# CADMIUM AND CADMIUM ALLOYS

## 1. Introduction

Cadmium (Cd) [7440-43-9] a name derived from the Latin *cadmia* and Greek *kadmeia*, which are ancient names for calamine or zinc oxide, is a member, along with zinc and mercury, of group 12 (IIB) of the periodic table of elements. It is generally characterized as a soft, ductile, silver-white or bluish-white metal, and was discovered almost simultaneously in 1817 by Strohmeyer and Hermann, both in Germany, as an impurity in zinc carbonate (1). Germany produced the first commercial cadmium metal in the late nineteenth century and was the only important producer of cadmium metal and cadmium sulfide [1306-23-6] pigments until World War I, recovering cadmium from the smelting of zinc ores from Upper Silesia. Production in the United States began in 1907 at the Grasselli Chemical Company in Cleveland, Ohio, where metallic cadmium was recovered as a byproduct of zinc smelting. Initial production in 1907 in the United States was 6.3 mt, which expanded to its peak production level of 5736 tonnes in 1969 but has declined to approximately 1200 tonnes today (2).

Cadmium metal may be recovered as a byproduct of zinc, lead, or copper smelting operations and is utilized commercially as a corrosion-resistant coating on steel, aluminum, and other nonferrous metals (see ZINC AND ZINC ALLOYS; COPPER; LEAD). Cadmium is also added to some nonferrous alloys to improve properties such as strength, hardness, wear resistance, castability, and electrochemical behavior or to other nonferrous alloys to obtain lower melting temperatures and improved brazing and soldering characteristics. Cadmium compounds are employed mainly as the negative electrode materials in NiCd batteries, as ultraviolet light and weathering stabilizers for polyvinyl chloride (PVC), and as red, orange, and yellow pigments in plastics, ceramics, glasses, enamels, and artists' colors.

## 2. Occurrence

Cadmium is a naturally occurring metallic element, one of the minerals present in minor amounts in the earth's crust and its oceans, and present everywhere in our environment. The crustal abundance of cadmium has variously been reported between 0.1 and 0.5 ppm, but much higher and much lower values have also been cited depending on a large number of factors. Igneous and metamorphic rocks tend to show lower values, 0.02–0.2 ppm, whereas sedimentary rocks have much higher values, from 0.1–25 ppm. Naturally, zinc, lead, and copper ores, which are mainly their sulfides and oxides, contain even higher levels of cadmium, 200–14,000 ppm for zinc ores and ~500 ppm for typical lead and copper ores. The raw material for iron and steel production contain approximately 0.1–5.0 ppm, while those for cement production contain about 2 ppm. Fossil fuels contain 0.5–1.5 ppm cadmium, but phosphate fertilizers may contain levels from 10 to as high as 200 ppm cadmium (3).

A number of cadmium-containing minerals have been identified, and are summarized in Table 1.

The most common cadmium-containing mineral is greenockite, which is not found in any isolated deposits, but is nearly always associated with the zinc ore, sphalerite. Approximately 80% of current cadmium production arises from primary zinc production; the remaining 20% is a result of lead and copper byproduct production and cadmium product recycling.

The average cadmium content in the world's oceans has variously been reported as low as <5 ng/L (4) and 5–20 ng/L (5,6) to as high as 110 ng/L (7) 100 ng/L (3) and 10–100 ng/L (8). Higher levels have been noted around certain coastal areas (8) and variations of cadmium concentration with the ocean depth, presumably due to patterns of nutrient concentrations, have also been measured (4,5). Even greater variations are quoted for the cadmium contents of rainwater, freshwater, and surface water in urban and industrialized areas. Levels from of 10–4000 ng/L have been quoted in the literature depending on specific location and whether total cadmium or dissolved cadmium is measured (3,4,7).

Ambient-air cadmium concentrations have generally been estimated to range within 0.1–5 ng/m$^3$ in rural areas, 2–15 ng/m$^3$ in urban areas, and 15–150 ng/m$^3$ in industrialized areas (4,5,8) although some much lower values have been noted in extremely remote areas and some much higher values have been recorded in the past near uncontrolled industrial sources. There are generally little or no differences noted in cadmium levels between indoor and outdoor

Table 1. **Cadmium-Containing Minerals**

| Name | Formula | CAS registry number | Cadmium, % |
|---|---|---|---|
| sphalerite | $ZnS$ | [1314-98-3] | 0.02–1.4 |
| wurtzite | $ZnS$ | [1314-98-3] | 0.02–1.4 |
| galena | $PbS$ | [1314-87-0] | 500 ppm |
| chalopyrite | $CuFeS_2$ | [1308-56-1] | 500 ppm |
| otavite | $Zn(Cd)CO_3$ | [513-78-0] | <1.2 |
| greenockite | $CdS$ | [1306-23-6] | 77.8 |
| monteponite | $CdO$ | [1306-19-0] | 87.5 |
| cadmoselite | $CdSe$ | [1306-24-7] | 58.7 |

Table 2. **World Production of Refined Cadmium Metal**

| Year | Production, t |
|---|---|
| 1991 | 21,268 |
| 1992 | 20,197 |
| 1993 | 19,497 |
| 1994 | 18,411 |
| 1995 | 19,478 |
| 1996 | 19,108 |
| 1997 | 19,946 |
| 1998 | 19,851 |
| 1999 | 18,767 |
| 2000 (estimated) | 18,065 |

air in nonsmoking environments. The presence of tobacco smoke, however, may substantially affect indoor ambient-air cadmium concentrations.

## 3. Sources and Supplies

World production of cadmium from 1990 through 1999 varied between 18,000 and 21,000 t/yr according to the World Bureau of Metal Statistics, and is summarized in Table 2. Historically, the Western world cadmium production trend growth has been 0.6% per year from 1970 through 1982 but increased to 0.8% per year during 1982–1995. This production trend could increase further as zinc production capacity increases, recycling of cadmium products increases, and production from countries such as China, Kazakhstan, Russia, and Canada increases. Overall, refined primary cadmium metal production has shown decreases in recent years as secondary or recycled cadmium production has increased.

The world production of cadmium continues to originate from the three principal producing areas—Europe, the Americas, and Asia—with lesser but still significant production from Australia and only very small production from Africa. The relative cadmium productions of these five areas in 1997 are summarized in Table 3.

Even though the cadmium production figures from countries in Asia such as China, Russia, Kazakhstan, and North Korea are often difficult to obtain and veriify, there is still no doubt that significant amounts of cadmium are being produced in Asia. Japan remains one of the largest cadmium producers in the world.

Table 3. **Geographic Summary of 1997 World Cadmium Production**

| Area | Production, t |
|---|---|
| Asia | 6,986 |
| Europe | 5,928 |
| Americas | 5,815 |
| Australia | 632 |
| Africa | 52 |

Table 4. **Leading Producers of Refined Cadmium Metal, 1994–1997**

| Country | Production, t | | | |
|---|---|---|---|---|
| | 1994 | 1995 | 1996 | 1997 |
| Canada | 2,167.8 | 2,342.6 | 2,832.3 | 3,082.6 |
| Japan | 2,614.1 | 2,628.5 | 2,356.7 | 2,373.3 |
| China | 1,282.0 | 1,471.0 | 1,300.0 | 1,300.0 |
| Belgium | 1,556.1 | 1,710.4 | 1,579.2 | 1,420.0 |
| United States | 1,125.7 | 1,361.8 | 1,238.4 | 1,179.1 |
| Germany | 1,145.0 | 1,144.8 | 1,144.8 | 1,144.8 |
| South Korea | 909.0 | 908.4 | 930.0 | 930.0 |
| Kazakhstan | 601.0 | 600.2 | 593.0 | 819.0 |
| Netherlands | 306.7 | 704.0 | 603.2 | 752.9 |
| Russia | 582.3 | 670.0 | 716.0 | 716.0 |
| Mexico | 646.0 | 689.0 | 784.0 | 784.0 |
| Australia | 909.5 | 838.1 | 638.9 | 631.5 |
| Peru | 507.0 | 560.0 | 405.0 | 562.0 |
| Finland | 548.0 | 540.0 | 540.0 | 540.0 |
| United Kingdom | 469.5 | 548.6 | 537.2 | 454.6 |
| Italy | 475.0 | 308.0 | 296.0 | 287.0 |

Countries which are leading producers of cadmium are listed in Table 4 along with their refined cadmium metal production according to the World Bureau of Metal Statistics.

The total amounts of secondary or recycled cadmium produced cannot accurately be estimated because in some recycling operations such as the processing of baghouse dusts from lead and copper smelters, the cadmium recovered subsequently enters primary cadmium production circuits at zinc refining operations and is assessed in the production statistics for primary cadmium metal. However, estimated figures are available from the recycling of spent NiCd batteries and manufacturing wastes based on plant capacities and tonnages of batteries and wastes processed, and these figures give some indication of the levels of cadmium recovered. Table 5 summarizes the estimated amounts of cadmium recovered in 1996 and 1997 at NiCd battery recycling plants around the world (10).

Although the estimates listed in Table 5 are very approximate and include NiCd battery manufacturing wastes which may be lower in cadmium content than the nominal level (12–15%) in spent NiCd batteries, it indicates that

Table 5. **Estimates of Cadmium Production from NiCd Recycling**

| Company | Country | Cadmium recycled, mt | |
|---|---|---|---|
| | | 1996 | 1997 |
| INMETCO | USA | 338 | 395 |
| SNAM | France | 650 | 975 |
| SAFT | Sweden | 225 | 225 |
| BAJ Program[a] | Japan | 600 | 613 |
| *Total* | | *1813* | *2208* |

[a] Battery Association of Japan Collection and Recycling Program.

Table 6. **Summary of U.S. DLA Cadmium Disposals**

| Fiscal year | Authorized limit | Cadmium sales, t |
|---|---|---|
| 1992/1993 | 227.3 | 148.9 |
| 1993/1994 | 340.9 | 339.8 |
| 1994/1995 | 340.9 | 360.9 |
| 1995/1996 | 443.2 | 0 |
| 1996/1997 | 544.3 | 141.7 |
| 1997/1998 | 544.3 | 118.8 |
| 1998/1999 | 544.3 | 544.3 |
| 1999/2000 | 544.3 | 329.2 |

recycling of NiCd batteries is adding more than 2200 t or more than 11% of current total production. If recycling of other manufacturing wastes such as filter cakes, electroplating sludges, electric-are furnace (EAF) dusts, and spent anodes is added to the NiCd battery recycling numbers, then cadmium recycling is probably 15–20% of the total supply rather than the 10–15% level currently suggested. Cadmium recycling rates are expected to continue to grow in the future.

Another factor in the cadmium supply situation in recent years has been the decision by the U.S. Defense Logistics Agency (DLA) in 1991 to dispose of its entire cadmium stockpile of 2877 t as excess material. As of September 2000, 1983.6 t of DLA stockpile cadmium has been sold into the market, mostly to traders and much of it at prices substantially below the existing market prices published in *Metal Bulletin*. In addition, the DLA has raised the authorized annual sales limit for any one fiscal year, which normally runs from October 1 to September 30, from the original level of 500,000 lb (227.3 t) to 1,200,000 lb (544.3 t). The status of DLA disposals and authorized disposal limits for fiscal years 1993–1999 are summarized in Table 6 (10).

Although the total amount of cadmium sold from the DLA stockpile is relatively small compared to total production and consumption, the continual availability of more than 500 t/yr of surplus cadmium does not help the cadmium market recover, especially in times of weak prices and general oversupply.

