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RECYCLING TECHNOLOGIES TO ABATE CADMIUM PRODUCT EMISSIONS

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Abstract

Cadmium metal, cadmium compounds and cadmium products account for approximately 2 5 % of total human exposure to cadmium, the majority of which arises from cadmium impurities in fertilizers, fossil fuels, iron and steelmaking, natural sources and cement production Nonetheless, it is important to minimize any exposure to cadmium from products to which cadmium is intentionally added as a functional component Emissions of cadmium from the manufacture and use of cadmium products are already well regulated and controlled, and have decreased significantly in the past twenty years. The present concern is the disposal of waste cadmium products after their useful life, and the industry has adopted collection and recycling strategies as the most logical and effective techniques to minimize that potential risk

Cadmium or cadmium compounds are intentionally added to six classes of products - nickel-cadmium (NiCd) batteries; red, orange and yellow pigments for plastics, glasses, ceramics and enamels; weathering stabilizers for polyvinylchloride (PVC); corrosion resistant coatings for ferrous and nonferrous metals; brazing, soldering, electrical contact and other specialty alloys; and semiconducting compounds such as cadmium sulfide and cadmium telluride for electronic applications. At present, NiCd batteries account for 72 % of total usage, pigments 13 %, coatings 8 %, stabilizers 6 %, alloys 1 %, and electronic compounds less than 0 1 %. These use patterns are expected to change in the future with batteries and electronic compounds growing, pigments and coatings stable, and stabilizers and alloys decreasing in market share. The cadmium content of these products range from a high of 20 % to a low of less than 0.1 %

Nickel-cadmium batteries, cadmium-pigmented plastics, cadmium-coated steels, cadmium alloys and cadmium telluride solar cells are cadmium products which can be recycled. Widespread efforts and programs have already been undertaken to collect and recycle NiCd batteries, cadmium's largest application, and recycling programs exist for the other products as well, although not on as large or as economic a scale. The programs and technologies for collection and recycling of cadmium products are described in detail with specific flowcharts shown for major cadmium recycling facilities around the world

SOURCES AND LEVELS OF ENVIRONMENTAL AND HUMAN CADMIUM EXPOSURE

Although the term "heavy metal" has no real scientific basis in fact, cadmium is one of the metallic elements which is often considered to be of human health and environmental concern. Cadmium and cadmium compounds are naturally occurring substances in the earth's crust and in its waters, but the concentration of cadmium in the environment may be increased by man-made or anthropogenic activities. The natural sources of cadmium include average levels of 0.1 to 1.0 parts per million (ppm) in the earth's crust, and average concentrations in the earth's oceans of 0.2 micrograms per liter (μg/l). Higher concentrations may arise naturally from forest fires, volcanoes, erosion of soils and weathering of rocks.

SOURCES OF CADMIUM EXPOSURE

Anthropogenic sources of cadmium are generally divided into two main classes, products to which cadmium is intentionally added to accomplish some engineering or performance function and products in which cadmium is present as an unintentional impurity and in which cadmium accomplishes no functional role. The products with cadmium impurities include:

- Nonferrous Metals (Zinc, Lead and Copper)
- Ferrous Metals (Iron, Steel, Coke and Limestone)
- Fossil Fuels (Coal, Oil, Gas, Peat and Wood)
- Fertilizers (Phosphates, Sewage Sludge and Composts)
- Cement and Cement Making Materials

The impurity levels in these materials may vary widely, from 15,000 ppm in zinc ores to 0.5 ppm in some steel making and cement making materials. Two factors are important to remember. The high levels of cadmium impurities in nonferrous metals are removed during smelting and refining operations and are not appreciable in the final products. While impurity levels are low in fossil fuels, irons and steels, and cement, the volumes of these products utilized are huge, so that total environmental loading and human exposure from these sources may be appreciable.

