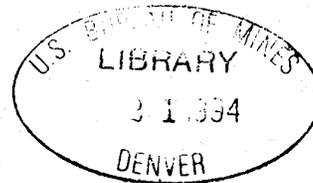


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BUREAU OF MINES
INFORMATION CIRCULAR/1994



Cadmium

(Materials Flow)

By Thomas O. Llewellyn



UNITED STATES DEPARTMENT OF THE INTERIOR

*U.S. Department of the Interior
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**UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary**

BUREAU OF MINES

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CADMIUM

(Materials Flow)

By Thomas O. Llewellyn¹

ABSTRACT

This U.S. Bureau of Mines (USBM) report presents a concise review on sources, processes, supply, and historical use patterns of domestic cadmium. It also covers a preliminary estimated cadmium material flow for the year 1989.

This preliminary study contains information on cadmium and cadmium-bearing products in the United States. The data in this report were obtained from both published and/or unpublished sources of information. However, in order to estimate the fate of cadmium in each operation or application stage, some assumptions, judgments, and correlations were made by the USBM in an attempt to determine the material flows and losses.

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BACKGROUND

Cadmium, a soft, malleable, ductile, bluish-white metal was discovered in Germany in 1817. Germany produced the first commercial cadmium metal later in the 19th century, and it was the only important producer of cadmium until World War I, recovering the metal as a byproduct of the smelting of cadmium-bearing zinc ores of Upper Silesia. Production in the United States began in 1907 when the Grasselli Chemical Company of Cleveland, OH, recovered metallic cadmium as a byproduct of zinc smelting. Before cadmium production started in the United States, about 85% of the cadmium content of the zinc concentrates was lost in roasting the concentrate and fractional distillation of zinc metal.

In the early 1900's, cadmium was imported from Germany as metallic sticks and as cadmium sulfide pigment. As supplies from Germany were curtailed during World War I, domestic production which started in 1907 increased dramatically. By 1917, the United States became the world's leading producer of cadmium, and held that position for more than 50 years.

Apparent consumption of primary cadmium in the United States during the years 1979-89 was at an average rate of 3,880 tons per year (data in metric tons, unless noted). Because not much of this metal was recycled until recently, it can be assumed that most of it either remains dispersed in products or has been released or could be released to the environment.

SOURCES OF CADMIUM

CONVENTIONAL SOURCES

Cadmium minerals are not found alone in commercially viable deposits. Cadmium's abundance in the Earth's crust is about 0.2 part per million (ppm). Greenockite (CdS), the only cadmium mineral of importance, is not found in any isolated deposits, but is nearly always associated with sphalerite (ZnS). Cadmium is usually produced as a byproduct in the recovery of primary zinc from zinc ores, and also from some lead ores or complex copper-lead-zinc ores. However, it is generally agreed that the cadmium in lead and copper ores is associated with the zinc sulfide present rather than with the other minerals.

The feed material for cadmium production consists of fume and dust, collected as flue dust in baghouses during the pyrometallurgical processing of zinc, and of residues resulting from electrolytic zinc production. The availability of cadmium is in most cases dependent on the amount of zinc production. However, smelter residues from which cadmium is recovered may be stockpiled in time of low demand or low prices or both, and can be used to recover metal at a later date.

OTHER SOURCES

No cadmium values are recovered from the sources listed below, except from dust generated during the operation of electric arc furnaces (EAF) used by steelmaking industries. However, these other sources could be considered as the main sources of environmental cadmium because atmospheric emissions from cadmium primary producers have been reduced substantially during the last decade.

Steel Operations

Cadmium is present as a trace element in the raw materials used in the manufacture of iron and steel products. Included in these products are iron ore, coal, limestone, scrap steel, and in the lead and zinc metals used to coat or treat specialty steel products. In the steel industry, cadmium is generated as a fugitive emission from EAF, and open hearth furnaces.

EAF technology has become an important part of the domestic steelmaking industry. EAF operations use steel scrap as feed material and currently represent about 30% of the total steel produced in this country. There are about 80 EAF plants in the United States, and the dust generated by these plants is listed as a hazardous solid waste by the U.S. Environmental Protection Agency (EPA) (1).²

At current production levels the total EAF dust generation, which is collected in baghouses, is estimated at about 550,000 metric tons per year. The total content of the dust by elements, in metric tons, has been calculated as: 100,000 zinc, 12,650 lead, 275 cadmium, 9,500 chlorine, and 2,750 fluorine (2).

Electrical Power Companies

Electric powerplants burn fossil fuels (coal and/or oil); those fossil fuels containing zinc sulfides also contain cadmium. As much as 170 ppm cadmium occur in mid-continental coals. When burned, a great portion of the cadmium reports to the bottom ash as well as the fly ash. About 9.0%, on the average, of coal is ash (3).

²Italic numbers in parentheses refer to items in the list of references preceding the appendixes at the end of this report.

Phosphate Industry

Phosphate rock contains varying amounts of cadmium, depending on the origin of the material. Florida and North Carolina phosphate rock may contain from 5 to 15 ppm cadmium, and phosphate rock from Idaho may contain from 30 to 300 ppm cadmium. During production of phosphoric acid, about 80% of the cadmium concentrates in the acid and 20% reports in the waste gypsum. The inorganic phosphate fertilizer produced, using the acid product, becomes a source of soil cadmium.

The cadmium content in phosphate fertilizers has been estimated at a range of 2 to 20 ppm. This cadmium is dispersed on farm land every year. How much of this

cadmium is absorbed by the crops every year is not known (4).

Municipal Treatment Plants

Almost all sewage treatment effluents contain cadmium as part of the sludge material (4).

Refuse Incinerators

Cadmium is released as a result of incinerating cadmium stabilized polyvinyl chloride (PVC) plastic and other products containing cadmium pigments or cadmium compounds that are found in commercial and household waste (5).

PROCESSING

MINING AND BENEFICIATION

Cadmium is mainly a byproduct of beneficiating and refining of zinc metal from sulfide ore concentrates. The mined zinc ores are crushed and ground to liberate the zinc sulfide particles from the waste host rock. The ground ore is usually treated by a differential flotation process to separate the zinc-bearing particles from the waste rock, yielding a high-grade zinc concentrate and a waste product called tailings. The cadmium content of the zinc concentrate is usually around 0.3% to 0.5%.

An estimated 90% to 98% of the cadmium present in zinc ores is recovered in the mining and beneficiating stages of the extraction process. Figure 1 shows a schematic flow of mining and beneficiating a typical lead-zinc ore.

SMELTING AND REFINING

Refining of zinc and its cadmium content, can be accomplished by treating the zinc concentrates and/or zinc-bearing secondary materials using either a hydrometallurgical or pyrometallurgical process. In both processes, the concentrate is converted from zinc sulfide to zinc oxide by roasting, and at the same time most of the sulfur is removed as sulfur dioxide (SO_2). The SO_2 offgas is stripped of all entrapped dust and other impurities and then converted to sulfuric acid in an acid plant.

