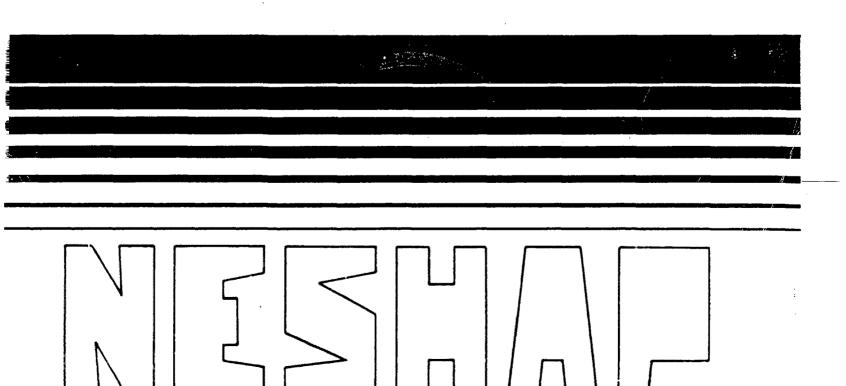
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Cadmium Emissions from Cadmium Refining and Primary Zinc/Zinc Oxide Smelting — Phase I Technical Report



Cadmium Emissions from Cadmium Refining and Primary Zinc/Zinc Oxide Smelting — Phase I Technical Report

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
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TECHNICAL REPORT:

CADMIUM REFINING AND PRIMARY ZINC/ZINC OXIDE SMELTING

I. DEFINITION OF SOURCE CATEGORIES

A. Cadmium Refining

Cadmium is principally a byproduct of zinc production and to a lesser extent of copper and lead production. It is a relatively rare element and in metal form is used for plating and alloying, accounting for about 34 percent of total demand in 1983. Cadmium compounds used in pigments, plastics, and batteries account for most of the remainder. 1

Because cadmium is recovered mainly as a byproduct of zinc ore processing, many producers of zinc and zinc compounds produce primary cadmium as an integral part of their operation. In some cases, residues and flue dusts from zinc producers are used directly by cadmium producers. Some cadmium also is recovered from flue dust generated by a lead smelter. 1

This report describes the sources of cadmium emissions from cadmium refining plants and primary zinc/zinc oxide smelters, documents the health risks attributable to these emission sources, and discusses the potential for improvements in existing levels of control.

1. Plants in operation. At present, there are four cadmium refining facilities in the U.S.: AMAX Zinc Company (AMAX) in East St. Louis, Illinois; ASARCO, Inc., Globe plant (ASARCO) in Denver, Colorado; Jersey Miniere Zinc in Clarksville, Tennessee; and St. Joe Resources Company, National Zinc Division (National Zinc) in Bartlesville, Oklahoma. The ASARCO plant produces only cadmium products. The other three cadmium refining facilities are colocated with primary zinc smelters. One additional cadmium refining operation, the ASARCO facility in Corpus Christi, Texas, was permanently closed in May 1985.

Crude cadmium oxide (CdO) is produced at the Asarco El Paso plant.

Refined CdO is produced at the Witco Chemical Corporation plastic stabilizer manufacturing plant in Brooklyn, New York. Although the Asarco-El Paso lead plant is currently shut down with indefinite plans for startup, the feed material for crude CdO production (blast furnace baghouse dust)

is supplied by Asarco's East Helena lead smelter. Cadmium emission data and risk values for Witco Chemical and Asarco-El Paso are included in the technical reports for pigments and stabalizer manufacturing (ESED 80/42 c) and primary lead and copper (ESED 80/42b), respectively.

2. <u>Processes</u>. Cadmium minerals do not occur in concentrations and quantities sufficient to justify mining them in their own right, but they are present in most zinc ores and are concentrated during zinc ore processing. Cadmium is a byproduct of the extraction and refining of zinc metal from zinc sulfide ore concentrates. Figure 1 is a general flow diagram for cadmium refining.

The first step in the refining of zinc metal is roasting the concentrates in a fluid bed roaster. This step removes up to 97 percent of the sulfur present in the concentrates and produces an impure zinc oxide product known as calcine.² Cadmium, in the form of CdO, is an impurity and must be removed as a part of the leaching and purification process.

All cadmium recovery processes comprise the dissolution or leaching of the cadmium-bearing feed material followed by various purification and cadmium displacement steps. Recovery processing can be performed by electrolytic and electromotive methods. In the former, cadmium is recovered by electrolyzing purified solutions where the cadmium is deposited on cathodes. After the deposition, the cathodes are removed from the cells and stripped, and the cadmium metal is melted and cast into the required shapes. This method is used at Jersey Miniere Zinc. In the electromotive method, metallic cadmium, called "sponge" because of its appearance, is displaced from the purified solutions by zinc dust. The sponge is then briquetted, melted, and cast into shapes for sale or further processing. This method is used at the other three plants; however, the feed material at ASARCO Globe plant is the impure CdO produced at the ASARCO El Paso plant from the lead smelter blast furnace baghouse dust received from ASARCO - East Helena.

Cadmium metal is produced in a variety of shapes. Slabs, ingots, and sticks are used in alloying, pigments, and in the production of CdO, which is often the initial input material for many cadmium uses. Balls and sheets are required for plating anodes.3