### 3.1. Stocks.

World stocks of cadmium built significantly during 1996 following a trend begun in 1994 after decreases during 1992–1994. In 1997, cadmium stocks decreased by ~14%, but still remained at >3800 t at the end of the year. The world stock situation by geographic area for 1993–1997 is summarized in Table 7. These figures do not include the DLA stockpile amounts and reflect mainly producer inventories rather than consumer inventories that have returned to more normal levels.

Table 7. **World Cadmium Stocks by Geographic Area**

| | Stocks, t | | | | |
|---|---|---|---|---|---|
| Area | 1993 | 1994 | 1995 | 1996 | 1997 |
| Europe | 1,424.5 | 1,142.4 | 1,401.9 | 1,746.5 | 1,370.2 |
| Americas | 920.0 | 733.4 | 1,029.2 | 1,855.7 | 1,686.5 |
| Other | 556.3 | 417.8 | 746.9 | 856.8 | 784.9 |
| *Total* | *2900.8* | *2293.6* | *3178.0* | *4459.0* | *3841.6* |

Table 8. **Natural Isotopes of Cadmium**

| Mass | Relative abundance, atomic % |
|---|---|
| 106 | 1.25 |
| 108 | 0.89 |
| 110 | 12.49 |
| 111 | 12.80 |
| 112 | 24.13 |
| 113 | 12.22 |
| 114 | 28.73 |
| 116 | 7.49 |

## 4. Properties

The electronic structure of elemental cadmium is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$, and its normal oxidation state in almost all of its compounds is +2, although the +1 oxidation state has been reported in rare instances. There are eight natural isotopes of cadmium and their mass and relative abundance are summarized in Table 8.

The standard electrochemical reducion potential for the reaction

$$\mathrm{Cd}^{2+} + 2e^- \longrightarrow \mathrm{Cd}$$

is −0.403 V at 25°C (7). Its electrochemical equivalent is 582.4 Mg/C. Because of its position in the electromotive series of elements, cadmium is displaced from solution by more electropositive metals such as zinc and aluminum but is more galvanically active than steel and thus protects it in a sacrificial manner.

The physical, thermal, electrical, magnetic, optical, and nuclear properties of cadmium metal are summarized in Table 9. The chemical properties of cadmimum metal in general resemble those of zinc, especially under reducing conditions and in covalent compounds. In oxides, fluorides and carbonates, and under oxidizing conditions, cadmium may behave similarly to calcium. It also forms a relatively large number of complex ions with other ligand species such as ammonia, cyanide, and chloride. Cadmium is a fairly reactive metal. It dissolves slowly in dilute hydrochloric or sulfuric acids, but dissolves rapidly in hot dilute nitric acid. All of the halogens, phosphorus, sulfur, selenium, and tellurum also react readily with cadmium at elevated temperatures.

Unlike zinc, cadmium is not markedly amphoteric, and cadmium hydroxide is virtually insoluble in alkaline media. Like zinc, however, cadmium forms a protective oxide film that reduces its corrosion/oxidation rate in atmospheric service. Both metals exhibit low corrosion rates over the range of pH $\sim$5−10. (1,11) In more acidic and alkaline environments, their corrosion rates increase dramatically. Cadmium is generally preferred for marine or alkaline service, whereas zinc is often as good or better in heavy industrial exposures containing sulfur or ammonia.

## 5. Manufacturing and Processing

**5.1. Production of Cadmium Metal.** Cadmium metal is produced mainly as a byproduct of the beneficiation and refining of zinc sulfide ore concentrates,

Table 9. **Physical Properties of Cadmium**

| Property | Value |
|---|---|
| atomic weight | 112.40 |
| melting point, °C | 321.1 |
| boiling point,°C | 767 |
| latent heat of fusion, kJ/mol[a] | 6.2 |
| latent heat of vaporization, kJ/mol[a] | 99.7 |
| specific heat, J/(mol · K)[a] | |
| 20°C | 25.9 |
| 321–700°C | 29.7 |
| coefficient of linear expansion at 20°C, μm/(cm.°C) | 0.313 |
| electrical resistivity, μω · cm | |
| 22°C | 7.27 |
| 400°C | 34.1 |
| 600°C | 34.8 |
| 700°C | 35.8 |
| electrical conductivity, % IACS[b] | 25 |
| density, kg/m$^3$ | |
| 26°C | 8642 |
| 330°C (liq>) | 8020 |
| 400°C | 7930 |
| 600°C | 7720 |
| volume change on fusion, % increase | 4.74 |
| thermal conductivity, W/(m · K) | |
| 273 K | 98 |
| 373 K | 95 |
| 573 K | 89 |
| vapor pressure, kPa[c] | |
| 382°C | 0.1013 |
| 473°C | 1.013 |
| 595°C | 10.13 |
| 767°C | 101.3 |
| surface tension, mN/m (= dyn/cm) | |
| 330°C | 564 |
| 420°C | 598 |
| 450°C | 611 |
| viscosity, mPaċs (= cP) | |
| 340°C | 2.37 |
| 400°C | 2.16 |
| 500°C | 1.84 |
| 600°C | 1.54 |
| molar magnetic susceptibility, cm$^3$/mol (= emu/mol) | $-19.8 \times 10^{-6}$ |
| Brinell hardness, kg/mm$^2$ | 16–23 |
| tensile strength, MPa[d] | 71 |
| elongation, % | 50 |
| Poisson's ratio | 0.33 |
| modulus of elasticity, GPa[e] | 49.9 |
| shear modulus, GPa[e] | 19.2 |
| thermal neutron capture cross-section at 2200 m/s, m$^2$/atom | $2450 \pm 50 \times 10^{-28}$ |

[a] To convert J to cal, divide by 4.184.

[b] IACS = International Annealed Copper Standard.

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] To convert MPa to psi, multiply by 145.

[e] To convert GPa to psi, multiply by 145,000.

and, to a lesser degree, from the processing of complex zinc, lead, and copper ores and their concentrates. Cadmium is also increasingly being recovered through the recycling of nickel–cadmium batteries. Mined zinc ores, which may contain 0.02–1.4% cadmium (3), are first crushed and ground to liberate Zn(C*d*)S particles from the host rock. Differential flotation techniques are employed to separate the sulfide particles from waste rock yielding a high grade zinc concentrate that normally contains 0.3–0.5% cadmium (2). It is estimated that 90–98% of the cadmium present in zinc ores is recovered in the mining and beneficiation stages of the extraction process. A schematic flowsheet of the mining and beneficiation processes for a typical lead–zinc ore is shown in Figure 1.

Refining of zinc/cadmium concentrates to separate and purify the two metals can be accomplished by either hydrometallurgical (electrolytic) or pyrometallurgical (high temperature) techniques. Today, most zinc is produced by electrolytic production techniques, but considerable cadmium may also be generated from cadmium fumes and dust from the processing of complex zinc–lead–copper concentrates. In both cases, the concentrate is first converted from a

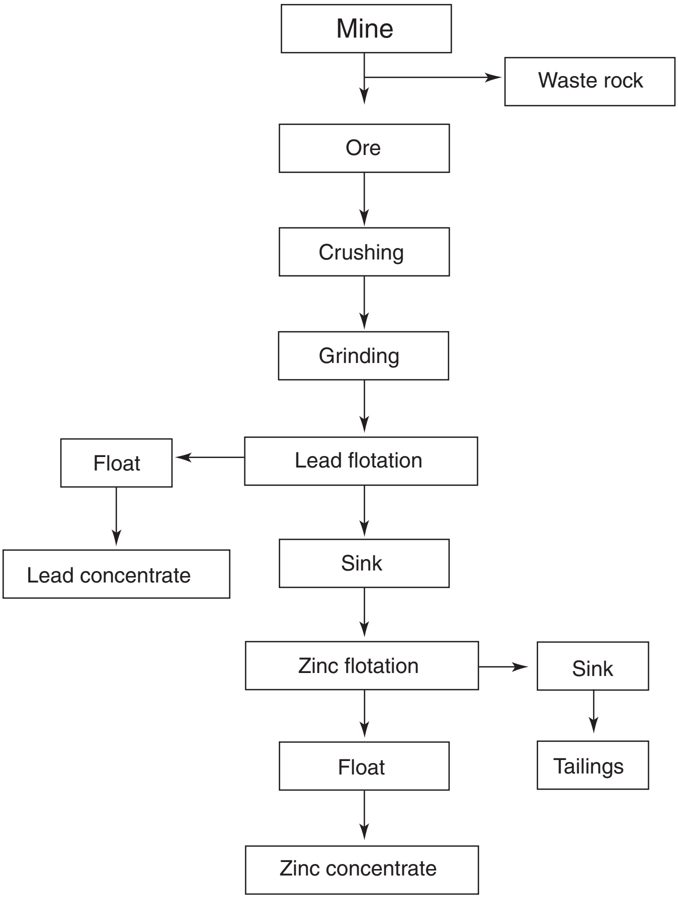

**Fig. 1.** Schematic flow sheet of the mining and beneficiation processes for a typical lead–zinc ore (2)

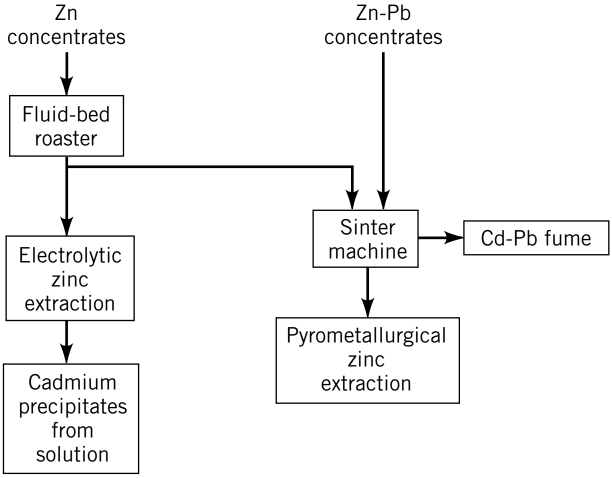

**Fig. 2.** Preliminary cadmium roasting processes.

zinc/cadmium sulfide to a zinc/cadmium oxide by roasting in a fluidized-bed roaster in an excess of oxygen usually at temperatures below 1000°C, which removes sulfur in the form of sulfur dioxide ($SO_2$). The $SO_2$ offgas is stripped of all entrapped dust and other impurities, which are recycled, and then converted to sulfuric acid in an acid plant. The preliminary roasting processes for zinc and zinc–lead concentrates results in cadmium recovery either as precipitates from solution or as cadmium–lead fume, respectively, as shown in Figure 2.

Precipitates are treated by a hydrometallurgical process and cadmium recovered by electrolytic extraction, while the cadmium present as fumes may be treated by several different methods to recover the lead and cadmium.