Hydrometallurgical Process

In the hydrometallurgical process, zinc, copper, and cadmium are dissolved in the sulfuric acid leach of the roasted zinc ore. The copper and cadmium are among the most common interfering impurities that are removed before the purified solution is subjected to electrolysis for zinc recovery. Copper is precipitated from the solution

using a determined amount of zinc dust. Most of the cadmium is precipitated in a second zinc dust addition, and any remaining dissolved cadmium is precipitated by a third stage of zinc dust addition. The purified zinc sulfate solution is sent to the cellroom and metallic zinc is recovered from the solution by electrowinning. The cadmium precipitate is sent to the cadmium plant where it is filtered and formed into a cake containing cadmium, zinc, and minor amounts of copper and lead. Through various steps of purification the impurities are separated and a

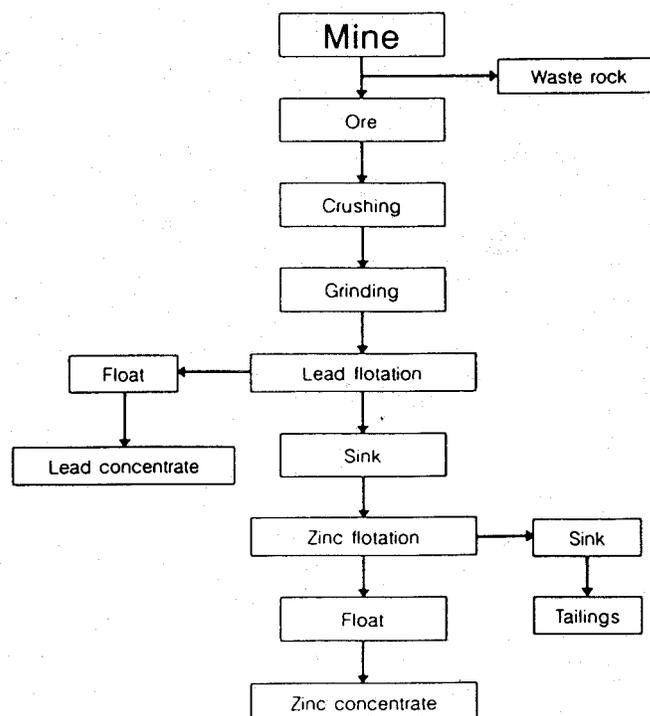


Figure 1.—Schematic flowchart of mining and beneficiating a typical lead-zinc ore.

sufficiently pure cadmium sponge is dissolved in sulfuric acid. Metallic cadmium is recovered by electrolyzing this solution where cadmium is deposited on cathodes. After deposition, the cathodes are removed from the cells and stripped, the cadmium metal is melted and cast into desired shapes. Figure 2 is a schematic flowchart of a hydrometallurgical refining process to produce zinc as well as cadmium metal from zinc concentrates.

Pyrometallurgical Process

In the pyrometallurgical process, cadmium is volatilized during the roasting and sintering of zinc concentrates, and the resultant fume and dust are collected as flue dust in baghouses or electrostatic precipitators. The initial cadmium content of the flue dust can be as high as 10%. A great deal of cadmium collects with the zinc metal and may be removed by refining of zinc by fractional distillation (the boiling point of cadmium is 767° C and that of zinc is 906° C). Figure 3 is a schematic flowchart of a pyrometallurgical refining process to produce zinc and cadmium metal from zinc concentrates.

The following process is usually used to obtain cadmium produced from flue dust collected at lead or copper smelters. Concentrates of copper, and especially lead, contain considerable amounts of cadmium. In copper smelters, the cadmium reports in flue dusts, which are collected and recycled through the smelter system to upgrade the cadmium content. At the lead smelters, the cadmium is fumed off and collected in the blast furnace baghouses. The baghouse dust is recycled to upgrade the cadmium content and later used as feed material for the cadmium refinery plant.

The cadmium-upgraded dusts are charged into a tank and dissolved with sulfuric acid. The resulting solution is filtered to remove impurities and obtain a purified cadmium sulfate solution. Next, metallic cadmium, called sponge because of its appearance, is precipitated from the solution using zinc dust. The sponge is usually briquetted, remelted, and cast into ingots. Some plants produce cadmium oxide and/or metallic cadmium powder. Cadmium oxide is produced by melting the ingots and keeping a controlled oxidizing atmosphere in the retort. To produce metal powder, the melted ingots in the retort are kept under an inert atmosphere while cadmium is distilled into a condenser as metallic powder.

The USBM estimated that about 95% of the cadmium content of zinc, lead, and copper concentrates is recovered in the smelting and refining process stages. As stated in

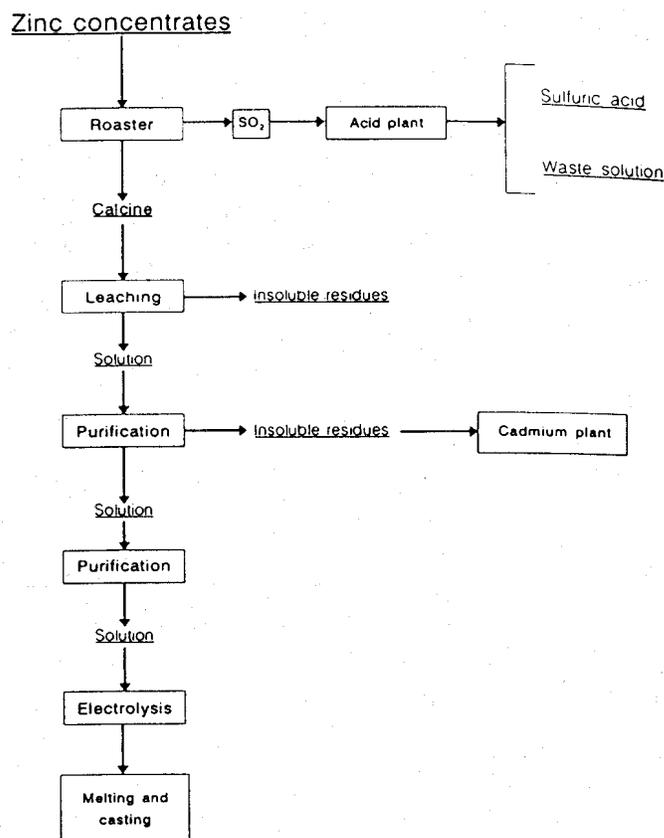


Figure 2.—Schematic flowchart for hydrometallurgical refining of zinc concentrates.

the introduction of this report, several assumptions and correlations were made to estimate recoveries and losses of cadmium in each operation or application stage. A search of the literature together with some personal contacts provided, in part, information on unavailable data.

Assumed loss ranges, throughout this report, should be used with caution, as the actual loss of each stage of treatment would have to be determined on a plant-by-plant basis, and also by identifying each particular area where cadmium losses occur.

Commercial grades of cadmium have 99.95% to 99.96% minimum purity, but for special applications such as semiconductors, grades up to 99.9999% purity are produced by vacuum distillation. Cadmium metal is produced in a variety of shapes such as slabs, ingots, and sticks, which are used in alloying, pigments, and in production of cadmium oxide. Balls and sheets are used for plating anodes.

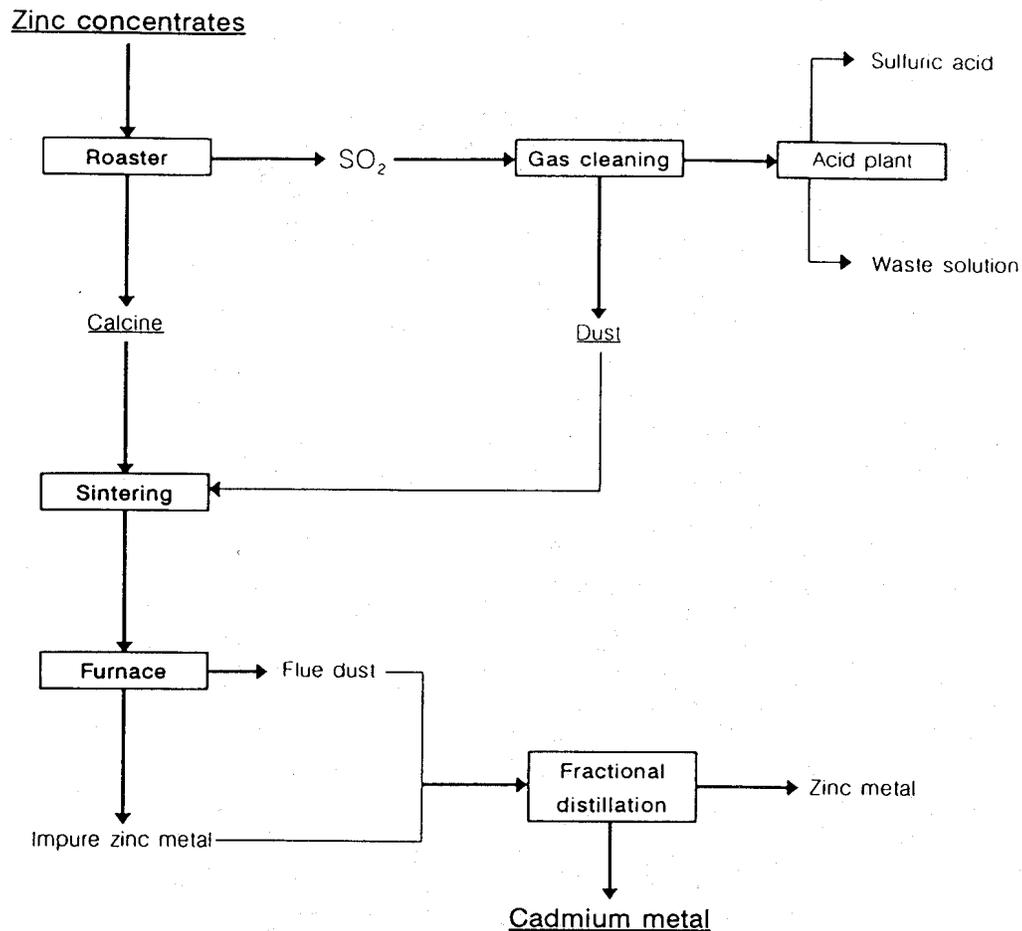


Figure 3.—Schematic flowchart for pyrometallurgical refining of zinc concentrates.

