may be formed by squeezing the oxide between two rubber rolls to form pellet nuclei.

2. Input Materials - The mix for a grate-type furnace is typically 50 percent sinter briquettes and 50 percent coal (1). The preferred type of coal is a fine-sized anthracite, used to minimize contamination of the vapor stream with soot and to prevent caking and slagging.

For the rotary kiln, the mix is usually 65 to 75 percent zinc-bearing material and the remainder crushed coal or anthracite (to give about 25 percent carbon in the charge) plus a small amount of sand to stiffen the bed, if desired (1).

The principal feed to the electrothermic furnace also consists of sinter and coke, but as much as 25 percent of the total zinc input is other zinc-bearing materials. Nominal coke rate is 44 percent of the weight of sinter (roughly equal volumes of coke and sinter) and approximately 300 percent of the stoichiometric carbon relative to the zinc in the sinter. Other zinc-bearing materials are fed in the form of almond-shaped briquettes, granules, 8 by 25 millimeter metallic screenings, and slab dross (2). High product purity is achieved by using low-volatility cokes and sinter that is low in impurities.

3. Operating Conditions - The grate-type furnace and rotary kiln operate at atmospheric pressures. Temperatures in the grate-type bed are reported to range from 1000° to 1950°C (1); operating temperatures for the rotary kilns are about 1300°C.

Electrothermic furnaces also operate at atmospheric pressures. Operating conditions are the same as in electrothermic furnaces for zinc metal production, with temperatures of 1200°C at the vapor ring elevation, 1400°C in the main smelting zone, 900°C near the walls, and 1300°C at the bottom electrode elevation (1). Further details on operating conditions of electrothermic furnaces are given in Process No. 9.

4. Utilities - No information is available regarding heat input per unit of product output for grate-type or rotary kiln processes. The bed is ignited by residual heat from the previous charge in grate-type furnaces, and gaseous fuel supplies the heat for reduction in rotary kilns. Air is added in all three furnaces in unspecified quantities.

The main factor influencing production in electrothermic furnaces is the quantity of electricity introduced. Josephtown's largest furnace operates at 10,000 kilowatts. Energy consumption averages 2800 kilowatt-hours per metric ton of metal (2).

5. Waste Streams - Combustion products and some zinc oxide are emitted from all three furnaces; again, quantities are unspecified.

There are no liquid wastes from the process.

A solid residue is produced, estimated at 350 kilograms per metric ton of zinc oxide. This residue contains approximately 6.2 percent zinc and 0.09 percent of other metals such as cadmium, chromium, copper, and lead (3). It may also contain slag, coke, and globules of ferrosilicon. One analysis of waste samples from oxide furnace residue revealed concentrations presented in Table 17.

TABLE 17. SELECTED CONSTITUENTS OF OXIDIZING FURNACE RESIDUE (3)

Constituent	Concentration, ppm
Cadmium	10
Chromium	17
Copper	810
Lead	68
Zinc	62,000

Further details on waste streams from electrothermic furnaces are given in Process No. 9.

6. Control Technology - Control techniques for direct zinc oxide processes are similar to those used in other reduction operations. Further details are given in Process No's. 7, 8, and 9. Uncondensed zinc (blue powder) in gases from the condenser is recovered by settling the water slurry in ponds. Solids can be dried and briquetted for furnace feed.

7. EPA Source Classification Code - None

8. References -

1. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

2. Lund, R.E., et al. Josephtown Electrothermic Zinc Smelter of St. Joe Minerals Corp. AIME Symposium on Lead and Zinc. Volume II. 1970.

3. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II, Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

Leaching

1. Function - Electrolytic production of zinc is an alternative to pyrometallurgical processing. The first step is to separate zinc from gangue minerals by leaching roasted calcine in recycled electrolyte solution. The zinc dissolves, and the insoluble gangue is separated from the solution by decantation, thickening, and filtration. The solution is purified (Process No. 12) and the waste solids are either discarded or, if their concentration warrants, further processed to recover lead and precious metals (1,2).

Two general leaching methods can be employed, described as either a single or a double leach. In a single leach, recycled electrolyte, which is a solution containing principally sulfuric acid, is brought only once into contact with the calcine. Zinc oxide in the calcine reacts with sulfuric acid to form soluble zinc sulfate and water. The single leach is not often practiced, however, since losses of sulfuric acid are excessive and recovery of zinc is poor.