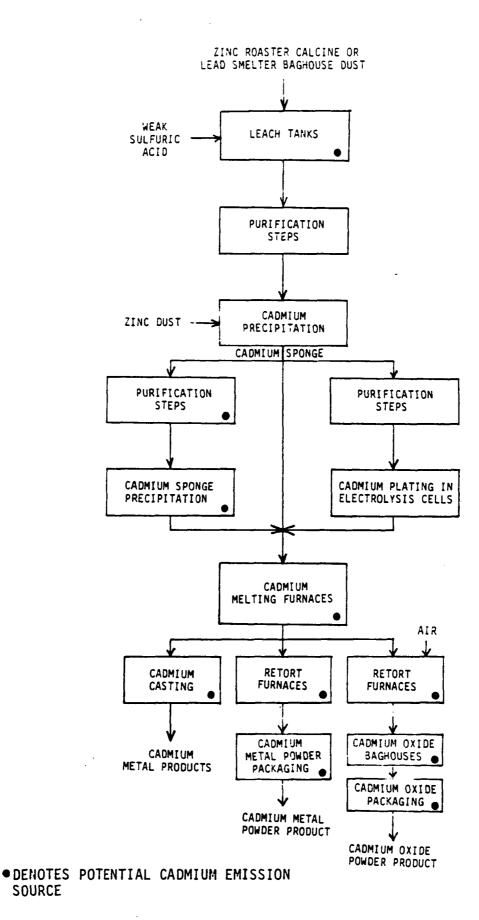


Figure 1. Flow diagram for cadmium refining. 11

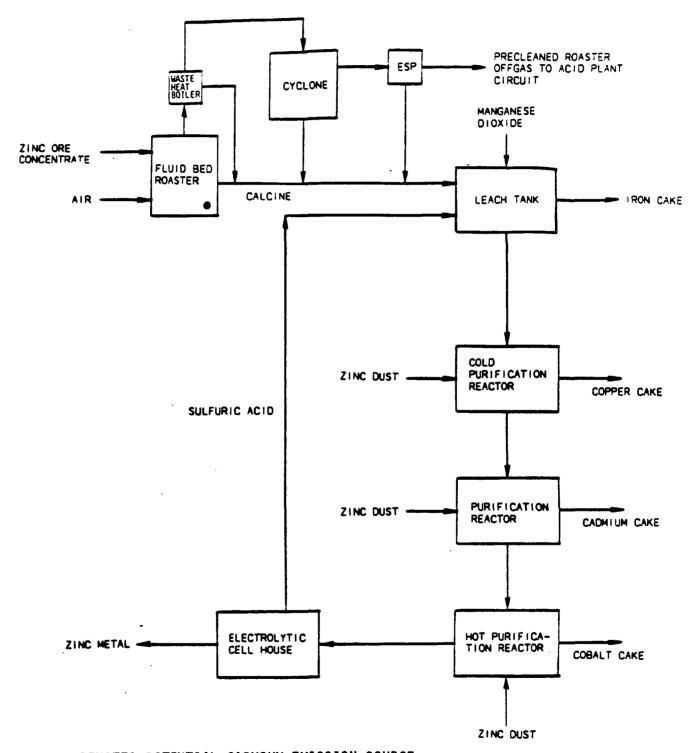
SOURCE

Two of the four cadmium refining plants produce only cadmium metal products, while the other two, ASARCO and AMAX, also produce cadmium metal powder and/or CdO powder. At these two plants, cadmium metal from the melting furnace is oxidized in air, and the CdO product is captured in a product collection baghouse and packaged for sale. In the production of cadmium metal powder, the entire system is purged with carbon dioxide and the neck of the furnace is sealed to prevent air from entering the system. Cadmium vapor from the retort furnace is rapidly cooled in a condenser to form cadmium metal powder.

3. <u>Projections of industry growth</u>. The forecast of U.S. demand for cadmium from 1983 to 2000, based on 1983 demand of 3,414 megagrams (Mg), is between 3,265 and 7,260 Mg. The probable demand of 4,540 Mg corresponds to an average annual growth rate of 1.7 percent for the period.⁴ One of the four plants is operating at 100 percent of capacity. The other three plants have the capacity to meet the expected demand because they are currently operating at 18, 61, and 88 percent of capacity. Therefore no new cadmium refining plants are expected.

B. Primary Zinc/Zinc Oxide Smelting

- 1. <u>Plants in operation</u>. At present, there are four primary zinc smelters in operation in the U.S.: AMAX, Jersey Miniere Zinc, National Zinc, and St. Joe Resources Company (St. Joe) in Monaca, Pennsylvania. There is one primary zinc oxide smelter in operation, the New Jersey Zinc Company in Palmerton, Pennsylvania. St. Joe also manufactures zinc oxide by refining zinc metal produced at the plant.
- 2. <u>Processes</u>. Of the primary zinc smelters, three are electrolytic smelters while one (St. Joe) is an electrothermic smelter. All four plants process zinc sulfide ore concentrates that contain from 0.1 to 0.8 percent cadmium by weight. The electrothermic smelter, due to the nature of the production process, also processes zinc secondary materials such as zinc skimmings, drosses, scrap metal, and oxides. The following two sections briefly discuss the two production processes. A third section discusses the production process at New Jersey Zinc.



• DENOTES POTENTIAL CADMIUM EMISSION SOURCE

Figure 2. Typical process flow diagram for an electrolytic zinc smelter. 12

- a. <u>Electrolytic zinc production</u>. A process flow diagram for a typical electrolytic zinc smelter is shown in Figure 2.
- (1) Roasting. The first step in the production of zinc metal from ore concentrates at both electrolytic and electrothermic zinc smelters is the roasting operation. Zinc roasting consists of heating the ore concentrates to 650° to 1000° C in an oxidizing environment. The roast is carried out below the melting temperature of the charge and has three primary functions: (a) elimination of sulfur as $S0_2$, (b) conversion of zinc sulfide to impure zinc oxide, and (c) removal of volatile impurities from the ore concentrate. The degree of sulfur elimination accomplished in a zinc roaster varies from about 93 to 97 percent.²

The fluid bed roaster is the newest roasting system for zinc sulfide concentrates and is currently the only type in use. The outlet gas stream from a fluid bed zinc roaster typically has an SO₂ concentration of 10 to 13 percent, and up to 85 percent of the roaster product (calcine) is carried out with the off-gas. Waste heat boilers, cyclones, and electrostatic precipitators (ESP's) are used in series to capture the entrained portion of the calcine.² The cleaned gas is then ducted to a sulfuric acid plant. At electrolytic zinc plants the collected materials are typically combined with the remaining portion of the calcine and stored prior to leaching and purification.²

(2) Leaching and purification. The roaster calcine is first leached in a dilute sulfuric acid solution to dissolve the impure zinc oxide. Manganese dioxide is generally added to the leach tank to cause the precipitation of an iron cake that contains iron and significant amounts of arsenic, antimony, and silicic acid. The leachate is then sent to a series of cold and hot purification tanks where cadmium, copper, and cobalt are removed from solution. The precipitation reactions that occur are induced by the addition of zinc dust, which reduces Cd^{+2} , Cu^{+2} , and Co^{+2} to their respective metallic forms. All three electrolytic smelters recover the precipitated cadmium and sell it as cadmium metal or CdO.

