

U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

MINERAL COMMODITY PROFILES

CADMIUM

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Reston, VA

Open-File Report 02-238

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MINERAL COMMODITY PROFILES CADMIUM

By W.C. Butterman and Jozef Plachy

OVERVIEW

Cadmium is a soft, low-melting-point metal that has many uses. It is similar in abundance to antimony and bismuth and is the 63d element in order of crustal abundance. Cadmium is associated in nature with zinc (and, less closely, with lead and copper) and is extracted mainly as a byproduct of the mining and processing of zinc. In 2000, it was refined in 27 countries, of which the 8 largest accounted for two-thirds of world production. The United States was the third largest refiner after Japan and China. World production in 2000 was 19,700 metric tons (t) and U.S. production was 1,890 t. In the United States, one company in Illinois and another in Tennessee refined primary cadmium. A Pennsylvania company recovered cadmium from scrap, mainly spent nickel-cadmium (NiCd) batteries. The supply of cadmium in the world and in the United States appears to be adequate to meet future industrial needs; the United States has about 23 percent of the world reserve base.

Three-fourths of the cadmium consumed goes into nickel-cadmium (NiCd) batteries. Most of the remainder is used in colorants and pigments, coatings, and stabilizers for organic polymers, but small quantities are used for more than 30 other uses. Although the NiCd battery is a growing application, some of the other uses are being phased out, or at least constrained, by concern about cadmium's toxicity and, consequently, its potential for pollution of the environment. Considering that many of cadmium's uses are essentially dissipative, this concern is understandable. All these uses together, however, add only a very small amount of cadmium to the environment. The major contributions come from the use of phosphate fertilizers, iron and steel production, the smelting of nonferrous metals, and the combustion of fossil fuels.

HISTORICAL BACKGROUND

Cadmium was discovered in 1817 by Friedrich Stromeyer, who isolated it from an anomalously colored sample of zinc ore and named it "cadmium" after cadmeia, the ancient Greek name for zinc ore. It was first used as yellow cadmium sulfide paint pigment later in the 19th century. The first commercial cadmium metal was produced in Germany in the 1880s as a byproduct of the smelting of zinc ores from Upper Silesia (now part of Poland). Germany remained the most important producer until the outbreak of World War I; its annual production peaked at about 43 t in 1912 (Siebenthal, 1918). Commercial production in the United States began in 1907 when the Grasselli Chemical Co. of Cleveland, Ohio, recovered 6 t of cadmium metal as a byproduct of the fractional distillation of zinc ores. As imports from Germany were curtailed during World War I, domestic production increased rapidly, and by 1917, the United States had six domestic producers and had become the world's leading producer of cadmium. The United States and Germany then accounted for practically the entire world production of cadmium. Production was spurred by the development of the cadmium electroplating process in 1919, which was applied mainly to the coating of iron and steel, and by the extensive use of cadmium alloy sleeve bearings in automobile engines for several years in the 1930s. The uses of cadmium had expanded to include dental amalgams, low-melting alloys, metal for stereotype plates, and as a strengthener for the copper used in telephone and telegraph lines. By the 1940s, electroplating represented about three-fourths of domestic cadmium consumption. Production of cadmium in the United States peaked in 1969 at 5,700 t; consumption peaked in the same year at 6,800 t (fig. 1). Since then, production and consumption have declined because of the migration of primary zinc production from the United States to other countries, and because of environmental concerns about the toxicity of certain forms of cadmium. During the second half of the 20th century, cadmium use came to be dominated by the application in NiCd electrical batteries. By 2000, about three-fourths of the cadmium consumed went into batteries, and the remaining one-fourth was used for pigments, coatings and platings, stabilizers for plastics, and miscellaneous small-volume uses (Plachy, 2001).

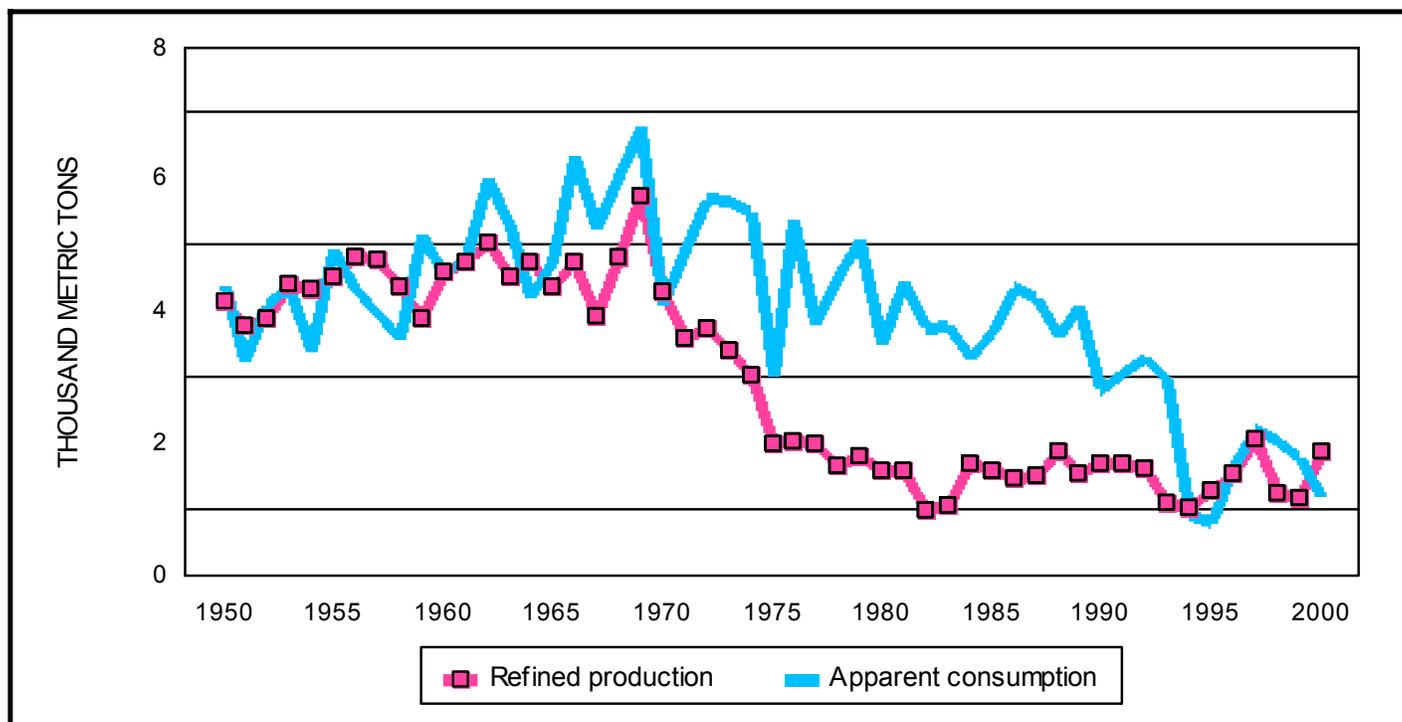


Figure 1. U.S. refined production and apparent consumption of cadmium, 1950-2000.
[Data from U.S. Bureau of Mines (1950-95); U.S. Geological Survey (1996-2001).]

DESCRIPTION

SALIENT FACTS

Cadmium is a soft, ductile, silver-white metal that has a wide range of industrial uses. Chemically, it is a divalent 4d transition element, atomic number 48, atomic weight 112.41, electron configuration $[\text{Kr}]4d^{10}5s^2$, located in period 5, group 12 (or IIB), of the periodic table. It crystallizes in a distorted hexagonal close-packed structure as do its neighbors in group 12, zinc and mercury. As a result of this relatively weakly bonded structure, cadmium has low tensile strength, is soft enough to be cut with a knife, and has the low melting point, for a metal, of 321.1 °C. Its density is 8.65 grams per cubic centimeter at room temperature. Of the 43 known isotopes of cadmium, 8 occur naturally. Cadmium is associated in nature with zinc (and, less closely, with lead and copper) and is extracted mainly as a byproduct of zinc smelting (Berry and Mason, 1959, p. 313, 316; Greenwood and Earnshaw, 1998, p. 1201-1226).

Cadmium metal quickly forms a surface oxide layer upon exposure to moist air. In general, it is susceptible to attack by acids but unreactive towards alkalis. When heated, it reacts with oxygen, the halides, sulfur, and phosphorus but is unreactive towards carbon, hydrogen, or nitrogen. Some cadmium compounds are highly toxic (Greenwood and Earnshaw, 1998, p. 1205-06).

PRINCIPAL FORMS, ALLOYS, COMPOUNDS

METAL AND ALLOYS

Cadmium is recovered in the form of metal sponge from the zinc-cadmium sludge generated at zinc refineries. Although this has some limited use, most of it is upgraded by distillation to commercial grade then melted and cast into marketable shapes. Cadmium forms numerous alloys with a variety of metals. One of its more important uses as an alloying agent is in the hardening and strengthening of copper used for electrical and thermal transfer applications. Cadmium is a component of a number of low-melting-point solders designed for use on electronics circuitry. Other cadmium-containing solders have been used for joining aluminum parts, and high-cadmium solders have been used for joining steel parts.

COMPOUNDS

Cadmium forms many divalent inorganic compounds that have a wide assortment of uses. Also, many organic compounds of cadmium have been synthesized, but only a very few are commercially important. Several dialkyl and diaryl cadmium compounds have found use. For example, diethylcadmium, $(C_2H_5)_2Cd$, and diphenylcadmium, $(C_6H_5)_2Cd$, are polymerization catalysts for several monomers. Dimethylcadmium, $(CH_3)_2Cd$, cadmium acetate, $Cd(CH_3COO)_2 \cdot nH_2O$, and cadmium salts of long-chain fatty acids, such as cadmium stearate and cadmium laurate, also are commercially important (Herron, 1992, p. 773-775). A selection of cadmium compounds, with their principal uses, is listed in table 1.

Table 1. Selected compounds of cadmium and their uses.

[Data from Mote, 1950; Herron, 1992.]