Double leaching is used most often. In several variations, the calcine is leached first in a solution that is neutral or slightly alkaline, then in an acidic solution, with the liquid passing countercurrently to the flow of calcine. In the neutral leach, the readily soluble sulfates from the calcine dissolve, but only a portion of the zinc oxide enters into solution. The second acidic leach solubilizes the remainder of the zinc oxide, but also dissolves many impurities, especially iron. Recycle of the liquor to the first neutral stage causes much of the iron to reprecipitate, so the neutral leach acts also as an initial stage of solution purification. In some of the more complex process variations, considerable overlap occurs between leaching and purification steps, and the calcine may be subjected to as many as four leaching operations in progressively stronger or hotter acids to bring as much of the zinc as possible into solution.

The leaching process is conducted most often in a series of agitated tanks. Batch operation is common, since it is thereby possible to compensate for variations in calcine composition. A few smelters, especially those processing ore of consistent quality, are equipped with continuous leaching equipment. In all of the leaching operations, the pH, temperature, and solution composition at each step are carefully regulated.

2. Input Materials - The principal input to the leaching process is calcined zinc concentrate from roasting (Process No's. 4, 5, and 6). If a pelletized feed is used in the roaster, the calcine must be ground prior to leaching. Air classification and grinding is occasionally practiced also with unpelletized material. One foreign plant grinds calcine to 95 percent through a 200-micron screen (about 70 mesh) (3). Wet grinding with a portion of the leach liquor is also practiced in some smelters.

The only other input specific to the leaching process is recycled spent electrolyte from Process No. 13, containing about 200 grams of sulfuric acid per liter (2).

3. Operating Conditions - Batch leaching processes usually operate at atmospheric pressure, whereas continuous processes may include pressurized steps up to 2.5 kilograms per square centimeter (1). Most leach operations take place around 50°C; exothermic chemical reactions maintain this temperature without requiring additional heat energy. Some hot acid process variations may employ temperatures up to 90°C(3).

4. Utilities - Electricity is required for pumping the solution and conveying the calcine and final residue. No estimates of energy consumption for the leaching process are given. In batch leaching, air at about 6.3 kilograms per square centimeter must be available to clear out accumulating deposits of coarse material at the bottom of the tanks. In continuous leaching, it is seldom necessary to use air at pressures higher than the normal operating pressure of 1.4 to 2.5 kilograms per square centimeter (1). Continuous leaching requires a larger total volume of air per tank, because agitation must be continuous. During agitation in either process, consumption ranges from 2.8 to 4.2 cubic meters of air per minute (1).

5. Waste Streams - As in the closely associated purification process, emissions of acid mist occur from the leach tanks. This waste is described more completely in Process No. 12.

Leach solution may be cooled in open towers, as described for electrolyte cooling in Process No. 13. Atmospheric mist may therefore be created from these towers, as described in connection with the electrolysis process.

Except for leaks and spills, no liquid waste is produced from this process.

After all leaching, the solid residue is filtered from solution and the filter cake is rinsed with fresh water. This cake will contain all the lead originally present in the concentrate, and also other acid-insoluble trace elements such as indium, gold, and the platinum-group metals. Other minerals present will be silica, alumina, and silicates of iron, aluminum, and calcium. The quantity and composition will vary with the characteristics of the ore concentrate; one measurement reports a quantity of 360 kilograms per metric ton of zinc produced (1).

6. Control Technology - Control of acid mist emissions is described in connection with the similar mists produced in Process Nos. 12 and 13.

The solid residue will frequently be sent to a lead smelter for recovery of the lead and other reclaimable elements. Alternatively, the residue may be batch-treated at the zinc smelter with cyanide for recovery of gold. In other cases, the concentrations of recoverable metals may be so small that the residue will be discarded in a dump. Ore residue from a double leach process should be inert; however, as generally practiced, the residue will also contain trace elements from Process No. 12. Single leach residues may also contain zinc oxide or zinc ferrites. The potential of this waste for secondary water pollution is unreported.

7. EPA Source Classification Code - None.

8. References -

1. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc., New York. 1967.

2. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75-032. Effluent Guidelines Division, Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

3. E. Van Den Neste. Metallurgie Hoboken-Overpelt's Zinc Electrowinning Plant. CIM Bulletin. August 1977.

Purifying

1. Function - The leaching of zinc calcine causes other elements in addition to zinc to dissolve. Unless impurities are removed from the solution, they will either contaminate the zinc product or interfere with the proper operation of the electrolysis process. The solution from leaching is therefore purified to remove metallic ions that are more electropositive than zinc.