- (3) <u>Electrodeposition</u>. The purified zinc sulfate solution from the purification system is passed to the cell room where an electric potential applied to the solution causes zinc metal to form on the surface of aluminum cathodes. Hydrogen gas is also evolved causing the formation of sulfuric acid, which is recycled to the leach tank.⁵ The zinc metal sheets are subsequently stripped from the cathodes and stored prior to melting and casting.
- charged to an electric induction furnace and melted down. Ammonium chloride typically is added to the zinc sheets as a flux. The molten zinc is then pumped to a holding furnace where pneumatic jets direct the molten zinc into molds. Any impurities that form on the top of the freshly poured zinc are skimmed off. Water is sprayed on top of the molds to aid in cooling. At some plants, the area in which this cooling takes place is enclosed. The zinc slabs are subsequently removed from the molds, stacked, and stored for sale.
- b. <u>Electrothermic zinc production</u>. The process flow diagram for the St. Joe electrothermic zinc smelter is shown in Figure 3.
- (1) Roasting and sintering. The zinc sulfide ore concentrates are dried in a rotary dryer prior to roasting. Emissions from the dryer are controlled by a venturi scrubber. The dried ore concentrates are then roasted in a fluid bed roaster. Emissions from the roaster are controlled in series by a cyclone, waste heat boiler, electrostatic precipitator, and a wet scrubber. The cleaned gas is then ducted to a double-adsorption sulfuric acid plant. 6

Roaster calcine, sand, coke breeze, electrothermic furnace residue, blue powder from the electrothermic furnaces' scrubbers, and return sinter fines are mixed together and pelletized. The pelletized material is then roasted in downdraft sinter machines at an operating temperature from 1200° to 1300° C. The sinter machine product is subsequently crushed and screened. Sinter fines from screening are recycled to the sinter machines. Emissions from the sinter machines and from the crushing and sizing operation are controlled by separate baghouses.⁶

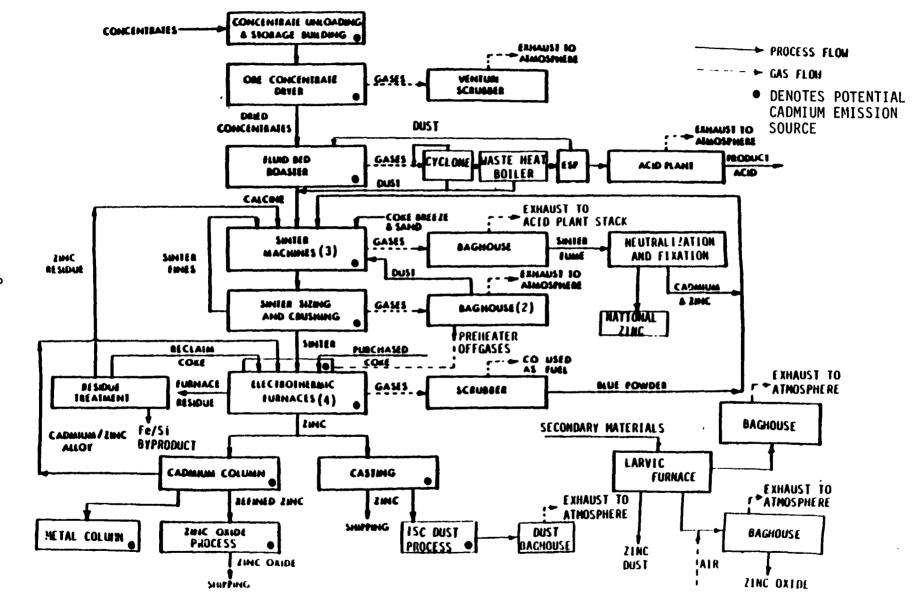


Figure 3. Process flow diagram, St. Joe Resources Company, Monaca, Pennsylvania.⁶

- (2) Electrothermic furnace operations. The advantage of the electrothermic process over the electrolytic process is that a significant portion of the feed may be comprised of secondary material. Sinter, coke, and secondary materials are heated and mixed in a rotary preheater and then charged to an electrothermic furnace. Emissions from the electrothermic furnace preheaters are controlled by a baghouse. Electricity is passed through eight pairs of graphite electrodes located at the top and bottom of the furnace to generate the heat required for smelting. Furnace vapors, including zinc vapor, are drawn through a water-cooled condenser and bubbled through a molten zinc bath. The gases vented from the condenser are scrubbed with water from high-velocity impingers. The clean gas, which contains about 80 percent carbon monoxide, is recovered and used as fuel. Any uncondensed zinc is recovered by settling the water slurry in ponds. This zinc, which is called blue powder, is recycled to the roaster. Furnace residue is discharged on a rotary table at the base of the furnace. It is then treated to recover coke and unsmelted zinc and to segregate slag and ferrosilicon by-products.6
- furnace condenser is passed to a holding furnace. The zinc may then be cast into 25-kilogram (kg) slabs, 227-kg blocks, or 1,090-kg jumbo blocks. The casting process is fully automated. Molten zinc from the holding furnace is tapped into molds which travel on a conveyor. Dross that forms on the surface of the molten zinc after tapping is skimmed off and stored for later use as furnace feed material. As the conveyor proceeds, water is poured on top of the molten zinc to aid in cooling the slabs. The slabs then pass into a hooding and ventilation system where more water is sprayed onto the slabs; the steam produced is drawn off to the atmosphere. The cooled slabs of zinc are then mechanically removed from the molds, stacked, and stored for shipment.
- (4) Zinc refining. Further refining of the zinc metal is accomplished using two types of refining columns known as cadmium columns and lead columns. Molten zinc from the electrothermic furnace is transferred to the cadmium column in large ladles. The molten zinc is

fed at a constant rate to the column and flows inside carbide trays. The column is operated at a temperature high enough to drive off metals, including cadmium, with a lower boiling point than zinc. Vapor from the column is condensed in a condenser. The resulting cadmium/zinc alloy contains approximately 3 percent cadmium by weight. This alloy is recycled to the electrothermic furnaces.⁶

The partially purified zinc collected at the bottom of the cadmium column is processed through another column known as the lead column. Here, the zinc is further purified by driving off zinc vapor and leaving behind higher boiling metals such as lead and iron. The zinc vapor is either condensed to produce high purity zinc metal slabs or oxidized to produce high purity zinc oxide. The zinc oxide powder is captured in product collection baghouses. Off-gases from the refining columns are vented to two other baghouses.