Compound	Composition	Uses
Inorganic compounds:		
Cd antimonide	CdSb	Semiconductor, thermoelectric generator.
Cd arsenide	CdAs	Semiconductor, photodetectors, thermodetectors.
Cd borates	$nCdO \cdot C \cdot mB_2O_3$, in ratios 1:3, 2:3, 3:2	Phosphors.
Cd borotungstate	$2Cd \cdot CB_2O_3 \cdot WO_3 \cdot 18H_2O$	Heavy-media mineral separation.
Cd bromide	CdBr ₂	Photography, lithography, process engraving.
Cd carbonate	$CdCO_3 \cdot C1/2H_2O$	Catalyst for organic reactions.
Cd fluoride	CdF ₂	Phosphors, glass, electric brushes, nuclear reactor control rods.
Cd fluoroborate	$Cd(BF_4)_2$	Electrolyte for plating high-strength steel.
Cd hydroxide	$Cd(OH)_2$	Positive anode material in NiCd batteries.
Cd iodide	CdI ₂	Phosphors, lubricants, photography, photoconductor, lithography.
Cd nitrate	$Cd(NO_3)_2$	Photographic emulsion, colorant for glass and ceramics, starting material for Cd hydroxide for NiCd batteries.
Cd oxide	CdO	PVC heat stabilizers, Cd cyanide plating baths, mixed with silver in electrical power contactors, lends heat resistance to plastics and rubber, phosphor, glass colorant, catalyst for organic reactions, starting material. for many important Cd compounds.
Cd phosphide	Cd ₃ P ₂	Semiconductor for laser use.
Cd phosphate	$Cd_3(PO_4)_2$	Phosphor, catalyst.
Cd dihydrogen phosphate	$Cd(H_2PO_4)_2$	Polymerization catalyst for gaseous olefins (ethylene, propylene, butylenes).
Cd metaphosphate	$Cd(PO_3)_2$	Exceptionally bright and stable phosphor.
Cd selenide	CdSe	Semiconductor, in solid solution with CdS as a pigment, photocells, rectifiers, luminous paints, ruby glass colorant.
Cd orthosilicate	Cd_2SiO_4	Phosphorescent and fluorescent phosphors.
Cd metasilicate	$CdSiO_3$	Phosphorescent and fluorescent phosphors.
Cd sulfide	CdS	Mainly as a pigment for glass, plastics, paint, ceramic glazes, textiles, solar cells.
Cd sulfate	$CdSO_4 \cdot 8/3H_2O$	Electroplating bath alternative to cyanide, and used in Weston cell (standard EMF cell).
Cd telluride	CdTe	Solar cells.
Cd tungstate	$CdWO_4$	Luminescent crystals for scintillation counters, x-ray screens, phosphors, and catalyst for organic reactions.
Organic compounds:		
Diethylcadmium	$(C_2H_5)_2Cd$	Polymerization catalyst.
Dimethylcadmium	$(CH_3)_2Cd$	Source of Cd for chemical vapor deposition.
Diphenylcadmium	$(C_6H_5)_2Cd$	Polymerization catalyst.
Cd acetate	$Cd(CH_3COO)_2 \cdot nH_2O$	Iridescent glaze for ceramics; colorant.
Cd laurate	$Cd(C_{12}H_{24}O_2)_2$	Plastics stabilizer.
Cd stearate	$Cd(C_{18}H_{36}O_2)_2$	Do.

COMMERCIAL GRADES, SHAPES, SPECIFICATIONS

Cadmium is sold in several forms and grades. Alloyers use slabs (20-60 pounds), bars (9 x ½ x 38 inches) or sticks (9 x ½-inch diameter); platers often use cast balls (about 2-inch diameter); and compound and pigments manufacturers use rods, flakes, powder, and sometimes sponge cadmium. Cadmium is also produced as 1–3 millimeter (mm) shot, in purities as high as 99.99999 percent. Pigment grade cadmium must be low in thallium, and cadmium used in solders must be completely free of aluminum. Three commercial grades of refined cadmium are on the market; the chemical requirements for them are listed in table 2. Under the unified numbering system for metals and alloys, these grades are designated, in order of increasing purity: L01951, L01971, and L01981.

Table 2. Chemical requirements for commercial grades of cadmium.
[Source: ASTM standard specification for cadmium B 440-00.]

Element	Grade		
	(L01951)	(L01971)	(L01981)
Cadmium, minimum ¹	99.95%	99.99%	100.00%
Iron	---	10	5
Copper	150	20	5
Nickel	---	10	5
Lead	250	100	20
Zinc	350	30	5
Thallium	35	35	5
Tin	---	---	1
Silver	---	---	1
Antimony	---	---	0.1
Arsenic	---	---	1
Mercury	---	---	0.1

¹Determined by difference; figures for other metals are maxima in parts per million.

SOURCES OF CADMIUM

PRIMARY CADMIUM

Cadmium is about as abundant in the earth's crust as are antimony and bismuth. At 0.16 gram per metric ton (g/t), it is 63d in order of crustal abundance of the elements. Cadmium is never found as a native metal, and only three cadmium minerals are known, none of which is found in sufficient concentration to be mined alone as an ore. Greenockite and hawleyite are the hexagonal and isometric polymorphic forms of cadmium sulfide, CdS. Otavite is cadmium carbonate, CdCO₃. Greenockite, hawleyite, and otavite are analogs of the zinc minerals wurtzite, sphalerite, and smithsonite, in which they are often occluded. Alternatively, cadmium may substitute, to a limited extent, for zinc in the lattices of the three zinc minerals. On altered or weathered zinc minerals, the cadmium minerals sometimes form coatings as does cadmium oxide in at least one known occurrence (in Sardinia) where it coats the zinc silicate mineral hemimorphite (Wedow, 1973).

Being similar to zinc in chemistry, cadmium is associated closely with zinc in ore deposits. It is produced mainly as a byproduct of zinc processing. Most zinc deposits contain at least traces of cadmium, but the bulk of the cadmium is associated with zinc sulfide ores. Because it is more chalcophile than zinc, cadmium tends to remain in solution in the magma more readily than zinc and, consequently, is concentrated most heavily, relative to zinc, in hydrothermal zinc ores formed in the later lower temperature stages of magmatic differentiation. It is concentrated even more heavily, relative to zinc, in low-temperature reducing environments, such as those in which black shales are formed. These latter, however, are very low-grade resources of zinc and—despite the higher concentration of cadmium—are neither mined nor considered part of the reserve base. The cadmium content of typical zinc ores can be as high as 1.3 percent but is more commonly in the range of 0.2 to 0.3 percent; the world average for zinc concentrates lies in this range (Wedow, 1973, p. 107-108).

RESERVES, RESERVE BASE, RESOURCES

Reserves and reserve base for several of the leading cadmium-producing countries are listed in table 3. All cadmium resources are associated with zinc resources.

Table 3. Cadmium reserves and reserve base, yearend 2000
[In metric tons, contained cadmium. All data are rounded to two significant digits; because of independent rounding, they may not add to totals shown. Plachy, 2001]

	Reserves	Reserve base
United States	90,000	270,000
Australia	110,000	300,000
Canada	55,000	160,000
China	13,000	35,000
Germany	6,000	8,000
Japan	10,000	15,000
Kazakhstan	25,000	40,000
Mexico	35,000	40,000
Russia	16,000	30,000
Other countries	240,000	330,000
World totals	600,000	1,200,000

“Reserves” refers to the in-place cadmium content of ores that can be mined and processed at a profit given the metal prices, available technology, and economic conditions that prevail at the time the reserves estimate is made. “Reserve base” is a more-inclusive term that encompasses not only reserves proper, but marginally economic reserves and a discretionary part of subeconomic resources—the part that is judged to have a reasonable potential for economic extraction in the future. “Identified resources” is an even more-inclusive category that comprises reserves, marginal reserves, all demonstrated subeconomic reserves, and an “inferred” component for each of these three subcategories. Inferred quantities are estimates that are based on an assumed continuity of resources beyond demonstrated resources for which there is geologic evidence that may or may not be supported by samples or measurements (U.S. Bureau of Mines and U.S. Geological Survey, 1980).

Identified world resources of cadmium, which are based on estimated zinc resources of 1.9 billion metric tons that contain, on average, 0.3 percent cadmium, are estimated to be nearly 6 million metric tons. Australia, Canada, and the United States have more than 60 percent of cadmium resources; the United States alone has 23 percent.

SECONDARY CADMIUM

Of the top four uses of cadmium, only NiCd batteries, which account for three-fourths of the cadmium consumed, are recycled extensively enough to provide significant quantities of secondary cadmium. The large industrial batteries, which use about 20 percent of battery cadmium, are recycled at a high rate—about 85 percent. The smaller sealed consumer cells and batteries, which account for the other 80 percent, used to be discarded. That practice is now banned or severely restricted in most industrial countries, and programs for collecting spent batteries are being promoted heavily. The cadmium in pigments, platings/coatings, and stabilizers for plastics, which together account for nearly one-quarter of consumption, is present in low concentrations in these products and cannot be reclaimed economically. The same is true of most of the other 32 end uses (listed in table 5 in the section “Uses”), which together account for only 1 percent of cadmium consumption. Cadmium-tellurium solar cells and silver-cadmium oxide electrical contacts are, however, recycled.

The only other significant source of postconsumer secondary cadmium is electric arc furnace (EAF) dust, which is generated during the recycling of galvanized steel; cadmium is a minor constituent associated with the zinc coating on the steel, and is often not recovered when cadmium prices are low, as they were in 2000. Also, some secondary cadmium is generated in diecasting and other manufacturing processes. An unrecorded amount of secondary cadmium is derived from baghouse dusts collected at copper and lead smelters. These dusts are usually sent to zinc refineries where they are fed into the cadmium recovery circuit and the recovered cadmium is counted as primary metal in the reported statistics.

The authors estimate that in 2000 about 200 t of refined secondary cadmium was produced in the United States. The International Cadmium Association estimates that in 2000 nearly 2,000 t, or about 10 percent of the world’s refined cadmium production, was secondary metal; for 2001, the estimate was raised to 2,500 to 3,000 t, or as much as 15 percent of the world’s total cadmium production (Morrow, 2002).

PRODUCTION TECHNOLOGIES

PRIMARY CADMIUM

Cadmium is recovered as a byproduct of the smelting of zinc ores and lead-zinc ores. Most cadmium is recovered by hydrometallurgical zinc plants—usually referred to as electrolytic zinc plants. Lesser amounts are recovered by pyrometallurgical zinc plants, and by lead smelters that process lead-zinc ores. Although a high percentage of the cadmium contained in zinc concentrates can be recovered, actual recovery is often dictated by the demand for cadmium and by environmental restrictions on the disposal of cadmium-containing wastes, and ranges from no recovery at all (in some countries) to as much as 90 percent. In the United States during the early years of production, less than 20 percent of the cadmium accumulated in smelter flue dusts was actually recovered (Siebenthal, 1918). During the 1970s, with a much larger demand for cadmium, the percentage recovered from smelted and hydrometallurgically processed concentrates typically was in the range of 60 to 75 percent (Roskill, 1990, p. 5).

Zinc processing is based on the reduction of the metal from oxides. The zinc concentrates, which are sulfides, and typically contain from 0.5 to 1.5 percent cadmium, are first roasted to convert the minerals to oxides and lesser amounts of sulfates. During roasting, cadmium oxide, along with lead and some other impurities, is volatilized and captured as flue dust in baghouses and electrostatic precipitators. The collected flue dust, which contains on the order of 10 percent cadmium, can, if desired, be re-fumed in a furnace or kiln to raise the cadmium content to as much as 45 percent. Refuming is necessary at lead and copper smelters where the cadmium content of the concentrates is lower than at zinc smelters.

At electrolytic zinc plants, the flue dust is mixed with the roasted zinc concentrate and dissolved in sulfuric acid. A zinc-cadmium sludge containing anywhere from 5 to 50 percent cadmium is then precipitated by adding zinc dust to the sulfate solution. The extraction of cadmium from this high-cadmium precipitate is effected through a multistep leach-precipitation-filtration process that yields cadmium sponge and, subsequently, a solution of cadmium sulfate that contains about 200 grams per liter (g/l) of cadmium. This solution is then electrolyzed between silver-lead anodes and aluminum cathodes. Cadmium metal is stripped from the cathodes periodically and melted at 380 to 400 °C under sodium hydroxide, which acts as a flux and as a scavenger of arsenic and zinc. The metal is then cast into commercial shapes.