The products to which cadmium is intentionally added are summarized in Table I. These include nickel-cadmium (NiCd) batteries; cadmium-sulfide based pigments utilized to color plastics, glasses, ceramics and enamels; cadmium and cadmium alloy coatings for corrosion protection and other specialized properties of ferrous and nonferrous metals; organic cadmium compounds such as laurates and stearates employed to prevent ultraviolet light degradation of polyvinylchloride (PVC); and a wide variety of cadmium-containing alloys and electronic compounds for many different applications.

The percent of market data are taken from 1997 and in the past three years the battery share of the market has continued to grow, pigments and coatings have remained the same, but stabilizers and alloys have decreased in usage. Thus, most of the cadmium intentionally utilized in

Table I – Products with Intentional Cadmium Contents

Product	Percent Cadmium	Percent of Market
Nickel-Cadmium Batteries	15	70
Cadmium Sulfide Pigments	1	13
Cadmium Coatings	0 2	8
Cadmium Stabilizers for PVC	1	7
Alloys and CdTe Solar Cells	0.1 - 20	2

products is concentrated in the NiCd battery application, and it is this sector which has today become the focus of intense recycling efforts to prevent the entry of disposed cadmium products into the environment.

The relative importance of the various sources of human and environmental cadmium exposure have been analyzed in a number of studies (Van Assche and Ciarletta 1992, Van Assche 1998, ERL 1990, SEI 1994). While the relative sources of environmental loading vary from country to country and from region to region, the relative sources of human exposure appear to depend more on individual differences such as smoking habits and/or occupational exposure. For the non-smoking, non-occupationally exposed general population, the chief sources of human cadmium exposure are fertilizers, fossil fuel combustion, iron and steel, and natural sources, which together account for about 88 % of general population human cadmium exposure. All product applications in which cadmium is present as an intentional addition account for only 2.5 % of total human cadmium exposure. Another 1 % may arise from the incineration of materials containing cadmium, which may or may not be products with intentional cadmium additions. The nonferrous metals industry and cement production industry also contribute small amounts to total human cadmium exposure. The relative contributions of these various sources are shown graphically in Figure 1.

Similarly, a U.S. Environmental Protection Agency report (U.S. EPA 1993) on cadmium air emissions indicated that the large majority of cadmium air emissions arise from the combustion of fossil fuels and that the contribution to air cadmium emissions to the environment from cadmium products is relatively small. These results are summarized in Table II.

Thus, both with regard to human and environmental sources of cadmium exposure, cadmium products are a relatively minor source. In the case of human exposure,

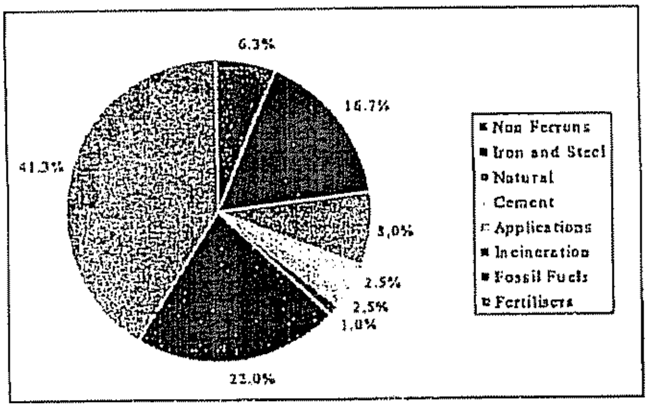

Figure 1 - Sources of Human Cadmium Exposure (Van Assche 1998)

Table II - Air Emissions of Cadmium in the United States (U.S. EPA 1993)

Industrial Activity	Metric Tonnes of Cadmium per Year
Combustion of Coal and Oil	243.8
Production of Zn, Pb and Cu	38.1
Waste Incineration	21.8
Cement Production1	3.0
Production of Cd & Cd Products	6.1

fertilizers would appear to be the major source. In the case of environmental exposure, at least for air emissions, fossil fuel combustion appears to be a major source.

