NATIONAL INVENTORY OF SOURCES AND EMISSIONS: CADMIUM - 1968

by

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PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. CPA 22-69-131 with the U. S. Public Health Service, U. S. Department of Health, Education, and Welfare, National Air Pollution Control Administration.

The inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of the emissions of cadmium in the United States for the year 1968.

Background information concerning the basic characteristics of the cadmium industry has been assembled and included. Process descriptions are given, but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact about twenty percent of the companies in each major emissions source group to obtain the required information. It was known that published data concerning emissions of the pollutant was virtually non-existent, and contacts with industry ascertained that atmospheric emissions were not a matter of record.

The cadmium emissions and emissions factors that are presented are

based on the summation of the information obtained from production companies that represent approximately forty percent of the total production, and the reprocessing companies that handle about forty-five percent of the cadmium used in consumer products. Emissions control equipment is in use at all the production facilities that were visited. It is a part of the process system for the recovery of zinc, and is not specifically for the control of cadmium emissions to the atmosphere. Cadmium emissions and emissions factors are considered to be reasonably accurate.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals in the cadmium industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to many branches of the Federal and State Governments.

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SUMMARY

The flow of cadmium in the United States has been traced and charted for the year 1968. The apparent consumption was 13.3 million pounds, and domestic production 10.6 million pounds.

Only a small amount of cadmium was recovered from scrap.

Emissions to the atmosphere during the year totaled 4.6 million pounds. Emissions from the metallurgical processing plants of the primary producers of cadmium, zinc, lead, and copper were more than 2 million pounds, and those from melting operations in the iron and steel industry were about the same.

Emission estimates for mining, metallurgical processing, and reprocessing operations are considered to be reasonably accurate. They are based on data obtained by personal contact with the processing and reprocessing companies. Further effort is recommended to confirm the accuracy of the emissions from the scrap containing cadmium.

SOURCES OF CADMIUM

Cadmium is a metal which is not found as a free mineral in nature. The most important mineral is sulfide greenockite which is dispersed in zinc sulfide ore. Since pure cadmium is never found in a natural state and cadmium minerals are not found in concentrated form, metallic cadmium is always prepared commercially as a byproduct of primary metal industries, principally the zinc industry.

Cadmium, a relatively rare element, is found not only in zinc ore but in lead ore, copper ore and other ores that contain zinc minerals. It is intimately associated with the zinc and when ore containing several minerals is separated, the cadmium remains with the zinc. Since the separation process is not exact, lead concentrates will contain a small quantity of zinc and a proportionately small amount of cadmium. The earth's crust contains 0.55 ppm of cadmium, \frac{1}{2} and field soil unfertilized 0.55 ppm to 2.45 ppm.\frac{2}{2} (wet wt.)

Ores containing cadmium are found in the following states:

Arizona, California, Colorado, Idaho, Illinois, Kansas, Kentucky,

Maine, Missouri, Montana, Nevada, New Jersey, New Mexico,

^{1 -} Schroeder, H. J., Cadmium, Mineral Facts & Problems, Bureau of Mines Bulletin 630, 1965

^{2 -} Schroeder, H. A., etal., Essential Trace Metals in Man: Zinc Relation to Environmental Cadmium, J. Chronic Diseases 20 (4) - 179, (1967)

New York, Oklahoma, Oregon, Pennsylvania, Tennessee, Utah, Virginia, Washington, Wisconsin. Not all of these states produce metallic cadmium and some other states do produce metallic cadmium from ores and concentrates shipped in from outside of the state. Ores mined in the United States account for 38 percent of the primary cadmium produced in the United States. The other 62 percent comes from imported ores and concentrates, and imported flue dust. The principal sources of imports were Canada, Peru and Mexico.

Some cadmium metal was imported which amounted to about 14 percent of total United States consumption. Principal imports were from Australia, Canada, Japan, Mexico and Peru. $\frac{1}{2}$

World production of cadmium is essentially a by-product of zinc smelting, and the situation is much the same in the United States. Very little cadmium is recovered from scrap, and even less is produced as a by-product of lead and copper refining.

^{1 -} Bureau of Mines Minerals Yearbook - 1968

MATERIAL FLOW

CADMIUM

MATERIAL FLOW CHART - 1968

(Thousand Pounds)

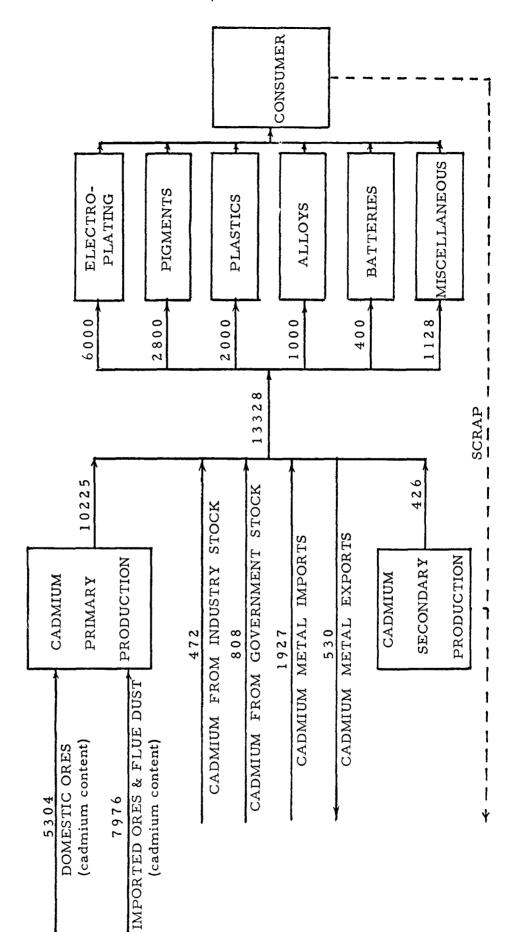


Figure I

MINING AND PROCESSING

In 1968 about ninety six percent of the cadmium produced in the United States was primary cadmium and 4 percent was from secondary production - 45 percent recovered from foreign ores; 36 percent from domestic ores; 15 percent from imported flue dust; 4 percent secondary metal derived from reprocessing scrapped alloys.