In the hydrometallurgical process, the crude zinc calcine is dissolved in the sulfuric acid leach of the roasted zinc ore to form an impure zinc sulfate solution, and then neutralized to precipitate any iron. Copper and cadmium are the most common impurities in these solutions, which are subjected to electrolysis for zinc recovery. Both may be precipitated from the solution by successive zinc dust additions in controlled amounts to produce a cadmium cake containing about 25% cadmium, 50% zinc, and minor amounts of copper and lead. The cadmium cake is redissolved in sulfuric acid with only zinc and cadmium going into solution. Two additional acid dissolution and zinc dust precipitation stages ultimately produce a relatively pure cadmium sponge, which is finally dissolved to produce a high purity cadmium solution from which high purity cadmium metal may be electrodeposited. After the electrodeposition process, cadmium metal is stripped from the cathodes and melted and cast into slabs, ingots, sticks, or balls generally of 99.95–99.99% minimum purity. Vacuum distillation techniques may be further employed to produce 99.999 and 99.9999% purity metals that are utilized in semiconductor and photovoltaic applications. A detailed flowchart of the electrolytic cadmium production process is shown in Figure 3.

In the pyrometallurgical or high temperature process, zinc concentrate is roasted as above under oxidizing conditions to remove sulfur and produce a granular sinter for the Imperial Smelting Furnace (ISF) lead–zinc blast furnace

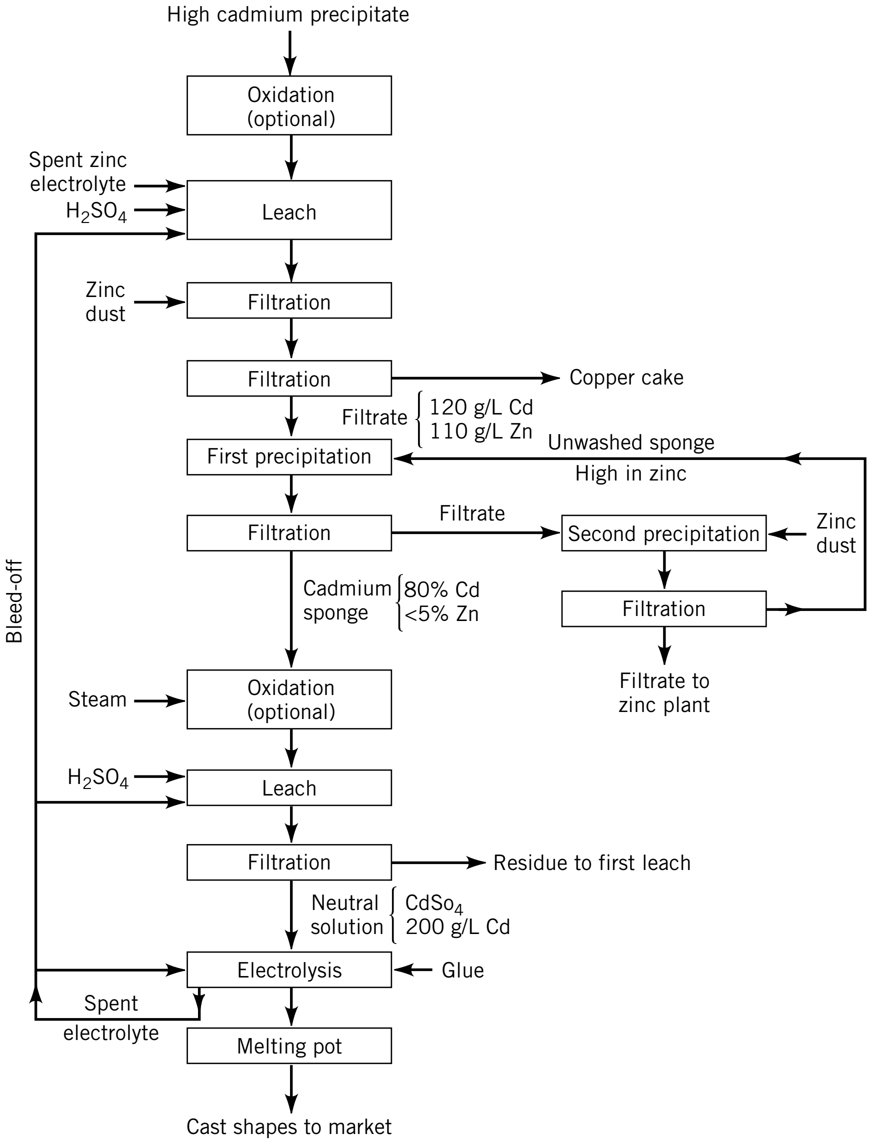

**Fig. 3.** Schematic flow sheet for electrolytic production of cadmium (12).

process. In the sintering operation, ≤70% of the cadmium content of the concentrate will volatilize and be collected as dust and fume. The collected material is leached with sulfuric acid to precipitate lead as lead sulfate and then treated with zinc dust to precipitate cadmium as a metallic sponge that is subsequently dried and refined by distillation to cadmium metal. In all pyrometallurgic processes, the calcine containing oxidized zinc and cadmium is heated to ~1100–1350°C, reduced by carbonaceous material, and the zinc and cadmium are volatilized. Most of the cadmium collects with zinc metal and may be removed by fractional distillation since the boiling points to the three metals (cadmium 767°C, zinc 906°C, lead 1750°C) are well separated. The dusts, powder, and alloy are repeatedly redistilled under reducing conditions to produce a pure metal. A flowchart for cadmium recovery from cadmium-bearing fumes is shown in Figure 4(12) illustrating several possible alternatives during the processing of these materials for cadmium recovery.

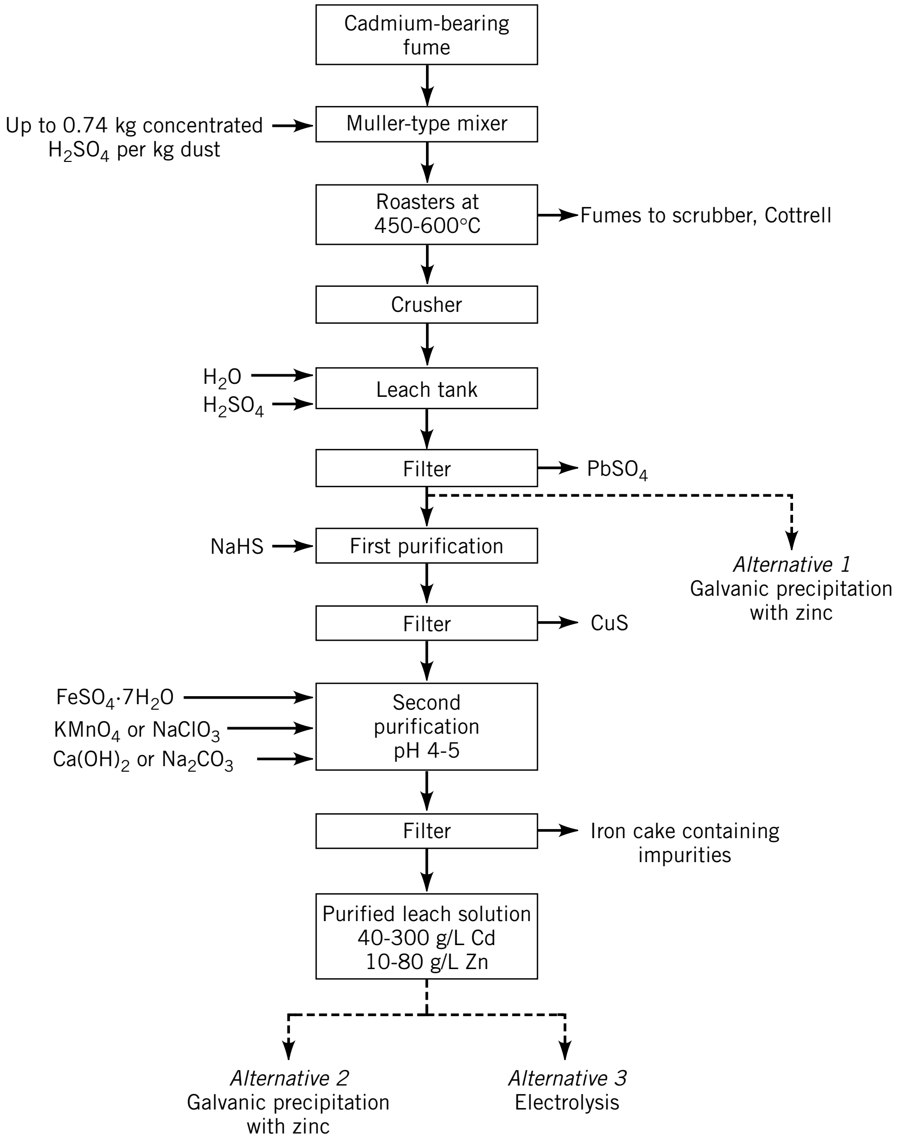

**Fig. 4.** Cadmium recovery from cadmium-bearing fumes (12).

Table 10. **World Consumption of Refined Cadmium Metal**

| Year | consumption, t |
|---|---|
| 1991 | 20,283 |
| 1992 | 17,870 |
| 1993 | 19,165 |
| 1994 | 18,149 |
| 1995 | 18,847 |
| 1996 | 17,726 |
| 1997 | 18,506 |
| 1998 | 18,104 |
| 1999 | 18,936 |
| 2000 (estimated) | 19,180 |

## 6. Economic Aspects

**6.1. Consumption.** Accurate cadmium consumption figures are more difficult to establish than those for cadmium production because of two important confounding factors: (1) the conversion of cadmium metal into cadmium oxide and other cadmium compounds and (2) shipments of cadmium-containing residues to zinc smelters from recycling operations. Once cadmium metal is produced, it may be converted to an intermediate product in one country, incorporated into batteries, pigments, stabilizers, or coatings in another country, and finally manufactured and sold in a product in a third country. It is difficult to establish consumption patterns accurately on a geographic basis, and the figures reported in Table 10 by the World Bureau of Metal Statistics (WBMS) refer to *apparent* consumption of refined metal and include the conversion of refined metal into compounds such as the oxide, hydroxide, sulfide, or carboxylate as would be utilized respectively in batteries and coatings, pigments, and stabilizers. Table 10 shows that refined cadmium metal consumption has decreased substantially since 1996, and that cadmium metal production has exceeded cadmium metal consumption, especially during 1997 and 1998.

The world's leading consumers of refined cadmium metal, according to the World Bureau of Metal Statistics, are summarized in Table 11.

Table 11. **World's Leading Consumers of Refined Cadmium Metal**

| | Apparent consumption | | | |
|---|---|---|---|---|
| Country | 1994 | 1995 | 1996 | 1997 |
| Japan | 6,615.3 | 8,363.5 | 6,527.2 | 7,247.0 |
| United States | 2,236.6 | 2,007.6 | 1,700.5 | 1,355.9 |
| Belgium | 2,944.0 | 2,017.0 | 2,017.1 | 2,017.2 |
| France | 1,969.0 | 1,968.0 | 1,476.0 | 1,476.0 |
| Germany | 750.0 | 750.0 | 750.0 | 750.0 |
| China | 600.0 | 600.0 | 600.0 | 600.0 |
| United Kingdom | 663.5 | 587.4 | 617.7 | 631.2 |
| India | 411.0 | 446.4 | 446.4 | 446.4 |
| South Korea | 380.4 | 380.4 | 380.0 | 380.4 |
| Sweden | 293.0 | 393.0 | 259.0 | 300.0 |

With regard to the data shown in Table 11, Belgium is not a large cadmium consumer producing cadmium-containing products, but it does convert an enormous amount of cadmium metal to cadmium oxide, which is then shipped to the NiCd battery manufacturers around the world. Japan is the largest cadmium consumer in the world for cadmium products because the world's two largest NiCd battery producers, Sanyo and Panasonic, manufacture NiCd battery electrode material there and then ship it to battery assembly plants all over the world. NiCd battery production accounts for over 90% of Japan's cadmium consumption.