At pyrometallurgical zinc plants or at smelters, the calcine from the roaster may be sintered with coke, a process that results in a considerable volume of cadmium-containing flue dust. Cadmium still remaining in the sinter follows the zinc through processing and may be recovered during purification of the zinc by distillation. The cadmium-rich flue dust travels a different route starting with (in some cases) a further roast and then through a multistep leach-and-filtration process that results in a purified cadmium-zinc leach solution that contains typically 40 to 300 g/l of cadmium and 10 to 80 g/l of zinc. Cadmium is recovered from the solution either by galvanic precipitation by zinc or by electrolysis (Plunkert, 1985; Carr, 1992).

SECONDARY CADMIUM

Secondary cadmium is recovered almost entirely from two sources—NiCd batteries and EAF dust, the latter generated in the recycling of galvanized or cadmium-coated steel scrap. The EAF dust is processed by some of the methods described above. The NiCd batteries are disassembled if they are large or shredded and incinerated if they are small. The cadmium battery plates are charged to a recovery furnace where they are reduced with carbon to metallic cadmium. The cadmium distills off, is precipitated, and then is cast into 4- to 6-mm-diameter flattened discs, minimum 99.95 percent pure cadmium.

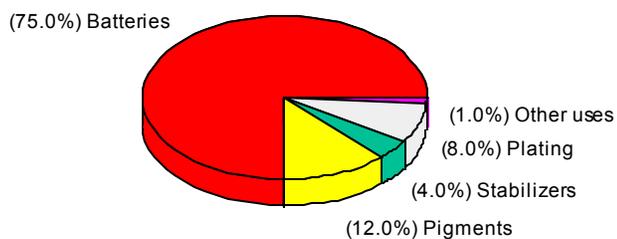
USES

Cadmium possesses chemical and physical properties that singly or in combination have led to a multitude of uses for the metal and its compounds. Properties contributing to cadmium's utility include the following:

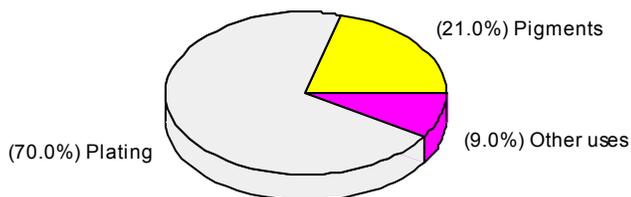
- Low melting point
- Excellent resistance to corrosion in neutral to alkaline and saline environments
- Ability to form ductile alloys with a variety of metals
- Softness combined with good fatigue strength
- Chemical and metallurgical similarity to zinc, and substitutability for zinc
- Formation of amalgam with mercury
- The great durability of cadmium sulfide pigments
- Efficiency as a neutron absorber in nuclear reactors
- Photoelectric parameters suitable for solar energy conversion
- With nickel, forms a good source of electrical energy

A list of three dozen selected applications for cadmium is given in table 4. In addition to these uses, at least two dozen minor uses are not listed. The first four uses in table 4 (listed in order of the amount of cadmium currently used) account for 99 percent of the cadmium consumed; the other 32 uses (listed in alphabetical order) collectively account for only 1 percent.

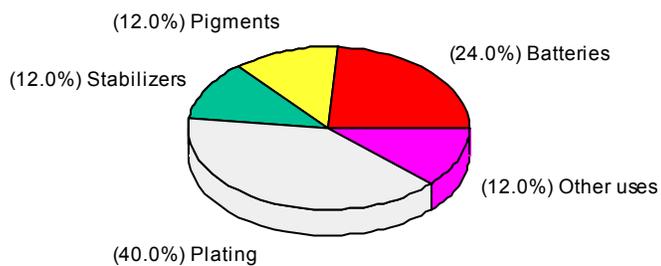
Cadmium is used for the same purposes worldwide, but the relative importance of individual end uses varies from country to country, and the pattern of consumption has changed considerably during the past several decades. Figure 2 shows the great change in the pattern of use in the years since 1960. In all the principal using countries, the trends in that same time period were similar—rapid growth in NiCd batteries, slow decline in pigments, and faster declines in all other use categories.



U.S. apparent consumption in 2000: 1,190 metric tons



U.S. apparent consumption in 1960: 4,560 metric tons



U.S. apparent consumption in 1980: 3,530 metric tons

Figure 2. Shifts in the pattern of cadmium use United States. [Data for 1960 and 1980 from U.S. Bureau of Mines. 1932-2000 from U.S. Geological Survey, 1996-2001.]

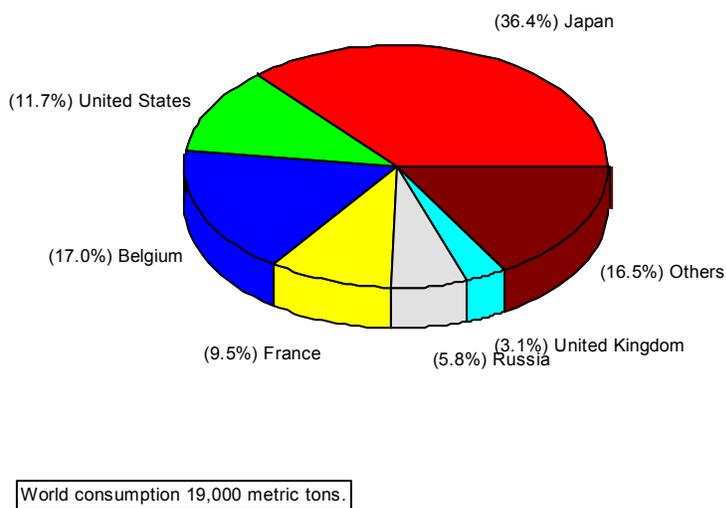


Figure 3. World cadmium consumption, 2000, [Data from World Bureau of Metal Statistics, 2001.]

Cadmium use is concentrated in the industrial countries, six of which account for 85 percent of world consumption (fig. 3). The United States is now the second largest consuming country, having been surpassed by Japan in the 1980s as that country's manufacture of NiCd batteries burgeoned, and, later, by Belgium. Belgium and France, which, like Japan, export a large share of their cadmium-containing products, are the second and fourth largest industrial consumers of cadmium, respectively.

BATTERIES

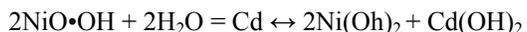
Table 4. Selected uses of cadmium, with alloys and compounds used

[Mote, 1950; Herron, 1992.]

End use process or product	Alloy/compound	Composition
Nickel-cadmium batteries	Cd hydroxide	$\text{Cd}(\text{OH})_2$
Pigments	Cd selenide, Cd sulfide	CdSe, CdS
Coatings and platings	Cd fluoroborate, Cd iodide, Cd oxide, Cd sulfate	$\text{Cd}(\text{BF}_4)_2$, CdI_2 , CdO, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$
Stabilizers for plastics	Cd oxide, Cd laurate, Cd stearate	CdO, $\text{Cd}(\text{C}_{12}\text{H}_{22}\text{O}_2)_2$, $\text{Cd}(\text{C}_{18}\text{H}_{36}\text{O}_2)_2$
Bearings (sleeve)	Cd with aluminum and silicon	Various
Brazing alloys	Cd with copper, zinc, or silver	Various
Cadmium copper	Copper-cadmium	0.1% to 1.5% Cd
Catalysts for organic reactions	Diethylcadmium, Diphenylcadmium, Cd carbonate, Cd tungstate, Cd dihydrogen phosphate	$(\text{C}_2\text{H}_5)_2\text{Cd}$, $(\text{C}_6\text{H}_5)_2\text{Cd}$, $\text{CdCO}_3 \cdot 1/2\text{H}_2\text{O}$, CdWO_4 , $\text{Cd}(\text{H}_2\text{PO}_4)_2$
Chemical intermediates	Cd nitrate, Cd oxide	$\text{Cd}(\text{NO}_3)_2$, CdO
Chemical vapor deposition	Dimethylcadmium	$(\text{CH}_3)_2\text{Cd}$
Colorants for glass, ceramics, plastics, etc.	Cd nitrate, Cd oxide, Cd selenide, Cd sulfide, Cd acetate	$\text{Cd}(\text{NO}_3)_2$, CdO, CdSe, CdS, $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$
Electric motor brushes	Cd fluoride	CdF_2
Electrical power contactors	Silver-cadmium	14% max. Cd as CdO
Electroplating	Cd fluoroborate, Cd iodide, Cd oxide, Cd sulfate	$\text{Cd}(\text{BF}_4)_2$, CdI_2 , CdO, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$
Heavy-media separation of minerals	Cd borotungstate	$2\text{Cd} \cdot \text{B}_2\text{O}_3 \cdot \text{WO}_3 \cdot 18\text{H}_2\text{O}$
Nuclear reactor control rods	Cd fluoride	CdF_2
Phosphors	Cd borates, Cd fluoride, Cd oxide, Cd phosphate, Cd metaphosphate, Cd orthosilicate, Cd chloride Cd tungstate, Cd sulfide	$n\text{CdO} \cdot m\text{B}_2\text{O}_3$, CdF_2 CdO, $\text{Cd}_3(\text{PO}_4)_2$ $\text{Cd}(\text{PO}_3)_2$ Cd_2SiO_4 , $\text{CdC}_{12} \cdot 5\text{H}_2\text{O}$ CdWO_4 , CdS
Photoconductive devices	Cd selenide, Cd telluride	Cd Se, Cd Te
Photodetectors	Cd selenide, Cd sulfide Cd arsenide, Cd iodide; Cd selenide Cd mercury telluride	CdSe, CdS CdAs, CdI_2 CdSe $\text{Cd}_x\text{Hg}_{(1-x)}\text{Te}$
Rectifiers	Cd selenide	CdSe
Scintillation counter crystals	Cd tungstate	CdWO_4
Semiconductors	Cd antimonide, Cd arsenide Cd phosphide, Cd selenide	CdSb, CdAs Cd_3P_2 , CdSe
Solar energy cells	Cd telluride Cd selenium telluride Cd mercury telluride	CdTe Cd_2SeTe $\text{Cd}_x\text{Hg}_{(1-x)}\text{Te}$
Solders	Cd with silver and zinc	Various
Standard emf cell (Weston cell)	Cd sulfate	$\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$
Thermal imaging	Cd arsenide Cd mercury telluride	CdAs $\text{Cd}_x\text{Hg}_{(1-x)}\text{Te}$
Thermoelectric generators	Cd antimonide	CdSb

Three-fourths of the cadmium consumed in the United States is used in the negative plates of the three types of commercial cadmium-containing batteries—NiCd, silver cadmium, and mercury cadmium (the production of which is being phased out). Silver cadmium and mercury cadmium batteries are excellent, but very expensive and, thus, are used only in specialized applications where performance outweighs cost, such as in space satellites, and in several kinds of military equipment (Roskill, 1990, p. 234-235). NiCd

is by far the most widely used cadmium battery, and accounts for nearly all of the cadmium used in batteries. By weight, it contains between two and three parts nickel to one part cadmium. The cell reaction can be written in simplified form as



In manufacture, the plates are packed with the two hydroxides corresponding to the fully discharged state, $\text{Ni}(\text{OH})_2$ in the positive plate, $\text{Cd}(\text{OH})_2$ in the negative plate. The plates, separators, and connectors are assembled in a stainless steel, nickel-plated steel, or polyethylene case; potassium hydroxide (KOH) or sodium hydroxide (NaOH) electrolyte is added (or absorbed in fiber mats that are assembled along with the plates), and the unit charged (Berndt, 1997, p. 177; Morrow, 2002).