LEVELS AND TRENDS OF CADMIUM EMISSIONS AND EXPOSURES

Levels of cadmium emissions and exposures have been studied extensively and have been summarized in a number of studies (OECD 1995, WHO 1992, Morrow 1998). One of the most important is the data which show that the daily human intake of cadmium for the general population today ranges from 10 to 20 micrograms (µg) per day for the average 60-kg woman and average 70-kg man. The daily tolerable cadmium intake levels established by the World Health Organization (WHO) range from 60 to 70 mg per day for the same average woman and man. These results are shown graphically in Figure 2. Thus, the general population today takes in far less than the tolerable levels established by WHO and the margin between the daily tolerable intake level and the actual intake levels appears to be widening, creating a larger margin of safety than in earlier years

Likewise, general levels of cadmium emissions to the environment have decreased substantially over the past twenty to thirty years as a result of strengthened regulations, improved pollution control technology, greater societal emphasis on environmental values, and the adoption of recycling as an appropriate risk

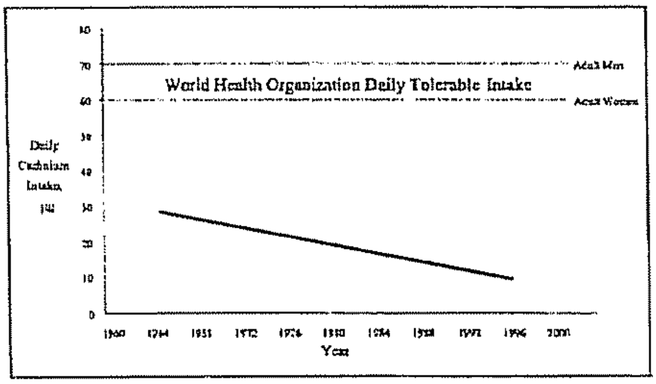

Figure 2 - Daily Cadmium Intake Levels for the General Population (WHO 1992, OECD 1995)

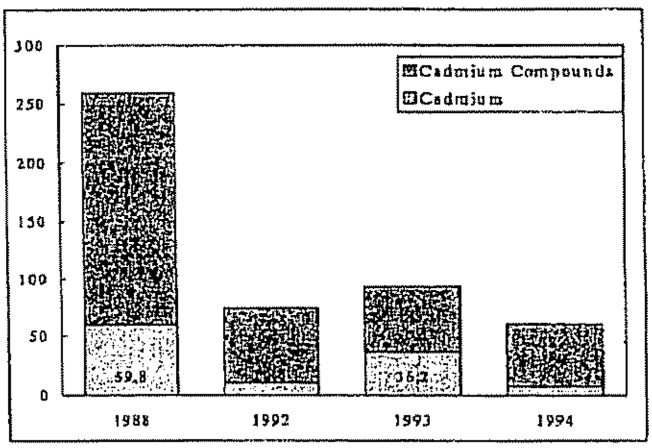

Figure 3 - United States Toxic Release Inventory (TRI) Cadmium Releases (tons), 1988 - 1994

management option to reduce any risks arising from cadmium products. The Toxic Release Inventory (TRI) data for cadmium and cadmium compounds for the United States for the period from 1988 through 1994, for example, show continuous decreases in total emissions (tons) to air, water and soil (Figure 3), while progress on reduction in emissions of respirable and soluble forms of cadmium under Canada's Accelerated Reduction and Elimination of Toxics (ARET) Program is shown in Figure 4. While the TRI data applies to air, water and soil emissions and differentiates cadmium metal from cadmium compounds, the ARET data is focused directly on those forms of cadmium which are of most concern to human health and the environment, namely the respirable and soluble forms (Mining Association of Canada 1999). Respirable forms of cadmium are most thoroughly absorbed by the human body, and soluble forms of cadmium interact most readily in the environment and are therefore more likely to enter the food chain. In addition, data on aqueous emissions of cadmium in the Rhine River Basin from 1970 through 1988 have similarly indicated decreases in cadmium emissions from the zinc and lead primary smelting and refining and nonferrous metals mining sectors, although little change in cadmium emissions from the secondary lead smelting industry (Elgersma et al. 1992). All in all, it is apparent that cadmium emission levels from anthropogenic sources in general have decreased substantially in the past 20 to 30 years, that sources other than products to which cadmium has been added intentionally are a much more important source of human and environmental exposure than cadmium products themselves, and that human cadmium intake for the general population is, in any event, well below levels of human health concern.