Purification is usually conducted in large agitated tanks. A variety of reagents is added in a sequence of steps that causes impurities to precipitate. The precipitates are separated from the solution by filtration. The purification techniques are among the most advanced applications of inorganic solution chemistry in industrial use, and vary from one smelter to another. Iron is often removed in conjunction with the leaching process (Process No. 12) by precipitation as a hydrated oxide (goethite) or a complex sulfate (jarosite). Some of these processes, which are patented, also reduce the concentration of arsenic and other elements. Almost all smelters then add zinc dust, often in the form of "blue powder" from the pyrometallurgical production of zinc. This addition causes a cementation reaction that precipitates cadmium, copper, and several other elements. The final steps remove all but trace quantities of a group of metals that includes arsenic, antimony, cobalt, germanium, nickel, and thallium. These metals severely interfere with electrolytic deposition of zinc, and their final dissolved concentrations are limited usually to less than 0.05 milligram per liter.

2. Input Materials - The principal input is the filtered, acidic, mineral-rich solution from Process No. 12. Reagents are mostly inorganic, primarily finely divided metals such as zinc, arsenic, and antimony. Fresh sulfuric acid may be added in small quantities, and lime may be used to remove excess sodium carbonate or sodium hydroxide may be used for iron precipitation. Organic materials such as 1-nitroso-2-naphthol may be used to remove cobalt (1). Inorganic salts such as copper sulfate may be added to catalyze or promote some precipitation reactions. Except for zinc dust, the quantities of these additives are small.

3. Operating Conditions - The purification process takes place at temperatures ranging from 40° to 85°C, and pressures ranging from atmospheric to 2.5 kilograms per square centimeter (2). The conditions at each step of precipitation are carefully regulated.

4. Utilities - Electricity is required to pump solutions and drive equipment agitators. Steam and noncontact cooling water may be used to heat and cool solutions. Quantities are not reported.

5. Waste Streams - The atmospheric emission from this process consists of a mist that develops from the ventilation of the leach and purification tanks. Ventilation is necessary since side reactions can cause evolution of small quantities of explosive hydrogen gas which must not be allowed to accumulate. The mist contains sulfuric acid and smaller quantities of zinc, calcium, and

arsenic (3). There is no estimate of the quantity of waste products released from this source.

Except for leaks and spills, no liquid waste is created by this process.

Precipitated solids consisting of impurity elements and excess reagent metals are accumulated as cakes from pressure filters. The composition of the cakes is variable, depending on the characteristics of the zinc concentrates and the details of the processing. All are highly metalliferous.

In some process modifications, much of the iron, and part of the arsenic and antimony originally present in the concentrate, are precipitated into and discarded with the insoluble residue from Process No. 12.

6. Control Technology - Ventilation of leach and purification tanks is usually controlled with impingement or centrifugal demisting equipment. The efficiency of these devices in this service has not been reported.

The disposition of most of the solid residues has also not been reported. With some zinc concentrates, a filter cake rich in copper is produced which is sold to copper smelters. Some residues are recycled to the roaster or leach tanks, or are separately treated to reclaim zinc and cadmium. Two companies are reported to have refined indium from some of the residues (4). Filter cakes rich in cobalt are apparently being stockpiled by a foreign refinery, and similar disposition may be practiced by some U.S. refineries (2). It is not known whether any of these materials are being discarded.

7. EPA Source Classification Code - None.

8. References:

1. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

2. E. Van DenNeste Metallurie-Hoboken-Overpelt's Zinc Electrowinning Plant. CIM Bulletin. August 1977.

3. Privileged communication, EPA files.

4. Commodity Data Summaries 1979. U.S. Department of Interior, Bureau of Mines. Washington, D.C. 1979.

Electrolysis

1. Function - In electrolysis, metallic zinc is recovered from the purified solution by passing current through an electrolyte solution, causing zinc metal to deposit on a cathode. Electrolysis takes place in rectangular tanks, or cells, each of which holds a number of closely spaced rectangular metal plates. Alternate plates are made of lead containing 0.75 to 1.0 percent silver; these are the anodes that are electrically connected to a positive potential. The remaining plates are made of aluminum, and are connected with a negative electrical potential. Purified electrolyte from Process No. 13 is circulated slowly through the cells, and water in the electrolyte dissociates, releasing oxygen gas at the anode. Electrode voltage is maintained sufficiently high so hydrogen is not released at the cathode; instead, zinc ions absorb electrons and deposit zinc metal. Hydrogen ions remain in solution, and thereby regenerate sulfuric acid for recycle to the leach process (1,2).

Zinc smelters contain a large number of electrolytic cells, often several hundred. They are most often made of concrete with a lead, plastic, or vitreous lining, and are electrically connected in series banks. A portion of the electrical energy is converted into heat, which increases the temperature of the electrolyte. Therefore, a portion of the electrolyte is continuously circulated through cooling towers. These are usually open towers, in which the electrolyte falls through a rising stream of air drawn through the tower by fans. This method both cools the electrolyte and evaporates the excess water (3). The cooled and concentrated electrolyte is repumped to the cells.