Cadmium in zinc concentrates from domestic mines is estimated at 5,304,000 pounds (Table II). This is based on mine production of recoverable zinc (Table I), a zinc recovery efficiency of 83 percent, and an average of 0.227 percent cadmium contained in 60 percent zinc concentrates.

Cadmium in imported zinc ores is estimated at 6,208,000 pounds (Table IV). This is based on imports from Canada, Mexico, and other countries (Table III), a zinc recovery efficiency of 83 percent, and an average of 0.283 percent cadmium contained in 60 percent zinc concentrates. Imported lead ores contained 163,000 pounds of cadmium, and flue dust from Mexico contained 1,605,000 pounds. 1/

^{1 -} Bureau of Mines Minerals Yearbook - 1968

TABLE I

MINE PRODUCTION OF RECOVERABLE ZINC UNITED STATES 1968

<u>STATE</u>	SHORT TONS
Arizona	5441
California	3525
Colorado	50258
Idaho	57248
Illinois	18182
Kansas	3012
Kentucky & Maine	9702
Missouri	12301
Montana	3778
Nevada	2104
New Jersey	25668
New Mexico	18686
New York	66194
Oklahoma	6921
Pennsylvania	30382
Tennessee	124039
Utah	33153
Virginia	19257
Washington	13884
Wisconsin	25711
TOTAL	529446

Bureau of Mines Minerals Yearbook - 1968

TABLE II

ESTIMATED CADMIUM CONTENT CONCENTRATES PRODUCED IN THE UNITED STATES

1968

	CADMIUM (Thousand	
ZINC CONCENTRATES		4827
WESTERN STATES	2083	
MISSOURI - KANSAS - OKLAHOMA	370	
ILLINOIS - TENNESSEE - WISCONSI	N 1560	
EASTERN STATES	814	
LEAD - OTHER CONCENTRATES		477
TOTAL		5304

(Estimates Based on Company Confidential Data)

TABLE III

UNITED STATES IMPORTS

ZINC ORES

1968

COUNTRY		SHORT TONS
AUSTRALIA		2267
BOLIVIA		9027
CANADA		310586
GERMANY, WEST		5942
HONDURAS		12959
MEXICO		142313
MOROCCO		15715
NETHERLANDS		3313
PERU		39899
SOUTH AFRICA		4287
OTHER		74
	TOTAL	546382

Bureau of Mines Minerals Yearbook - 1968

TABLE IV

ESTIMATED CADMIUM CONTENT UNITED STATES IMPORTS ZINC ORES AND FLUE DUST

1968

CADMIUM CONTENT (Thousand Pounds)

ZINC ORE

	CANADA		1755	
	MEXICO		3430	
	OTHER		1023	6208
LEAD	ORE			163
FLUE	DUST			1605
		TOTAL		7976

(Estimates Based on Company Confidential Data)

Cadmium production during the year was 10,651,000 pounds, including primary and secondary metal, and the equivalent metal content of cadmium sponge used directly in the production of compounds. $\frac{1}{2}$

CADMIUM METAL IMPORTS & EXPORTS

Cadmium metal imports totaled 1,927,000 pounds. These were mostly from Australia, Canada, Japan, Mexico, and Peru. Exports during the year were 530,000 pounds. $\frac{2}{}$

CADMIUM STOCKS

Total industry stocks of cadmium metal at the beginning of 1968 were 1,541,000 pounds, but by the end of the year the total was only 1,069,000 pounds. This was a 472,000 pound difference. At the same time there was a 808,000 pound draw-down of Government stocks. $\frac{3}{}$ During 1968, 1,280,000 pounds of cadmium from stocks went to reprocessing.

^{1-2-3 -} Bureau of Mines Minerals Yearbook - 1968

REPROCESSING

The apparent consumption of cadmium in the United States during 1968 has been reported at 13,328,000 pounds. $\frac{1}{2}$

ELECTROPLATING

For many years the chief use of cadmium metal in the United States has been for electroplating, and most has been used for plating of iron and steel. The industrial and commercial applications for cadmium plating are numerous, including: components for aircraft, automobiles, electrical and electronic apparatus, household appliances, radio and television sets, hardware, and fasteners. It offers an effective protective coating against corrosion, especially for such environments as salt water and tropical atmospheres.