**6.2. Prices.** Cadmium has always shown a high price volatility as a byproduct metal with an inelastic supply dependent primarily on zinc production and as a heavily regulated "heavy metal" subject to many proposed product and production restrictions, especially in the European Union. Another problem with cadmium pricing is that the published price very largely reflects trader spot sales, which make up only a relatively small part of total cadmium sales volume. Thus, cadmium prices have varied from as high as \$10/lb in the late 1980s to as low as \$0.20/lb, their levels in 1998 and 1999. Cadmium prices began at \$0.70–0.85/lb in early 1997 for 99.95 and 99.99% purity grades as published in *Metal Bulletin*. Prices decreased steadily throughout the year, and by the end of the year stood at \$0.35–0.45/lb, close to the all-time lows recorded in 1993. Cadmium metal prices were as high at \$2.50/lb in late 1994 and late 1995, but declined to < \$0.50/lb for all of 1998. The published *Metal Bulletin* prices for 99.99% Cd from 1993 through September 1998 are shown in Figure 5.

Prices for cadmium chemicals and for high-purity cadmium metal command a substantial premium over the base metal prices, depending on the specific chemical required, its purity and particle size, lot size, shipping arrangements, and

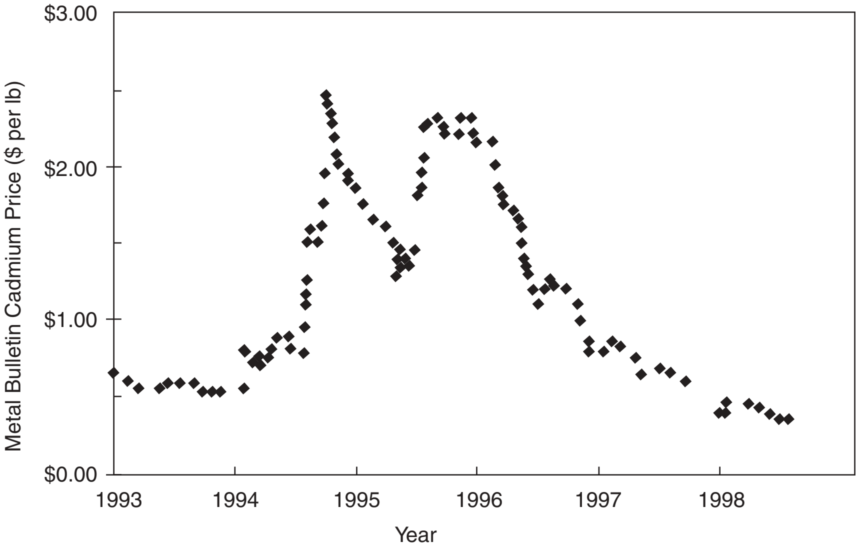

**Fig. 5.** Metal Bulletin Prices for 99.99% cadmium, 1993–1998 (10).

Table 12. **Specifications for Cadmium and Its Alloys, Compounds, and Products**[a]

| Number | Title |
|---|---|
| | *ASTM Specifications* |
| B201-89 | *Testing Chromate Coatings on Zinc and Cadmium* |
| B440-00 | *Cadmium* |
| B635-91 | *Coatings of Cadmium-Tin Mechanically Deposited* |
| B696-91 | *Coatings of Cadmium Mechanically Deposited* |
| B699-93 | *Coatings of Cadmium Vacuum Deposited* |
| B766-93 | *Electrodeposited Coatings of Cadmium* |
| B774-95 | *Low Melting Point Alloys* |
| B781 | *Silver-Cadmium Oxide Contact Material Guide* |
| B816-91 | *Coatings of Cadmium-Zinc Mechanically Deposited* |
| F326 | *Electronic Hydrogen Embrittlement Test for Cadmium Electroplating Processes* |
| F1135-93 | *Cadmium or Zinc Chromate Organic Corrosion Protective Coating for Fasteners* |
| | *ISO Specifications* |
| ISO 2082-86 | *Electroplated Coatings of Cadmium on Iron or Steel* |
| ISO 3613-80 | *Chromate Conversion Coatings on Zinc and Cadmium—Test Methods* |
| ISO 4520-81 | *Chromate Conversion Coatings on Electroplated Zinc and Cadmium Coatings* |
| | *National and Military Specifications* |
| A-A-50800(1) | *Cadmium Oxide* (U.S.A) |
| A-A-51126A | *Cadmium Anodes* (U.S.A) |
| ANSI C18.2-1984 | *Sealed Rechargeable Nickel-Cadmium Cylindrical Bare Cells* (U.S.A.) |
| BS 2868:1968 | *Cadmium Anodes and Cadmium Oxide for Electroplating* (U.K.) |
| MIL-C-8837B(1) | *Cadmium Coating, Vacuum Deposited* (U.S.A) |
| MIL-C-81562B(1) | *Mechanically Deposited Cadmium, Cadmium Tin and Zinc Coating* |
| MIL-F-14072D | *Finish for Ground Signal Equipment* (U.S.A) |
| MIL-P-23408B(1) | *Plating, Tin-Cadmium (Electrodeposited)* (U.S.A) |
| MIL-S-5002D(1) | *Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapons Systems* (U.S.A) |
| MIL-STD-171E | *Finishing of Metal and Wood Surfaces* (U.S.A) |
| MIL-STD-870BB | *Electrodeposited Cadmium Plating, Low Embrittlement* (U.S.A) |
| MIL-STD-889B(3) | *Dissimilar Metals* (U.S.A) |
| MIL-STD-1500 | *Electrodeposited Cadmium-Titanium Plating, Low Embrittlement* (U.S.A) |
| NAS672 | *National Aerospace Standard for Electrodeposited Cadmium* (U.S.A) |
| QQ-P-416F | *Electrodeposited Cadmium Plating* (U.S.A) |
| | *Commercial Specifications* |
| AMS/SAE 2400S | *Cadmium Plating* |
| AMS/SAE 2401D | *Cadmium Plating, Low Hydrogen Content Deposit* |
| AMS/SAE 2416G | *Diffused Nickel-Cadmium Plating* |
| AMS/SAE 2419A | *Cadmium-Titanium Alloy Plating* |
| AMS/SAE 2426B | *Cadmium Plating, Vacuum Deposition* |

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[a] *Nomenclature:* ASTM = American Society for Testing and Materials; ISO = International Standards Organization; ANSI = American National Standards Institute; BS = British Standard; NAS = National Aerospace Standard; AMS = Aerospace Materials Specification; SAE = Society of Automotive and Aerospace Engineers.

many other commercial factors. For example, in May 1999, when the price of cadmium metal was published in *Metal Bulletin* at approximately \$0.19–0.24/lb, the corresponding prices for various cadmium chemicals were published in the *Chemical Market Report* ranging from \$6.75/lb pound for cadmium nitrate to \$25.24/lb for chemically pure, dark red cadmium sulfide used for pigment applications. Cadmium/zinc sulfide yellows are priced at approximately \$12–13/lb, while the cadmium selenide lithopones are priced in the \$5–12/lb range. Depending on specific purity and particle size requirements, cadmium oxide and cadmium hydroxide for NiCd battery production generally may be priced at several times the base price for the high purity (99.99% Cd) metal. The 1999 prices for high purity cadmium powder were \$5.00–7.00/lb, compared to base metal prices of \$0.25/lb for cadmium sticks and balls.

## 7. Specifications for Cadmium and Cadmium Compounds

There are a number of specifications for cadmium, cadmium compounds, and cadmium products, some of which are listed in Table 12.

In addition, there are many specific specifications for cadmium products prepared by various materials and products manufacturers. For example, each NiCd battery producer has a specific requirement for the cadmium compounds such as cadmium oxide, cadmium hydroxide, or cadmium nitrate, which they may utilize in the production of their NiCd batteries. Similarly, pigment and stabilizer producers have specific compositional, particle size, and other requirements for the cadmium compounds used in their formulations. Many different zinc-, lead-, and copper-based products also have maximum cadmium contents levels.

## 8. Analytical Methods

Analytical methods for cadmium are broadly classified into techniques for determining the impurity levels of antimony, arsenic, copper, lead, silver, thallium, tin, and zinc in cadmium metal and cadmium alloys, and methods for establishing cadmium impurities in other base metals such as aluminium and aluminum alloys, nickel, uranium oxide, and zinc and zinc alloys. The ASTM specifications for determining the impurity levels of certain metals in cadmium and of cadmium impurities in certain other systems are summarized in Table 13.

Excellent, if somewhat dated, reviews of the analytical techniques used for the determination of cadmium have been presented by Farnsworth (1) and Fernando and Freizer (13). Farnsworth, for example, summarizes the various analytical techniques available and their sensitivity and accuracy, and her summary is shown in Table 14.

More information (13) indicates that the sensitivity of a number of these techniques has improved greatly and that it is now possible to detect cadmium ion concentrations down to 0.01 parts per billion (ppb) (see CHROMIUM COMPOUNDS).

Table 13. **ASTM Specifications for Analysis of Cadmium**

| Number | Title |
|---|---|
| E34-94 | *Chemical Analysis of Aluminum and Aluminum-Base Alloys* |
| E227-90 | *Optical Emission Spectrometric Analysis of Aluminum and Aluminum Alloys by the Point-to-Plane Technique* |
| E396-98 | *Standard Test Methods for Chemical Analysis of Cadmium* |
| E402-95 | *Standard Test Method for Spectrographic Analysis of Uranium Oxide* ($U_3O_8$) *by Gallium Oxide-Carrier Technique* |
| E536-98 | *Standard Test Methods for Chemical Analysis of Zinc and Zinc Alloys* |
| E607-90 | *Standard Test Method for Optical Emission Spectrometric Analysis of Aluminum and Aluminum Alloys by the Point-to-Plane Technique, Nitrogen Atmosphere* |
| E1277-96 | *Standard Test Method for Chemical Analysis of Zinc-5%* Aluminum-Mischmetal Alloys by ICP Emission Spectrometry |
| E1587-94 | *Standard Test Methods for Chemical Analysis of Refined Nickel* |

A 1986 summary of analytical techniques for cadmium (14) estimates the following detection limits for cadmium ions by various analytical techniques:

| Method | Detection limit, ppb |
|---|---|
| Atomic absorption spectroscopy (graphite furnace) | 0.008 |
| Polarography (square-wave) | 10 |
| X-ray fluorescence (energy-dispersive) | 5,000 |
| Neutron activation analysis | 1 |
| Isotope dilution | 10 |
| Inductively coupled plasma emission spectra | 1 |

At higher concentrations, cadmium may be estimated gravimetrically following precipitation with sulfide, β-naphthoquinoline, or after plating from a cyanide-containing solution onto a stationary platinum cathode. Volumetric

Table 14. **Analytic Techniques for Cadmium**

| Technique | Sensitivity ppb | Accuracy, % |
|---|---|---|
| spectrophotometry | | |
| dithizone | 50 | 5–10 |
| electrochemistry | | |
| d-c polarography | 1000 | 5–10 |
| pulse polarography | 10 | 10 |
| anodic stripping voltammetry | 1 | 20 |
| spectroscopy | | |
| arc/spark emission | 20,000 | 30 |
| atomic emission | 50 | 5 |
| atomic absorption | 10 | 5 |
| atomic absorption with extraction | 1 | 10 |
| atomic absorption with furnace | 1 | 10 |
| atomic fluorescence | 1 | 10 |
| neutron activation | 1–10 | 20 |
| mass spectroscopy | | |
| spark source | 10–100 | 20 |
| isotope dillution | 1 | 5 |

*Source*: Ref. 1.

procedures rely on preliminary precipitation of the sulfide that is purified and then dissolved in acid whereupon the liberated $H_2S$ may be titrated with iodine. An alternative, should zinc be a likely contaminant, is to precipitate with diethyldithiocarbamate and then to redissolve in acid and titrate with sodium ethylenetriaminetetraacetate (EDTA) using Eriochrome Black T as indicator (see CHROMIUM COMPOUNDS).