Every 24 to 48 hours, each cell is shut down and the zinc-coated cathodes are removed, rinsed, and the zinc is mechanically stripped from the aluminum plates. Stripping is accomplished manually in some smelters, while others use specialized automated equipment. The aluminum cathodes are then chemically cleaned, replaced in the cells, and the cell is restored to normal operation. Stripped zinc is sent to Process No. 15 for melting and casting.

2. Input Materials - The principal input is purified electrolyte, which is a water solution containing about 70 grams of zinc per liter and about 200 grams of sulfuric acid per liter (4). Barium hydroxide or manganese sulfate may be added to the electrolyte in order to form insoluble coatings on the cell anodes, thereby minimizing both anode corrosion and lead contamination of product zinc. Colloidal materials are also usually added to prevent uneven deposition of zinc on the cathodes; materials used include glue, goulac, gum arabic, and a mixture of agar-agar, sodium silicate, and cresylic acid (2).

3. Operating Conditions - Electrolytic cells operate at 30° to 35°C and atmospheric pressure (4).

4. Utilities - Electrolysis consumes the major amount of energy in an electrolytic zinc smelter. Most plants use direct current at a current density of about 600 amperes per square meter of cathode surface. Voltage drop is 3.3 to 3.5 volts per cell, and current efficiency is 85 to 94 percent. Approximately 3300 kilowatt-hours of power are needed to electrolyze a metric ton of cathode zinc (4).

Electricity in much smaller quantity is used to operate pumps and fans.

5. Waste Streams - There are two sources of atmospheric emissions from this process. Escape of oxygen at the cell anodes causes the formation of a mist of approximately the same composition as the electrolyte that escapes into the air of the cell room. Another mist of the same approximate composition is released from the atmospheric cooling towers. Cell emission has been estimated to be 3.3 kilograms per ton of zinc produced (1). No estimate of cooling tower emissions has been reported.

If the ore concentrate contains quantities of sodium or halogen compounds, a portion of spent electrolyte must be routinely removed and discarded. This is not known to be occurring regularly in U.S. smelters. In general, there is no loss of electrolyte or other liquid waste other than leaks and spills.

A sludge accumulates in the cells which is periodically removed. Table 18 provides reported analyses of this material.

TABLE 18. ANALYSES OF ANODE SLUDGES FROM ELECTROLYTIC ZINC REFINING (5).

	Concentration, ppm				
	Cd	Cr	Cu	Pb	Zn
Fresh anode sludge	12	10	85	170,000	12,800
Old anode sludge (from dump)	1,400	8	1,900	89,000	39,200

6. Control Technology - Cell rooms must be well ventilated to avoid accumulation of oxygen. This ventilation also serves to remove mist from the room. There are no reports of treatment being applied to this air stream, although this is apparently the largest source of air pollution from the electrolytic process (6).

Treatment of mist from the electrolyte cooling towers is also not documented. An opinion has been expressed that the concentration of these emissions is so diluted by the large volumes of air that it is not a nuisance to nearby residents (3).

Disposition of anode sludge is also unreported. The material is a rich source of recoverable minerals, and is probably reprocessed or recycled, as are the filter cakes from Process No. 13.

7. EPA Source Classification Code - 3-03-030-06.

8. References -

1. Background Information for New Source Performance Standards: Primary Copper, Lead, and Zinc Smelters. EPA-405/2-74-002a. Office of

Air and Waste Management, U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. October 1974.

2. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

3. E. Van DenNeste. Metallurie-Hoboken-Overpelt's Zinc Electrowinning Plant. CIM Bulletin. August 1977.

4. Krupkowa, D., and A. Udrycki. New Electrolytic Zinc Plants. Chemical Age of India. August 1975.

5. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II, Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

6. Privileged communication, EPA files.

Melting and Casting

1. Function - The process involves melting and casting the zinc from an electrolytic or pyrolytic plant into a marketable form. Pyrolytic zinc is usually in a molten state whereas electrolytic stripped zinc sheets must always be melted. Recent practice utilizes induction heating, possibly combined with a gas-fired furnace. The molten zinc is cast into 27-kilogram slabs on an in-line casting machine. Some zinc is cast into 640- to 1100-kilogram blocks in stationary molds (1).

Cathode zinc sheets from electrolytic plants are dried, melted, and cast into various forms of slab zinc. Alloys of zinc are also prepared and cast. Depending on market conditions, lead and other constituents may be added to a relatively high grade of zinc to make a select grade for galvanizing. Zinc dust is made at the plants for use in purification of solutions.