For the period 1940-44, 71 percent of the cadmium used in the United States was for electroplating (averaging 5.4 million pounds per year). $\frac{2}{}$ In 1968 the consumption for that purpose was 6 million pounds or about 45 percent of the total cadmium used during that year. $\frac{3}{}$ While this is a decrease of 26 percent, the

^{1 -} Bureau of Mines Minerals Yearbook - 1968

^{2 -} Mentch, Robert L. and Lansche, Arnold M., Cadmium A Materials Survey, Information Circular 7881. Bureau of Mines - 1958

^{3 -} Frawley, E. V., American Metal Market, August 25, 1969

amount consumed is still larger than for the 1940-44 period, and the electroplating industry is still the largest user of cadmium. Industry does report that there is a definite relationship between the amount of cadmium used for electroplating and the price of the metal.

The electroplating industry has the largest number of users of cadmium metal. The American Electroplaters Society has a membership of about eight thousand. There are many small users and they are located in the United States near small industry; thus they are widely distributed. The large users are located near industrial areas; such as, automotive manufacturing centers, etc.

In this report on cadmium the term electroplating is used to cover all types of plating operations.

PIGMENTS

Cadmium, first used in the sulfide form in paint pigments more than one hundred years ago, is used today in colors for many different purposes, including, durable enamels and finishes, plastics, coated fabrics, textiles, rubber, glass, printing inks, baking enamels, ceramic glazes, artists colors, etc. It is used where extreme color retention is required and in cases of exposure where heat resistance is essential.

Until about 1930, the cadmium red and yellow pigments were essentially in the concentrated form and their use was limited; however the subsequent manufacture of the lithopones caused a tremendous demand for the cadmium colors.

Two cadmium compounds important in the pigment industry are the sulfide and sulfoselenide which are often extended with barium sulfate and then known as cadmium lithopones. The color range of cadmium sulfide is from lemon yellow to orange, and that of cadmium sulfoselenide from orange and light red to deep maroon.

Large quantities of the extended reds were used by the automotive industry until 1955 when there was a world shortage of selenium and the automotive industry turned to other coloring agents. It is doubtful that the cadmium color industry would have shown any

growth since the middle 1950's were it not for the rapidly expanding plastics industry. Cadmium colors, being both heat and light stable in plastics, found immediate acceptance; particularly because of high molding temperatures which would cause less stable pigments to fail.

During 1968 cadmium used in pigments totaled nearly 2.8 million pounds or about 21 percent of all cadmium used in the United States. The principal use was in plastics as a coloring agent.

PLASTICS

An important use of cadmium that is growing rapidly is in plastics. It is used not only in pigments, but in the stabilizers that are added to polyvinyl chloride compounds to prevent discoloration during processing as well as to maintain stability during the useful life of the end product.

Polyvinyl chloride plastics are used for many purposes, such as clear bottles, medical tubing, shoe soles, clear vinyl packaging film for fresh meat, flexible tubing, garden hose, hi-fi and stero records, house siding, wall covering, flooring, furniture, upholstery, automobile upholstery, toys, pipe, table tops, and many other extensively used products. The use of cadmium based stabilizers for plastics used in food packaging has not been approved by the USDA.

During 1968, organic and inorganic colors used in plastics totaled 112 million pounds, up ten percent from 1967, and cadmium pigments used were 4.4 million pounds $\frac{1}{2}$ (cadmium metal content - 1.8 million pounds). During the same period the consumption of heat stabilizers in vinyls was 65 million pounds with barium-cadmiums and the chelates together accounting for 34 million pounds $\frac{2}{2}$ (cadmium metal content 2 million pounds).

^{1-2 &}quot;Modern Plastics", September 1969, p.p. 92 & p.p. 96

ALLOYS

Alloying is an important use of cadmium in solders, low-melting point alloys, bearings and brazing alloys.

Typical cadmium solders contain tin, lead, zinc, cadmium and sometimes a small amount of copper. Others contain only cadmium and zinc. The cadmium content in the various solders varies from approximately ten to forty percent.

Low-melting-point alloys that contain cadmium ore are used for fusible elements in automatic sprinkler heads, fire-detection apparatus, fire-door release links and safety plugs for compressed-gas cylinders and tanks.

Cadmium-base bearings were previously used to a greater extent than they are today. During World War II, this was the second largest use of cadmium, exceeding one million pounds per year.

In brazing the use of silver-cadmium alloys make it possible to join both ferrous and non-ferrous metals with strong, leak-tight corrosion resistant joints. The alloys used for this purpose normally contain from 15 to 25 percent cadmium.

In 1968 cadmium metal used in alloys totaled about one million pounds. $\frac{1}{2}$

^{1 -} Frawley, E. V., "American Metal Market" Aug. 25, 1969

BATTERIES

Although the nickel-cadmium battery has been well known in the United States for many years, its use has been somewhat limited. It has many advantages, including - long life, simple maintenance, maximum current delivery with minimum voltage drop, quick charging, and the ability to operate effectively over a wide temperature range, but its price is considerably higher than for a comparable lead-acid battery.

End uses of the nickel-cadmium battery vary from the small rechargeable items, such as - flashlights, electric shavers, and cordless carving knives, to heavy equipment, such as - busses, diesel locomotives, airplanes, and spacecraft.

In 1968, cadmium metal used in batteries is estimated to be 400,000 pounds, based on information received from manufacturers.

MISCELLANEOUS

More than 90 percent of the cadmium used in 1968 was for electroplating, pigments, plastics, alloys, and batteries. Smaller quantities, totaling about 1.1 million pounds, were used in fungicides, nuclear energy applications, phosphors for television tubes, photography, lithography, process engraving, glass, x-ray screens, compounds for curing rubber, and various other applications.