U.S. CADMIUM SUPPLY

PRODUCTION

Before production started in the United States, about 85% of the cadmium content of zinc concentrates was lost in the roasting of the concentrates and fractional distillation of zinc metal. It is assumed that part of the remaining 15% was contained in the zinc metal and part went with the smelter residues.

Production in the United States began in 1907 when the Grasselli Chemical Co. of Cleveland, OH, recovered metallic cadmium as a byproduct of zinc smelting. The cadmium output consisted of metallic sticks and cadmium sulfide. Gradually, other companies started producing cadmium, and by 1917, there were six domestic producers. In 1956, the United States reached its peak cadmium

production of 4,810 metric tons with 14 producing plants. Currently, there are only four domestic primary cadmium-producing plants.

In 1989, primary cadmium was produced by ASARCO Incorporated, Denver, CO; Big River Zinc Corp., Sauget, IL; Jersey Miniere Zinc Co., Clarksville, TN; and Zinc Corp. of America, Bartlesville, OK. The companies in Illinois, Oklahoma, and Tennessee recovered cadmium as a byproduct of smelting domestic and imported zinc concentrates. The company in Colorado recovered cadmium from other sources such as lead smelter baghouse dust. About 3 kilograms of cadmium are produced for every ton of zinc produced. Zinc and lead producers do not have the option of not producing cadmium metal; neither can they avoid generating residues that contain cadmium.

All four domestic cadmium producers use foreign and domestic cadmium-containing ores as feed material for their processes to obtain high-grade refined cadmium. These producers reportedly do not generate any process wastes at their cadmium refinery plants because all residues are recycled to the zinc recovery system (6).

The most reliable numbers for cadmium statistics are those for production of primary cadmium. The average yearly production of cadmium content (metal plus sulfide) for 1907-89, is presented in figure 4.

IMPORTS

In the early 1900's, cadmium was imported from Germany as metallic sticks and as cadmium sulfide pigment. Supplies from Germany were curtailed during World War I, and no cadmium was imported from 1916 to 1920. Imports were resumed in 1921, but in much smaller amounts, and none was imported in 1923, 1925, and 1926.

The average annual quantity of cadmium metal imported into the United States during 1975-89 was 2,581 tons,

which was about 1.6 times the average annual production for the period (see appendix A). For the last 15 years, about 64% of the domestic requirements for cadmium have been met by imported metal and metal contained in imported zinc ores and concentrates. Figure 5 shows the average yearly imports for 1907-89.

EXPORTS

Complete statistics of the exports of cadmium before 1941 were not available, but it is known that domestic cadmium was exported during World War I as well as in other years after the war. The Department of Commerce, which had previously recorded data on cadmium exports in combination with other commodities, began to report them separately in 1941.

The average annual quantity of domestic cadmium metal exported during the years 1975-89 was 212 tons, which represents only about 13% of the average cadmium production for the period, according to appendix A. Exports for 1941-89 are presented in figure 6.

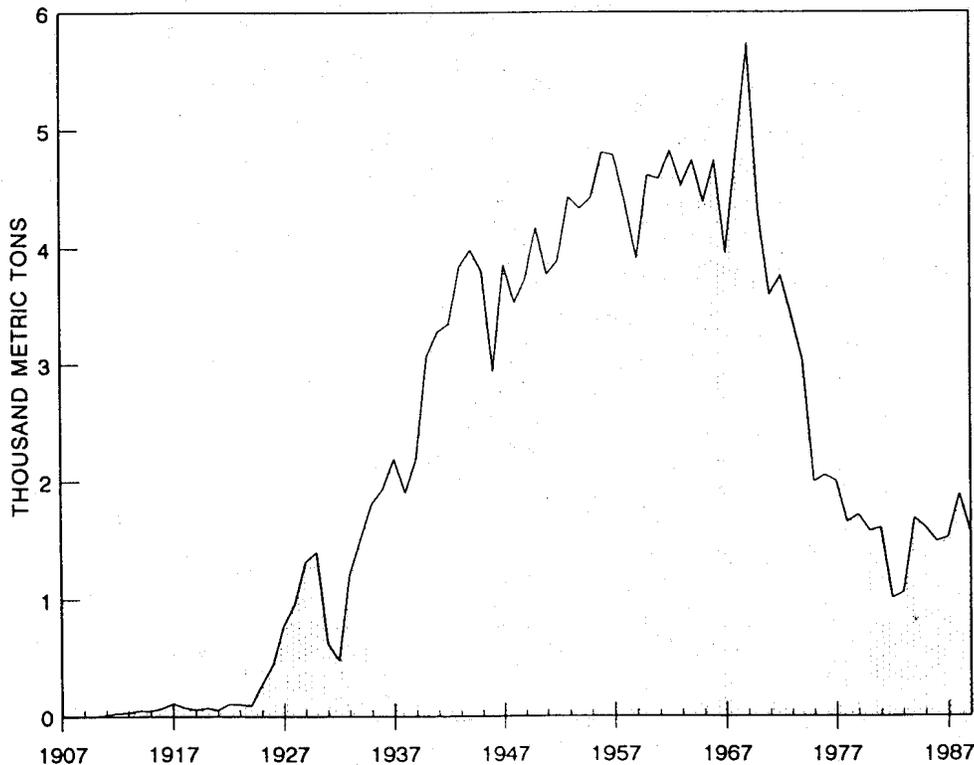


Figure 4.—Annual cadmium production, 1907-89.

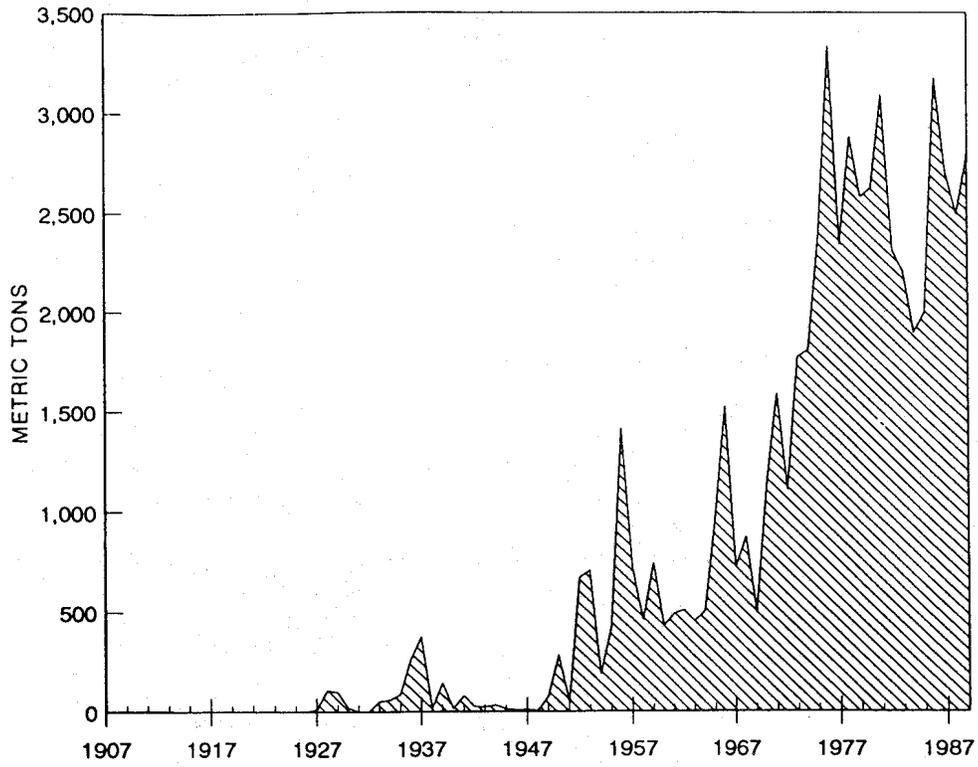


Figure 5.—Annual cadmium imports, 1907-89.