New Jersey Zinc plant in Palmerton, Pennsylvania, is currently the only plant in the U.S. producing zinc oxide using the American process. In the American process, zinc ore concentrates or steel furnace fume are used as the zinc feed material. Another process known as the French process uses high purity zinc metal as a raw material and is, therefore, a secondary zinc process and not considered in this study. As mentioned in the Federal Register, October 16, 1985, the risk estimate for the secondary zinc category is considered to be negligible as sources have excellent control equipment. Two other plants formerly produced zinc oxide using the American process. The ASARCO plant in Columbus, Ohio, was permanently closed in April 1986, and the ASARCO plant in Hillsboro, Illinois, now produces zinc oxide using only the French process.

The process flow diagram for New Jersey Zinc is shown in Figure 4. This plant can process a low-sulfur zinc ore known as Sterling crude ore and steel furnace fume that have cadmium contents of about 0.004 and 0.01 to percent by weight, respectively. Because the Sterling mine has been closed, steel fume is the feedstock currently used by New Jersey Zinc. Ore and coal are fed to the Waelz kilns where metals are volatilized and

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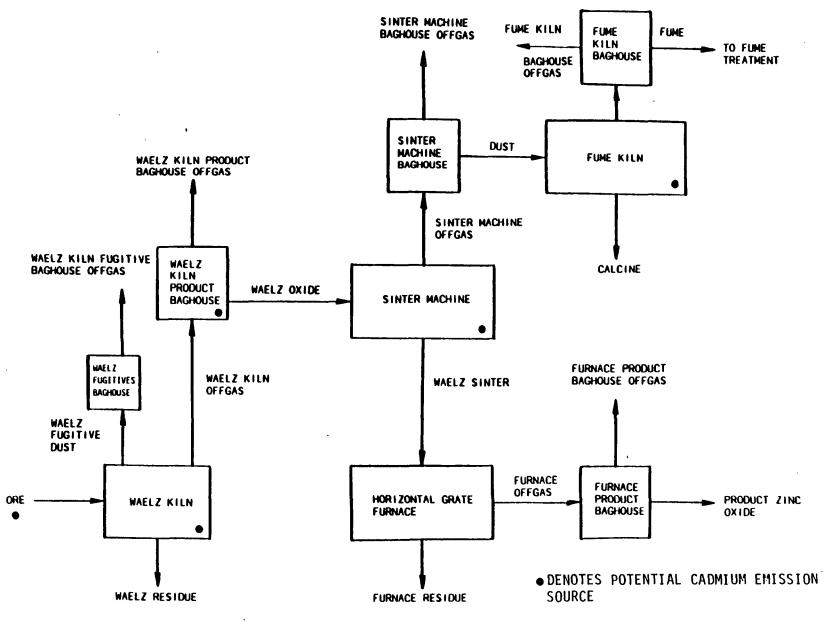


Figure 4. Process flow diagram for the American Zinc Oxide Process, New Jersey Zinc Company, Palmerton, Pennsylvania. 13

oxidized.⁸ The Waelz oxide product is cooled and collected in a baghouse collector.⁹ The oxide is then sintered in a downdraft sinter machine to reduce impurities such as lead and chloride. The last step in the process is the final oxidation and purification. The sinter is mixed with coal and fed to a moving-grate furnace. The oxide is volatilized, reduced to metallic zinc, and then oxidized again. The purified zinc oxide is then collected in a baghouse.⁹

3. <u>Projections of industry growth</u>. The forecast of U.S. demand for zinc in the year 2000 is 1.4 million metric tons. The demand in 1983 was 930,000 metric tons. During the forecast period, U.S. dependence on metal imports is expected to remain between 55 and 70 percent. No new primary zinc smelters are expected to open because idle capacity is available at the ASARCO Corpus Christi primary zinc smelter. The reopening of this plant is unlikely and is dependent on an increase in both mine production and the price of zinc:

II. EMISSIONS AND CONTROLS

A. Cadmium Refining

An inventory of cadmium emission sources at currently operating cadmium refining plants showing estimated emissions and existing controls is presented in Table 1. The cadmium emission estimates were generated from Section 114 responses, emission test reports, trip reports, and the previous cadmium source survey (Radian, 1985). Also, the methodologies for determining these estimates were sent to each plant and the estimates were revised based on industry comments. The two types of process emission sources are cadmium melting furnaces and cadmium retort furnaces. These process emission sources and their controls are discussed below.

Cadmium melting furnaces are used to melt either cadmium "sponge" or sheets. A layer of caustic on the molten metal surface is used to prevent oxidation, to help remove impurities, and to provide some control of particulate matter at three cadmium refining plants. The other plant uses a layer of resin.

TABLE 1. INVENTORY OF CADMIUM EMISSION SOURCES AND CONTROLS FOR CADMIUM REFINING PLANTS

		•	Emissions		
Plant	Source	Type ^{ā.}	Maximum operation	Normal operation	Control device ^b
AMAX Zinc Company,	Cadmium melting furnace	Н	70	55	UNC
East St. Louis,	Cadmium holding furnace	Н	93	54	UNC
Ill.	Cadmium casting furnace	F	-68	<1	UNC
	Cadmium oxide furnace	н	$\frac{814}{1,040}$	496 605	ВН
Jersey Miniere Zinc, Clarksville, Tenn.	Cadmium melting furnace	Н	<1	<1	вн
National Zinc, Bartlesville, Okla.	Cadmium melting/casting furnace	Н	<1	<1	WS
•	Cadmium tapping/casting	Н	<1	<1	UNC
ASARCO Globe,	Dust charging	Н	194	72	UNC
Denver, Coĺo.	Premelt department	Н	1,580	707	UNC
	Casting/holding furnace	Н	792	2	UNC
	Purification sponge tank	Н	5	2	UNC
	Purification dept. stack	Н	9	4	UNC
	Solutions heating tanks	Н	421	203	UNC
	CdO baghouse No. 1	Н	5	1	вн
	CdO baghouse No. 2	Н	99	18	ВН
	Cd metal powder packaging	Н	18	16	BH
	Fugitives packaging dust collector No. 1	Н	86	15	ВН
	Fugitives packaging dust collector No. 2	Н	196	175	ВН
	Gypsum storage piles ^c (tailing piles)	Н	<1 3,400	<1 1,220	DS

aH=point source; F=fugitive source. bUNC=uncontrolled; BH=baghouse; WS=wet scrubber; DS=dust suppressant. CBased on AP-42 methodology which was developed for aggregate materials.