A relatively new use for cadmium in the rubber industry is in the curing process. A product containing cadmium is used, instead of zinc oxide, as an activator. Reports indicate that this product is not used for tires but mainly for mechanical rubber goods.

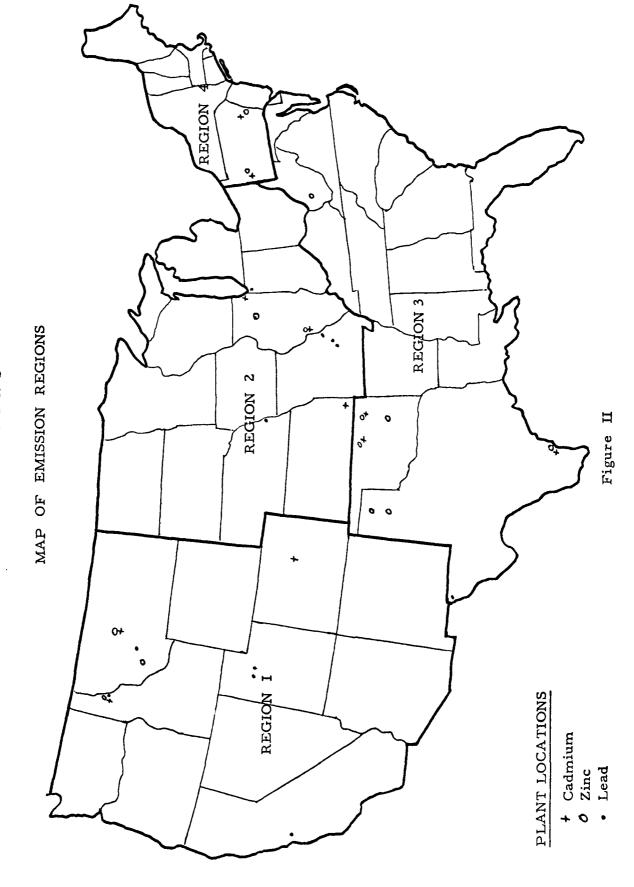
Cadmium in nuclear reactors has been used in the control rods which regulate the fission rate and in other parts as a shielding material.

Cadmium acetate is used in pottery and porcelain to produce an iridescent effect.

Fungicides are another use of cadmium. Reports indicate the larger quantities of the fungicides containing cadmium are used for golf courses. During 1968, cadmium used for

this purpose was more than 25,000 pounds.

Cadmium oxide is used for phosphors in television tubes. It is contained in the black and white tubes, and the blue and green in the color tubes. Other similar applications include: x-ray screens, fluorescent lamps, luminescent dials, etc.



EMISSIONS

CADMIUM EMISSIONS

1968

SOURCE CATEGORY	SOURCE GROUP	SOURCE GROUP PO		
MINING			530	
	Mining	530		
METALLURGICAL PROCESSING			2,100,000	
	Cd Separation			
	from Ores	2,100,000*		
REPROCESSING			33,528	
	Pigments	21,000		
	Plastics	6,000		
	Alloys	5,000		
	Batteries	400		
	Miscellaneous	1,128		
CONSUMPTIVE USES			14,630	
	Rubber Tires	11,400	·	
	Motor Oil	1,820		
	Fungicides	500		
	Fertilizers	910		
INCINERATION OR OTHER				
DISPOSAL			2,440,000	
	Plated Metal	2,000,000*	• •	
	Radiators	250,000		
	Other	190,000		
TOTAL EMISSIONS TO	THE ATMOSPHERE IN T	HE U. S.	4,588,688	
			or	
			2,294 Tons	
EM	MISSIONS BY REGION			
	<u>PLANTS</u>		POUNDS	
Region No. 1	212		920,000	
Region No. 2	758		1,414,000	
Region No. 3	334		996,000	
Region No. 4	496		774,000	
*Source groups (representing 89	percent of total emissi	ons) in regional		
distribution. Undistributed - 11 percent			484,688	

CADMIUM EMISSIONS FACTORS

MINING

Mining and Ore Concentration	NC	0.2 lb/ton of cadmium in ore
METALURGICAL PROCESSING		
Cadmium Recovery from Zinc Concentrates	C	284.0 lb/ton of cadmium charged
Cadmium Recovery from Lead Concentrates	С	1310.0 lb/ton of cadmium charged
Cadmium Refining Units	С	25.0 lb/ton of cadmium charged
REPROCESSING		
Pigment Production	С	15.0 lb/ton of cadmium charged
Production of Stabilizers for Plastics	С	6.0 lb/ton of cadmium charged
Production of Brazing Alloys and Solders	С	10.0 lb/ton of cadmium charged
Nickel-Cadmium Battery Manufacture	NC	2.0 lb/ton of cadmium charged
CONSUMPTIVE USES		
Automobile Tire Wear	NC	0.01 lb/million vehicle miles
Automobile Motor Oil (burned in engine)	NC	0.002 lb/million vehicle miles
Fungicide Spraying	NC	0.05 lb/1000 gallons of spray
INCINERATION & OTHER DISPOSAL		
Production of Iron & Steel	NC	0.015 lb/ton of iron/steel produced
Production of Secondary Copper (from automobile radiators)	NC	3.9 lb/ton of scrap processed
Solid Waste (63,500,000 tons incinerated)	NC	0.003 lb/ton of incinerated solid waste

C - Controlled

NC - Not Controlled

MINING AND PROCESSING

Since no ore is mined solely for the recovery of cadmium, the cadmium emissions to the atmosphere resulting from mining operations are those that occur during the mining and concentration of zinc-bearing ores.