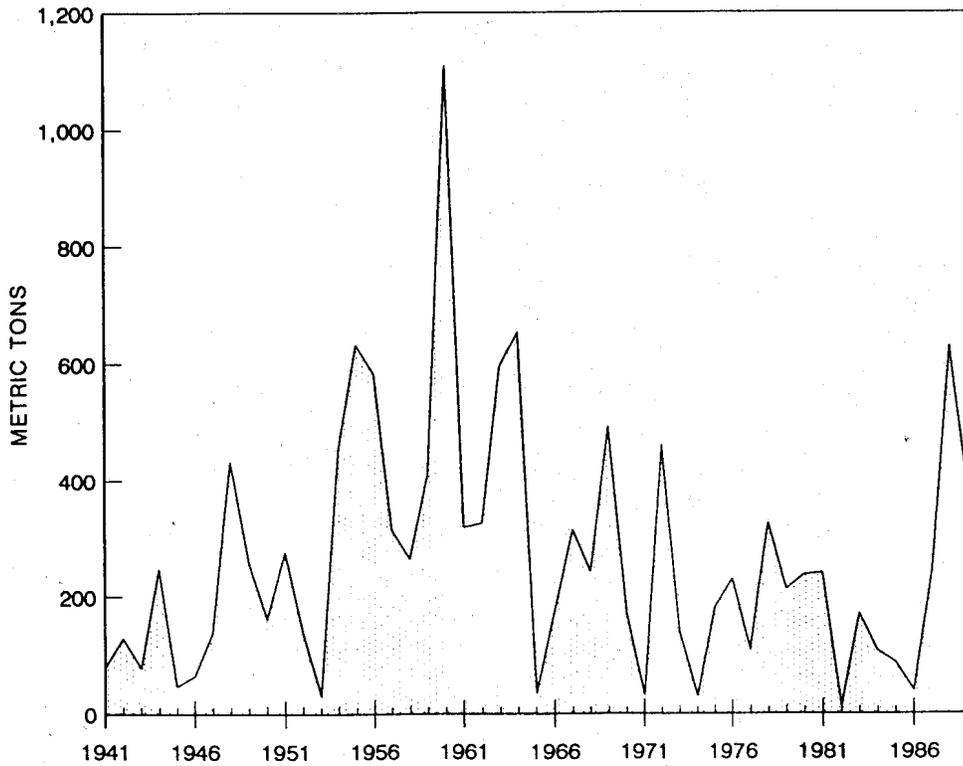


Figure 6.—Annual cadmium exports, 1941-89.

MANUFACTURE/FABRICATION AND USES

HISTORICAL USE PATTERN

For about 70 years after its discovery, cadmium was used primarily in the sulfide form in small amounts in paint pigments. Some reports, which have not been confirmed, suggested that during the time of the Roman Empire the bright yellow colors on paintings were produced using natural cadmium sulfide. In the early part of this century, cadmium sulfide was used in this country mainly as pigment. Minor amounts of metallic cadmium were used in amalgams, and other alloys. The common dental amalgam of those days consisted of 26% cadmium and 74% mercury.

During World War I cadmium was used mainly as a substitute for tin. The consumption of tin in the manufacture of food containers for U.S. and Allied troops (combat rations, popularly known as "C-rations") resulted in a scarcity of tin in this country. To conserve tin, the quantity of tin metal in solder formulas was reduced, and cadmium was used in solders as a substitute for tin.

The adoption of cadmium electroplating for rustproofing parts and accessories by the automobile industry was an important factor in making plating the biggest end use for cadmium for many years. Manufacturing of storage batteries using nickel-cadmium cells started in the United States during World War II. For the period 1940-45, the estimated consumption of cadmium in batteries was less than 1%, while that of plating was about 70%. However, by 1989, the consumption of cadmium in batteries reached 35%, and plating had gone down to 30%. The remaining 35% was distributed as follows: pigments, 15%; plastics and synthetic products, 10%; and alloys and other uses, 10%.

Batteries

Batteries are classified as primary or secondary. Primary batteries can be used only once because the chemical reaction that produces the electrical current is irreversible. Secondary batteries, also known as storage batteries or accumulators, are used, recharged if needed, and reused. The chemical reaction, that provides the electrical current from the battery, can be reversed by supplying the electrical current to the battery.

Cadmium is used in secondary batteries, and its use has grown in importance during the last two decades and now represents the major use for cadmium. Cadmium is used in the negative plates of nickel-cadmium (Ni-Cd), mercury-cadmium, and silver-cadmium batteries. Ni-Cd batteries are by far the most popular of the three, and production of mercury-cadmium batteries is being phased out. The other two types of cadmium batteries are more specialized and expensive. These batteries are manufactured in two

basic types - the smaller sealed cell and the large vented cell (7, 8).

Sealed cell Ni-Cd batteries have a wide range of industrial and domestic applications which include: portable electric appliances, tools, portable telephones and televisions, toys, calculators, data processing and computer memory retention, and several others. Sealed cells do not require servicing nor maintenance other than recharging.

The vented cell Ni-Cd batteries also have a wide range of industrial applications such as: engine starting for locomotives, aircraft, and vehicles; alarm systems; military communication systems; TV cameras; and navigation systems.

The ratio of cadmium to nickel in nickel cadmium batteries is reported to be 1:3, and the cadmium content of these batteries can vary from about 5% to 20%, depending on the battery type and size.

Limited data are available on the amount of cadmium used to manufacture batteries in the United States. The USBM estimated an apparent consumption of 1,434 metric tons of cadmium for manufacturing batteries in 1989. In order to estimate how much cadmium was lost during the manufacturing of batteries, the literature cited in this report (3, 9), consultations with industry representatives (whenever possible), and the USBM's own assumptions were correlated in an attempt to assign cadmium losses for each manufacturing process throughout this report. Based on the correlations mentioned before, it was assumed that cadmium losses during battery manufacturing could vary from 0.1% to 0.3%. An average loss of 0.2% or about 3 tons was assigned to environmental losses, and 54 tons were probably recycled within the manufacturing process for producing batteries. Of the 1,377 tons cadmium content in batteries entering the market for the year, most likely none were recycled during the year; all the tons were assigned to products in use. Ni-Cd batteries manufactured in 1989 are mostly still in use. Depending on its use, sealed cell Ni-Cd batteries can last about 10 years, and an average lifetime of 5 years is not unusual for these products. For the large vented cell Ni-Cd batteries, a lifetime of 20 to 30 years is often cited (9).