NiCd batteries are manufactured as either vented or sealed units. The vented types tend to be the largest, with capacities of up to perhaps 1,500 ampere-hours (Ah), and are commonly used to provide starting power for aircraft, locomotives, and other vehicles; automatic signaling devices; emergency and standby power and lighting systems; mobile work flood-lamps; television cameras, and many other devices. Low-maintenance vented NiCds are being actively considered for powering electric highway vehicles and are, in fact, being used in three models of electric cars in France (Rand, Woods, and Dell, 1998, p. 252). The larger, less portable sizes of the vented batteries are fitted with pocket plates (strips of perforated nickel-plated iron in which tablets of the active materials are pressed). The more portable types, with capacities of up to perhaps 360 Ah, are fitted with sintered plates—thin (0.5- to 1-mm) strips that consist of porous nickel powder that has been sintered onto a nickel screen support and then impregnated with the hydroxides; this type is used in aircraft and military equipment. Sintered plate batteries, as compared with pocket plate batteries, have higher energy densities and lower internal resistance, which makes them suitable for handling heavy electrical loads. They are also more expensive.

The sealed NiCd batteries use either sintered plates or pressed plates or a combination. Pressed plates are “thin tablets of active material, pressed and enclosed in a nickel-wire gauze” (Berndt, 1997, p. 369). The electrolyte is immobilized by absorption on felted mixtures of polyamide and polypropylene fibers, thus allowing the battery to be used in any orientation. Sealed NiCds are fitted with safety vents to relieve the excessive internal gas pressure that might be generated during very severe discharge or overcharge conditions. Sealed batteries are typically much smaller than the vented types, are maintenance free, and are used in such devices as power hand tools, camcorders, small personal appliances (toothbrushes, razors, cordless telephones, and notebook computers), and for powering equipment on space vehicles, for emergency lighting, and for many other uses. They are produced in rectangular, cylindrical, or button shapes; the cylindrical is by far the most often used. Some are enclosed in the appliance along with a charger and are recharged in place. Others are removed to a separate charger as needed.

NiCd batteries have several advantages compared with lead-acid and some other commercial types, as follows:

- They are mechanically and electrically rugged and are long-lived (up to 25 years, or 2,500 charge/discharge cycles).
- They can be stored for extended periods of time in any state of discharge without harm and with loss of only 10 percent of charge per month, compared with 25 percent per month for lead-acid batteries and even higher rates for nickel-metal hydride batteries.
- Wide operating range; can be as large as from about -50 to $+50$ °C.
- The electrolyte freezes over the range -24 to -65 °C (depending on the concentration used), making freezing much less of a problem than with lead-acid batteries.
- Their energy density in kilowatt-hours per kilogram of battery weight is 60 or more, versus about 30 for lead-acid batteries.
- Vented NiCds are inherently low-maintenance, and sealed cells are maintenance-free.

Some of their disadvantages are as follows:

- They are more expensive than lead-acid batteries. The higher cost is ascribed to the high purity required for the active materials (99.95 percent pure CdO; 99.8 percent pure NiSO_4 , with Cu and Pb each limited to 0.001 percent).
- Compared with lead-acid batteries, they are not as well suited as for float service (prolonged constant current/constant voltage charging) as is typical of use in emergency lighting devices, and in the starting/lighting/ignition use in nonelectric powered vehicles.
- The so-called memory effect, which is a temporary and reversible loss of storage capacity observed when the battery is subjected to repetitive and similar partial discharge-recharge cycles, such as happens when the battery is routinely plugged into a trickle charger overnight to “top off” the charge. Improved separator technology has reduced the effect in modern NiCds and it is no longer a major disadvantage.

PIGMENTS

About 12 percent of the cadmium consumed in the United States currently (2000) goes into pigments. Cadmium pigments are some of the most durable pigments known—little affected by exposure to light, harsh weathering conditions, or use in high temperature environments. They yield bright colors, possess good opacity, and resist bleeding (migration). Cadmium sulfide (CdS), which is golden yellow, is the base cadmium pigment. By substituting zinc for some of the cadmium in CdS a range of yellows is produced—deep gold [1.9 percent zinc sulfide (ZnS)] through gold and lemon yellow to primrose yellow (20 percent ZnS). Substituting mercury for some of the cadmium yields a range of orange-reds—deep orange [11 percent mercury sulfide (HgS)] through light red, medium red, and dark red to maroon (26.5 percent HgS). The mercury-containing pigments are less costly but are

less stable at high temperature and weather poorly. Substitution of selenium for some of the sulfur in CdS also produces a range of orange-reds—light orange [15 percent cadmium selenide (CdSe)] through light red, medium red, and dark red to maroon (65 percent CdSe). Cadmium lithopones, which are cadmium pigments extended with barium sulfate (BaSO₄), are also used. These comprise typically about 40 percent cadmium pigment and 60 percent BaSO₄, although the proportions can be varied.

More than 85 percent of cadmium pigments go into plastics, valued for their strong, bright colors, their ability to withstand the high processing temperatures (300-400 °C) required for some polymers, and their resistance to bleeding. A small share, perhaps 5 percent, of cadmium pigments are used as premium pigments in paints, in applications where the high cost is justified by a requirement for resistance to alkalis and other chemicals (but not to acids), to heat, and to fading. For example, they may be used for color-coded pipes and cables that are used in high-temperature environments. In some applications, cadmium-pigmented paint has been used as the top coat over a base of more-economical color, such as chrome yellow. Cadmium pigments are also used in artists' colors.

About 5 percent of cadmium pigments are used in ceramic ware, and less than 1 percent in glass. In ceramics, they are used to produce brilliant reds and yellows. In glass, they are said to be the only pigments that yield the clarity and brightness needed for the yellow and red glass lenses in traffic signals and hazard lights. The remaining 2 or 3 percent of cadmium pigments is used in such products as decorative coatings for metals, printing inks, and rubber (Plunkert, 1985, p. 114; Roskill, 1990, p. 243-251; Roskill, 1995, p. 100-104).

Because of their high cost and the perceived toxicity of the metal component (toxicity actually is minimal in these virtually insoluble pigments), cadmium pigments are generally used only in applications in which there are, as yet, no satisfactory substitutes. The development of replacement pigments, such as cerium sulfide, mixed metal oxides, and various organics, was stimulated in the 1990s by environmental restrictions in Western Europe and is continuing.

COATINGS AND PLATINGS

This category of use accounted for about 8 percent of the cadmium consumed in the United States in 2000, compared with about 60 percent in a year typical of the 1960s. Although cadmium is an excellent protective coating, it is highly toxic, and the necessary environmental restrictions have curtailed this end use greatly in the past 30 years, especially in the 1990s. Cadmium provides excellent corrosion resistance in most environments to products made of aluminum, brass, iron, steel, and titanium. It is very effective against alkalis, detergents, and salt spray but is subject to corrosion by acid environments. Most cadmium coatings are applied by electroplating, but some are applied by ion deposition, mechanical plating, or vacuum spraying; they range in thickness typically from 5 to 25 micrometers. Most are applied to such steel products as aircraft landing gear components, automotive brake parts, fasteners of all types, and springs. When used on bolts, nuts, and other types of fasteners, a cadmium coating or plate has the advantage of predictable torque, which is a consequence of its low coefficient of friction and its low-specific volume (dense) corrosion products, which do not interfere much with metal-against-metal movement. It also is ductile enough to resist cracking when abused and wrenched. In addition, cadmium plating is a sacrificial coating that protects against galvanic corrosion. This is of particular value where aluminum is in contact with other metals, as in aircraft structures. In addition, cadmium coatings possess good electrical conductivity, and are easily soldered. They have been widely used on electrical and electronic components, such as connectors, equipment housings, and switches. The prime substitutes for cadmium in specific coating/plating applications are various organic polymers, tin alloys, zinc, and binary alloys of zinc with cobalt, iron, manganese, nickel, and silicon.

POLYMER STABILIZERS

Organic polymers, such as polyvinyl chloride (PVC), are subject to decomposition by heat or incident light. Cadmium salts of long-chain fatty acids, such as cadmium carboxylate, cadmium laurate, and cadmium stearate, have been used extensively with barium compounds of the fatty acids as heat and light stabilizers for PVC in applications where it is not used in the packaging of foodstuffs or the distribution of potable water. They have proven especially effective in stabilizing flexible PVC, such as extruded and injection molded products, and calendered PVC products, such as clear sheet and film (Herron, 1992, p. 761; Roskill, 1990, p. 252-257; 1995, p. 104-108). However, the availability of alternatives, such as barium-zinc, calcium-zinc, and organotin stabilizers has led to decreased use of cadmium stabilizers. In the United States, for example, cadmium-barium stabilizers accounted for only about 4 percent of the cadmium consumed in 2000, compared with 15 percent in the 1980s. They have been supplanted in the United States mainly by barium-zinc and calcium-zinc stabilizers, and in some countries by lead and antimony stabilizers, although use of the latter two is also being restricted by concerns for their effects on the environment.

OTHER USES

METALLIC USES

The addition of 0.1 to 1.5 percent cadmium (0.6-1.2 percent is the more-usual range) to electrical grade copper enhances strength and wear resistance and raises the softening point while leaving the electrical conductivity and thermal transfer characteristics of the copper almost unaffected. Cadmium copper alloys can be used at considerably higher temperatures than pure copper and are resistant

to abrasive wear. By virtue of a coating of refractory cadmium oxide that forms on the copper during arcing, cadmium copper becomes resistant to further arc erosion, a factor that is important for its use in electric motors and as trolley power wires for electrified railroads and urban bus lines.

In the past, cadmium has been used in a number of bearing alloys. It provides excellent strength and load-bearing capacity at high temperatures, it is resistant to fatigue cracking, and is unreactive towards steels. In the 1930s, it was used extensively in automotive engines but was phased out because of its susceptibility to corrosion by combustion products and the organic acids that build up in engine oil as it oxidizes in use.

With silver and zinc, cadmium is a third component in a number of low-melting solders. Two noneutectic compositions have been especially useful in the soldering of aluminum, a 60 percent Cd–40 percent Zn alloy, with a melting range of from 265 to 335 °C ; and a 95 percent Cd–5 percent Ag alloy, with a melting range of from 338 to 393 °C. Other compositions find limited use in electronics work, and yet others, high in cadmium, have been used to solder steel parts.