Regardless of the type of mine (underground or open-pit) the processing is basically the same - ore removal, ore handling, crushing, grinding, and concentration. The ore is dry or perhaps damp when removed from the mine, but is wet during the grinding. It is also wet during concentration which is accomplished by means of a flotation process.

While this study was in progress, many mining companies were contacted concerning the quantity of ore mined, its cadmium content, and the cadmium emissions occuring during mining and concentration. Most stated there were no emissions to the atmosphere, and others indicated there were slight emissions, mostly a wind loss from tailings.

Due to the wind loss from tailings the cadmium emissions from sources of mining are estimated at 0.2 pounds per ton of cadmium mined. This would give a total figure of 530 pounds of cadmium emissions to the atmosphere for 1968.

METALLURGICAL PROCESSING

In the United States primary cadmium is recovered principally from foreign and domestic zinc concentrates processed at zinc smelters and refineries. Eight of the fourteen domestic zinc plants that produce primary zinc have the cadmium purification facilities required to produce cadmium metal. These eight plants normally produce about 75 percent of the domestic primary cadmium. The other 25 percent is produced by two cadmium plants that receive their feedstock from other locations. At one of the plants feedstock is principally cadmium flue dust imported from Mexico. At the other plant the feedstock is cadmium bearing zinc ore from which most of the cadmium is recovered before the ore is shipped elsewhere for zinc recovery.

Processing procedures followed at each zinc smelter or refinery are different and the efficiency of dust collection varies from plant to plant, even though many of the plants are of the same general type. This difference is accounted for by the type, age, condition, and arrangement of dust collecting equipment and the number of times the fume is recycled.

Most of the atmospheric emissions occur during the roasting and sintering of zinc concentrates as impurities are removed.

Cadmium is volatilized and condensed to be collected as dust

in the bag houses and/or in the electrostatic precipitators.

From the standpoint of cadmium emissions to the atmosphere, the zinc metallurgical processing plants are the most important.

Lead and copper smelters also process concentrates containing cadmium and even though the cadmium content is low, the losses are relatively high. The concentration of cadmium in the fume from roasting and smelting operations is low; thus the fume is recycled many times to increase its cadmium content to 8 or 10 percent before it is removed from the circuit for further processing. Each time it is recycled some cadmium is lost to the atmosphere so the actual percentage of cadmium lost is rather high. Recycling of fume is practiced to some extent in nearly every plant, including zinc smelters.

Very few operators were found who actually knew the particle size of the emissions. The operators who had collected samples of emissions advised that the emissions vary in size from 4 to 8 microns. This does not necessarily represent the size of the actual cadmium particle. The emissions are composed of cadmium and other materials. Cadmium oxide dust, as it leaves the process, is in a very finely divided state. It is actually a fume, and the minute particles may act as a nucleus to form a larger particle or other material may act as a nucleus to catch

the cadmium fume. The cadmium contained in the fume may be in the form of cadmium oxide. It may be combined with sulphur, iron, or some other element. Field and lab testing were not a part of this contract and operators were not aware of the exact analysis of the emissions, but always referred to it as cadmium oxide or cadmium sulfate.

All zinc and lead smelters that were visited during this study were equipped with electrostatic precipitators and/or bag filters. It is understood that all such smelters in the United States are equipped with similar emission control equipment. Some systems operate more efficiently than others due to the type of process and to the management.

During 1968 cadmium emissions to the atmosphere resulting from metallurgical processing of cadmium-bearing ores totaled more than 2.1 million pounds. This estimate is based on material balance data obtained from processing companies during field trips to lead, zinc, copper, and cadmium plants. The results of stack tests were not available.

Cadmium emissions factors based on data obtained are as follows:

Type Of Plant	Pounds Cd Emissions per ton Cd processed					
Cadmium Recovery Unit	<u>Range</u> 20-30	Average 25				
Zinc Plant (not including Cadmium unit)	220-560	284				
Lead & Copper Plant	1200-1400	1310				

REPROCESSING

The reprocessing companies contacted during field trips, without exception, reported that cadmium was too expensive to be wasted, and their emissions were insignificant.

From data received from reprocessing companies, the estimated cadmium emissions to the atmosphere for the year 1968 - 33,528 pounds.

ELECTROPLATING

Electroplating with cadmium is a process consisting of setting up articles to be coated as cathodes in an electrolytic bath, the anode being metallic cadmium. As direct current electricity is passed through the bath, ions from the electrolyte are deposited on the objects to be coated and an equivalent amount of cadmium is dissolved at the anode.

Virtually all commercial plating is from cyanide baths although cadmium can be deposited from acid baths. Nearly every bath characteristic of importance favors the cyanide-cadmium bath because of its ability to give a dense, fine grained deposit, the excellent covering power, and the good plate distribution on recessed articles.

None of the electrolytic processes operate at one hundred per-

cent efficiency, and some of the electric energy decomposes water in the bath, evolving hydrogen and oxygen gases. If the efficiency is low and the rate of gassing high, the constituents of the electrolyte are discharged to the atmosphere. Fortunately from the standpoint of air pollution, the electrolytic efficiency in cadmium plating is near one hundred percent.