Figure 7 shows a comparison of U.S. estimated apparent consumption of cadmium in 1980 and 1990. In 1980, the estimated cadmium consumption in batteries was 16% and for plating, 34%. However, by 1990, the consumption of cadmium in batteries reached 40%, and plating was down to 26%. During each of the years 1966, 1968, and 1969 domestic cadmium consumption was more than 6,000 tons, according to appendix B. The universal acceptability of cadmium plating provided a continuing high demand level for the metal. Plating was the largest application for cadmium due to its high corrosion resistance

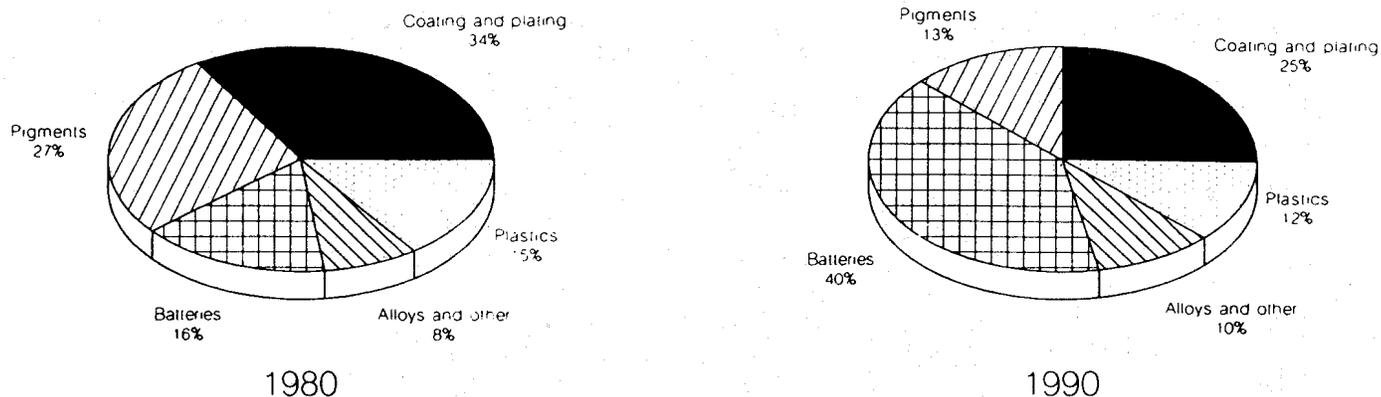


Figure 7.—Comparison of estimated U.S. cadmium consumption, 1980 and 1990.

in parts for automobiles, appliances, aircraft, industrial machinery, and fasteners in general. Cadmium-plated titanium fasteners were a growing market in military aircraft to prevent corrosion failure of aluminum-titanium junctions. But, technological improvements in zinc plating and the economic appeal of zinc started reducing the growth of cadmium after those 3 peak years of consumption. A graphical representation of the domestic consumption for the last 86 years is shown in figure 8, and the corresponding table is in appendix B.

Electroplating and Coating

Cadmium coatings on iron, steel, aluminum, and brass make these metals highly resistant to corrosion in most conditions and especially in marine and alkaline environments. Cadmium coatings also provide a low coefficient of friction, good electrical conductivity, protection from galvanic corrosion, and easy solderability. Cadmium coatings may be applied using several different procedures: by vacuum deposition and sputtering, mechanical deposition by tumbling, and by electroplating using different types of solutions. Cadmium is usually electroplated from an alkaline cyanide solution prepared using cadmium metal or oxide, cadmium or sodium cyanide, and sodium hydroxide together with brightening agents (10).

Non-cyanide plating solutions have also been used in recent years, in an attempt to control water pollution caused by cyanide solution waste (11).

Cadmium coatings are particularly useful in the electrical, electronic, automotive, and aerospace industries. In the electrical and electronic industries, cadmium is used because of its low contact resistance, good solderability, and lack of corrosion buildup. Cadmium plating on contacts, such as silver-cadmium oxide contacts, is said to give excellent corrosion protection in switches. In the automotive industry, cadmium plating is mainly used to protect springs and other brake parts from exposure to salt used

for deicing of roads. The aerospace industry uses cadmium plating to minimize the galvanic corrosion between steel fasteners and aluminum alloys.

The USBM estimated an apparent consumption of 1,229 metric tons of cadmium for coating and plating operations in 1989. To estimate how much cadmium was lost during coating and plating operations, the same procedure of obtaining this information as for batteries was used (3, 9). It was assumed that cadmium losses during coating and plating could vary from about 1% to 3%. An average loss of 2% or about 25 tons was assigned to environmental losses. Of the 1,204 tons cadmium content in coated and plated parts entering the market for the year, most likely none were recycled during the year, all the tons were assigned to products in use. It was assumed that about 20% of the parts will eventually go to waste disposal or will be dissipated to the environment during years of service by wear and corrosion. The other 80% of the cadmium will probably end up in steel scrap, which can be recycled.

Pigments

Cadmium pigments are stable inorganic coloring agents, which have essential properties such as high temperature stability, high resistance to degradation by light, insolubility in organic solvents, and a wide range of excellent brilliant colors and opacity for applications such as ceramics, coatings, plastics, and artists' colors. The pigments are based upon the compound cadmium sulfide, which produces a golden yellow pigment. Partial substitution of cadmium by zinc or mercury and the substitution for sulfur by selenium in the crystal lattice forms a series of intercrystalline compounds making up the intermediate colors in the lemon yellow to maroon range of cadmium colors. Their high heat stability makes them ideal for use in high-temperature plastic moldings. Cadmium compounds are also used as pigments in plastics, paints, enamels, and lacquers. The

amount of cadmium used in 1989 to manufacture pigments was estimated by the USBM at 614 tons. To estimate how much cadmium was lost during the manufacturing of pigments, assumptions were made based on available published information (3, 9), and the USBM's own estimates based on consultations with industry representatives. About 37 tons was considered lost in the manufacturing process. Of that total amount, 3 tons was assigned as loss to the environment, and 34 tons were most likely recycled within the manufacturing plant itself. Of the 577 tons cadmium content in pigments entering the market for 1989, about 85% was used in plastic products, and the other 15% or less was used in ceramics, glass, and paints. Because the lifetime of these products is not known, and the cadmium sulfide in these pigments is not leached when stored outdoors, the cadmium content in these products is assumed to be immobile. The total amount of 577 tons of cadmium content entering the market in these products, would eventually end up in the waste disposal pile, or could be dissipated during years of service, and/or probably a minor amount of it incinerated.

Plastic and Synthetic Products (Stabilizers)

Cadmium is used in liquid or solid form as a stabilizer in plastics. Liquid stabilizers contain from 2% to 5% cadmium and constitute about 1% to 3% of the total weight in polyvinyl chloride (PVC) plastics. Solid stabilizers contain 4% to 12% cadmium by weight and are also present in PVC (12).

Cadmium-bearing stabilizers prevent the degradation of PVC and related polymers by ultraviolet light rays which may cause discoloration and/or mechanical breakdown of the material. Carboxylates of cadmium and barium are mixed to produce the most common stabilizer formulations. The stabilizer is mainly used in liquid form.

In 1989, the apparent cadmium consumption in stabilizers was estimated by the USBM at 410 tons. Cadmium losses during stabilizer manufacturing processes for that year were assumed to be 2 tons, based on published information (3, 9), and the USBM's own assumptions. The 2-ton loss was probably absorbed by the environment because none was recycled. Of the 408 tons of cadmium contained in stabilizers entering the market for 1989, and used almost exclusively in PVC products, all the tons would end up in the waste disposal pile, or could be dissipated during years of service, and/or probably a minor portion of it incinerated; but during 1989 all the tons would remain as products in use.

Cadmium stabilized PVC is used mainly in window frames and other external profiles. The lifetime of these products has been estimated between 25 to 30 years. Producers of cadmium stabilizers are considering using other metal or metals instead of cadmium, because of environmental concerns and regulatory proposals related to cadmium. Argus Witco, considered until now one of the larger producers of cadmium stabilizers for PVC in the United States, is prepared to assist stabilizer users in obtaining non-cadmium alternatives for their applications. The company is now promoting methyltin stabilizers (13).