Because molten zinc exhibits a strong tendency to form dross, ammonium chloride flux is usually added to the melting furnace to retard oxidation at the surface and to collect any oxides formed. Ordinary slab zinc can be melted in a reverberatory furnace with the formation of 1 percent or less of dross; electrolytic cathodes lose 6 to 17 percent under these circumstances, depending on the presence of glue, cobalt, and the like in the electrolyte (1).

2. Input Materials - Inputs are zinc, ammonium chloride flux, and various alloying materials to meet special requirements. Quantities are not specified.

3. Operating Conditions - Melting and casting are at atmospheric pressure. Zinc must be heated above its melting point (420°C) to form liquid zinc.

4. Utilities - Gas- or oil-fired melting pots are used for melting zinc. Heat requirements are not specified. Water is used in some plants to cool the molds rapidly, but usually does not come into contact with the metal.

5. Waste Streams - Some zinc oxides and chloride compounds are emitted by the melting pots into the atmosphere; quantities are not given. To achieve high overall melting efficiency, dross is skimmed from the melting pot so that the globules of metal may be separated from thin oxide shells.

Casting cooling water generally contains suspended solids and oil and grease in the form of metal oxides, mold washes, and lubricants from casting equipment.

The only solid waste is the dross produced if the slab zinc is melted in an electrolytic furnace.

6. Control Technology - Control of atmospheric emissions is with scrubbers or fabric filters. Any processing to recover the zinc values from the control residue must deal with its chloride content. In electrolytic plants the reaction is very sensitive to the deleterious effects of chloride.

The dross is treated by liquation, centrifugal separation of metal, fluxing, etc. Recovered metal may be used to make zinc dust for electrolytic purification or it may be returned to the melting pots.

7. EPA Source Classification Code - None

8. References -

1. Schlechten, A.W., and A. Paul Thompson. Zinc and Zinc Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

Cadmium Leaching

1. Function - Leaching selectively dissolves as much cadmium as possible from various cadmium-bearing dusts, fumes, and sludges from primary zinc plants, precipitating lead and other impurities without precipitating any of the dissolved cadmium. There is no separate primary cadmium industry in the United States. Cadmium recovery processes use by-products of other operations, all involving zinc, in four major categories (1):

(1) Fumes and dusts from roasting and sintering of zinc concentrates.

(2) Recycled zinc metal containing cadmium.

(3) Dusts from smelting of lead-zinc or copper-lead-zinc ores.

(4) Purification sludge from electrolytic zinc plants.

The first and fourth of these categories are of concern here, since they provide the inputs to the leaching process. The second category involves recycled zinc metal, and is not relevant here; cadmium-bearing dusts from lead and copper smelting, the third category above, are sent directly to cadmium purification, Process No. 18.

During sintering, cadmium, lead, and thallium chlorides form and are drawn off as a fume to be recovered in ESP's. After collection, the fumes and dusts are leached with dilute sulfuric acid and sodium chlorate to ensure complete dissolution of cadmium sulfide. Cadmium goes into solution by the following reaction:

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2O$$

Sodium chlorate is a strong oxidizing agent, added to prevent reduction of any sulfur to sulfide and to prevent reprecipitation of cadmium or thallium as sulfides. Cadmium and lead are converted to sulfates and chlorides. The cadmium compounds remain in solution, but lead is almost completely converted to insoluble lead sulfate. This is filtered out and sent to lead recovery together with other insoluble materials such as quartz and silicates. The lead residue may contain small but significant quantities of gold, silver, and indium (2). More sulfuric acid is then added to the solution in order to bring the concentration up to 10 percent and to raise the temperature.

Instead of a direct leach with sulfuric acid, in at least one plant the dust is first roasted and then water leached. The sinter fume is heat-treated in a four-hearth roaster, which selectively sulfates the cadmium and makes about 90 percent of it water-soluble. The water leach that follows produces relatively pure cadmium solutions containing about 40 grams per liter cadmium and 10 grams per liter zinc. Addition of sodium bichromate to this solution removes about 90 percent of the soluble lead. The residual solids are batch treated with scrubber liquor and concentrated acid (3).

Another element in the flue dusts from roasting and sintering that is economically recoverable is thallium; this processing is not done at primary zinc smelters. One refiner in Colorado is the sole domestic producer of thallium (4).

Another source of high-cadmium residues for leaching is electrolytic zinc processing. In the purification stage, both copper and cadmium are eliminated from solution by treating the electrolyte with powdered zinc. Generally this is done in stages making possible rough separations such as high-copper and high-cadmium precipitates. Copper sulfate and arsenic trioxide may be added during these stages. The cadmium precipitate is high in zinc and contains virtually all the cadmium originally present in the electrolyte. This purification sludge constitutes the raw material for the cadmium plant. It is oxidized, either by allowing it to stand exposed to air or on a steaming platform. The acid-soluble cadmium is leached out by sulfuric acid and spent electrolyte. Filtration to remove insoluble copper may follow.