Although most cadmium plating is by electrodeposition, a small amount of special purpose plating is by vacuum evaporation. For this process a special vacuum vessel is required. After the cadmium and the articles to be plated are placed in the vessel, the vessel is sealed and evacuated. Electric heat is applied to the cadmium which soon vaporizes and deposits on the articles to be coated.

During the search for sources of atmospheric emissions, many in the plating industry were contacted concerning their use of cadmium. They reported as follows:

- 1 Low gassing rates
- 2 Agitation of the electrolyte not required
- 3 Masks for workmen not required
- 4 Air pollution control equipment not required
- 5 No cadmium emissions to the atmosphere

During 1968 the cadmium emissions to the atmosphere as the result of electroplating operations were negligible.

PIGMENTS

Cadmium sulfide, also known as cadmium yellow, may be prepared in several ways. One process is by heating cadmium oxide with sulfur and another is to disolve cadmium oxide in sulfuric acid and then precipitate the sulfide from the solution with hydrogen sulfide. Two other methods also include a precipitation step, and it is interesting to note that the color of the sulfide precipitated depends on the particle size. The color is light yellow when the cadmium sulfide is precipitated from a cold solution of low cadmium content and deep orange when it is precipitated from hot acid solutions with hydrogen sulfide.

Cadmium lithopone is prepared by mixing solutions of cadmium sulfate and barium sulfide which yields cadmium sulfide and barium sulfate. This is filtered and calcined in a reducing atmosphere to give it a uniform color. The shade or color of the product depends on the calcining process. The orange shades are obtained when the product is not calcined, but simply dried.

Cadmium sulfoselenide pigments are prepared by adding selenium to a solution of barium sulfide or nitrate, reacting the solution with cadmium sulfate, and calcining with excess sulfur to remove unreacted selenium. This process and many others in commercial use are similar regarding the requirement for a heating or calcining

step.

All major compounders of pigments were contacted during this study and pertinent information was obtained including: the quantity of cadmium used, the type of air pollution control equipment in service, general information concerning the end use of products. None maintained cadmium emissions records but their estimates averaged 15 pounds cadmium emissions per ton of cadmium processed. All reported that they used bag filters for emission control.

The cadmium atmospheric emissions for 1968 would be 21,000 pounds.

PLASTICS

Barium-cadmium stabilizers are now used extensively in the making of plastics so its compounding process is important from the stand-point of cadmium emissions. It is reported that the weight loss of cadmium to the atmosphere is very low during the actual wet processing as the cadmium oxide is reacted with fatty acids to form cadmium soaps. The oxide is charged into the reactor after the fatty acids and the vessel is then sealed; however there is some loss when handling the cadmium oxide prior to and during the time it is introduced into the reactor.

The compounding of cadmium-containing stabilizers can be a significant source of cadmium emissions to the atmosphere. At one facility visited during a field trip permission to view the operations was denied; however from the outside of the plant emissions of particulate matter were quite noticeable. At another plant where operations were observed, no emissions were visible, and the inside of that plant was relatively clean. There were bag filters and the emissions were reported to be less than one-half of one percent.

In this study the emissions reported are based on the manufacturer's estimates, and the emissions factor is 6 pounds of cadmium emissions per ton of cadmium processed. All manufacturers of

stabilizers reported that they use bag filters for emission control.

For 1968 the estimated cadmium emissions from the manufacture of plastic stabilizers is 6000 pounds.

ALLOYS

In the United States about 160 companies produce alloys that contain cadmium, and the quantity used by each company varies from 1000 pounds to 150,000 pounds per year. Products produced are low-melting point solders and brazing alloys that are used by home-owner as well as by manufacturers of appliances and various types of equipment. One common use is in the manufacture of condensers for air conditioners. Another use is in the alloying of copper which is used chiefly for automobile radiators. Several other reported reprocessing operations of cadmium in alloys were explored - use in bearings, and in copper for electrical transmission lines. More than one million pounds annually were used in bearings during World War II but currently the requirement for this purpose is relatively small. Electrical cable manufacturers were contacted but none reported using cadmium during 1968.

Emissions are based on the estimates obtained from manufacturers. The emissions factor is 10 pounds cadmium per ton of cadmium processed. In 1968 the cadmium emissions to the atmosphere were 5000 pounds.

BATTERIES

In the nickel-cadmium battery of the sintered-plate type, the grids of both positive and negative plates consist of sintered carbonyl nickel powder. The active material of the positive plate, when charged is nickel oxide and that of the negative plate is cadmium. Each plate of the core assembly has as its foundation a screen of nickel-wire mesh. This screen is converted into a sheet as nickel powder is deposited in its meshes by a sintering process. It is the active material electrochemically deposited within the pores of the sheets that distinguishes between negative and positive plates.

Manufacturers report nickel emissions in the making of these batteries to be greater than cadmium emissions which are only 2 pounds per ton of cadmium processed.

In 1968 the cadmium emissions to the atmosphere were 400 pounds.

MISCELLANEOUS

Fungicides containing cadmium are used extensively on golf courses, and to a lesser extent on lawns and ornamentals. One such product, used principally on golf courses, is formulated using cadmium oxide in solution with nitric acid and water.

Other formulators report the use of cadmium chloride or cadmium carbonate in their solutions. All those contacted have stated atmospheric losses of cadmium during formulation of fungicides are negligible and that emission controls are not required.