TABLE 2. INVENTORY OF CADMIUM EMISSION SOURCES AND CONTROLS FOR PRIMARY ZINC/ZINC OXIDE SMELTERS

			Emissions	
Plant	Source	Typea	kg/yr	Control device ^b
AMAX Zinc Company,	Raw material storage & unlo	adinaCF	54	UNC
	Zinc melting furnace		<1	ВН
East St. Louis, IL		H		
	Zinc tapping/casting	F	<1	UNC
	Zinc dust process	H	<1 /	ВН
	Roadways ^C	F		load sweeper/water spra
	Leach residue dryer	Н	17	ВН
			100	
Jersey Miniere Zinc,	Raw material storage ^C	Н	1	вн
Clarksville, TN	Calcine handling	H	4	вн
•	Zinc melting furnace	Н	- <1	ВН
	Zinc metal powder process	Н	<1	ВН
	Zinc tapping/casting	F	<1	UNC
	Gypsum storage ^C	F	<1	UNC
		F		
	Roadways ^C		22	Road_sweeper
	Screening tower	Н	<1	ВН
			28	
National Zinc,	Raw material storage & unloa	adingCF	7	DS
Bartlesville, OK	Zinc tapping/casting	F	<1	UNC
•	Zinc metal powder process	Н	<1	ВН
	Zinc melting furnace	Ĥ	<1	ВН
	Roadwaysc	F		_
		H		load sweeper/water spra
	Purified cooler		<1	Demister
	Electrolyte cooler	Н	<1 12	Demister
		0=		
St. Joe Resources	Raw material storage & unloa	adingCF	2	Building and DS
Company, Monaca, PA	Zinc ore dryer	Н	1	WS
, , ,	Zinc holding furnace	Н	<1	ВН
	Zinc tapping/casting	F	2	UNC
	Zinc metal powder process	H	< <u>1</u>	ВН
	Sinter machine	H	1,430	ВН
		• •		
	Sinter sizing/crushing	Н	147	BH
	Zinc furnace preheaters	H	262	ВН
	Refining column No. 1	H	<1	ВН
	Zinc oxide furnace	Н	1	ВН
	Roadways ^C	F	<1	Road sweeper
	Refining column No. 2	Н	<1	ВН
	Nuisance dust collector	H	< <u>1</u>	ВН
			1,840	
The New Jersey Zinc	Sterling ore storage ^C	F	<1	UNC
Company, Palmerton,	Waelz kiln fugitives	H	<1	ВН
PA	Waelz kiln product	Н	1	ВН
	Sinter machine	Н	110	ВН
	Fume kiln	Н	102	ВН
			215	

aH=point source; F=fugitive source. bUNC=uncontrolled; BH=baghouse; WS=wet scrubber; DS=dust suppressant cBased on AP-42 methodology which was developed for aggregate materials. Process cadmium emissions from the melting furnace are controlled by a baghouse at Jersey Miniere Zinc and by a wet scrubber at National Zinc. Jersey Miniere Zinc also has a hooding system that controls process fugitive emissions from the charging/drossing port and from the tapping/casting area. There is no such hooding system at the other three plants. At AMAX, ventilation to the atmosphere for the cadmium melting furnace is accomplished via natural draft. At ASARCO, forced ventilation is in place during furnace operation and during charging and tapping/casting. Cadmium emissions from all of these sources were estimated based on data from stack tests performed at two of the plants.

Cadmium retort furnaces are used at AMAX and ASARCO. The processes involved at these plants are similar in that cadmium metal is vaporized and/or oxidized to produce cadmium metal powder or CdO. Cadmium oxide is collected in product collection baghouses at both plants. Cadmium metal powder is collected in a condenser at ASARCO. Cadmium emissions from the retort sources at these two plants were estimated based on data from tests performed on each stack.

B. Primary Zinc/Zinc Oxide Smelting

An inventory of cadmium emission sources at currently operating primary zinc and zinc oxide smelters showing estimated emissions and existing controls is presented in Table 2. The cadmium emission estimates were generated from Section 114 responses, emission test reports, trip reports, and the previous cadmium source survey (Radian, 1985). Also the methodologies for determining these estimates were sent to each plant and the estimates were revised based on industry comments.

Ore concentrate storage and handling and roasting operations at electrolytic and electrothermic primary zinc smelters are similar. Emissions from ore concentrate storage and handling are controlled by a storage building equipped with three baghouses at Jersey Miniere Zinc (typically only one baghouse operates). At two of the other three plants, ore concentrates are enclosed to varying degrees in storage buildings. At National Zinc, a latex dust suppressant is sprayed on the outside storage piles once a year.

Emissions from the roasters at all of the primary zinc smelters are controlled by a variety of gas cleaning equipment including cyclones, ESP's, waste heat boilers, wet scrubbers, and mist eliminators; after leaving the gas cleaning equipment, roaster emissions enter a sulfuric acid plant. Emissions of cadmium from the roasters at each plant are assumed to be insignificant due to the extensive gas cleaning system and the fact that any particulate matter entering the acid plant would be caught in one of the four catalyst beds.

The leaching and purification operations associated with the electrolytic process are wet operations and as such are not considered to be sources of atmospheric cadmium emissions. At AMAX, however, the leach residue material is dried and sold for further metals recovery. The leach residue dryer is controlled by a baghouse. Other minor sources of cadmium emissions at electrolytic plants are the zinc melting furnace, zinc tapping/casting operations, and the zinc dust process. At each plant, the zinc melting furnace and zinc dust processes are controlled by baghouses. The zinc tapping/casting operations are uncontrolled and ventilated to the atmosphere at Jersey Miniere Zinc and National Zinc. This operation is uncontrolled and is not ventilated at AMAX. In general, emissions of particulate matter, including cadmium, are well controlled at electrolytic plants.

In the electrothermic process, cadmium is removed from the zinc-bearing calcine mainly by volatilization of the material in sinter machines. This is in contrast to the removal of cadmium by wet chemical means in the electrolytic process. As a result, the potential for cadmium emissions is greater in the electrothermic process than in the electrolytic process. Separate baghouses are used to control emissions from the following sources: sinter machines; sinter sizing/crushing, sinter feed preparation, and the sinter machine feed bins and transfer points; and the electrothermic furnace preheaters, furnace plant residue, sinter residue, and coke sizing operations. The electrothermic furnaces are each controlled by a condenser and scrubber system with the carbon monoxide scrubber off-gases being used as fuel. The zinc furnace is

controlled by a baghouse, while tapping/casting is uncontrolled and ventilated to the atmosphere. The seven zinc refining columns (normally a maximum of six operate at any one time) are controlled by two baghouses. The zinc oxide produced by volatilizing the refined zinc from the refinery columns is collected in one of three product collection baghouses.