Alloyed with copper, zinc, and silver, cadmium finds use in brazing alloys—joining alloys that melt at temperatures above about 420 °C. Roskill (1990, p. 263) listed a selection of 15 such alloys that range in cadmium content from 12 to 25 weight percent and in melting temperature from 605 to 780 °C. The presence of cadmium yields a lower brazing temperature and improved flow characteristics, and economizes on silver, the most expensive component (Cross, 1981).

Cadmium, along with bismuth, tin, and lead, is a common component of low-melting point alloys, the so-called fusible alloys. These alloys have a number of diverse uses that include the heat-activation of fire-prevention sprinklers, as temporary jigs to hold complex shapes for machining, and as temporary fillers for electrical conduit and similar types of tube, which function to prevent collapse of the conduit wall when the conduit is being bent into a desired shape.

Cadmium in small amounts is added to several metals to enhance mechanical properties and corrosion resistance. For example, cadmium in amounts of up to 5 percent has been used in some sterling silver and some gold alloys (Roskill, 1990, p. 247). A 0.1 percent addition to zinc imparts corrosion resistance and strength to the zinc used as casings for alkaline dry cells; it is also added to the zinc used as sacrificial anodes, where it inhibits uneven corrosion of the anode. An 80 percent silver–15 percent indium–5 percent cadmium alloy is one of the two most commonly used control rod materials in pressurized water nuclear power reactors. Cadmium is also alloyed with either tin or bismuth for use in some types of selenium rectifiers (Roskill, 1990, p. 267–270).

USES IN COMPOUND FORM

The more-commercially significant uses for cadmium compounds are listed in table 5. Cadmium oxide (CdO) is a refractory compound that is dispersed in a silver matrix for use as high-current electrical switch contacts to quench arcing and thus prevent sticking or welding of the contacts. The CdO, which is used in amounts up to about 14 percent by weight of the cadmium oxide–silver composite, interferes only minimally with silver’s superior electrical and thermal conductivity and low surface contact resistance.

Among the very few commercially important organic cadmium compounds, several dialkyl and diaryl cadmium compounds have found use as catalysts. For example, diethylcadmium, $(C_2H_5)_2Cd$, is a polymerization catalyst (in some instances used with $TiCl_4$) for several monomers, including vinyl chloride and vinyl acetate, methyl methacrylate, polyethylene, and polypropylene. Diphenylcadmium, $(C_6H_5)_2Cd$, is also a polymerization catalyst.

Dimethylcadmium, $(CH_3)_2Cd$, has been used as a source of Cd in metal organic chemical vapor deposition for the production of semiconductor thin films such as cadmium sulfide, cadmium mercury telluride, or cadmium manganese telluride.

Cadmium acetate, $Cd(CH_3COO)_2 \cdot nH_2O$, is used as an iridescent glaze for ceramics, a colorant for glass and textiles, and as an alternative to cyanide in cadmium electroplating baths (Herron, 1992, p. 773–775).

Table 5. U.S. supply and demand for unfabricated cadmium.

[In metric tons. NA, Not available. ----, Zero. Data include estimates. All data are rounded to three significant digits: because of independent rounding, they may not add to totals shown. Note change at 1995 from 5- to 1-year intervals]

	1950	1955	1960	1965	1970	1975	1980	1985	1990	1995	1996	1997	1998	1999	2000
Components of U.S. supply															
Refined production 1/	4,170	4,540	4,620	4,390	4,290	1,990	1,580	1,600	1,680	1,270	1,530	2,060	1,240	1,190	1,690
Imports, cadmium metal	286	420	427	962	1,130	2,380	2,620	1,990	1,740	848	843	790	514	294	425
Imports, cadmium sulfide	NA	45	11	31	7	14	35								
Sales from U.S. Govt. Stockpile	----	----	----	----	3	----	----	----	----	220	230	161	128	554	319
Net deliveries from industrial stocks	64	596	621	----	----	----	----	215	73	----	----	50	331	----	----
Total U.S. supply	4,520	5,560	5,670	5,350	5,420	4,360	4,200	3,810	3,490	2,380	2,610	3,090	2,220	2,050	2,470
Distribution of U.S. supply															
Exports, cadmium metal, alloys, scrap	160	632	1,110	33	170	180	236	86	698	1,050	201	554	180	20	312
Exports, sulfide	NA	394	620	310	22	83	864								
Purchases for U.S. Govt. Stockpile 2/	600	600	----	----	----	----	----	----	----	----	----	----	----	----	----
Net additions to industrial stocks	----	----	----	559	1,150	1,150	425	----	----	121	150	----	----	164	107
Apparent consumption	3,760	4,330	4,560	4,760	4,110	3,030	3,530	3,720	2,800	818	1,640	2,230	2,020	1,780	1,190
Total Distribution of Supply	4,520	5,560	5,670	5,350	5,420	4,360	4,200	3,810	3,490	2,380	2,610	3,090	2,220	2,050	2,470
U.S. cadmium consumption, estimated 3/															
Electrical batteries	4/	4/	5/	95	140	490	940	1,000	1,260	550	1,100	1,560	1,450	1,320	889
Pigments	1,310	1,480	957	714	590	650	550	595	447	122	247	312	262	233	142
Coatings and platings	2,530	2,860	3,190	2,850	1,250	990	1,450	1,260	559	65	132	178	161	142	95
Polymer stabilizers	4/	4/	5/	714	1,080	600	470	557	335	65	132	156	122	71	48
Nonferrous alloys and other uses	523	591	410	380	250	300	124	298	196	16	32	22	20	18	12
Total apparent consumption	4,360	4,930	4,560	4,760	4,110	3,030	3,530	3,720	2,800	818	1,640	2,230	2,020	1,780	1,190

1/ Includes primary and secondary production, from domestic and imported ores, zinc refinery flue dust, and scrap.

2/ From 1948 through 1958, about 6,400 tons were purchased for the stockpile, but amounts for individual years are not available; figures shown are rounded estimates based on 10-year annual average.

3/ Data on end-use distribution are scarce. Estimates shown are based on percentage distributions reported in U.S. Bureau of Mines' Minerals Yearbooks and Mineral Facts and Problems, and, after 1995, U.S. Geological Survey's Minerals Yearbooks.

4/ If any, included in "Pigments and chemicals," a category used in these years but represented in this table as "Pigments."

5/ If any, included in "Nonferrous alloys and other uses."

TRENDS IN USE

As mentioned earlier with reference to figure 2, the usage trends in the past few decades have been similar in all the principal using countries—rapid growth in NiCd batteries, a slow decline in coatings and pigments, and faster declines in alloys and stabilizers. As awareness of the health dangers of heavy metals in general, and cadmium in particular, has grown, Governments, principally in Western Europe have imposed restrictions on the use of cadmium for some purposes, and more are expected in the future (in the United States, restrictions have thus far been limited to the disposal of cadmium waste and scrap). Nonetheless, overall world cadmium consumption actually grew, if very slowly (less than 1 percent per year), during the past three decades (fig. 4). Among the five largest consuming countries of that period, consumption fell in Germany and the United States, but, buoyed by the growing deployment of the nickel-cadmium battery, grew in Belgium, France, and Japan. As was shown in figure 1, consumption in the United States peaked at 6,800 t in 1969 and declined until it fell below 1,000 t in 1994 and 1995; in 2000, it was just under 1,200 t.

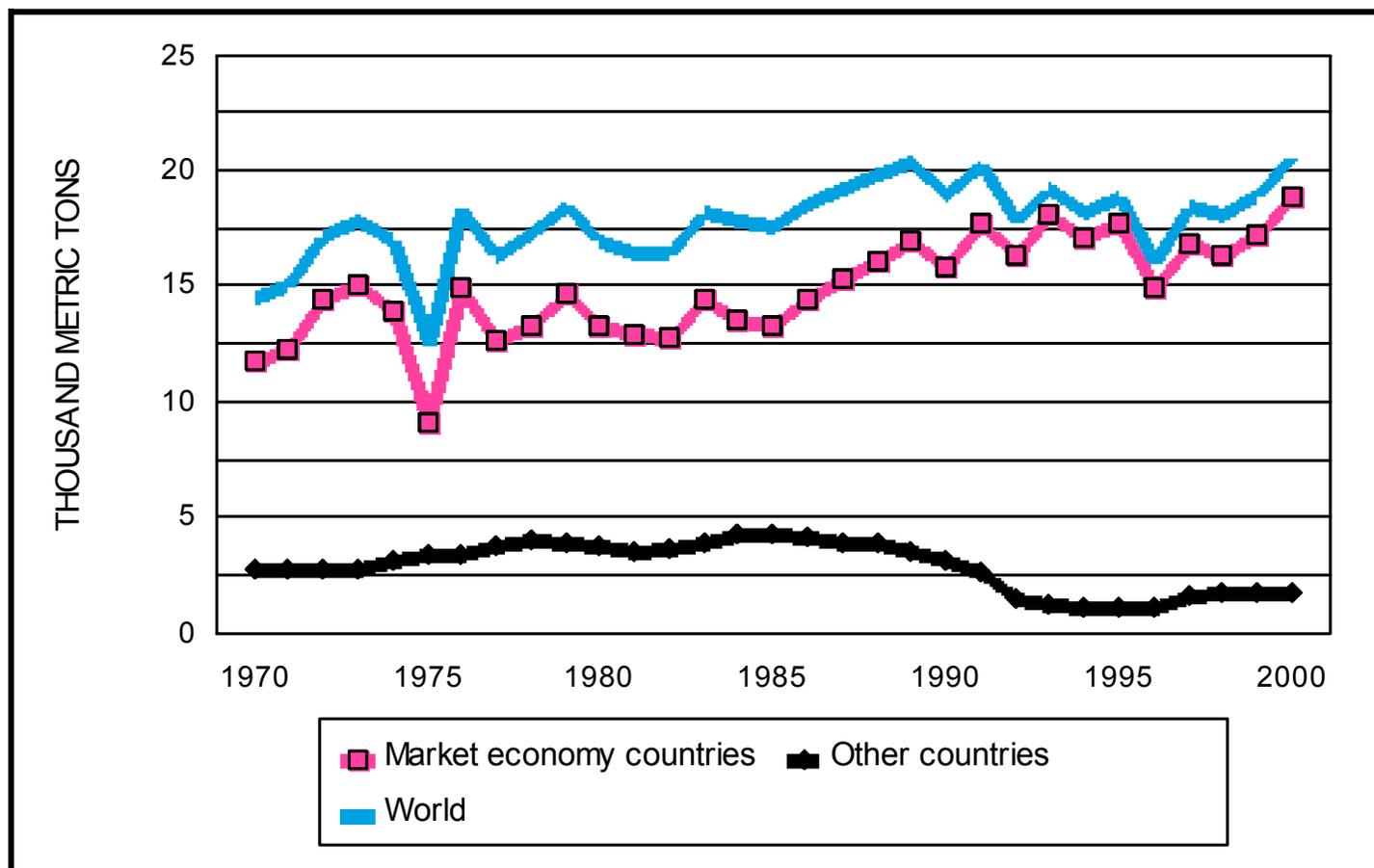


Figure 4. World cadmium consumption, 1970-2000 [Data from Roskill, 1990; World Bureau of Metal Statistics, 2001.]