The miscellaneous uses of cadmium include: the curing of rubber, x-ray screens, cathode ray tubes, nuclear reactor components, etc. Based on 2 pounds per ton of cadmium processed, their emissions to the atmosphere are estimated at 1128 pounds.

CONSUMPTIVE USES

Thousands of household and commercial products contain some cadmium even though it was not purposely used in the manufacturing process.

Rubber Tires

Reported tests have shown the cadmium content of motor vehicle tires of different brands to range from 20 to 90 ppm. 1/ This cadmium content, no doubt, was due to the impurity in the zinc oxide used as an accelerator. Nearly all industrial processes involving zinc are subject to the presence of cadmium because both metals derive from the same ores.

Zinc oxide used by the rubber industry in 1968 totaled 111,800 short tons, $\frac{2}{-}$ / and the cadmium content of the zinc oxide was about 0.05% or 111,800 pounds. The rubber used totaled 2,477,000 long tons; $\frac{3}{-}$ / a ratio of 20.2 pounds of cadmium per million pounds of rubber which is in correlation with the test data reported above.

^{1 -} Lagerwerff, J. V. and Specht, A. W., Unpublished data, United States Department of Agriculture, Beltsville, Md.

^{2 -} Bureau of Mines Minerals Yearbook - 1968

³⁻ Chemical & Engineering News, July 14, 1969, pp 46.

Data concerning the wear and cadmium content of motor vehicle tires

Vehicle miles during 1968	1,010,000,000,000
Number of tires per vehicle	4
Pounds of rubber per tire	14
Percent of rubber worn away	
when tire is discarded	20
Percent of cadmium in the rubber	.00202
Mileage life of tire	20,000

Based on the above figures, cadmium emitted by the wear of tires was 11,400 pounds during 1968.

Motor Oil

Oil companies contacted during this study have stated that they add no cadmium to motor oil; however test results show the average cadmium content of five samples of motor oil as 0.48 ppm. $\frac{1}{}$

Vehicle miles during 1968 Oil burned - qts. per 500 mi.	1,010,000,000,000		

Based on oil burned in the engine at the rate of one quart per 500 miles, cadmium emitted by the burning of oil in motor vehicles during 1968 was 1820 pounds.

^{1 -} Letter dated Jan. 16, 1970, Enrione, Richard E. to Spangler, C. V., Project Officer, Air Pollution Control Administration

Fungicides

The fungicides containing cadmium are used mostly on golf courses and applied in liquid form. Actual losses to the atmosphere during spraying vary depending on spray particle size, wind velocity, type of spray equipment, and other factors. Atmospheric losses of cadmium for 1968 are estimated at 500 pounds based on an average loss of 2 percent during application of the fungicides.

<u>Fertilizers</u>

It has been reported that some fertilizers contain cadmium, and that fertilized soils contain more cadmium than unfertilized soils. During this study the large fertilizer companies were contacted, and without exception, they reported no cadmium used in fertilizers. It is known that the cadmium content of superphosphate is about 110 ppm, $\frac{1}{-}$ / and this may be the reported source of cadmium in fertilizers.

During 1968 the production of superphosphate in the United States totaled 4,148,829 short tons. 2/ Cadmium emissions resulting from the use of fertilizers that contain superphosphate are 910 pounds based on an average loss of 0.1 percent.

^{1 -} Caro, J. H., Superphosphate: Its History, Chemistry, and Manufacture, U. S. Department of Agriculture and TVA, pp-273-305.

^{2 -} Current Industry Reports - M Series: M28D(68)-12 U. S. Dept. of Commerce, Bureau of Census.

INCINERATION AND OTHER DISPOSAL

Numerous references that list the major emission sources of cadmium include the metal industries engaged in extraction and refining, but few include or make reference to the emissions that may occur with disposal of scrap.

From 1954 through 1968 the annual use of cadmium in the United States ranged from 7.5 million to 14.8 million pounds; a total of 165 million pounds used during 15 years. (Table V) In the same period the recovery of secondary cadmium from scrap averaged less than 500,000 pounds per year. $\frac{1}{2}$ More than 95 percent of the 165 million pounds of cadmium that was placed in use is still in use or has been disposed of as waste.

Plated Metal

For fifty years the largest use of cadmium in the United States has been for electroplating; mostly for plating iron and steel. It has been reported that cadmium consumed in electroplating in 1955 was about 6.2 million pounds, $\frac{2}{}$ / while steel produced that year totaled 117 million tons: $\frac{3}{}$ / a ratio of 0.053 pounds cadmium used in electro-

^{1 -} Bureau of Mines Minerals Yearbooks - 1952 through 1968.

^{2 -} Mentch, R. L. et al, Cadmium - A Materials Survey, Info. Circ. 7881, Bureau of Mines, 1958, pp 13.

^{3 -} Metal Statistics 1969, The American Metal Market Company Somerset, New Jersey.