2. Input Materials - The fumes and dusts from roasting and sintering processes and the purification sludge from electrolytic plants are the primary inputs to leaching. Copper sulfate and arsenic trioxide may be added during preleaching purification stages. Dilute sulfuric acid and/or spent electrolyte are the leaching agents. The electrolyte contains 200 grams per liter sulfuric acid and 65 grams per liter zinc. Sodium chlorate is added to serve as an oxidizing agent, and in some plants water is used to leach the fumes and dusts. The residual solids from water leaching are batch-treated with scrubber liquor bolstered with concentrated acid. Sodium bichromate may be added to remove soluble lead; one plant reported using 7.5 grams per kilogram of cadmium product. Sixty-five grams of caustic per kilogram of cadmium produced are added (3). Quantities for other inputs are not specified.

3. Operating Conditions - Cadmium leaching takes place at atmospheric pressure. A temperature of 80°C is reached after the final addition of sulfuric acid (1).

4. Utilities - Electricity in unspecified quantities is used to pump liquids. The water leaching process requires 1.3 cubic meters of natural gas per kilogram of cadmium product to roast the dust, followed by the addition of an unspecified quantity of water (3).

5. Waste Streams - No data were found on the quantities of residuals from acid leaching, but they are probably very small. Typical analysis of this residue at one plant is 32 percent lead, 8 percent zinc, 0.7 percent cadmium, 0.13 percent indium, 0.45 percent arsenic, 0.30 percent copper, 0.23 percent silver, and 4 grams per metric ton gold. The residue may also contain other insolubles such as quartz and silicates (3). Water vapor is released from purification and leacning. An exhaust gas temperature of 60°C from leaching was reported at one electrolytic plant, which also reported exhaust gases from preleaching purification stages ranging from 60 to 90°C (3).

6. Control Technology - Lead sulfate is filtered out from the solution along with other insolubles. All residues are recycled. They are typically high in lead content and are sent to a lead recovery plant.

7. EPA Classification Code - None

8. References -

1. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II, Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

2. Howe, H.E. Cadmium and Cadmium Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

3. Battelle Columbus Laboratories. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-68-01-1518. Draft data.

4. Commodity Data Summaries 1977. U.S. Department of Interior, Bureau of Mines. Washington, D.C. 1977.

Cadmium Precipitation

1. Function - The purpose of precipitation is to treat the cadmium-zinc sulfate solution from the leaching process with zinc dust to precipitate cadmium as a metallic sponge and then to separate it from most of the zinc dust while the solution is agitated. To avoid excess zinc contamination, usually only 90 to 95 percent of the cadmium in solution is precipitated. The initial cementation with zinc dust may result in a liquor containing a residual 0.2 gram per liter of cadmium and 30 to 40 grams per liter of zinc. To further decrease overall cadmium discharge, the stripped liquor is heated to 40°C and recemented with 1.6 times the stoichiometric amount of zinc to reduce the liquor to 0.04 gram per liter of cadmium and 30 to 40 grams per liter of zinc (1).

The cadmium sponge is then filter-pressed. It contains about 69 percent cadmium, 30 percent moisture, and small amounts of lead and zinc (2). It is steam dried or dewatered in a centrifuge. The solution from filtration, containing practically all of the zinc added and about 10 percent of the cadmium as chlorides and sulfates, is returned to the sintering operation.

For cadmium production at electrolytic plants, the leach liquor is first filtered to remove insoluble copper introduced from the electrolyte. The filtrate is then precipitated with zinc dust in two or three stages to minimize zinc concentration in the cadmium sponge. Strontium carbonate may be added in one of these stages. The sponge will contain about 80 percent cadmium and less than 5 percent zinc. Because the electrolysis step that follows is not highly sensitive to the presence of impurities, the purification step with zinc dust is usually adequate. If further purification is desirable, cobalt may be precipitated with nitroso-2-naphthol or potassium xanthate, and thallium precipitated with potassium chromate or dichromate. The sponge is then oxidized again by steam drying to enhance the solubility of cadmium and is leached in spent electrolyte and filtered. The filtrate contains about 200 grams per liter of cadmium as sulfate and is ready for introduction into the electrolytic cells (1).