Because the Sterling Mine, the source of zinc ore concentrates for New Jersey Zinc, has been closed, the storage and handling of the concentrate are unlikely to be sources of fugitive cadmium emissions. The plant is currently using steel furnace fume with a cadmium content that ranges from 0.01 to 0.4 percent by weight. This material is stored inside a building and is, therefore, not considered to be a source of fugitive cadmium emissions. Process fugitive emissions from the Waelz kilns are collected by capture hoods and ducted to a baghouse. Process emissions from the Waelz kilns are controlled by a baghouse. Process emissions from the sintering operation are controlled by a baghouse. Process fugitive emissions from the sintering operation and material handling also are controlled by baghouses. Two other process sources, the fume kiln and horizontal-grate furnace also are controlled by baghouses.

III. PUBLIC HEALTH RISKS

A. Risk Assessment

1. <u>Background</u>. Risk assessment is the process used by EPA to develop quantitative estimates of public health risks associated with individual and population exposure to a hazardous or toxic air pollutant. The resultant estimates are considered by EPA to be rough but plausible upperbound approximations of the risks. Two measures of risk are calculated. One is maximum individual risk (MIR) and the other is aggregate risk. Maximum individual risk is an estimate of the probability of contracting cancer experienced by the person or persons exposed to the highest predicted annual average concentration of the pollutant. Aggregate risk is an estimate of the increased number of cancer cases for the entire population after 70 years of continuous exposure. It is expressed in terms of annual incidence or number of cancer cases per year. Non-carcinogenic health risks are not addressed in this study.

The estimates are calculated by coupling a numerical constant that defines the statistical exposure-risk relationship for a particular hazardous pollutant with estimates of public exposure to the pollutant. The numerical constant used by EPA in its analysis of carcinogens is called a unit risk factor. It represents an estimate of the increase in cancer risk occurring to a hypothetical individual exposed continuously over a lifetime (70 years) to a concentration of 1 microgram per cubic meter (ug/m³) of the pollutant in the air the individual breathes. For cadmium, the unit risk factor is estimated to be 1.8×10^{-3} or 1.8 chances in 1,000.

Estimates of public exposure are derived using dispersion models and census data contained in EPA's Human Exposure Model (HEM). Dispersion models are used to predict concentrations of a pollutant in the ambient air at varying distances in all directions within a 50 kilometer radius from a stationary emission source. With inputs of emission estimates and stack parameters such as height, gas velocity, gas temperature, and diameter, the model is able to predict ambient pollutant concentrations around the plant. By combining the predicted ambient concentrations with population data, both the number of people exposed and their levels of exposure can be estimated. More details on the methodology and assumptions used in HEM are contained in User's Manual for the Human Exposure Model (HEM) (EPA-450/5-86-001).

2. Approach. Emission estimates were generated for each of the sources at all of the plants in both categories. The number of sources at each plant varied from 5 to 13 sources for zinc/zinc oxide smelters and from 1 to 12 sources for cadmium refining plants. Each source at each plant was modeled separately, and individual values for MIR (expressed as a probability for an individual) and aggregate risk (expressed as statistical cases per year) were generated for each source. The risks from all sources at a particular plant were then summed to provide MIR and aggregate risk for that plant. Details of the methods used to develop the health risk estimates for both source categories are described below.

TABLE 3. SUMMARY OF EMISSIONS AND RISKS FOR CADMIUM REFINING PLANTS AT TYPICAL OPERATING CONDITIONS

Plant	Cadmium emissions, kg/yr	Maximum individual risk	Annual incidence, case/yr
AMAX Zinc Co., East St. Louis, Ill.	605	2.0x10 ⁻⁴	0.018
Jersey Miniere Zinc, Clarksville, Tenn.	<1	1.0x10 ⁻⁷	<0.0001
National Zinc, Bartlesville, Okla.	<1	4.9x10 ⁻⁷	<0.0001
ASARCO, Denver, Colo.	1,220	1.4x10 ⁻³	0.041
Total	1,830	1.4x10-3	0.059

TABLE 4. SUMMARY OF EMISSIONS AND RISKS FOR AMAX AND ASARCO AT MAXIMUM OPERATING CONDITIONS

Plant	Cadmium emissions, kg/yr	Maximum individual risk	Annual incidence, case/yr
AMAX Zinc Co., East St. Louis, Ill.	1,040	4.6x10-4	0.034
ASARCO, Denver, Colo.	3,410	3.6x10-3	0.11
Total	4,450	3.6x10 ⁻³	0.14

TABLE 5. SUMMARY OF HIGH RISK SOURCES AT CADMIUM REFINING PLANTS

Plant	Source	Operating conditions	Cadmium emissions, kg/yr	Maximum risk	Annual incidence
AMAX Zinc Co.,	CdO furnace	Norma1	496	1.1x10 ⁻⁴	0.014
East St. Louis, Ill.	CdO furnace	Maximum	814	1.8x10 ⁻⁴	0.024
ASARCO, Denver, Colo.	Dust charging	Norma 1	72	1.5x10 ⁻⁴	0.0026
	Premelt department	Normal	707	6.2×10^{-4}	0.023
	Solution heating tanks	Norma1	203	3.1x10 ⁻⁴	0.0070
	Dust collector No. 2	Normal	175	1.7x10 ⁻⁴	0.0058
	Dust charging	Maximum	194	4.0×10 ⁻⁴	0.0069
	Premelt department	Maximum	1,580	1.4×10^{-3}	0.052
	Casting furnace	Maximum	792	4.7×10 ⁻⁴	0.025
	Solution heating tanks	Maximum	421	6.4×10^{-4}	0.014
	Dust collector No. 2	Maximum	196	1.9×10 ⁻⁴	0.0064
	CdO baghouse No. 2	Maximum	99	2.3x10 ⁻⁴	0.0036
	Dust collector No. 1	Maximum	. 86	2.0x10 ⁻⁴	0.0031

B. <u>Cadmium Refining</u>

The inputs to the HEM, including cadmium emission estimates and stack parameters for cadmium refining plants, were generated from Section 114 request responses, test reports, trip reports, and the previous cadmium source survey (Radian, 1985). Also, the methodologies for determining these estimates were sent to each plant and the estimates were revised based on industry comments, as appropriate.