TABLE V

APPARENT CONSUMPTION OF CADMIUM

<u>Year</u>		<u>Pounds</u> (thousands)
1954		7499
1955		10684
1956		12711
1957		10966
1958		8242
1959		11589
1960		10126
1961		10184
1962		12146
1963		11482
1964		9365
1965		10431
1966		14780
1967		11561
1968		13328
	Total	165094

TABLE VI

ZINC USED IN GALVANIZING - STEEL PRODUCTION
(Short Tons-Thousands)

Year	Zinc Used In Galvanizing	Steel <u>Production</u>	
1961	382	98014	
1962	389	98328	
1963	420	109261	
1964	456	127076	
1965	482	131462	
1966	474	134070	
1967	459	126920	
1968	<u>459</u>	131098	
	3521	956229	

Pounds of Zinc Used In Galvanizing per ton of steel produced - 7.4

Metal Statistics - 1969

plating per ton of steel produced. In 1963, cadmium consumed in electroplating was reported as 6.3 to 6.9 million pounds, $\frac{1}{2}$ / and steel produced as 109 million tons: $\frac{2}{2}$ / a ratio of 0.058 to 0.063 pounds of cadmium per ton of steel. In this report a ratio of 0.05 pounds of cadmium per ton of steel is used to calculate the amount of cadmium in steel due to cadmium plating.

Galvanized Metal

Steel scrap also contains galvanized metal and the zinc used in galvanizing averages 7.4 pounds per ton of steel produced (Table VI). Since the cadmium content in zinc (for galvanizing) is reported to average about 0.04 percent, the cadmium content in steel due to zinc galvanizing is about 0.003 pounds per ton of steel.

Steel producing companies contacted have indicated that scrap steel they use contains nickel, chromium, copper, manganese, cadmium, zinc and other metals, and that nickel, chromium, and copper will not be emitted to the atmosphere; that manganese will stay in the slag; that other metals will be released as vapors. There are no records showing the cadmium content of the scrap.

^{1 -} Schroeder, H. J., Cadmium - Mineral Facts and Problems; Bureau of Mines Bulletin 630, 1965, pp 165

^{2 -} Metal Statistics 1969, The American Metal Market Co., Somerset, New Jersey.

The 38.5 million tons of steel scrap purchased by the steel industry in 1968 \(\frac{1}{2} \) is estimated to contain 2.04 million pounds of cadmium based on cadmium plated and zinc galvanized steel in the scrap. Cadmium emissions to the atmosphere during steelmaking are estimated at 2.0 million pounds or 0.0152 pounds of cadmium per ton of steel produced.

<u>Auto Radiators</u>

Cadmium is used to harden copper and in automobile radiators the copper contains about 0.2 percent cadmium. 2/ During 1968 auto radiators accounted for 64,394 short tons of copper scrap consumed by secondary producers. 3/ According to information obtained during this study there is no recovery of cadmium by secondary producers of copper and cadmium contained in the scrap is released to the atmosphere during copper recovery operations.

Cadmium emissions to the atmosphere during recovery of copper from scrapped auto radiators are estimated at 250,000 pounds.

^{1 -} Metal Statistics 1969, The American Metal Market Co., Somerset, New Jersey

^{2 -} Trends in the Usage of Cadmium, Materials Advisory Board, Publication MAB-255

^{3 -} Bureau of Mines Minerals Yearbook - 1968.

Other

Solid waste includes many different kinds of articles that contain cadmium. Plastic bottles, auto seat covers, furniture, floor coverings, and numerous items made of polyvinyl chloride, other than food containers, are likely to contain cadmium as a coloring agent and as a stabilizer. There were millions of tons of waste discarded in 1968 that contained cadmium in plastics, pigments and miscellaneous items. These items were using cadmium produced mostly prior to 1968.

During the past ten years cadmium used in plastics and pigments has averaged about 2.3 million pounds annually, and miscellaneous uses during the same period has averaged about 0.9 million pounds. It is estimated that 40 percent of these annual averages were contained in solid waste in 1968, and that 15 percent of the solid waste was incinerated. Based on these estimates, cadmium emissions to the atmosphere from incineration were 190,000 pounds.

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APPENDIX A

PLANTS PRODUCING CADMIUM, LEAD AND ZINC

COMPANY	LOCATION	METAL PRODUCE
American Smelting & Refining Company	Amarillo, Texas Corpus Christi, Tex. Denver, Colo. East Helena, Mont. El Paso, Texas Glover, Missouri Omaha, Nebr. Shelby, California	Zn Zn - Cd Cd Pb Pb Pb Pb Pb
American Zinc Company	Dumas, Texas East St. Louis, Ill.	Zn Zn – Cd
Anaconda Company	Anaconda, Mont. Great Falls, Mont.	Zn Zn - Cd
Blackwell Zinc Company	Blackwell, Okla.	Zn - Cd
The Bunker Hill Company	Kellogg, Idaho	Zn - Cd - Pb
Eagle - Pitcher Industries, Inc.	Galena, Ks. Henryetta, Okla.	Cd Zn
International Smelting & Refining Company	Tooele, Utah	Pb
Matthiessen & Hegeler Zinc Co.	Meadowbrook, W. Va.	Zn
Missouri Lead Operating Co.	Boss, Mo.	Pb
National Zinc Company, Inc.	Bartlesville, Okla.	Zn - Cd
New Jersey Zinc Company	Depue, Ill. Palmerton, Pa.	Zn Zn – Cd
St. Joseph Lead Company	Josephtown, Pa. Herculaneum, Mo.	Zn - Cd Pb
United Refining & Smelting Co.	Franklin Park, Ill	Cd
U. S. Smelting Lead Refinery, Inc.	East Chicago, Ind.	Pb
U. S. Smelting, Refining and Mining Co. Bureau of Mines Minerals Yearbook - 1968 \$\times U. S. GOVERNMENT PRINTING OFFICE: 1973—746771/4185	Midvale, Utah	Pb

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