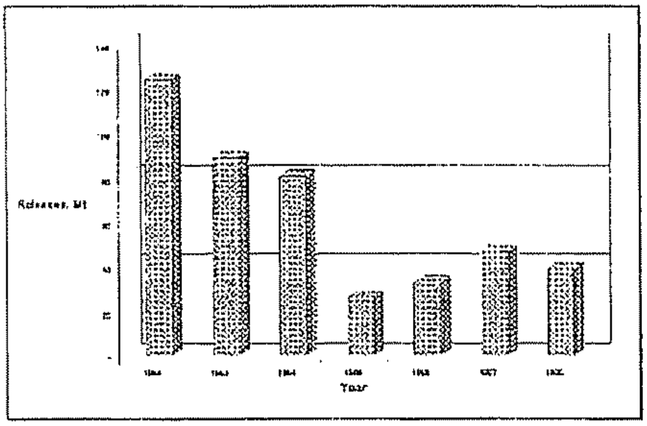

Figure 4 – Releases of Respirable and Soluble Inorganic Forms of Cadmium in Canada, 1988 – 1998

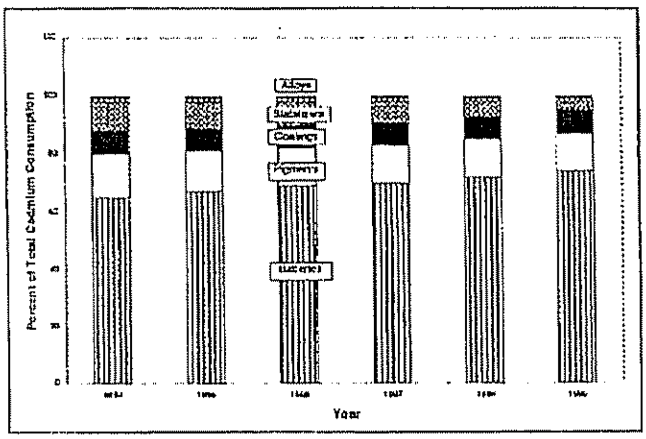

Figure 5 – Western World Cadmium Consumption Patterns, 1994 – 1999

EMISSIONS RESULTING FROM CADMIUM PRODUCTS MANUFACTURE

Products intentionally containing cadmium are generally divided into five major market areas – batteries, pigments, coatings, stabilizers and alloys and other minor uses. The relative trends in these uses are summarized in Figure 5. During the past twenty years, the nickel-cadmium (NiCd) battery market has grown substantially, while the traditional cadmium markets in pigments, coatings, stabilizers and alloys have declined. Today, the pigments and coatings markets have stabilized at 13% and 8% of the total market respectively, but stabilizers and alloys applications continue to decline because of the more widespread availability of substitutes.

With respect to the use of these cadmium products, earlier studies (Stockholm Environmental Institute 1994, Yost 1983) and estimates from the International Cadmium Association updating these studies have indicated generally accepted lifetimes, dissipation rates and recycling rates, all of which are summarized in Table III. As will be subsequently shown, however, the degree of recycling cadmium products has increased markedly in the past five years, especially in the nickel-cadmium battery market sector.