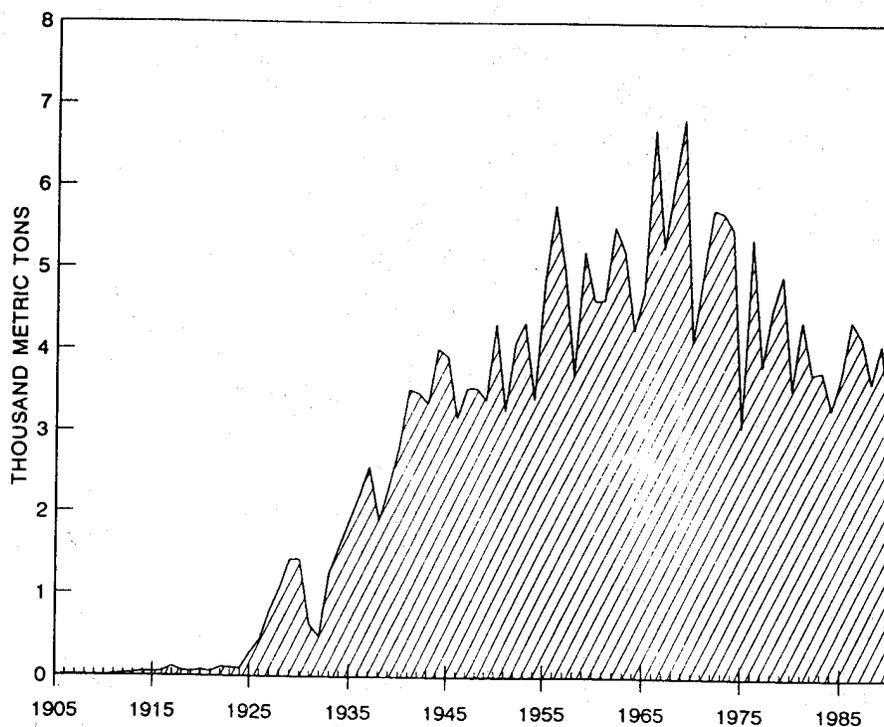


Figure 8.—Annual cadmium consumption, 1905-90.

Alloys and Other

There are several commercial cadmium alloys. The two principal cadmium alloys are copper-cadmium alloys and solders. The presence of small cadmium quantities in alloys can enhance their hardness, wear resistance, and mechanical properties. Addition of 0.5% to 1.2% cadmium increases the strength and wearing qualities of copper without greatly reducing the conductivity, as many other hardening agents do. These improved mechanical properties of copper-cadmium alloys make them attractive for applications in railway catenary and trolley wires.

Other uses for cadmium and cadmium compounds are television screens, fluorescent light phosphors, electrical contacts, solar cells, catalysts for the production of primary alcohols, nuclear reactor controls, and several other minor uses.

The USBM estimated an apparent consumption of 409 tons of cadmium for alloys and other applications in 1989. No specific information has been located regarding

cadmium manufacturing losses in alloys and other uses. However, it is estimated that the losses from manufacture of cadmium-containing alloys are mainly to the air, and in small amounts. To determine how much cadmium was lost in this stage, assumptions were made based on a published European study (9), and 2 tons was assigned to environmental losses. Of the 407 tons cadmium content in these products entering the market for 1989, most likely none were recycled during the year; all the tons were assigned to products in use for 1989 and beyond.

A flowchart representation of losses and recovery of cadmium in smelting and refining, manufacture/fabrication, and products in use is shown in figure 9. This attempted materials balance of each stage covers only 1989. The reader should be advised, once more, to use these numbers with caution as they are only assumed quantities. The actual loss and recycle quantities would have to be determined on a plant-by-plant basis, and in cooperation with each particular industry.

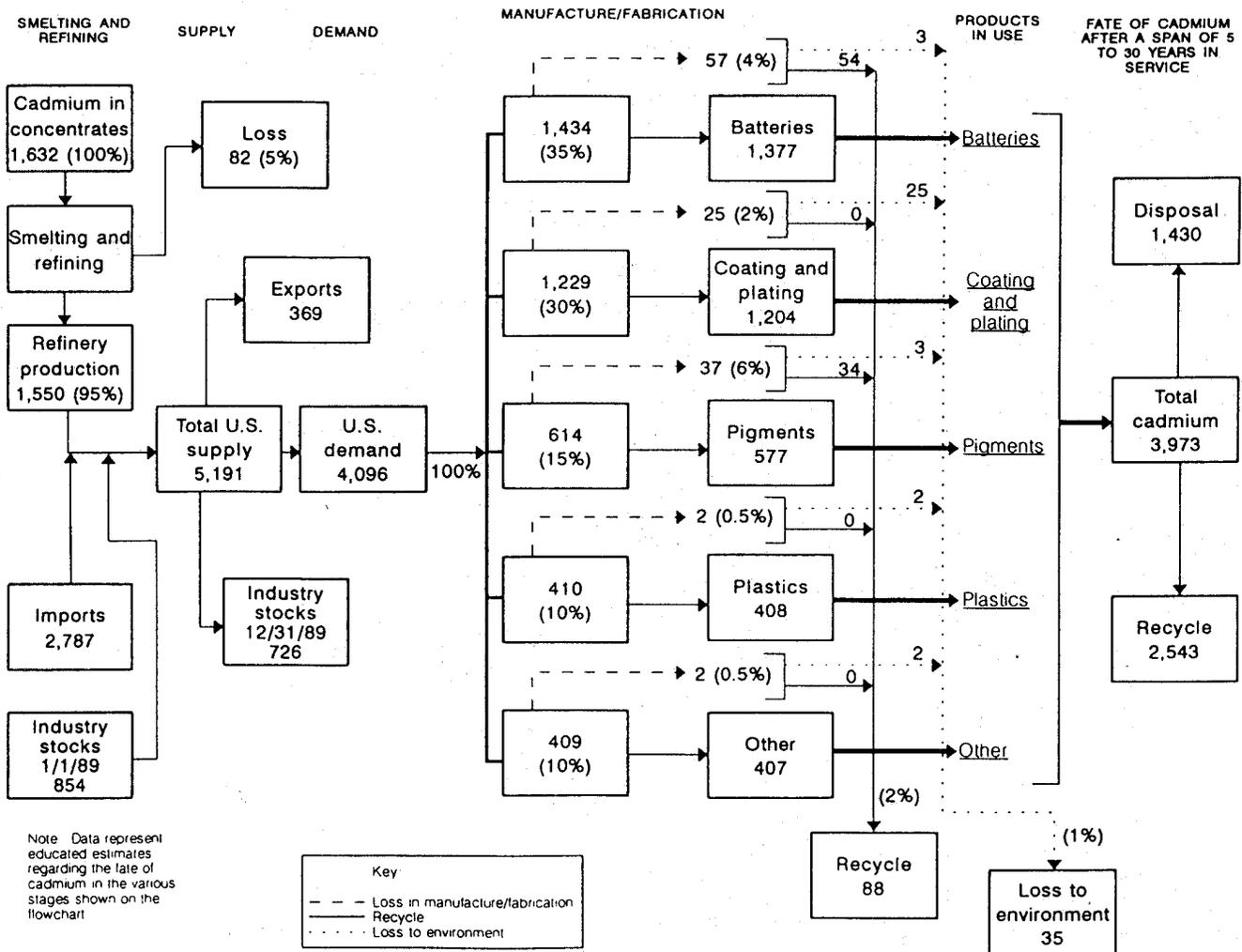


Figure 9.—Materials flow of cadmium in the United States, 1989, in metric tons.

HUMAN EXPOSURE TO CADMIUM

Cadmium is widely distributed in the Earth's crust, and it is principally associated with zinc and other metals. It is usually found in trace amounts as a component of surface soil, underground and surface water, and in air. However, most of the cadmium in the environment results directly from human activities.

The amount of cadmium added to the environment is directly proportional to the level of national industrialization. The highly industrialized countries in Europe, North America, and Japan in Asia, are concerned with the

amount of cadmium entering the environment as a result of manufacturing, uses, and generation of waste products that contain cadmium. The sources of environmental cadmium and how this dissipated metal reaches humans is shown in figure 10.

As shown in figure 10, cadmium is loaded into the environment through several sources, such as: air, surface and ground water, soil, and plants. Human potential exposure to cadmium results from inhaling contaminated air, eating food, drinking water, and by smoking tobacco.

RECYCLING

Currently, most uses for cadmium are dissipative; therefore, not much old scrap is available for recycling. Exceptions are the recycling of some cadmium-bearing alloys and batteries. Cadmium from spent nickel-cadmium batteries and cadmium alloys can be recovered using a pyrometallurgical or hydrometallurgical process. Most of the battery-recycling plants employ pyrometallurgical processes. Large cadmium batteries, normally heavier than 1 to 2 kilograms, are emptied of their electrolyte and dismantled mechanically. The separators are then removed together with the plastic casings, and the cadmium is

recovered by distillation of the plates in specially designed furnaces. The plastic casings and separators of the small sealed batteries are burned off at a lower temperature prior to a higher temperature treatment required for volatilization and condensation of cadmium content.