SUBSTITUTES FOR CADMIUM

The principal alternatives to NiCd batteries are, depending on the application, fuel cells and lead-acid, nickel-metal hydride, and lithium-ion batteries. Cadmium pigments are already restricted in the European Union to applications in which they are difficult to replace. Nevertheless, rare-earth pigments (especially cerium sulfide pigments) and, less successfully, various organic pigments, are being developed as substitutes for cadmium pigments. Cadmium stabilizers for polymers are being phased out in many plastic products in favor of antimony, barium-zinc, calcium-zinc, organotin, and organic compound stabilizers. Cadmium coatings and platings are being restricted in the European Union in favor of tin and zinc alloys, and organic polymers.

INDUSTRY AND MARKET

Cadmium is refined in more than two dozen countries. Several of the producing countries refine only part of the cadmium they mine, and others depend on imports of cadmium-containing zinc concentrates, flue dusts, and sludges. The cadmium is refined at zinc and lead refineries that have cadmium recovery circuits and at secondary refineries, where cadmium is usually only one of several metals recycled. The cadmium feedstocks are derived from the ores of more than 200 zinc and lead-zinc mines worldwide (Roskill, 1995, p. 2-14). Those refineries located in market economy countries are operated by about 40 companies. In 2002, only one company was refining primary cadmium in the United States.

Secondary cadmium is recovered mainly from NiCd battery scrap and secondarily from flue dust from the steel industry's electric arc furnaces, where it originates in the zinc coating on galvanized steel scrap or from cadmium-coated steel. In 2002, about eight plants, located mainly in Japan, the United States, and Western Europe, recovered cadmium from scrapped NiCd batteries (Morrow, 2002). In the United States in 2002, one company recovered cadmium from scrapped NiCd batteries; recovery from EAF dust, if any, was negligible.

More than 90 percent of the cadmium used is accounted for by Japan, Russia, the United States, and Western Europe (American

Metal Market, 2000, p. 71). A few dozen companies located in the industrial countries account for nearly all the cadmium consumed for batteries, pigments, and polymer stabilizers; however, there are many cadmium coaters.

Cadmium metal is traded by about 240 companies worldwide; cadmium oxide, by nearly 30 companies; and scrap NiCd batteries, by about 60 companies (Metal Bulletin, 1996, p. 495-496; 1997, p. 446-450). Prices for cadmium metal, oxide, and sulfide are quoted in trade journals.

CADMIUM AND THE ENVIRONMENT

Cadmium in ionic form, as derived from its soluble compounds, is toxic. It accumulates very slowly in animals, mainly in the liver and, especially, the kidneys (its half-life in human kidneys is about 15 years). At sufficiently high levels, it can cause kidney failure, and at levels below the failure threshold, it may—it is still a controversial claim—lower the retention of calcium, which leads indirectly to decalcification of bone mass. Inhaled cadmium fumes or smoke can produce a chemical pneumonitis; fatalities can result from massive pulmonary edema. The carcinogenic potential of cadmium is in dispute, as is its potential for causing birth defects, emphysema, and hypertension (Reesal and others, 1987).

About 95 percent of the cadmium uptake (referred to as “internal exposure”) in the general population of humans not living in proximity to an environmental point source comes from the ingestion of food, and only 5 percent from inhalation of cadmium aerosols from the atmosphere. Food plants absorb cadmium from irrigation water, phosphate fertilizers, manure, sewage sludge, and deposition from the atmosphere. The atmosphere receives most of its airborne cadmium from the combustion of fossil fuels; natural sources, such as volcanic eruptions and forest fires; ferrous and nonferrous metallurgical plants; and cement manufacture.

A recent study of the several pathways of cadmium transfer to humans assessed the relative importance of the principal sources of cadmium to human exposure (Van Assche, 1998). The results of the assessment, which are shown in figure 5, were based on mass transfer data from Europe in the early 1990s and did not take into account differences in the bioavailability of cadmium in its various compounds. By the 1990s, the production, use, and disposal of manufactured cadmium-containing products were clearly contributing very little cadmium to human exposure. The main contributors among anthropogenic activities were those that concentrated naturally occurring cadmium (as does the manufacture of phosphate fertilizers from phosphate rock), or released impurity cadmium to the atmosphere (as do the combustion of fossil fuels and the processing of metallurgical ores).

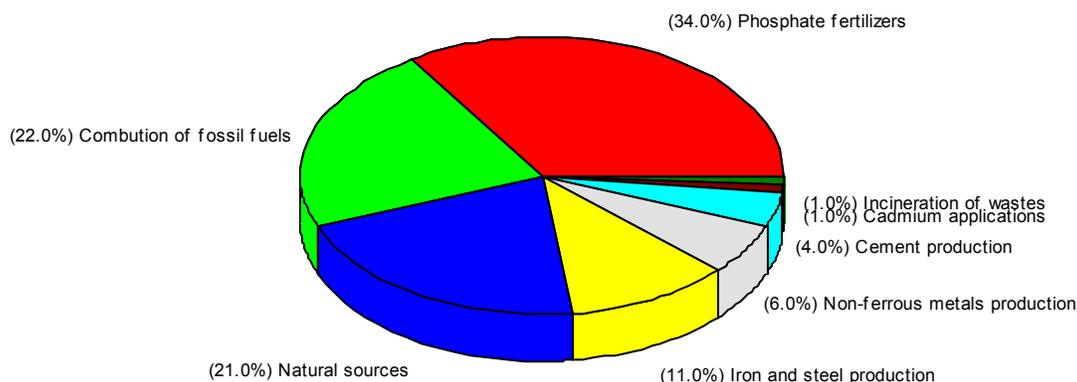


Figure 5. Relative contributions of the different sources of cadmium to human exposure, in percent. [Von Assche, 1998]

Manufactured cadmium products must still be respected as potential point sources of pollution by those who manufacture, use, or scrap them. For example, fatalities have occurred among welders who unknowingly worked with cadmium-coated metal components in an inadequately ventilated workspace. Likewise, fumes from the melting of cadmium-rich silver solders can be dangerous. Cadmium products can, however, be produced, used, and disposed of safely. For example, materials that contain cadmium dispersed in a matrix, such as plastics containing cadmium pigments and/or stabilizers, lose very little cadmium to leaching when they are landfilled (Van Assche, 1998). Products that contain larger or more-concentrated quantities of cadmium, such as batteries, can be recycled safely, and if collection and recycling is encouraged by government or required by law, as it is for NiCd batteries in some countries, then a high degree of recovery is achievable.

The toxicity of cadmium in some of its compound forms was recognized even as its use grew in the 20th century. For example, it was excluded from use as a coating for steel food containers because organic acids in the food would have released toxic ionic cadmium into the contents of the containers. At midcentury, awareness of cadmium's toxicity was heightened by the recognition that cadmium was a principal contributing cause, along with deficiencies in iron and other minerals, of the "itai-itai" ("ouch-ouch") disease that afflicted some 200 residents in and near the village of Fuchu, Japan. The cadmium had leached from wastes at a nearby lead-zinc mine and contaminated the village water supply. During a period of about 15 years, the residents had ingested cadmium in drinking water and in rice that had been grown in paddies irrigated by the same water. Of the victims, nearly all of the most seriously afflicted were postmenopausal women with low iron stores; these victims suffered severe bone decalcification.

Since then, Governments in many countries have become sensitive to the dangers that accompany the use of cadmium and have mandated reductions in point-source cadmium emissions and emissions levels in the workplace and have regulated the postconsumer disposal of cadmium-containing manufactured products. Thus, the level of cadmium in the environment, which peaked in the 1960s, declined steadily thereafter and by 2000, for the general population, was well below the tolerable daily limit established by the World Health Organization (International Cadmium Association, undated, a). The cadmium industry, as represented by the International Cadmium Association, takes the position that further restrictions or bans on cadmium products are undesirable and unnecessary. The Association points out that substitutes perform less satisfactorily than cadmium in some products and that most cadmium exposure comes from the use of fertilizers and the combustion of fossil fuels. It continues, "From an ecological point of view, it is important to develop and maintain functional products with long service lives, . . . to minimize the input into the world's waste stream. . . . Cadmium will invariably be present in our society, either in useful products or in controlled wastes [from zinc mining and smelting]" (International Cadmium Association, undated, b). Nonetheless, several European countries have imposed further restrictions, and in some cases have scheduled outright bans on the manufacture and use of specific types of cadmium-containing products.

SUPPLY, DEMAND, SUSTAINABLE DEVELOPMENT

SUPPLY AND DISTRIBUTION

Refined cadmium was produced in 27 countries in 2000; the 8 largest producing countries accounted for two-thirds of world production (fig. 6) (U.S. Geological Survey, 2001). World refined production leveled off at about 20,000 metric tons per year (t/yr) in the 1990s; U.S. production has averaged about 1,500 t/yr since 1980 (fig. 7). Some countries, such as Australia and Canada, extract much less cadmium than is contained in the zinc concentrates they produce; others, such as Belgium and Japan, depend on imported cadmium feedstocks; the predominant flows of cadmium-containing zinc concentrates are from Australia and North America towards eastern Asia and Europe (Roskill, 1995, p. 1).

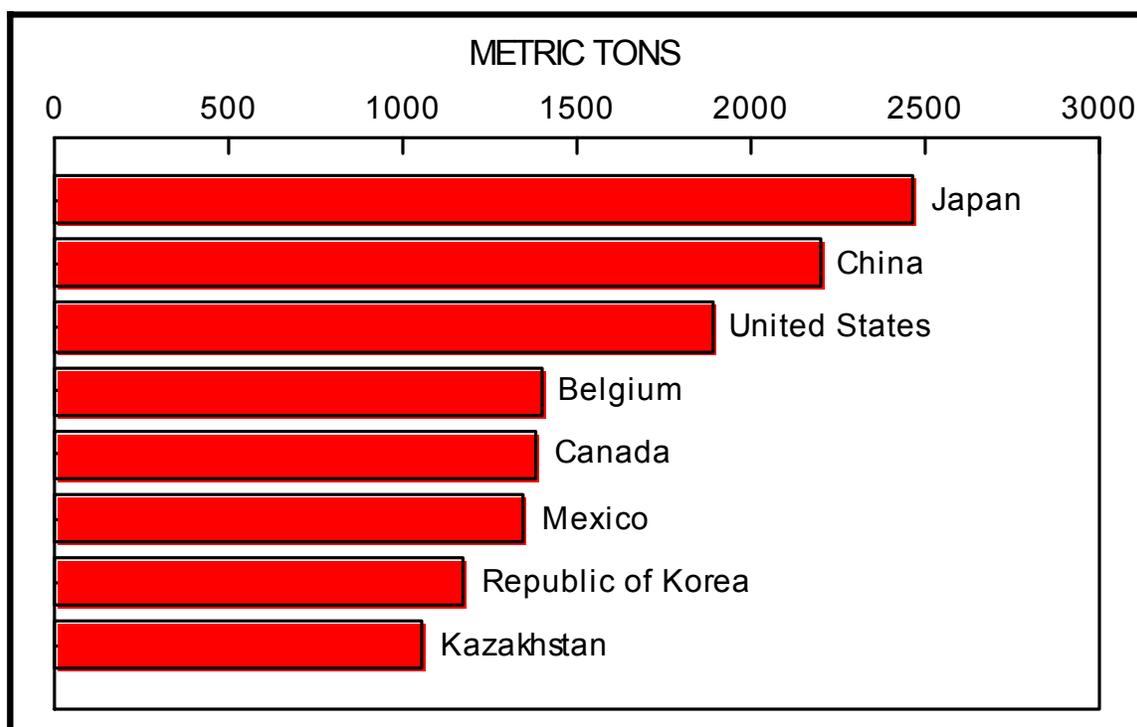


Figure 6. Cadmium principal refining countries in 2000. Eight countries refined two-thirds of the 19,700-ton world total. [Data from U.S. Geological Survey, 2001.]