Cadmium-containing products are, in general, long-lived products with low dissipation rates. The environmental and human health concerns for cadmium products arise mainly from their ultimate disposal and not during their manufacture or use. Recycling rates, according to the Stockholm Environmental Institute (SEI) in 1994, were high only for industrial NiCd batteries. More recent estimates from the International Cadmium Association, shown in parentheses in Table III, have placed these at somewhat higher levels. In most Western World countries, such as Europe, the United States and Japan, consumer NiCd battery recycling, for example, has now increased to the 25 % to 35 % range. On the other hand, estimates of cadmium coatings recycling have probably dropped because of the more recent practice of

Table III – Factors in the Use of Cadmium Products

Product	Life (yrs)	Dissipation (pct per yr)	Recycling Rate (percent)
Nickel-Cadmium Batteries			
• Industrial	25	0.01 (0.00)	50 (85)
• Consumer	5	0.01 (0.00)	4 (15)
Cadmium Sulfide Pigments	10	0.01	0 (0)
Cadmium Stabilizers	25	0.01	0 (0)
Cadmium Coatings	10 (20)	2.00 (1.00)	30 (50)
Cadmium-Containing Alloys	15	1.00	35 (35)

land filling electric arc furnace (EAF) dust rather than recycling it to recover zinc, lead and cadmium. More recently, cadmium sulfide based pigments have also been recycled in certain plastics and certain applications, and it appears as if this trend will continue in the future.

There are also numerous studies (SEI 1994, OECD 1995) to indicate how cadmium partitions during the manufacture of cadmium-containing products. These results are summarized in Table IV with both the SEI data shown and the lower emission levels derived from OECD studies coupled with ICdA estimates of cadmium consumption in product manufacturing areas in Europe. It is readily apparent that the vast majority of the cadmium utilized in the manufacture of cadmium-containing products partitions to the final product and is not released to the environment. The main differences between the two sets of data are that the SEI Report is based largely on data from Yost and other investigators from the late 1970s and early 1980s while the OECD numbers rely mostly upon the 1990 study performed by Environmental Resources Limited (ERL) for the European Commission. One of the main problems in reaching any conclusions regarding cadmium emissions is that they have constantly been decreasing over the past twenty to thirty years. Thus, it is most important to establish the present levels rather than to draw conclusions based on data which are ten to twenty years out-of-date. For example, the data in Table IV from SEI indicate that 97.00 to 97.50 percent of the cadmium in the production of NiCd batteries goes into the product. The corresponding numbers from the 1994 OECD report, based on the 1990 ERL data and 1995 ICdA estimates, indicate that 99.46 percent of the cadmium goes into the final product. Data from major NiCd battery manufacturers in 1998 and 1999 have placed cadmium emission levels during manufacture in the 0.001 to 0.01 percent range, meaning that 99.99 to 99.999 percent of the cadmium processed goes into the final product. These changing levels are the result of increasingly stringent regulations and constantly improving pollution control technology.

The decreasing levels of cadmium emissions during product manufacturing has been borne out by several studies (Elgersma et al 1992, Mukunoki and Fujimoto 1996, Environment Canada 1996) which illustrate continuously decreasing cadmium emissions from different product manufacturing areas to different environmental compartments. Some of these trends are shown in Figures 6 through 9 for the Rhine River Basin in Europe, Japan, and Canada.

Table IV - Partitioning of Cadmium During Product Manufacture

Product	Percent of Total Cadmium			
	Air	Water	Soil	Product
NiCd Batteries				
• Industrial	0.01–0.10*	0.03–0.15*	0.50–2.75*	97.00*–99.46
• Consumer	0.00*–0.01	0.03–0.05*	0.50–2.45*	97.50–99.46
Pigments	0.05*	0.20*	2.25*	97.50*
Stabilizers	0.01*	0.20*	2.04*	97.75*
Coatings	0.00*	0.02–1.25*	0.08–3.75*	95.00*–99.90
Alloys	0.50*	0.00*	0.00*	99.50*

* Stockholm Environmental Institute 1994
Other Data: OECD 1995 and ICdA Estimates