Cadmium from spent batteries is also being recovered in France, Japan, and the Republic of Korea. Currently Denmark, Germany, the Netherlands, and the United Kingdom are planning to develop recycling facilities. These countries have neither a collection nor a sorting infrastructure in place to generate the supply of spent

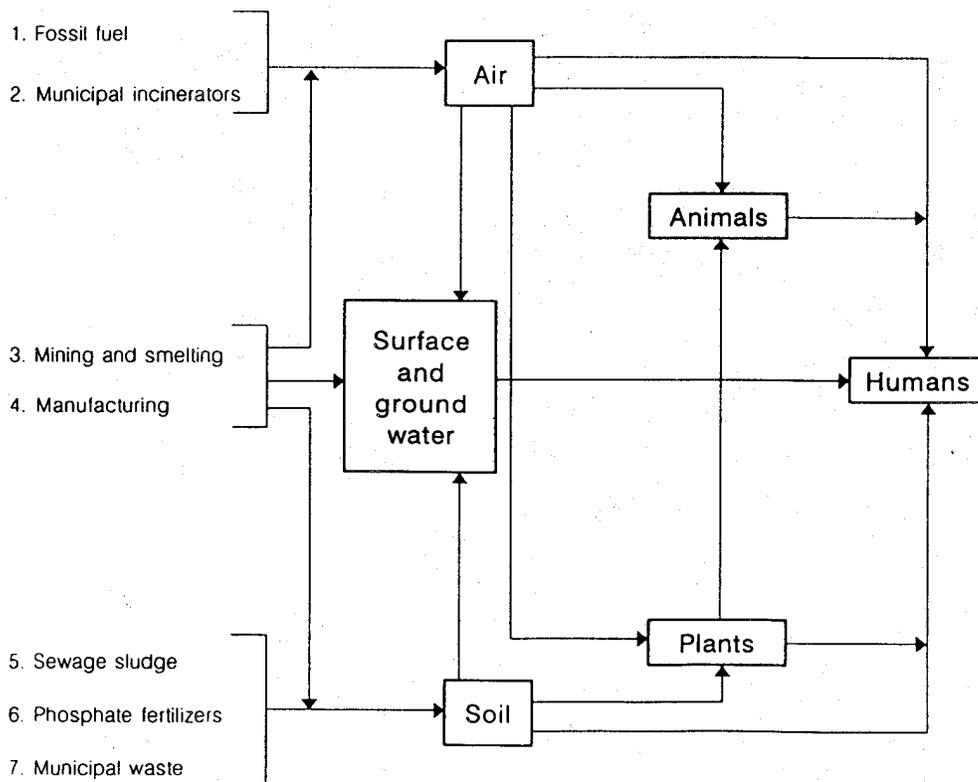


Figure 10.—Schematic representation by which dissipated cadmium reaches humans.

batteries for feedstock, but are actively developing an adequate infrastructure system for future recycling operations.

In 1990, Inmetco, an American company located 35 miles northwest of Pittsburgh in Ellwood City, PA, started recovering cadmium from industrial type Ni-Cd batteries, mainly used in the railroad and telecommunication industries. Inmetco is working with Ni-Cd battery manufacturers and end users to define procedures to recycle their spent batteries. This company has a capacity to process 10,000 tons of spent batteries per year, and it can also use household batteries as feed material.

SAFT NIFE, a battery company in Sweden, has been operating a recycling plant continuously since 1977, and now recovers about 200 metric tons per year of cadmium (14).

Recycling of spent batteries in the United States is expected to reach more than 90% by the end of this century

because of the battery industry's commitment to reclaim most of the cadmium, as well as other mineral content in batteries.

A study sponsored by the steel industry with support of the Center for Metals Production, found that in 1985 only about 15% of EAF dust was reprocessed for zinc and cadmium recovery. Landfill sites absorbed about 73% while the remaining 12% of the cadmium went to other uses or disposal systems (15). However, the amount of EAF dust being processed for its mineral values keeps increasing all the time, and for 1989 was estimated at about 20%. Recycling of EAF dust is expected to reach close to 90% before the year 2000 because of the hazardous nature of its mineral content and a strong commitment by industry to maintain a safe and healthy environment.

ENVIRONMENTAL REGULATIONS

Cadmium has long been recognized as a toxic metal that must be handled with care to avoid prolonged exposure to cadmium fumes and/or dust. Cadmium poisoning can result from inhalation of cadmium dust and fumes or the ingestion of contaminated food and water. Chronic exposure to cadmium can lead to kidney dysfunction.

Because of its toxicity, Sweden's ban on the use of cadmium for coating and plating, stabilizers, and pigments was introduced in 1979. The ban has resulted in a significant reduction in the use of cadmium not only in Sweden but in many other countries. Sweden's cadmium consumption in these sectors was about 100 tons in 1975, by 1985, 10 tons per year, and by 1989, it was reportedly less than 5 tons per year.

On February 6, 1990, the Occupational Safety and Health Administration (OSHA) published a proposed rule to reduce the existing limit for occupational exposure to airborne cadmium. The rule, as proposed, would lower the existing permissible 8-hour exposure limit (PEL) of 100 micrograms per cubic meter for cadmium fumes and 200 micrograms per cubic meter for cadmium dust, to an 8-hour time-weighted exposure limit of either 1 or 5 micrograms per cubic meter as alternatives for all forms of cadmium (16).

The proposed rule also covers supplementary provisions for employee protection, including exposure monitoring, medical surveillance, record keeping, and proper selection and maintenance of personal protective equipment.

OSHA held two public hearings, one in Washington, DC, in June, and the other in Denver, CO, in July 1990. These hearings were held to obtain further information on the feasibility of meeting a 1 or 5 micrograms per cubic meter PEL for cadmium using engineering controls and/or administrative controls.

On August 31, 1992, OSHA, meeting a court-imposed deadline, issued its final decision on permissible 8-hour exposure limit (PEL) to airborne cadmium in the workplace. OSHA's final ruling requires that cadmium fumes or dust levels be lowered to an average of 5 micrograms per cubic meter of air over an 8-hour period. The previous allowable average PEL levels for an 8-hour period were 100 micrograms per cubic meter for cadmium fumes and 200 micrograms per cubic meter for cadmium dust.

OSHA has determined that some processes in six industries would be unable to achieve the PEL of 5 micrograms per cubic meter through engineering controls and work practice alone. Therefore, OSHA established separate engineering control air of either 15 or 50 micrograms for those processes. The six industries were nickel-cadmium battery manufacturing, zinc and cadmium refinery, pigments manufacturing, plastic stabilizers, lead smelting, and plating. These final standards took effect 90 days from their publication in the Federal Register dated September 14, 1992 (17).

RECOMMENDATIONS

Future studies should be made, covering more detailed information on the flow of cadmium into the environment.

Quantitative identification of all sources and losses, as well as chemical and physical presence of cadmium should be

determined to make a comprehensive material balance. This comprehensive study of actual industrial losses and recycling of cadmium must cover all the primary producers, manufacturers of products containing the element,

and those industries that do not use nor produce cadmium but use cadmium-bearing materials in their daily process operations.