2. Input Materials - The cadmium-zinc sulfate solution from leaching and zinc dust are the principal inputs to precipitation. Strontium carbonate may be added during purification in electrolytic processing. Impurities may be removed by the addition of nitroso-2-naphthol, potassium xanthate, and potassium chromate or dichromate. Quantities for these inputs are not specified.

3. Operating Conditions - Precipitation takes place at atmospheric pressure. Temperatures range from ambient to 40°C (1).

4. Utilities - Electricity is used to pump liquids, and natural gas or oil is used to heat the stripped liquor. Quantities are not cited.

5. Waste Streams - Water vapor is released from both purification and precipitation operations at temperatures ranging from 45° to 60°C.

The filtration solution from this process contains almost all of the zinc added as well as about 10 percent of the cadmium as chlorides and sulfates (2). The purification precipitates may contain arsenic and mercury, both of which are relatively low in concentration in ores and concentrates. One plant reported that a materials balance established 8 ppm mercury and 23,000 ppm arsenic in an iron precipitate from the cadmium process, the only place where significant concentrations were found (3).

6. Control Technology - Much of the residual zinc and cadmium in the filtration solution can be precipitated by lime treatment. It has been shown that freshly precipitated cadmium hydroxide leaves approximately 1 milligram per liter of cadmium in solution at pH 8; this is reduced to 0.1 milligram per liter at pH 10. Even lower values of 0.002 milligram per liter have been shown at pH 11 (2). Evidence has been presented that high levels of iron are beneficial for removal of cadmium during lime precipitation. The resultant light slurry goes to settling ponds, where the solids can be retained for recycling. At one plant the slurry is mixed with the neutralized roaster scrubber liquor before being sent to a series of settling ponds.

7. EPA Source Classification Code - None

8. References -

1. Howe, H.E. Cadmium and Cadmium Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

2. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II. Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

3. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA-440/1-75/032. Effluent Guidelines Division Office of Water and Hazardous Materials. U.S. Environmental Protection Agency. Washington, D.C. November 1974.

Cadmium Purification and Casting

1. Function - The purification and casting step purifies the cadmium sponge by melting it with a caustic flux, with distillation and perhaps redistillation, or by redissolving the sponge with sulfuric acid and collecting the cadmium by electrolysis.

In pyrometallurgical processing, the dried cadmium sponge is first mixed with coal or coke and lime. It is then transferred to a conventional horizontal-type retort, where the cadmium is reduced and collected as molten metal in a condenser. Occasionally, for ultra-purity, the metal is distilled in graphite retorts. Thallium is removed by treatment with zinc ammonium chloride or sodium dichromate. The metal may then be cast into a marketable form or further purified by redistillation. Typical impurities in the product cadmium are 0.01 percent zinc, 0.003 percent copper, 0.015 percent lead, less than 0.001 percent thallium, less than 0.0005 percent tin, and less than 0.001 percent antimony (1). Cadmium recovery has been reported as 94 percent from the feed to the leach plant and 67 percent from the zinc concentrates.

Electrolytic processing of cadmium is carried out in banks of cells similar to zinc cells. The sponge is first dissolved in dilute sulfuric acid (return electrolyte). The anodes are lead. The cathodes of cadmium are 97 percent pure and represent 90 to 95 percent total recovery of cadmium from ore to metal. Recovery in the electrolytic step is 96 percent from the cadmium sponge. The stripped cathode metal is washed, dried, and melted under a flux, such as caustic or rosin, and cast into various shapes. Total depletion of cadmium from the solution is not carried out. When the ratio of the thallium to cadmium sulfate in the electrolyte reaches 1:10, the cadmium cathodes must be removed and replaced with new insoluble cathodes. Continuing electrolysis deposits an alloy containing 5 to 20 percent thallium. These cathodes are then leached with steam and water to separate thallium into the filtrate, leaving cadmium as a residue. Small amounts of cadmium in solution are precipitated with sodium bicarbonate. Thallium is precipitated with hydrogen sulfide, then dissolved in sulfuric acid. This sulfate solution can be electrolyzed for recovery of pure sponge thallium. The sponge is washed, pressed into blocks, melted, and cast.

Processing of concentrated lead smelter baghouse dust in an electrolytic cadmium plant is similar to processing of cadmium sponge. Since the dust is generally higher in impurities than the sponge, some additional purification is necessary. The dust is mixed with sulfuric acid and water to form a paste, then calcined to a sulfated cake which is crushed and agitated with spent electrolyte. Milk of lime may be added to neutralize the solution, and sodium sulfide or impure cadmium sulfide is added to precipitate copper and other metal impurities. After filtration to remove a lead cake, an agent such as sodium chlorate oxidizes the iron and lime precipitates iron and arsenic. Heating ensures complete precipitation. Precipitated thallium chromate or dichromate is filtered off after the addition of a soluble chromate or dichromate. Excess chromate remaining may be reduced by sodium sulfide and precipitated by neutralizing with caustic. The filtered solution

is fed to the electrolytic plant. Where chlorine is present, irons high in silicon are used as anodes instead of lead. The finished cathodes are melted and cast (2).