## 9. Recycling

There has been increasing emphasis on the collection and recycling of spent cadmium products to reduce any risk to human health and the environment from the disposal of cadmium products. Since NiCd batteries account for the vast majority (75%) of cadmium consumption, the main efforts have centered on the collection and recycling of NiCd batteries. However, cadmium-coated products, cadmium alloys, and CdTe photovoltaic modules are also recyclable and efforts have been made to collect and recycle these products as well. For example, cadmium coatings may be recycled through the treatment of electric-arc furnace (EAF) dust, which is generated by the remelting of large quantities of scrap steel, some of which may be cadmium-coated or contain cadmium as an impurity in galvanized coatings. In this case, EAF dust is processed mainly to recover zinc and lead, but could be processed to recover cadmium as well if the economics were more favorable. Similarly, certain types of cadmium-containing brazing and soldering alloys are recycled, mainly to recover more valuable metals such as silver and nickel, but in the process cadmium can be recovered as well. More recently, First Solar LLC. in the United States has developed successful techniques for recycling both cadmium and tellurium from CdTe manufacturing scraps and spent solar panels. However, the large volumes recycled and the massive programs that the cadmium and NiCd battery industries have developed arise from the recycling of nickel–cadmium batteries.

Nickel–cadmium batteries, as well as other cadmium-containing products, are relatively easy to recycle and may be recycled by either pyrometallurgical (high temperature) or hydrometallurgical (wet chemical) processes. There are also processes that include both hydrometallurgical and pyrometallurgical components in their overall flowcharts. The principal materials present in NiCd batteries are iron, nickel, cadmium, potassium hydroxide electrolyte, some copper contact materials, plastic (polypropylene or polyethylene) casings, and organic separator materials. In the recycling of large industrial NiCd batteries, the electrolyte is normally drained off, and plastic casings and separator materials are diverted from the metallic waste stream of mainly iron, nickel, and cadmium and their oxides or hydroxides. The objective of most recycling operations is to convert the metal oxide/hydroxide back to a metal with a purity, quality, and form that can subsequently be utilized for the manufacture of new batteries.

Since nickel, iron, and cadmium all have relatively low ($<200$ kJ) negative free energies of formation of their respective oxides, they are easier to reduce than are the oxides of other battery metals such as zinc, manganese, chromium, titanium, vanadium, aluminum, zirconium, and the rare-earth elements, all of which have higher ($>400$ kJ) negative free energies of formation of their

Table 15. **World's Major NiCd Battery and NiCd Scrap Recycling Plants**

| Company | Location | Type | Capicity, tonnes |
|---|---|---|---|
| INMETCO | USA | Stainless Steel | 3,000 |
| Hanil Metal Recycle Co. | Korea | NiCd Recycler | 3,000 |
| Mitsui Mining & Smelting | Japan | Zinc Refinery | 1,800 |
| Toho Zinc Co., Ltd. | Japan | Zinc Refinery | 1,700 |
| Kansai Catalyst | Japan | Zinc Refinery | 500 |
| Hydrometal S.A. | Belgium | Hydrometallurgical | 1,300 |
| SAFT | Sweden | NiCd Recycler | 1,500 |
| SNAM | France | NiCd Recycler | 1,000 |
| ACCUREC | Germany | NiCd Recycler | 1,0000 |

respective oxides. Therefore, NiCd and NiFe batteries will require less energy to recycle than do alkaline manganese and zinc–carbon batteries, which, in turn, require less energy to recycle than NiMH and lithium-ion batteries. Cadmium may be recycled indefinitely from spent NiCd batteries and manufacturing scrap, and continually produced to the same specifications as cadmium produced from zinc ore and meeting all the requirements of NiCd battery manufacturers. Some of the details of the various types of pyrometallurgical and hydrometallurgical NiCd battery processes are summarized below, including a listing of the world's major NiCd battery recycling plants and detailed process flowcharts. More complete details, including an extensive bibliography on NiCd battery recycling, are available in an OECD document (15).

Nickel–cadmium battery and manufacturing scrap recycling systems are usually based on pyrometallurgical (high temperature) or hydrometallurgical (wet chemical) processes, and the pyrometallurgical processes are further divided into three basic types: stainless-steel recyclers, dedicated NiCd battery recyclers, and primary zinc refineries. A summary of the world's NiCd battery and battery manufacturing scrap recycling facilities indicating their basic type and recycling capacity is shown in Table 15. In the case of the three hydrometallurgical recyclers listed, these are not commercially processing NiCd batteries or scraps at the present time and are included to illustrate both types of recycling processes.

Recycling of cadmium coatings and cadmium alloys is accomplished primarily by pyrometallurgical or high temperature techniques, while processing of CdTe manufacturing scraps and spent modules is carried out utilizing a hydrometallurical process. Details of all of the processes described above are available in the OECD *Guidance Document* (15) on nickel–cadmium battery recycling.

## 10. Environmental Concerns

**10.1. Cadmium Emissions.** Cadmium emissions arise from two principal source categories: natural sources and man-made or anthropogenic sources. Emissions occur to the three major compartments of the environment—air, water, and soil—but there may be considerable transfer between the three compartments after initial deposition. Emissions to air are considered more mobile than those to water, which in turn are considered more mobile than those to soils.

*Natural Cadmium Emissions.* Even though the average cadmium concentration in the earth's crust is generally placed between 0.1 and 0.5 ppm, much higher levels may accumulate in sedimentary rocks, and marine phosphates and phosphorites have been reported to contain levels as high as 500 ppm (3,4). Weathering and erosion of parent rocks result in the river transport of up to 15,000 t per annum of cadmium to the world's oceans (4,5). Volcanic activity is also a major natural source of cadmium release to the atmosphere, and estimates have been placed as high as 820 t per year (4,5,16,17). Forest fires contribute to cadmium air emissions, with estimates of 1–70 t emitted to the atmosphere each year (16).

*Anthropogenic Cadmium Emissions.* Man-made cadmium emissions arise either from the manufacture, use and disposal of products intentionally utilizing cadmium, or the presence of cadmium as a natural but not functional impurity in noncadmium-containing products. The former category of cadmium-containing products includes.

- Nickel–cadmium batteries
- Cadmium-pigmented plastics, ceramics, glasses, paints, and enamels
- Cadmium-stabilized PVC products
- Cadmium-coated ferrous and nonferrous products
- Cadmium alloys
- Cadmium electronic compounds

The latter category of noncadmium-containing products includeds:

- Nonferrous metals and alloys of zinc, lead, and copper
- Iron and steel
- Fossil fuels (coal, oil, gas, peat, and wood)
- Cement Phosphate fertilizers

Anthropogenic cadmium emissions have declined dramatically since the late 1960s and are still declining today. Studies in Europe, Japan, and the United States have all shown significant decreases in cadmium emissions in the time period from approximately 1960 to 1995 (13,18–21). Considerable progress is now also being made in reduction of diffuse contamination from cadmium products through collection and recyling programs of cadmium-containing products (3,9,19,22). Cadmium emissions from products where cadmium is present as an impurity have not been reduced as significantly (3,18,21) and appear to be the one remaining area where additional reductions might be achieved.

*Cadmium in Municipal Solid Waste.* There are many sources of cadmium in municipal solid waste, not just products to which cadmium has intentionally been added. As noted above, other sources include products such as iron and steel; gypsum, cement, and other construction debris; nonferrous (Zn, Pb, Cu) metal and alloy products; fossil fuels and fossil fuel residues; and natural substances such as grass, plants, and foods, all of which may contain cadmium (23). Some studies have determined that incineration accounts for only ~1% of the total sources of human cadmium exposure (5,21,24–26). The human exposure resulting from the disposal of cadmium-containing products by incineration is even less and is generally considered insignificant for all of these reasons (24–26).

*Partitioning of Cadmium Emissions to Compartments.* The vast majority of cadmium emissions, approximately 80–90%, partition initially to soils. Although some transfer does occur from soils back to the air or water compartments, the net flux into the soil is generally regarded as positive since there is deposition from both air and water onto soils. Thus, most cadmium emissions eventually return to soil. In soils, cadmium is largely bound to the nonexchangeable fraction, such as on clays and manganese and iron oxides. For this reason, its mobility and transfer into the animal and human food chain is limited. The remaining 10–20% of anthropogenic cadmium emissions partition between air and water and depend largely on the emission source. For example, cadmium electroplating operations result in no air emissions but, in the past, did result in water emissions. Today, water effluent regulations ensure that even cadmium electroplating water emissions are negligible. Any cadmium waste from cadmium electroplating is now contained in electroplating sludge from the pollution control equipment, which may be recycled to recover valuable metals.

*Sources of Cadmium Emissions to Air, Water, and Soil.* Cadmium emissions to air arise, in decreasing order of importance, from the combustion of fossil fuels, iron and steel production, nonferrous metals production, and municipal solid-waste combustion (3,21,27,28).Cadmium emissions to water arise, in decreasing order of importance, from phosphate fertilizers, nonferrous metals production, and the iron–steel industry (15,21,24).

Cadmium emissions to soils must be considered in three distinct categories: as inputs to agricultural soils, as emissions to nonagricultural soils, and as depositions in controlled landfills. In the first case, the main inputs to agricultural soils that are of primary relevance to human exposure to cadmium arise from atmospheric deposition, sewage sludge application, and phosphate fertilizer application (6,21). In the second case, inputs to nonagricultural soils arise mainly from the iron–steel industry, nonferrous metals production, fossil-fuel combustion, and cement manufacture (5,24,27).

In the case of cadmium present in controlled landfills, these amounts can arise from disposal of spent cadmium-containing products, products with cadmium impurities, and wastes such as grass, food, and soil with naturally occurring trace levels of cadmium (23). Cadmium input to agricultural soils is of far greater relevance to human health than cadmium input to nonagricultural soils. Input to controlled landfills is of even less importance because cadmium is largely immobilized in controlled landfills. For example, numerous studies of the leachate from municipal solid-waste landfills have conclusively demonstrated that, even after long periods of time, the leachate from these landfills meets the WHO cadmium drinking-water standards of 3 μg/L (29,30).

*Cadmium Emissions vs. Natural Cadmium Emissions.* Earlier estimates of anthropogenic versus natural cadmium emissions had indicated approximately 8000–10,000 t/yr for anthropogenic emissions compared to 800–1000 tonnes per year for natural cadmium emissions (4,16,17). Anthropogenic cadmium emissions, however, have decreased by $\leq$98%. Thus, natural cadmium emissions, expressed in terms of contained cadmium, which in the past have been stated to be only about 10% of the level of anthropogenic cadmium emissions, are more nearly equal to synthetic emissions today. This parity is becoming increasingly likely because of the rapidly decreasing anthropogenic cadmium emissions to the environment compared to the relatively stable natural cadmium emissions.