The ASARCO cadmium refining plant at Corpus Christi, Texas is permanently shut down. The ASARCO lead and copper smelting plant in El Paso, Texas, and the Witco Chemical Corporation plastic stabilizer manufacturing plant in Brooklyn, New York, both CdO producers, were included in the health risk modeling performed for the Primary Lead and Copper Smelting (ESED 80/42b) and Pigment and Stabilizer Manufacturing (ESED 80/42c) projects, respectively. Therefore, only the four currently operating cadmium refining plants were included in the health risk assessment. Table 3 shows the emissions, MIR, and annual incidence for each plant based on typical operating conditions. Two plants, AMAX and ASARCO, had MIR's exceeding 1x10-4. The highest MIR (1.4x10-3) occurs at ASARCO, and the annual incidence for this plant (0.041) is 69 percent of the entire category's annual incidence. Both National Zinc and Jersey Miniere Zinc had total plant MIR's far below the 1x10-4 level (4.9x10-7 and 1.0x10-7, respectively.)

For AMAX and ASARCO, the HEM was run a second time using a cadmium emission estimate for each source at maximum operating conditions. Maximum operation is considered unlikely due to the depressed state of the cadmium refining industry. The Jersey Miniere Zinc and National Zinc typical operating rates are 88 and 100 percent of capacity, respectively. Because both plants' MIR's were very low, the HEM was not run again using maximum operating conditions for these plants. Table 4 shows emissions, MIR, and annual incidence for AMAX and ASARCO based on maximum operating conditions. Again, ASARCO has the highest MIR (3.6×10^{-3}) , and the annual incidence for this plant (0.11) is 76 percent of the annual incidence for the two plants.

A summary of the individual sources that contribute the most to the risk at each plant is presented in Table 5 for both typical and maximum operating conditions. At typical operating conditions, the CdO product collection baghouse at AMAX is responsible for more than 78 percent of the annual incidence attributable to this plant. At maximum operating conditions, this baghouse is responsible for more than 71 percent of the annual incidence. Although the outlet particulate matter concentration is low, 0.018 grains per dry standard cubic foot (gr/dscf), based on emission test data, 30 - 69 percent of the particulate matter in cadmium.

At typical operating conditions, four sources at ASARCO are responsible for 94 percent of the annual incidence attributable to this plant: dust charging to the leaching process, the premelt department, the solutions department heating tanks stack, and fugitive packaging dust collector No. 2.

Impure CdO dust is charged to the leaching process. Emissions are vented to the atmosphere uncontrolled. A test conducted by ASARCO shows the outlet particulate emissions to be 0.004 gr/dscf.

A hooding system is in place to vent cadmium emissions from tapping and casting operations to the atmosphere uncontrolled. All emissions are vented through the same stack. A test conducted by ASARCO shows the outlet particulate emissions from this stack to be 0.021 gr/dscf.

Emissions from the solution heating tanks are vented to the atmosphere uncontrolled. A test conducted by ASARCO shows the outlet particulate emissions to be 0.018 gr/dscf.

In the retort department, fugitive emissions from the packaging operations are captured by fugitive dust collector No. 2. A test conducted by ASARCO shows the outlet particulate emissions to be 0.0002 gr/dscf.

At maximum operating conditions, three other sources at ASARCO Globe have MIR's greater than $1x10^{-4}$: the casting/holding furnace, CdO product collection baghouse No. 2, and the fugitive packaging dust collector No. 1.

Cadmium metal bricks are melted and cast into either balls or sticks. Emissions are vented to the atmosphere uncontrolled. Test data for this source are unavailable, and emissions were estimated based on emissions from the premelt department stack test.

Cadmium metal bricks are oxidized in air, and the CdO product is captured in a product collection baghouse. A test conducted on the No. 2 baghouse by ASARCO shows the outlet particulate emissions to be 0.003 gr/dscf.

Fugitive dust collector No. 1 performs the same function as fugitive dust collector No. 2 in the retort department. A test conducted by ASARCO shows outlet particulate emissions to be 0.001 gr/dscf.

C. Primary Zinc/Zinc Oxide Smelting

The HEM inputs for zinc/zinc oxide smelters were generated from Section 114 responses, trip reports, and the previous cadmium source surveys (Radian, 1985; GCA, 1981). Also, the methodologies for determining these estimates were sent to each plant, and the estimates were revised based on industry comments, as appropriate. Only those currently operating primary zinc/zinc oxide smelters were included in the analysis. Table 6 shows the emissions, MIR, and annual incidence for each plant based on current operating conditions. Because all of the primary zinc/zinc oxide smelters are currently operating at or near 100 percent of capacity, the maximum MIR's and annual incidences are reflected in Table 6. None of the primary zinc/zinc oxide smelters have MIR's greater than $1x10^{-4}$.

IV. POTENTIAL FOR IMPROVED CONTROL

Cadmium Refining

The results of the risk analysis indicated that two plants, AMAX and ASARCO, had MIR's from cadmium exposure in excess of 1×10^{-4} and annual incidences in excess of 0.01 case. Therefore, each point source of cadmium at each of these two plants was evaluated to determine the potential for improvements in existing control. If the existing particulate matter emissions were less than or equal to 0.005 gr/dscf (the lowest particulate matter standard that would likely be technically enforceable for these

TABLE 6. SUMMARY OF EMISSIONS AND RISKS FOR PRIMARY ZINC/ZINC OXIDE SMELTERS

Plant	Cadmium emissions, kg/yr	Maximum individual risk	Annual incidence, case/yr
AMAX Zinc Co., East St. Louis, Ill.	100	8.3x10-5	0.0029
Jersey Miniere Zinc, Clarksville, Tenn.	28	5.0x10 ⁻⁵	0.0002
National Zinc, Bartlesville, Okla.	12	1.8x10 ⁻⁵	<0.0001
St. Joe, Monaca, Pa.	1,840	5.6x10-6	0.0076
New Jersey Zinc, Palmerton, Pa.	215	2.6x10 ⁻⁵	0.0011
Total	2,200	8.3x10 ⁻⁵	0.011

TABLE 7. SUMMARY OF OPTIONS FOR IMPROVED CONTROL AND ASSOCIATED IMPACTS AT TYPICAL OPERATING CONDITIONS (April 1986 Dollars)