2. Input Materials - Cadmium sponge from precipitation or lead smelter baghouse dust are the principal inputs to purification and casting. In pyrometallurgical processing, coal or coke and lime or sodium hydroxide are added, and zinc ammonium chloride or sodium dichromate is used to remove thallium. One plant reported using 65 grams of caustic per kilogram of cadmium. In electrolytic processing, dilute sulfuric acid or return electrolyte, a flux such as caustic or rosin, water, sodium bicarbonate, and hydrogen sulfide are the inputs. The cell feed may run 100 to 200 grams cadmium, 30 to 80 grams zinc, and 70 to 80 grams sulfuric acid per liter (1). Processing of lead smelter baghouse dust may entail addition of sulfuric acid, water, milk of lime, sodium sulfide or cadmium sulfide, sodium chlorate, a soluble chromate or dichromate, and a caustic, added at different stages. Quantities are not specified for any of these inputs.

3. Operating Conditions - Cadmium retorting furnaces are not pressurized. Operating temperatures of 455°C have been reported for the gas melting and ammonium chloride stages, and 790° to 910°C in the furnace itself. Electrolysis also takes place at atmospheric pressure, with the temperature held at about 30°C (1).

4. Utilities - Electricity, oil, or natural gas is used for melting the cadmium product. Air is brought into the furnace. Specific quantities were not found. In electrolysis, current density may range from 140 to 360 amperes per square meter (2).

5. Waste Streams - Particulates are released at several stages in the process. One plant reported the release of 20 kilograms per hour of ammonium chloride from fluxing and 108 kilograms per hour of cadmium from the retorting furnace (1).

Residues from retorting furnaces contain 1.5 to 6.0 percent cadmium, together with varying amounts of zinc and lead. Filter cakes may also include iron, arsenic, indium, mercury, and copper (2). Thallium is not regarded as a serious impurity since it is removed during processing. A sample of a cadmium filter cake residue was obtained from one electrolytic plant. After cadmium had been recovered from the flue dust, this waste amounted to 514 kilograms per day. Analysis was as follows: cadmium - 280 ppm, chromium - 24 ppm, copper - 1150 ppm, lead - 21.5 percent, zinc - 3.9 percent, and thallium - 40 ppm. The filter cake amounts to 1.8 kilogram per metric ton of zinc product (3).

6. Control Technology - Particulates can be controlled with fabric filter systems. The filter cake derived from purification is returned to the sintering operation. In some cases it is disposed of by open dumping or transferred to unlined ponds for liming and settling. Sludge dredged from the lagoons is stored on the ground for variable periods of time before shipment to lead smelters. No plants are known to use lined lagoons or to treat soil areas where dredged sludges are stored. In electrolytic pro-

cessing, the spent electrolyte is returned to various leaching stages in the circuit. In some cases the electrolytic cadmium process cycle is completely closed with no discharge.

7. EPA Source Classification Code - None

8. References -

1. Battelle Columbus Laboratories. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Zinc Segment of the Nonferrous Metals Manufacturing Point Source Category. EPA Contract No. 68-01-1518. Draft data.

2. Howe, H.E. Cadmium and Cadmium Alloys. In: Kirk-Othmer. Encyclopedia of Chemical Technology. Interscience Division of John Wiley and Sons, Inc. New York. 1967.

3. Calspan Corporation. Assessment of Industrial Waste Practices in the Metal Smelting and Refining Industry - Volume II, Primary and Secondary Nonferrous Smelting and Refining. Draft. April 1975.

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15. SUPPLEMENTARY NOTES

Project Officer: John O. Burckle

16. ABSTRACT

The catalog of Industrial Process Profiles for Environmental Use was developed as an aid in defining the environmental impacts of industrial activity in the United States. Entries for each industry are in consistent format and form separate chapters of the study.

The primary zinc industry as defined for this study consists of mining, beneficiation, smelting, and refining. A profile of the industry is given including plant locations, capacities, and various statistics regarding production and consumption of zinc, co-products, and by-products. The report summarizes the various commercial routes practiced domestically for zinc production in a series of process flow diagrams and detailed process descriptions. Each process description includes available data regarding input materials, operating conditions, energy and utility requirements, waste streams produced (air, water, and solid waste), and control technology practices and problems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Exhaust Emissions Smelting Trace Elements Pollution	Zinc Production	13B

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