## 11. Levels of Cadmium in the Enviroment

**11.1. Cadmium in Air.** Three distinct categories may be recognized with respect to cadmium-in-air concentrations: cadmium in ambient air, cadmium air levels in occupational exposure situations, and cadmium in air from the smoking of tobacco. Cadmium in ambient air represents, by far, the majority of total airborne cadmium. Inputs from all three categories may affect human cadmium intake and human health, but the levels and the transfer mechanisms to humans are substantially different for the three. Whereas cadmium emissions from occupational environments and from cigarette smoke are transferred directly to humans, cadmium in ambient air is generally deposited onto waters or soils, then eventually transferred to plants and animals, and finally enters the human body through the food chain. Thus the amount of cadmium transferred through occupational exposure or cigarette smoking will be much higher than the amount transferred through atmospheric deposition.

*Cadmium in Ambient Air.* Ambient-air cadmium concentrations have generally been estimated to range from 0.1 to 5 ng/m$^3$ in rural areas, from 2 to 15 ng/m$^3$ in urban areas, and from 15 to 150 ng/m$^3$ in industrialized areas (4,5,8), although some much lower values have been noted in extremely remote areas and some much higher values have been recorded in the past near uncontrolled industrial sources. There are generally little or no differences noted in cadmium levels between indoor and outdoor air in nonsmoking environments. Smoking, however, may substantially affect indoor ambient-air cadmium concentrations.

*Cadmium in Occupational Enviroments.* Cadmium air concentrations may be elevated in certain industrial settings, but these exposures are closely controlled today by national occupational exposure standards. Historically, average exposure levels and regulatory permissible exposure limits (PELs) have decreased markedly in since late 1950s in recognition of the importance of cadmium inhalation to human health and with the significant improvements in air-pollution-control technology over that period (4,8). Occupational exposure standards that were formerly set at 100–200 μg/m$^3$ are now specified at 2–50 μg/m$^3$ along with requirements to maintain biological indicators such as cadmium-in-blood and cadmium-in-urine below certain levels to assure no adverse human health effects from cadmium occupational exposure (31–33).

*Cadmium in Tobaco Smoke.* Tobacco leaves naturally accumulate and concentrate relatively high levels of cadmium, and therefore smoking of tobacco is an important source of air cadmium exposure for smokers. It has been reported that one cigarette contains about 0.5–2 μg of cadmium and that ~10% of the cadmium content is inhaled when the cigarette is smoked (4,8). Smokers generally exhibit significantly higher cadmium body burdens than do nonsmokers.

**11.2. Cadmium in Water.** The average cadmium content in the world's oceans has variously been reported as low as <5 ng/L and as high as 110 ng/L (3–8). Higher levels have been noted around certain coastal areas and variations of cadmium concentration with the ocean depth, presumably due to patterns of nutrient concentrations, have also been measured (4,5). Even greater variations are quoted for the cadmium contents of rainwater, freshwater, and surface water in urban and industrialized areas. Levels of 10–4000 ng/L have been quoted in the literature depending on specific location and whether total cadmium or dissolved cadmium is measured (4,5,8).

Cadmium is a natural, usually minor constituent of surface and groundwaters. It may exist in water as the hydrated ion; as inorganic complexes such as carbonates, hydroxides, chlorides, or sulfates; or as organic complexes with humic acids (5). Much of the cadmium entering freshwater may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment (4). Some data shows that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0.1 ppm cited above for fresh waters (3). Partitioning of cadmium between the adsorbed-in-sediment state and dissolved-in-water state is therefore an important factor in whether cadmium emitted to waters is or is not available to enter the food chain and affect human health.

Rivers containing excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source (4). Nonetheless, studies of cadmium contamination in major river systems in the late twentieth century conclusively demonstrated that cadmium levels in these rivers decreased significantly since the 1960s and 1970s (13,18,19,21). For example, studies on the Rhine River Basin during 1973–1987 indicated that the point source cadmium discharges to the Rhine River decreased from 130 to 11 tonnes/year over that 14-year timespan, a reduction of over 90% (18). Similarly, data on total cadmium and dissolved cadmium at the Dutch/German border during 1971–1987 have shown comparable reductions (34).

**11.3. Cadmium in Soil.** *Sources.* Cadmium is much less mobile in soils than in air and water. The major factors governing cadmium speciation, adsorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, clay content and type, presence of organic and inorganic ligands, and competition from other metal ions (5). The use of cadmium-containing fertilizers and sewage sludge is most often quoted as the primary reason for the increase in the cadmium content of soils in Europe (6). Atmospheric cadmium emissions deposition onto soils has generally decreased significantly over that same time period (13,19). Indeed, studies in Europe have documented that atmospheric emissions do not have a significant impact on the cadmium content of soils (35).

*Cadmium in Agricultural Soils.* Numerous agencies have focused on the presence of cadmium in agricultural soils, the means by which agricultural soils may be enriched by cadmium, the degree to which cadmium is taken up by foodstuffs, and the subsequent transfer of cadmium to humans via foodstuffs. Because cadmium is a naturally occuring component of all soils, all foodstuffs contain some cadmium and therefore all humans are exposed to natural levels of cadmium. Although much attention has been focused on the cadmium content of agricultural soils, it is important to recognize that the cadmium content of food items varies more as a function of the nature of the crop grown and the agricultural practices followed. Except in cases of extreme contamination, the concentration of cadmium in soils is not the primary determinant of cadmium in the human diet. For example, leafy vegetables and potato tubers naturally accumulate higher levels of cadmium than do fruits and cereals (36). Moreover, tillage and crop rotation practices similarly have a greater impact on the cadmium content of food than does the concentration of cadmium in soils (46). Cadmium absorption may also depend on other factors as well, as described below.

*Cadmium Levels in Foodstuffs.* Cadmium levels can vary widely in various types of foodstuffs. Leafy vegetables such as lettuce and spinach and certain staples such as potatoes and grain foods exhibit relatively high values from 30 to 150 ppb. Peanuts, soybeans, and sunflower seeds also exhibit naturally high values of cadmium with seemingly no adverse health effects. Meat and fish normally contain lower cadmium contents, from 5 to 40 ppb. Animal offal such as kidney and liver can exhibit extraordinarily high cadmium values, up to 1000 ppb, as these are the organs in animals where cadmium concentrates (4,37). The cadmium contents of foodstuffs may vary widely with the agricultural practices utilized in the particular areas such as phosphate fertilizer, sewage sludge and manure application, the types of crops grown, and atmospheric cadmium deposition from natural or anthropoenic sources. Since various studies have shown that human cadmium intake, as least for nonsmokers, comes principally (~95%) from the ingestion of foods rather than from inhalation of cadmium in air, it is the cadmium levels of foods which most affect the general population. There are strong indications that cadmium levels in foodstuffs have substantially decreased with the progressive control of cadmium emissions to the environment (38–40). More recent studies have further documented that the cadmium content of food crops in Europe and many other countries are now stable and not increasing with time (41).

*Cadmium Contamination of Agricultural Soils.* In the past, there were examples of marked cadmium contamination in areas where food has been grown. This was particularly so for rice crops in Japan in the 1950s and 1960s where cadmium concentrations of 200–2000 ppb were found (8). In general, soils that have been historically contaminated with cadmium from industrial operations are no longer used for agricultural purposes. In those cases where old industrial installations that are cadmium-contaminated are subsequently employed for growing crops, suitable remediation techniques do exist to immobilize the cadmium present in the soil and thus to control the risk to human health. There is, however, no doubt that old sites that are so contaminated do require proper risk management and control by cleaning up or immobilizing the existing excess cadmium in the soil.

## 12. Health and Safety Factors

It has been well established that excess cadmium exposure produces adverse health effects on human beings. For virtually all chemicals, adverse health effects are noted at sufficiently high total exposures. For certain elements such as copper and zinc, which are essential to human life, a deficiency as well as an excess can cause adverse health effects. Cadmium is not regarded as essential to human life. The relevant questions with regard to cadmium exposure are the total exposure levels and the principal factors that determine the levels of cadmium exposure and the adsorption rate of the ingested or inhaled cadmium by the individual, in other words, the pathways by which cadmium enters the food chain, which is the principal pathway of cadmium exposure for most human beings.

## 13. Principal Factors that Determine Levels of Human Exposure

Human normally absorb cadmium into the body by either ingestion or inhalation. Dermal exposure (uptake through the skin) is generally not regarded to be of signifigance (42). It is widely accepted (14,37) that approximately 2–6% of the cadmium ingested is actually taken up into the body. Factors influencing cadmium absorption are the form in which cadmium is present in the food, and the iron status of the exposed individual. In contrast, 30–64% of inhaled cadmium is absorbed by the body, with some variation as a function of chemical form, solubility, and particle size of the material inhaled. Thus, a greater proportion of inhaled cadmium is retained by the body than when cadmium is taken in by ingestion. For the non–occupationally exposed individual, inhalation exposure to cadmium does not usually contribute significantly to overall body burden. The exception to this generalization is the cigarette smoker. One model for human cadmium intake (26) has estimated that ingestion accounts for 95% of total cadmium intake in a nonsmoker. For a smoker, this model estimates that roughly 50% of their cadmium intake arises from cigarettes with the balance due to ingestion and the low levels of cadmium naturally present in ambient air. In the past, occupational exposure was also a significant contributor to total cadmium intake, but with very stringent occupational standards in place today, occupational cadmium intake is much less of a consideration than it was in the late 1970s. Thus, the principal determinants of human cadmium exposure today are smoking habits, diet, and, to a lesser extent, occupational exposure.

**13.1. Human Intake of Cadmium.** *Ingestion.* Much of the cadmium that enters the body by ingestion comes from terrestrial foods, or from plants grown in soil or meat from animals that have ingested plants grown in soil. Thus, directly or indirectly, it is the cadmium present in soil and the transfer of that cadmium to food plants together with the cadmium deposited from the atmosphere on edible plant parts that establishes the vast majority of human cadmium intake. Some have estimated that 98% of the ingested cadmium comes from terrestrial foods, whereas only 1% comes from aquatic foods such as fish and shellfish, and 1% arises from cadmium in drinking water (27).

*Cadmium Intake from Foods.* Many studies have attempted to establish the average daily cadmium intake resulting from foods. In general, these studies show that the average daily diet for nonsmokers living in uncontaminated areas is at present at the low end of the range of 10–25 μg of cadmium (5,8,37). This general trend is confirmed by decreasing blood cadmium levels in the general population in several countries during this time period (43,44). In another evaluation, the International Programme on Chemical Safety (IPCS) assessed the average daily intake at the lower end of this range (4).

The World Health Organization (WHO) has established a provisional tolerable weekly intake (PTWI) for cadmium at 7 μg/kg of body weight. This PTWI weekly value corresponds to a daily tolerable intake level of 70 μg of cadmium for the average 70-kg man and 60 μg of cadmium per day for the average 60-kg woman (4). Clearly, the daily cadmium intake for the general population from food, which is by far the dominant source of cadmium, is well below the guidelines established by the World Health Organization. The average daily cadmium intake for the general population in the Western world has shown a distinct downward trend from 1970 through 1992 (31), a reduction presumed to be due to the marked decreases in direct atmospheric deposition of cadmium onto crops and soils. Other studies have suggested that, over the timeframe of 1980–1985, levels of cadmium intake have been relatively constant (5). At an absorption rate of 5% from ingestion, the average person is believed to retain about 0.5–1.0 μg of cadmium per day from food.