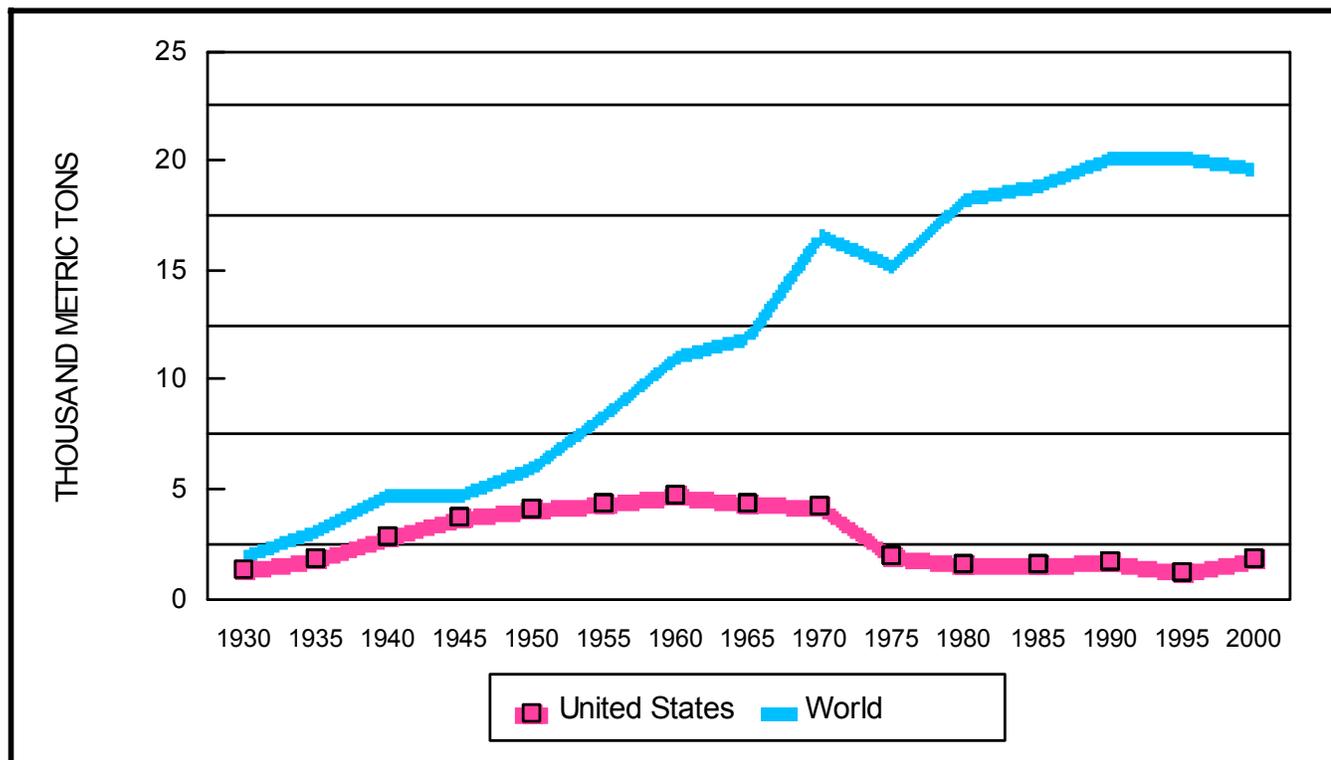


Figure 7. Production of refined cadmium, 1930-2000. [Data from U.S. Bureau of Mines (1930-95); U.S. Geological Survey (1996-2001).]

More than 80 percent of the cadmium consumed in the world is consumed in six countries and more than 90 percent in the market economy countries collectively (figs. 3, 4). World cadmium consumption peaked in 1989 at about 20,400 t, and after growing slowly, on average about 1.2 percent per year from 1970 through 1990, leveled off and underwent a very slow decline through the 1990s (fig. 4).

Cadmium supply-distribution relationships for the United States for 2000 are shown in figure 8. Of total domestic refinery output, 66 percent was derived from domestic ores, 22 percent from imported ores, and the remaining 12 percent from domestic scrap and steel furnace flue dust. Total supply comprised domestically refined metal (68 percent), imported metal and sulfide (19 percent), and sales from the National Defense Stockpile (13 percent). Of that supply, 48 percent went to domestic fabricators, 13 percent was exported as metal and 35 percent as sulfide, and the remaining 4 percent was added to industrial stocks. Overall, the United States was a net exporter (345 t) of cadmium in 2000.

U.S. supply-distribution statistics for the past half-century are shown in table 5. During the span of years shown in the table, most of the cadmium delivered to the domestic market was refined in the United States. The refinery feed was derived largely from domestic ores; from the 1930s to the 1970s, however, zinc smelter flue dust from Mexico was a significant feedstock and averaged about 600 t/yr contained cadmium. Net imports of metal was a much smaller part of supply, except for the period from 1970 to 1993 when it was the major component in some years (fig. 9). A surge in exports of cadmium sulfide (trade data for which have been available only since 1994) contributed to the net cadmium export balance of 2000. Sales of surplus cadmium from the National Defense Stockpile have been a minor but significant component of supply in some of the years between 1963 and 1976 and again from 1993 through 2000.

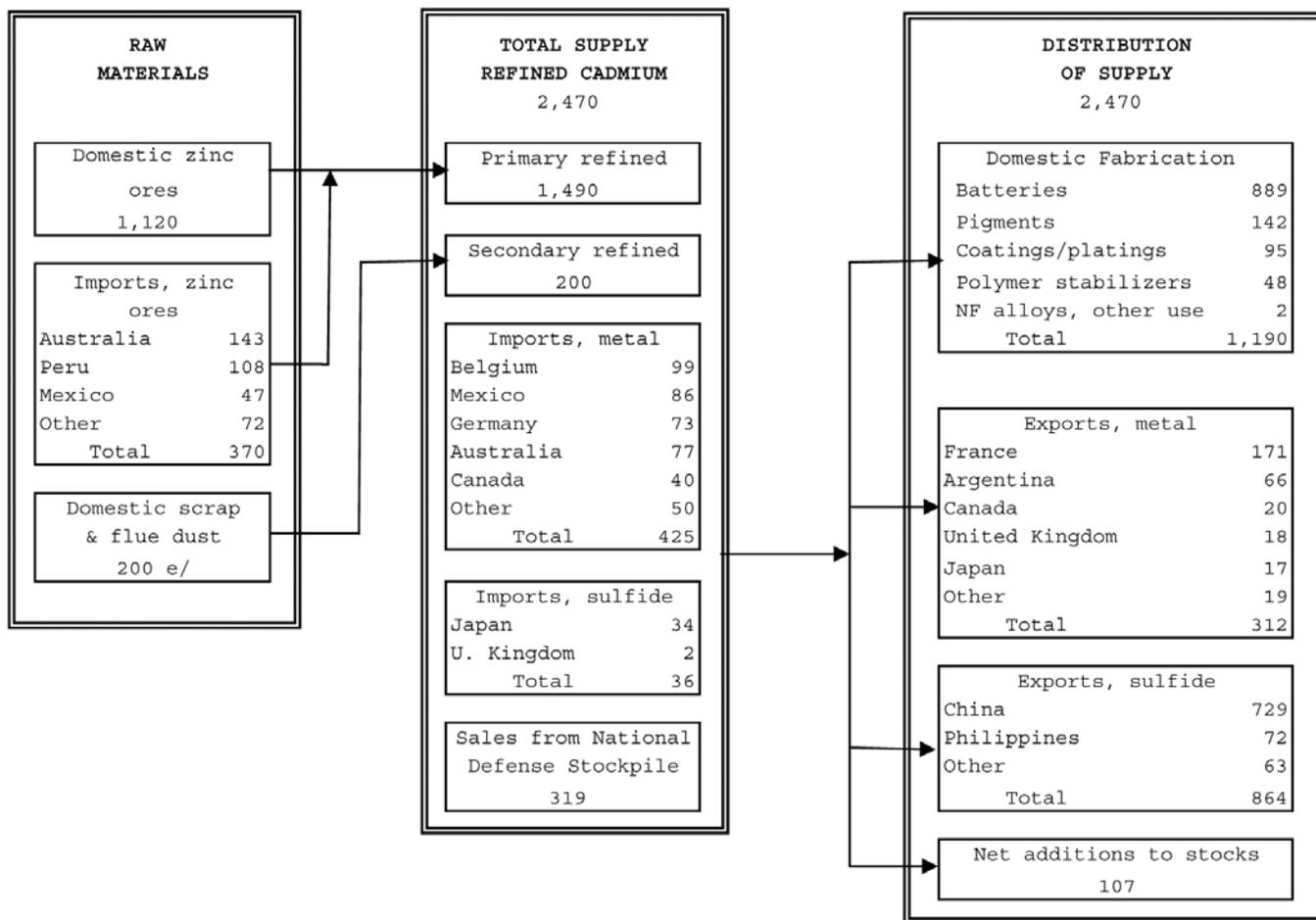


Figure 8. U.S. cadmium supply and demand. [In metric tons contained cadmium 2000. Excludes foreign trade in manufactured products. Exports of metal include waste and scrap. Data are rounded to three significant digits; because of rounding, they may not add to totals shown. E, Estimate. Estimates of end-use categories are based on percentage data from U.S. Geological Survey (2000).]