P1 ar	nt/source	Existing control	Improved control	Emission reduction, kg/yr	Incidence reduction, case/yr	Capital cost, \$	Annualized cost, \$a b	\$/life saved ^b
	Zinc Co., t St. Louis, IL							
1. 2.	Cadmium melting furnace Cadmium holding furnace	UNCC	One baghouse for control of sources 1, 2, and 3; 99.5% efficiency	109	0.0034	350,000	77,600	22,800,000
3.4.	Cadmium casting furnace Lead anode furnaces (2) ^e	BHq nnc	One baghouse for control of sources 1 through 4; 99.5% efficiency	109	0.0034	580,000	120,000	35,200,000
	CdO furnace CO, Inc.,	ВН	Increased pressure drop to improve baghouse efficiency to 99.98%	356	0.008	0 MIR: 2.	4,550 .0x10 ⁻⁴ to 6	569,000
6. 7. 8. 9.	Dust charging Premelt department Casting furnace Solution heating tanks	UNC UNC UNC UNC	Baghouse for control of sources 7, 8, and 9; 99.5% efficiency Wet scrubber (pressure drop= 12 in. w.c.)	778 162	0.0256 0.0058 0.031	670,000 89,000 MIR: 1.	174,000 30,000 4x10 ⁻³ to 3	6,810,000 5,170,000 .4x10-4

aIncludes a particulate recovery credit of \$3,300/Mg.
bValues presented here have been rounded. Exact values were used in the calculation of \$/life.

CUNC=Uncontrolled.

dBH=Baghouse. eNot a cadmium source.

TABLE 8. SUMMARY OF OPTIONS FOR IMPROVED CONTROL AND ASSOCIATED IMPACTS AT MAXIMUM OPERATING CONDITIONS (April 1986 Dollars)

) I an	t/source	Existing control	Improved control	Emission reduction, kg/yr	Incidence reduction, case/yr	Capital cost, \$	Annualized cost, \$a b	\$/life saved ^b
	Zinc Co., t St. Louis, IL							
1.	Cadmium melting furnace	NNCc	One baghouse for control of sources 1, 2, and 3;	230	0.0072	350,000	119,000	16,600,000
2.	Cadmium holding furnace	UNC	99.5% efficiency					
3.	Cadmium casting furnace	UNC	One baghouse for control of sources 1 through 4;	230	0.0072	580,000	177,000	24,600,000
4.	Lead anode furnaces (2)e	ВНФ	99.5% efficiency					
5.	CdO furnace	ВН	Increase pressure drop to improve baghouse efficiency	584	0.017	0	7,490	441,000
			to 99.98%		0.024			
SAR	CO, Inc.,					MIR:	4.6x10 ⁻⁴ to 8	.5x10 ⁻⁵
	nver, CO							
6. 7. 8.	Dust charging Premelt department Casting furnace	UNC UNC UNC	Baghouse for control of sources 7, 8, and 9; 99.5% efficiency	2,560	0.084	670,000	192,000	2,290,000
9.	Solution heating tanks	UNC	Wet scrubber (pressure drop= 12 in. w.c.)	337	0.012	89,000 MIR:	46,400 3.6x10 ⁻³ to 7	4,000,000 .4x10-4

aIncludes a particulate recovery credit of \$3,300/Mg.
bValues presented here have been rounded. Exact values were used in the calculation of \$/life.

CUNC=Uncontrolled.

dBH=Baghouse.
eNot a cadmium source.

source categories), no further evaluation of improved control was performed. If the particulate matter emissions were greater than 0.005 gr/dscf, control options were developed and control costs were calculated. Fugitive emission sources, regardless of emission rate, were also evaluated to determine the potential for improved control.

For AMAX, the following control sources were identified for improved control: the holding, melting, and casting furnaces (all currently uncontrolled), and the CdO baghouse. Tables 7 and 8 show the possible control improvements for these sources together with associated costs and cost effectiveness (including a particulate recovery credit of \$3,300/Mg) for typical and maximum operating conditions, respectively. Improved control options evaluated included applying baghouse control to the three cadmium furnaces that are currently uncontrolled and operating the existing CdO baghouse at a higher pressure drop. An emission test was conducted by AMAX on the existing CdO baghouse after this document was sent for review. Particulate emissions for this test were less than 0.005 gr/dscf. The bag life prior to this test was much shorter than the bag life prior to EPA's test. Thus, increased maintenance, as well as increased pressure drop, can also reduce emissions to 0.005 gr/dscf. The combined effect of improved control reduces the total plant MIR from 2.6×10^{-4} to 6.5×10^{-5} for typical operating conditions and from 4.6×10^{-4} to 8.5×10^{-5} for maximum operating conditions.

For ASARCO, the following sources were identified for improved control: the dust charging to leaching operation, the premelt department, the casting furnace, and the solutions department heating tanks. Tables 7 and 8 show the possible control improvements for these sources together with associated costs and cost effectiveness for both typical and maximum operating conditions. Improved control options evaluated included installation of a baghouse for control of the dust charging operation, premelt department, and casting furnace that are currently uncontrolled, and installing a wet scrubber on the uncontrolled solution heating tanks. The combined effect of improved control reduces the total plant MIR from 1.4×10^{-3} to 3.0×10^{-4} for typical operating conditions and from 3.6×10^{-3} to 7.2×10^{-4} for maximum operating conditions. Implementing these improved controls will not reduce the MIR below 1×10^{-4} ; however, each source at the plant would be controlled to a level less than or equal to 0.005 gr/dscf.

The information concerning operating hours and emissions for ASARCO's Globe plant as discussed above, is based on information submitted to EPA and the State of Colorado by ASARCO. Estimates of operating hours and emission rates for the maximum operating conditions are based on information supplied by ASARCO to the State of Colorado. Draft estimates and calculations prepared by EPA for typical operating hours were submitted to ASARCO for review. ASARCO's initial comments on these estimates and calculations were incorporated into a draft report.

The draft report and the subsequent dispersion analysis were then reviewed by ASARCO and they provided additional comments on the operating hours for the typical maximum operating conditions. Resolution of the differences between ASARCO's comments on the draft report and the dispersion analysis versus their original submittals and comments has not been possible. Since this plant has been assigned for further study under the State Initiative Program, the State of Colorado will further investigate the process, operating hours and emissions.

V. REFERENCES

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16. ABSTRACT

A technical report on cadmium emissions from cadmium refining and primary zinc/zinc oxide smelting. Descriptions of these industries and associated air pollution control equipment are presented. Cadmium emissions from all plants in the U.S. in these two source categories are presented. Health risks from exposure to cadmium air emissions from each plant is also discussed.

17.	KEYW	ORDS AND DOCUMENT ANALYSIS	
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