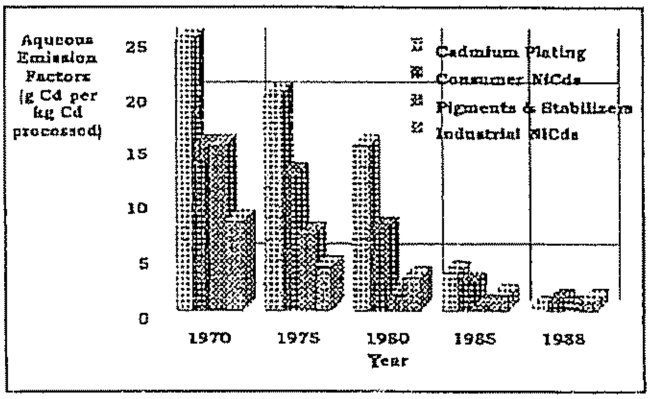

Figure 6 – Aqueous Emission Factors for Rhine River Basin, 1970 – 1988 (Elgersma et al. 1992)

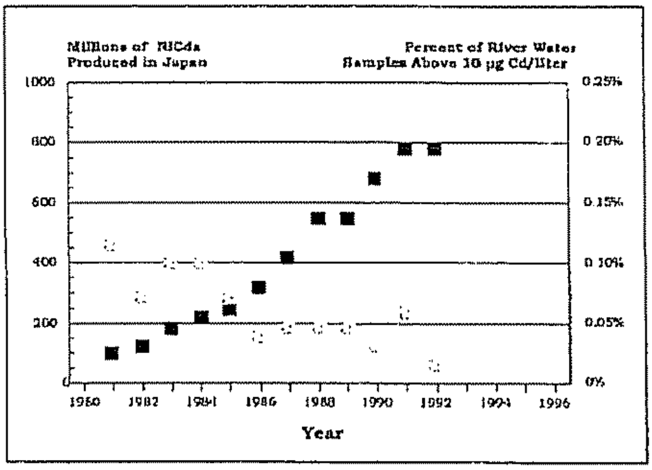

Figure 7 – NiCd Battery Production and Japanese River Water Cadmium Concentration, 1980 – 1992 (Mukunoki and Fujimoto 1996)

In the study performed by the International Institute of Applied Statistical Analysis (Elgersma et al. 1992), significant decreases in aqueous emissions were noted for the four major cadmium product manufacturing areas – plating, consumer NiCd battery production, pigments and stabilizers, and industrial NiCd battery manufacturing (see Figure 6). The decreases in aqueous emission factors in the plating, pigments and stabilizer areas cannot be attributed to the imposition of product restrictions in Switzerland, Denmark, Sweden and The Netherlands during these years as the data are expressed not as total emissions but in terms of grams cadmium emissions per kilogram of cadmium processed. The simultaneous reductions in aqueous emission factors from both industrial and consumer NiCd battery manufacture are even more remarkable in that they were accomplished during the 1980s which were the years of explosive market growth in the consumer NiCd battery market.

However, this same trend was also observed in Japan, the world's largest producer and consumer of cadmium through NiCd battery manufacturing. Data gathered by the Battery Association of Japan (BAJ), formerly the Japan Storage Battery Association (JSBA), are shown in Figures 7 and 8 for river water cadmium concentration and ambient air cadmium concentration from 1980 through 1992, again the years of greatest growth in the NiCd battery market.