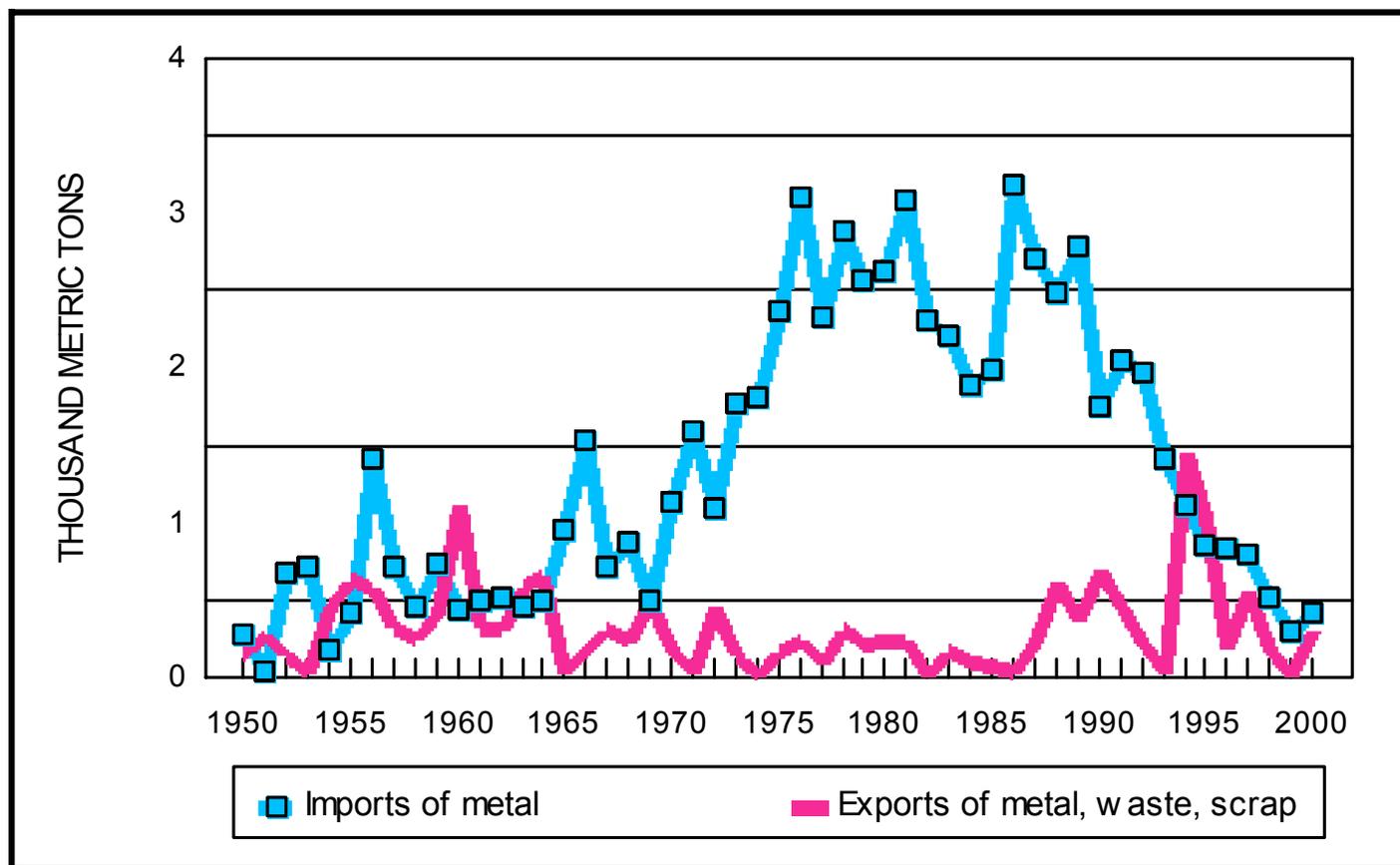


Figure 9. U.S. trade in cadmium metal, 1950-2000. [Data from U.S. Bureau of Mines (1950-95); U.S. Geological Survey (1996-2001).]

After peaking at nearly 6,800 t in 1969, U.S. apparent consumption declined at an average rate of about 3.8 percent per year through the rest of the century; this is a reflection of the shrinkage in markets for all uses except NiCd batteries (fig. 1). Exports of metal, scrap, and waste varied widely from year to year but, in general, were small compared with domestic consumption (fig. 9). Purchases for the National Defense Stockpile (or its predecessors) were a factor in the distribution of supply only through 1958.

POTENTIAL SUPPLY

Identified world resources of cadmium are estimated to be about 6 million metric tons, of which the United States has about 23 percent. At present rates of production, world resources would be adequate for nearly 300 years, providing they could all be mined and processed economically. World reserves would be adequate for about 30 years and the reserve base for 60 years. At the rate of refinery production seen in 2000, U.S. reserves (90,000 t) would be adequate for nearly 48 years, and the reserve base (270,000 t), for 143 years.

Secondary cadmium, which comes almost entirely from spent NiCd batteries, contributed 8 percent of the U.S. supply of cadmium in 2000. Should NiCd batteries be adopted on a large scale for use in electric vehicles, the inventory of spent batteries could become a much more important component of supply.

STRATEGIC CONSIDERATIONS

The U.S. Government began stockpiling cadmium in 1948 to insure its availability for critical uses in military hardware and had filled its initial requirements by 1955. From 1956 through 1963, more cadmium was acquired for a supplemental stockpile by means of a program in which surplus U.S. perishable agricultural goods were traded for foreign-produced stockpile commodities, which included cadmium metal. By yearend 1962, more than 7,800 t of cadmium metal had been stockpiled. Stockpile goals have been revised several times since then, and the revisions have made large quantities of surplus cadmium metal available to the market. Surplus cadmium was sold from 1963 to 1976; sales were begun again in 1993 and continued through 2000. As of the end of fiscal year 2000, the National Defense Stockpile contained 799 t of cadmium metal, all of which was authorized for disposal on the open market.

SUSTAINABILITY OF PRODUCTION AND USE

Cadmium's toxicity is of concern in zinc mining and smelting, but a relatively small concern, one that should not constrain zinc production. The extraction of cadmium from zinc concentrates is a closely controlled process that actually reduces the toxic pollution of mine and concentrator wastes that would otherwise occur.

The use of cadmium, however, has been and will continue to be constrained by concerns about the fate of cadmium delivered to the environment in most scrapped cadmium-containing products. The use of cadmium in coatings and platings, pigments, polymer stabilizers, and several other uses is largely dissipative—it is impractical, even impossible in some instances, to collect and recycle these manufactured goods. Thus, efforts to find substitutes for cadmium in these uses will continue. The use of cadmium in NiCd batteries, however, will not necessarily be constrained by environmental concerns. Large-scale successful collection and recycling programs for NiCds are in place in several of the industrial countries. Even the possibility of much wider use of large NiCd batteries in electric vehicles does not arouse much concern because comprehensive battery recycling programs appear to be quite manageable.

ECONOMIC FACTORS

Because cadmium is always a byproduct of zinc or lead-zinc mining, its exploration and mining costs are embedded in those of the two base metals, especially zinc. Its refinery extraction costs, likewise, are not readily available. The price of cadmium has been rather volatile at times, as exemplified in recent years by the price spike of 1988-89, which was caused by a supply squeeze. The price, however, was generally low during the 1990s, and has been lower in both current and constant dollar terms since 1998 than at any time in the 20th century (fig. 10). The New York dealer price averaged \$0.14 per pound in 1999 and \$0.16 per pound in 2000. Although the cadmium price typically could be expressed as a multiple of the zinc price for the past century, it was less than one-third

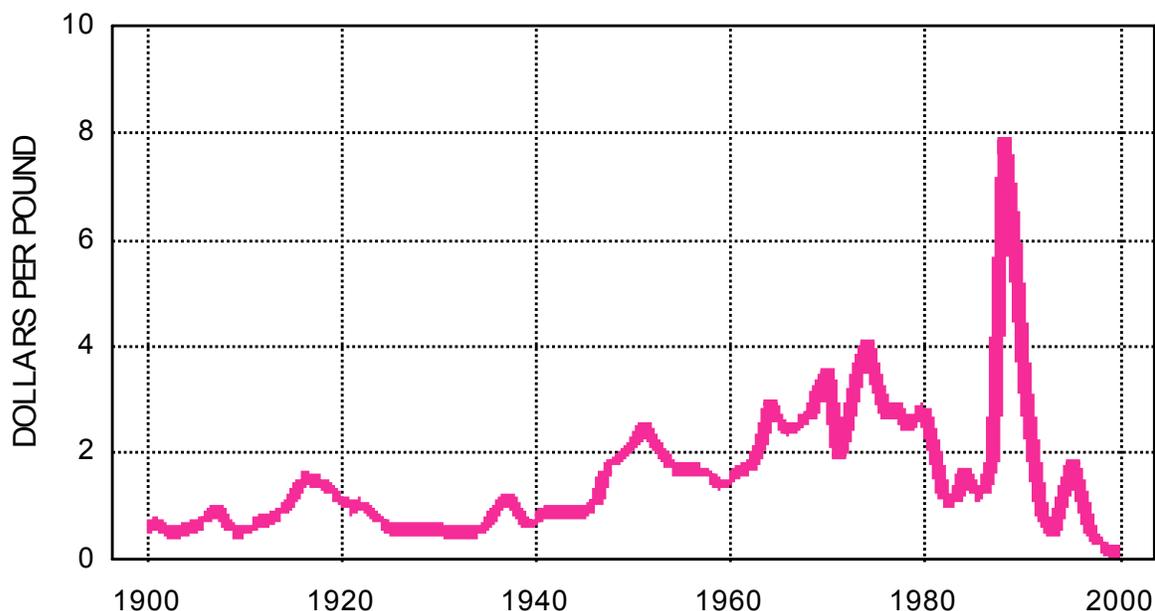


Figure 10. U.S. annual average cadmium price, 1900-2000. [Plachy, 1999.]

of the zinc price in 1999 and 2000. At such prices, zinc producers do not find cadmium extraction to be profitable except insofar as the extraction costs are outweighed by the environmental disposal costs that would be incurred were the cadmium not extracted from smelter wastes. Unless demand rises sharply, which appears unlikely, the price will remain low for the foreseeable future.

In the United States, the recycling of NiCd batteries provides the only appreciable quantity of secondary cadmium from domestic sources. It is encouraged by the alternative—the costs of complying with environmental regulations that require “proper disposal” of cadmium-bearing wastes. NiCd batteries, however, are a more concentrated source of cadmium than are low-grade materials, such as EAFdust and thus, their recycling is more likely to be profitable

Cadmium producers receive a depletion allowance of 22 percent on domestic mine production and 14 percent on foreign production. Unwrought cadmium metal and scrap may be imported duty free, but a 3.1 percent ad valorem duty is imposed on the importation of cadmium sulfide and pigments and preparations based on cadmium compounds.

OUTLOOK

The supply of primary cadmium is adequate and appears likely to remain so in the years ahead. At 2000 rates of production, the world reserve base could supply industrial requirements for 60 years, and the U.S. reserve base could satisfy domestic requirements for about 140 years.

The use of NiCd batteries, which today accounts for three-fourths of the cadmium consumed, is likely to continue to grow at a modest rate, sustained by the clear advantages of NiCds in certain applications, such as power tools and aircraft and traction batteries, but constrained mainly by competition in the small battery sector from lithium-ion and nickel-metal hydride batteries. Expansion of the large battery sector, which is uncertain, will depend on the enactment of legislation mandating the manufacture of electric vehicles, on the price of petroleum fuels, and on expansion of the telecommunications sector.

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