There is considerable information in the literature regarding the cadmium contents of foods grown in contaminated areas (4,5,8). Detailed studies have indicated that only a small percentage of these contaminated areas were actually utilized for growing foods that were subsequently consumed with the exception of rice fields in Japan, where considerable cadmium did find its way into the average person's diet through rice grown on contaminated rice beds (8). In specific cases, management measures to reduce the transfer of cadmium from historically contaminated soils into the local food chain have proved successful (45).

*Inhalation.* Cadmium inhalation is a far smaller contributor to total cadmium body burden except, as previously noted, in the cases of smokers or some highly exposed workers of the past. Today, the inhalation route is well controlled in the occupational setting, and is well controlled from point sources such as those which directly pertain to the nonferrous, cadmium, or cadmium products industries. Ambient-air emissions from fossil-fuel power generation plants, the iron–steel industry, and other major industries where cadmium may be present as a low concentration impurity, on the other hand, may be substantial because the volumes of the waste gases generated are substantial.

*Cadmium Intake from Cigarette Smoking.* Smokers absorb amounts of cadmium comparable to those from food, about 1–3 μg of cadmium per day, from cigarettes smoking. It has been reported that one cigarette contains ~1–2 μg of cadmium and that ~10% of the cadmium content is inhaled when the cigarette is smoked (4). Cigarette construction, the use of filters, and variations in the cadmium contents of tobaccos could decrease cadmium exposure by this route, but in general cigarette smoking is a habit that can more than double the average person's daily cadmium intake. Cigarette smokers who are also occupationally exposed may increase their total cadmium intake even further.

*Cadmium Intake from Occupational Exposure.* Before the 1960s, elevated cadmium in air exposure levels were measured in some workplaces, sometimes as high as 1 mg/m$^3$. Since that time, workplace exposures and standards have decreased markedly so that most occupational exposure standards today are in the range of 2–50 μg/m$^3$. The result has been that occupational exposures today are generally below 5 μg/m$^3$, and most cadmium workers are exposed at levels considered safe (37). In rare cases where cadmium air levels are higher, the use of personal protective equipment is obligatory. Extensive preventative hygiene programs and medical follow-up programs have been developed to control the risk related to cadmium exposure at the workplace (32,33,42,46). Considering present levels of occupational exposure cadmium intake, general dietary intake, and cigarette smoking intake, it still would appear, however, that today's average daily cadmium intake is well below the values recommended by the World Health Organization.

*Human Health Effects of Cadmium.* The kidney is the critical target organ for the general population as well as for occupationally exposed populations. Cadmium is known to accumulate in the human kidney for a relatively long time, from 20 to 30 years, and, at high doses, is also known to produce health effects on the respiratory system and has been associated with bone disease. Most of the available epidemiological information on cadmium has been obtained from workers occupationally exposed at high levels or on Japanese populations in highly contaminated areas. Most studies have centered on the detection of early signs of kidney dysfunction and lung impairment in the occupational setting, and, in Japan, on the detection and screening for bone disease in general populations exposed to cadmium-contaminated rice. More recently, the possible role of cadmium in human carcinogenesis has also been studied in some detail.

*General Population.* The actual levels of cadmium intake resulting from food ingestion varies as a function of multiple factors. For example, certain crops (eg, sunflowers) and shellfish contain naturally elevated amounts of cadmium. Individuals who consume large amounts of these materials might thus at first seem to be at increased risk. However, recent studies have demonstrated that foods which are naturally enriched in cadmium are also enriched in substances that inhibit the uptake of cadmium into the body. Thus, individuals who ingest large amounts of sunflower seeds may ingest up to 100 μg cadmium per day, yet these individuals do not have levels of cadmium in blood or urine higher than those of individuals with far lower levels of cadmium intake (47). Similarly, consumption of a diet rich in shellfish can double the intake of dietary cadmium without producing significant impacts on blood cadmium (48). These studies illustrate that the cadmium content of food is just one of a number of factors that determine the actual uptake of cadmium into the body. Indeed, more recent studies (48) have suggested that overall nutritional status is a more important determinant of cadmium uptake into the body than is the actual amount of cadmium ingested. For example, women subsisting on a vegetarian diet and with reduced iron stores have increased uptake of ingested cadmium. For these women, iron deficiency is a more important determinant of cadmium uptake than is the actual amount of cadmium ingested.

The present levels of cadmium intake in most European countries are far below the PTWI recommended by WHO. Indeed, as a result of numerous public health policies implemented during the late twentieth century, the cadmium body burden of the general population appears to be rapidly declining (49). Present exposure levels in many European countries are now comparable to, or lower than, those that characterize "unacculturated populations" residing in the jungles of South America (50).

Present levels of general population exposure to cadmium have no known adverse health consequences. Existing standards such as the PTWI are based on biological models that associate cadmium exposure and increased urinary excretion of low molecular weight proteins. This has been estimated to occur in humans with a lifelong daily intake of approximately 200 μg. Only in highly contaminated agricultural areas, and only if the cadmium levels in the food grown there were significantly increased, can levels of exposure be sufficient so as to produce kidney dysfunction. Such a situation did occur in the 1950s and 1960s in Japan, where heavy cadmium contamination of rice fields, along with nutritional deficiencies for iron, zinc, and other minerals, led to renal impairment and bone disease (Itai Itai disease) in exposed populations. Studies utilizing very sophisticated biomarkers have detected mild alterations in kidney functions at lower levels of exposure (51). However, more recent studies in the occupational setting have suggested that such alterations have no actual clinical consequences (52).

*Occupationally Exposed Populations.* Occupational exposure to cadmium is mainly by inhalation but also may include additional intakes through food, tobacco, and poor personal hygiene practices. In the past, the total cadmium in air level in the workplace has varied according to the type of industry, type of workplace, and industrial hygiene programs in place. Depending on the level and duration of cadmium exposure, a wide variety of effects have been observed in occupationally exposed groups. For acute exposure by ingestion, the principal effects are gastrointestinal disturbances such as nausea, vomiting, abdominal cramps, and diarrhea. Acute poisoning by inhalation may lead to respiratory manifestations such as severe bronchial and pulmonary irritation, subacute pneumonitis, and lung emphysema, and, in the most severe situations, death from pulmonary edema may occur (42).

Chronic obstructive airway disease has been associated with long-term high level occupational exposure by inhalation (4,5). Although there have been suggestions in past studies that such exposure may cause lung or prostate cancer, more recent epidemiologic analyses of cadmium-exposed cohorts have dismissed the prostate cancer association and indicate that arsenic rather cadmium may be responsible for the observed increase in lung cancer mortality rates (53,54). In addition, most of the other data cited as evidence for the carcinogenicity of cadmium (43) relies on studies that are confounded by the presence of other carcinogenic substances such as nickel, asbestos, or tobacco smoke as well as arsenic.

For chronic cadmium exposure, effects occur mainly on the kidneys, lungs, and bones. A relationship has been established between cadmium air exposure and proteinuria (an increase in the presence of low molecular weight proteins in the urine and an indication of kidney dysfunction (4,5). Cadmium is known to accumulate in the renal cortex, and there is evidence that the level of cadmium in the renal cortex associated with increased urinary excretion is about 200–250 μg/g (wet weight). Depending on exposure level and other sources of cadmium, this level might be reached after 20 years of occupational exposure.

However, more recent work has demonstrated that these effects are reversible at low exposure levels once the cadmium exposure has been removed or reduced (52). With today's low occupational exposure standards, coupled with required biological monitoring of cadmium exposure levels (eg, cadmium-in-blood and cadmium-in-urine) and kidney funcion parameters (eg, $\beta_2$-microglobulin, a low molecular weight protein), there is every assurance that kidney dysfunction or other effects will not develop in occupationally exposed workers as they did in the past.

**13.2. Sources of Human Cadmium Exposure.** Although sources of cadmium emissions to the environment have been listed in some detail in this report and others (3–6,17,21,24,27,28,55), there have been very few attempts to quantitatively partition human cadmium exposure to its various sources. Van Assche (21,26) has developed a model for cadmium exposure for human beings and allocated this exposure to its various sources. Some of the assumptions and the data inputs for the model have been based in large part on actual data from Belgium and the European Community, and, in particular, on the Environmental Resources Limited report on the sources of human and environmental contamination in Europe (24) and the updated data on cadmium emissions contained in the OECD Monograph on Cadmium (5).

The analysis acknowledges that, for the general population, most human cadmium exposure comes from ingestion of food, and most of that arises from the uptake of cadmium by plants from fertilizers, sewage sludge, manure, and atmospheric deposition. Specifically, the model estimated that the relative importance of various cadmium sources to human exposure is as follows (26):

| | |
|---|---|
| Phosphate fertilizers | 41.3% |
| Fossil-fuel combustion | 22.0% |
| Iron and steel production | 16.7% |
| Natural sources | 8.0% |
| Nonferrous metals | 6.3% |
| Cement production | 2.5% |
| Cadmium products | 2.5% |
| Incineration | 1.0% |

Clearly, of the anthropogenic sources of cadmium, phosphate fertilizers, fossil-fuel combustion, and some industrial activities contribute far more to human cadmium exposure than do production, use, and disposal of cadmium products and incineration of all cadmium-containing materials. However, as shown earlier, this observation should be put in the perspective of average daily cadmium intakes well below those necessary to ensure human health. Thus no action seems required to reduce cadmium from its existing levels.

## 14. Uses

Cadmium metal and cadmium compounds are utilized in five principal product areas that include NiCd batteries, pigments, stabilizers, coatings, and alloys and other miscellaneous products. Definitive consumption figures for these markets do not exist, but the International Cadmium Association has for some years

Table 16. **Western World Cadmium Consumption Patterns**

| | Percent of Total Cadmium Consumption | | | | |
|---|---|---|---|---|---|
| Market Segment | 1993 | 1994 | 1995 | 1996 | 1997 |
| Batteries | 63 | 65 | 67 | 69 | 70 |
| Pigments | 15 | 15 | 14 | 13 | 13 |
| Stabilizers | 11 | 10 | 9 | 8 | 7 |
| Coatings | 8 | 8 | 8 | 8 | 8 |
| Alloys etc | 3 | 2 | 2 | 2 | 2 |

made estimates of cadmium consumption patterns by various end-use categories, which are summarized in Table 16 (10).

Approximately 80% of the cadmium consumed in the NiCd battery market is for the small consumer cells utilized in power tools, cellular telephones, camcorders, portable household appliances, laptop computers, and other cordless devices, while the remaining 20% is utilized in the large industrial NiCd batteries for railroad, aerospace, and other industrial applications. The total NiCd battery market, particularly its consumer cell portion, is continuing to grow at the expense of some of the traditional cadmium markets such as pigments, stabilizers, and alloys. Cadmium coatings, which accounted for more than 50% of cadmium consumption in the late 1960s, have decreased substantially but now appear to have stabilized at about 8% of total cadmium consumption. At present the total NiCd battery market, which is growing at a rate of about 4% per year, is expected to account for more than 75% of all cadmium consumption.