The Japanese river water data indicate that, in spite on an eight-fold increase in NiCd battery production during

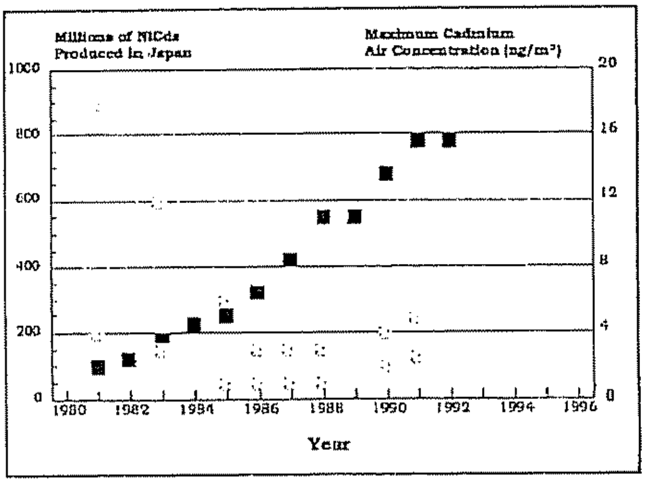

Figure 8 - NiCd Battery Production and Japanese Ambient Air Cadmium Concentration, 1980 - 1992 (Mukunoki and Fujimoto 1996)

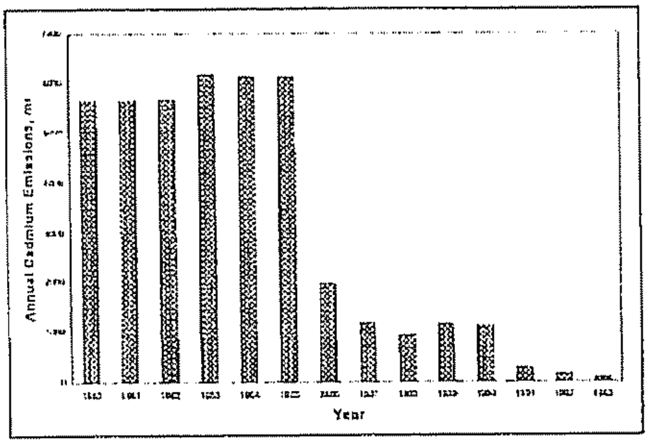

Figure 9 - Annual Cadmium Emissions to the Greater Montreal Sewer System, 1980 - 1993 (Environment Canada 1996)

the years from 1980 through 1992, the percentage of river water cadmium concentration samples exceeding the 10 µg per liter Japanese standard decreased from approximately 0.12 % to 0.02 %.

Similarly, the data for ambient air cadmium concentrations over the same time period and likewise compared against the backdrop of NiCd battery production, indicate even more marked decreases in cadmium levels to which the general population might be exposed. These data, which include measurements in both rural and industrial areas, are shown in Figure 8 (Mukunoki and Fujimoto 1996). As expected, the cadmium air levels in industrial areas are higher than those in rural areas, most likely due to the burning of fossil fuels, which, as previously shown, is the chief contributor to cadmium air emissions. It is also worth noting that the air cadmium levels in Japan today are very low, in the range from one to five nanograms per cubic meter, which is virtually a background air cadmium concentration level.

Finally, total annual cadmium emissions to the Montreal, Quebec sewer system in Canada have been determined and are shown graphically in Figure 9 (Environment Canada 1996). These emissions probably reflect changes in emission levels mostly from the cadmium electroplating industry over the years from 1980 through 1993.

It should be fairly clear from the above data that the levels of cadmium emissions associated with the manufacturing and use of cadmium containing products have now reached very low levels, and any analysis of the risks associated with these products should consider the present and not the past levels of these emissions. Any risks to the environment from cadmium-containing products are now most likely to arise from their ultimate disposal after use since occupational exposure is rigidly controlled in most countries today.