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APPENDIX A.—U.S. CADMIUM SUPPLY—1903-89

(Metric tons)

Year	Number of refineries	Production ¹ (a)	Imports (b)	Exports (c)	Apparent supply (a + b - c)
1903	—	—	3.9	NA	3.9
1904	—	—	3.5	NA	3.5
1905	—	—	3.7	NA	3.7
1906	—	—	6.3	NA	6.3
1907	1	6.3	.9	NA	7.2
1908	1	3.6	1.6	NA	5.2
1909	2	2.4	4.0	NA	6.4
1910	2	2.1	1.8	NA	4.0
1911	2	12.7	2.4	NA	15.1
1912	2	26.9	2.4	NA	29.3
1913	2	30.5	.7	NA	31.2
1914	4	49.2	.2	NA	49.4
1915	4	45.1	.1	NA	45.2
1916	4	68.9	—	18.0	51.1
1917	6	111.1	—	NA	111.1
1918	6	75.3	—	19.0	56.3
1919	6	55.9	—	NA	55.9
1920	6	69.6	—	NA	69.6
1921	7	51.8	.1	NA	51.9
1922	9	105.5	.9	NA	106.4
1923	9	100.0	—	NA	100.0
1924	10	90.0	.5	NA	90.5
1925	10	279.3	—	NA	279.3
1926	10	443.2	—	NA	443.2
1927	10	780.0	10.2	NA	790.2
1928	10	959.7	105.7	NA	1,065.4
1929	10	1,322.1	97.2	NA	1,419.3
1930	10	1,403.5	18.2	NA	1,421.7
1931	6	629.5	.1	NA	629.6
1932	6	480.5	—	NA	480.5
1933	10	1,214.9	49.4	NA	1,264.3
1934	10	1,516.9	57.1	NA	1,574.0
1935	10	1,807.8	84.1	NA	1,891.9
1936	13	1,932.3	261.3	NA	2,193.6
1937	14	2,189.1	375.8	NA	2,564.9
1938	14	1,899.0	10.21	6.4	1,892.8
1939	15	2,186.3	140.6	23.6	2,303.3
1940	13	3,069.0	12.5	175.5	2,906.0
1941	19	3,281.0	77.9	77.9	3,270.0
1942	13	3,343.4	24.2	128.6	3,239.0
1943	18	3,840.6	22.2	76.8	3,786.0
1944	18	3,982.5	30.2	248.6	3,764.1
1945	18	3,802.8	13.0	46.4	3,769.4
1946	15	2,935.3	7.9	63.7	2,879.5
1947	16	3,859.3	9.2	137.6	3,730.9
1948	14	3,527.0	4.4	433.5	3,098.9
1949	16	3,731.6	71.3	256.8	3,546.1
1950	14	4,175.9	285.8	160.1	4,301.6
1951	16	3,770.0	40.8	276.0	3,534.5
1952	16	3,886.0	670.8	136.5	4,420.3
1953	16	4,330.4	705.4	29.9	5,105.9
1954	16	4,332.6	182.5	453.1	4,062.0
1955	15	4,424.2	420.7	632.3	4,212.6
1956	14	4,810.1	1,413.2	582.5	5,640.8
1957	14	4,785.0	719.4	314.3	5,190.1
1958	13	4,387.6	454.5	263.1	4,579.0
1959	12	3,901.8	743.0	408.2	4,236.6

See footnotes at end of table.

U.S. CADMIUM SUPPLY—1903-89—Continued

(Metric tons)

Year	Number of refineries	Production ¹ (a)	Imports (b)	Exports (c)	Apparent supply (a + b - c)
1960	16	4,617.6	427.3	1,110.4	3,934.5
1961	16	4,588.1	489.4	318.4	4,759.1
1962	16	4,826.7	506.7	325.2	5,008.2
1963	15	4,531.4	449.5	595.6	4,385.3
1964	12	4,743.7	500.8	652.7	4,591.8
1965	12	4,386.7	962.1	33.1	5,315.7
1966	12	4,744.6	1,523.2	171.9	6,095.9
1967	11	3,945.8	719.8	313.4	4,352.2
1968	12	4,831.3	874.1	240.4	5,465.0
1969	12	5,736.2	489.0	492.1	5,733.0
1970	12	4,293.3	1,130.4	169.2	5,254.5
1971	12	3,597.0	1,587.1	29.9	5,154.2
1972	11	3,560.3	1,098.6	461.3	4,397.6
1973	10	3,402.9	1,767.2	138.8	5,031.3
1974	9	3,023.7	1,800.8	28.1	4,796.4
1975	8	1,989.5	2,375.0	179.6	4,184.9
1976	7	2,047.0	3,332.0	229.0	4,912.0
1977	7	1,999.0	2,332.0	107.0	4,224.0
1978	7	1,653.0	2,881.0	326.0	4,208.0
1979	7	1,715.0	2,572.0	211.0	4,076.0
1980	7	1,578.0	2,617.0	236.0	4,196.0
1981	6	1,603.0	3,090.0	239.0	4,454.0
1982	5	1,007.0	2,305.0	11.0	3,301.0
1983	5	1,052.0	2,196.0	170.0	3,078.0
1984	5	1,686.0	1,889.0	106.0	3,469.0
1985	5	1,603.0	1,988.0	86.0	3,505.0
1986	4	1,486.0	3,174.0	38.0	4,622.0
1987	4	1,515.0	2,701.0	241.0	3,975.0
1988	4	1,885.0	2,482.0	631.0	3,736.0
1989	4	1,550.0	2,787.0	369.0	3,968.0

NA Not available.

¹Metallic cadmium plus cadmium content in sulfide.

**APPENDIX B.—COMPARISON OF U.S. CADMIUM PRODUCTION
AND APPARENT CONSUMPTION—1903-89**

(Metric tons)			(Metric tons)		
Year	Production	Apparent consumption	Year	Production	Apparent consumption
1903	—	3.9	1947	3,859.3	3,538.4
1904	—	3.5	1948	3,527.0	3,536.7
1905	—	3.7	1949	3,731.6	3,395.7
1906	—	6.3	1950	4,175.9	4,330.0
1907	6.3	7.2	1951	3,770.0	3,252.7
1908	3.6	5.3	1952	3,886.0	4,085.8
1909	2.4	6.4	1953	3,430.4	4,340.9
1910	2.1	4.0	1954	4,332.6	3,401.4
1911	12.7	15.1	1955	4,424.2	4,846.1
1912	26.9	29.3	1956	4,810.1	5,765.7
1913	30.5	31.2	1957	4,785.0	4,989.1
1914	49.2	49.4	1958	4,387.6	3,709.0
1915	45.1	45.2	1959	3,901.8	5,204.6
1916	68.9	51.1	1960	4,617.6	4,611.0
1917	111.1	111.1	1961	4,588.1	4,619.0
1918	75.3	63.1	1962	4,826.7	5,509.0
1919	55.9	48.9	1963	4,531.4	5,208.2
1920	69.6	69.6	1964	4,743.7	4,247.5
1921	51.8	51.8	1965	4,386.7	4,731.5
1922	105.5	105.5	1966	4,744.6	6,704.2
1923	100.0	100.0	1967	3,945.8	5,251.7
1924	90.0	90.5	1968	4,831.3	6,045.5
1925	279.3	279.3	1969	5,736.6	6,832.0
1926	443.2	443.2	1970	4,293.3	4,110.9
1927	780.0	790.2	1971	3,597.0	4,932.0
1928	959.7	1,065.4	1972	3,760.3	5,727.1
1929	1,322.1	1,419.3	1973	3,402.9	5,685.4
1930	1,403.5	1,421.7	1974	3,023.7	5,488.5
1931	629.5	629.6	1975	1,989.5	3,055.0
1932	480.5	480.5	1976	2,047.0	5,381.0
1933	1,214.9	1,264.3	1977	1,999.0	3,818.0
1934	1,516.9	1,574.0	1978	1,653.0	4,510.0
1935	1,807.8	1,891.0	1979	1,715.0	4,928.0
1936	1,932.3	2,193.6	1980	1,578.0	3,534.0
1937	2,189.1	2,564.9	1981	1,603.0	4,378.0
1938	1,899.0	1,892.8	1982	1,007.0	3,728.0
1939	2,186.3	2,303.3	1983	1,052.0	3,763.0
1940	3,069.0	2,802.0	1984	1,686.0	3,300.0
1941	3,281.1	3,522.6	1985	1,603.0	3,720.0
1942	3,343.4	3,474.1	1986	1,486.0	4,385.0
1943	3,840.6	3,347.0	1987	1,515.0	4,178.0
1944	3,982.5	4,021.1	1988	1,885.0	3,620.0
1945	3,802.8	3,920.3	1989	1,550.0	4,096.0
1946	2,935.3	3,167.7			