**14.1. Batteries.** Nickel–cadmium (NiCd) batteries are characterized by higher energy and power densities and longer cycle lives than are rechargeable lead acid batteries, but are generally more expensive in initial cost and less expensive in lifecycle cost. NiCd batteries also exhibit excellent high and low temperature performance, marked resistance to mechanical and electrical abuse, and rapid charge and discharge characteristics. Because of their high discharge capability, they are the only battery chemistry presently suitable for portable power tools and other high drain rate applications. They are also utilized extensively in cellular and cordless telephones and pagers, emergency lighting and security, household appliances, and hobby and toy uses. Their earlier usage in portable computers and camcorders is being replaced by higher energy desity batteries such as the lithium-ion battery. A breakdown of the Japanese consumer NiCd battery market, which accounts for approximately 70% of the world's consumer NiCd batteries, is summarized in Table 17 for 1994–1997.

Applications for industrial NiCd batteries are fairly evenly divided between aviation starting and emergency power applications and railroad/subway emergency power, switching, and signaling uses. Some production of industrial NiCd batteries for electric vehicles has begun, and future opportunities exist as starters for small engines and in telecommunications uses. (see BATTERIES, LEAD-ACID SECONDARY CELLS)

**14.2. Pigments.** Cadmium sulfide–based pigments are bright yellow, orange, and red colors used in plastics, ceramics, glasses, enamels, and artists'

Table 17. **Japanese NiCd Consumer Battery Market, 1994–1997**

| | Market Share by Year, (Percent of Total) | | | |
|---|---|---|---|---|
| Application | 1994 | 1995 | 1996 | 1997 |
| Home appliances | 27 | 31 | 28 | 25 |
| Power tools | 15 | 17 | 22 | 24 |
| Communications | 34 | 25 | 19 | 18 |
| Emergency power | 7 | 8 | 11 | 13 |
| Miscellaneous | 5 | 7 | 7 | 9 |
| Office equipment | 10 | 9 | 7 | 6 |
| Retail sales | 2 | 3 | 6 | 5 |

colors. A wide spectrum of colors from golden yellow to maroon can be produced by substituting zinc or mercury for cadmium and selenium for sulfur in the CdS crystal lattice. These pigments are characterized by extremely low solubility and high stability, and resistance to high temperature and high pressure, which makes them excellent pigments in applications where high temperature or high stress processing are employed. The approximate breakdown of cadmium pigments usage by applications is summarized in Table 18 (56–58).

Cadmium pigments are widely used to color polymers such as acrylonitrile butadiene styrene (ABS) and other high impact polystyrenes, polyamides (nylon), polycarbonates, high density polyethylene (HDPE), high density polypropylene (HDPP), and silicone resins. It has been very difficult to substitute for cadmium pigments in these polymers, although some substitution has occurred in other polymers processed at lower temperatures.

**14.3. Coatings.** Cadmium coatings are generally applied by electroplating, mechanical plating, or vacuum coating onto iron and steel, aluminum, and titanium surfaces to obtain a superior combination of high corrosion resistance, particularly in saltwater or alkaline media, plus either low coefficient of friction, low electrical resistivity, or good brazing and soldering characteristics (see CORROSION AND CORROSION INHIBITORS). No other galvanically protective coating on steel, is able to match cadmium's combination of these properties. Estimates of U.S. cadmium coatings applications were made by the U.S. Department of Commerce in 1989 and by Morrow in 1992 and are summarized in Table 19 (59). Cadmium coatings are usually deposited from alkaline cyanide, acid sulfate, neutral chloride, or acid fluoborate baths; the cyanide process is the most widely utilized because of its ability to produce bright, uniform deposits. At one time, cadmium coatings accounted for almost half of total cadmium consumption, but this amount has decreased substantially in the face of product restrictions in Europe. The usage of cadmium coatings in the United States remains much

Table 18. **Applications for Cadmium Pigments**

| Application | Percent of total |
|---|---|
| plastics | 80 |
| ceramics | 8 |
| paints | 7 |
| others | 5 |

Table 19. **U.S. Cadmium Coatings Markets (1989 vs 1992)**

| | Percent of total | |
|---|---|---|
| Category | 1989 | 1992 |
| automotive | 30.0 | 15.0 |
| communications | 22.5 | 31.0 |
| fasteners | 17.5 | 20.0 |
| aircraft | 12.5 | 15.0 |
| ammunition | 6.0 | 10.0 |
| shipbuilding | 5.0 | 5.0 |
| railroads | 2.5 | 2.5 |
| hardware | 2.5 | 1.0 |
| appliances | 1.5 | 0.5 |

higher than in Europe, and environmental and human health concerns are managed by regulation and pollution control technology as well as increased recycling of cadmium products.

**14.4. Stabilizers.** Cadmium-bearing stabilizers are utilized to retard the degradation processes in PVC on exposure to heat and ultraviolet light (sunlight). These stabilizers normally consist of mixtures of lead, cadmium, and barium organic salts, which may include cadmium laurate or cadmium stearate, and that are incorporated into the PVC during processing to arrest any degradation processes. They ensure that the PVC develops good initial color and clarity, allows the use of high temperature processing, and promotes a longer service life. The most common type of cadmium-bearing stabilizers are the barium/cadmium stabilizers, which may be either liquid stabilizers containing octoates, phenolates, neodecanoates, naphthenates, and benzoates or the solid barium/cadmium stabilizers, which contain laurates and stearates.

Barium/cadmium-stabilized PVC may be prepared by three different processing techniques: extrusion, calendaring or dispersion coated resins. Typical applications of cadmium-stabilized extruded PVC include pipe for water and for sewage, electrical conduits, shaped profiles, hoses, electrical insulation, credit card stock, automotive exterior trim, belts, fencing, and PVC film and sheet. Applications for cadmium-stabilized calendered PVC include decals, waterbeds, swimming pool liners, adhesive and magnetic tape, laminating materials, ceiling tile, shower curtains, tarps, Band-Aids, and roofing membranes. Barium/cadmium-stabilized products are also formulated into dispersion coated resins used for vinyl flooring, raincoats, coated cloth, and automotive undercoating. There has also been a tendency to replace barium/cadmium stabilizers where feasible with barium/zinc, calcium/zinc or organotin type stabilizers.

**14.5. Alloys.** Cadmium-containing alloys are generally considered in two groups: those where small amounts of cadmium are utilized to improve some feature of the base alloy and those where cadmium is part of a complex low melting point alloy where the presence of cadmium helps to lower the melting point (60). Examples in the former category include

- Copper alloys where additions of 0.8–1.2% Cd double the mechanical strength and wear resistance of copper but result in only a 10% loss in conductivity. Major uses include telephone wires, contact wire, catenary strand for railway overhead electrification, and automotive radiators and fittings.
- Zinc alloys containing small amounts of cadmium exhibit improved mechanical properties such as strength, drawability, and extrudability, and may be used in applications such as the battery can material in carbon–zinc and alkaline–manganese primary batteries. Zinc alloys containing 0.025–0.15% Cd are used as sacrificial anodes for the corrosion protection of structural steel immersed in seawater.
- Lead alloys with $\leq$0.075% Cd are sometimes used as sheaths for cables subject to cyclic stress.
- Tin-bearing alloys with $\leq$1% Cd have improved tensile and fatigue strength for use in marine engines and gearboxes.
- Precious-metal alloys incorporate cadmium to improve strength and hardness. Levels of $\leq$5% Cd in gold–silver–copper alloys make Greek gold, a greenish-tinged gold.
- Silver electrical contact alloys utilize 10–15% cadmium or cadmium oxide for heavy-duty electrical applications such as relays, switches, and thermostats. Cadmium suppresses electrical arcing and improves resistance to electric erosion and material transfer.

Examples and applications of the low melting joining and fusible alloys include

- Lead–tin–bismuth–cadmium alloy (“Woods Metal”) is used in the bonding of metallized ceramic and glass components to metal frames and chassis where higher soldering temperatures are not possible. Other cadmium-containing solders are used in light electrical and electronic assemblies and when it is necessary to make a lower temperature second joint adjacent to a conventional tin–lead solder joint.
- Intermediate temperature soldering alloys include alloys of silver, zinc and/or tin alloyed with cadmium. These alloys have higher tensile strengths than do most common solders in this temperature range, and are used in applications where temperature sensitivity prohibits the use of silver solders with higher tensile strength. Zinc–cadmium alloys are used to solder aluminum, while cadmium–zinc–tin alloys are employed for soldering magnesium.
- Silver brazing alloys are quaternary alloys of silver, copper, zinc, and cadmium, which are distinguished by their ability to produce high strength joints at working temperatures more than 100°C below the melting points of the ternary silver–copper–zinc brazing alloys.
- Fusible alloys include a wide variety of very low melting and rapidly solidifying materials that can be utilized as heat-sensitive fusible links in fire safety devices or as control devices in kilns and ovens. Woods metal is utilized in water sprinkler valves to automatically activate water flow when

the temperature exceeds 70°C. These alloys are also employed to mount firmly complex or delicate parts during machining or grinding operations.

**14.6. Minor Applications.** Cadmium forms a number of compounds that exhibit semiconducting or electronic behavior that makes them useful for a wide variety of applications. The amounts utilized are usually quite small, but these minor uses often have major technological and social importance. For example, cadmium–telluride (CdTe) and cadmium–sulfide [1306-23-6] (CdS) are both used in photovoltaic or solar cells that convert sunlight directly into energy. Cadmium sulfide photoconductive cells are used in photographic exposure meters. Cadmium sulfide is also used as a highly sensitive photoreceptor in electrophotographic systems in photocopiers. Other cadmium compounds, including those containing sulfide, tungstate, borate, and silicate, are essential in the preparation of light-emitting phosphors that are activated by electron beams. These phosphors are utilized in color displays, X-ray instruments, luminescent dials, fluorescent lamps, and cathode-ray tubes.

Cadmium mercury telluride is utilized in infrared imaging systems, and cadmium selenides are used in thin-film transistors for switching applications.

Cadmium salts of organic acids are also used as polymerization catalysts in the production of a wide variety of organic compounds, as ethylating agents and as antiwear additives. Diethyl cadmium is a polymerization catalyst for production of vinyl chloride, vinyl acetate, and methylmethacrylate. Admixed with titanium tetrachloride, it catalyzes the polymerization of the respective monomers to form polyethylene and a highly crystalline polypropylene suitable for filaments, textiles, glues, and coatings.

Silver–indium–cadmium alloys are utilized as control rods in some pressurized-water nuclear reactors, and cadmium sheet is used for nuclear shielding applications because of its high neutron absorption characteristics (61).

**14.7. Future Applications.** Applications that show promise for the future include NiCd battery–powered electric vehicles, hybrid electric vehicles and electric buses. NiCd batteries offer an excellent compromise between low price–low performance lead acid batteries and high price–high performance NiMH or lithium-ion technologies. Renault and PSA Peugeot in France have already selected NiCd batteries for their initial electric vehicle production. Another area of promise for future cadmium applications is CdTe solar cells and NiCd batteries for energy storage of the output from those solar cells. This area has become one of increasing interest, especially in Third World nations in tropical zones, where solar power is a viable option and extensive power infrastructures are not available.

Whatever new applications are developed for cadmium for the future, they will have to be recyclable. Today, batteries, coatings and alloys are all recyclable, and major industry efforts have been and are being undertaken to ensure that these products are recycled. Likewise, the CdTe solar cell industry and the electric vehicle NiCd battery industry are making sure that recycling is part of the lifecycle of their respective products. In addition, the plastics industry has undertaken research to determine the feasibility of recycling cadmium pigments and stabilizers from plastics.

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