DISPOSAL OF CADMIUM CONTAINING PRODUCTS

There are really only four ways to dispose of spent products - incineration, composting, land filling or recycling. Composting is rarely carried out on cadmium-containing products because they are not readily biodegradable. Incineration is, in general, not a preferred method of cadmium product disposal because most cadmium products possess a low calorific value and do not result in significant reductions in volume when incinerated. Moreover, when some cadmium products are incinerated, the cadmium generally partitions preferentially to the fly ash resulting in a hazardous waste disposal problem even though better than 99% of the cadmium in fly ash is captured by modern incinerator emission control devices (Chandler 1995) and only a very small amount may be emitted to the air. Land filling is the most widely used disposal option for cadmium products today, although many nations are running out of available land fill space and must increasingly look to other disposal methods. There is concern that land filling of cadmium products may pose environmental and human health risks, although a number of studies have shown that cadmium in land fills is largely immobilized, does not diffuse for great distances through soils, and does not leach out of land fills to any appreciable extent (Thornton 1994, Eggenberger and Waber 1998, Oda 1990). Even if cadmium ions are released from land filled products, there is data to indicate that they tend to complex in sediments to a marked degree and be unavailable for plant and animal uptake. In addition, plant and animal uptake of cadmium has been found to depend very much on the presence or absence of other elements such as iron and on dissolved organic matter (Cook and Morrow 1995). In more recent years, recycling has been increasingly utilized

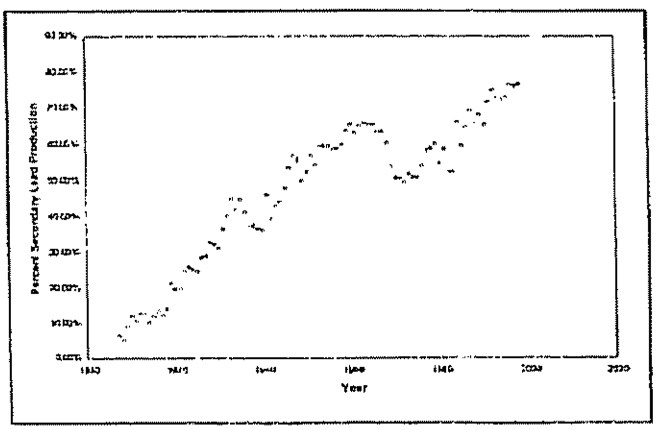

Figure 10 - Percentage Secondary Lead Production in the United States, 1900 - 1998

Table V - Cadmium Emissions from Production and Recycling of NiCd EV Batteries

	Production Emissions (grams Cd per KW-hr)	Recycling Emissions (grams Cd per KW-hr)
Air	0.28 to 3.6	0.0062
Water	0.40 to 2.4	0.0014
Land	Negligible	Negligible

as a cadmium product disposal option. A recent study (OECD 1998) indicated that an average of 63 % of all municipal solid waste (MSW) was land filled, an average of 17 % was incinerated, and the balance of 20 % was either composted or recycled.

These caveats notwithstanding, there is little argument that the preferred option for the disposal of spent cadmium products is obviously recycling. Not only does this option greatly reduce any human health or environmental risk associated with cadmium products, but it conserves valuable natural resources as well. Lead and lead acid battery recycling have already achieved impressive recycling rates, better than 95 % for lead acid batteries in the United States, and are growing all over the world (see Figure 10).

Today, recycling of cadmium products, particularly NiCd batteries, is viewed as the best human health and environmental option for the disposal of cadmium products and it is the fastest growing option. Collection and recycling programs for NiCd batteries have already been established in dozens of countries, and harmonization programs have been developed within OECD to promote NiCd collection and recycling on a worldwide basis. Recycling of cadmium products prevents the major portion of the product from ever being emitted to the environment or even having the potential of being emitted to the environment.

Another factor is certainly that the emissions associated with the production of cadmium by a recycling process have generally been found to be substantially less than the emissions associated with the production of cadmium from conventional mining and smelting sources. There have been studies, for example, which demonstrate that production of cadmium metal by recycling requires far less energy, and thereby less fossil fuel emissions and greenhouse gases, than production of cadmium from virgin ore (Gaines 1994). Another report on NiCd batteries for electric vehicles (Geomet Technologies 1993) shows that cadmium, nickel and cobalt emissions from recycling of batteries are roughly 10 to 100 times lower than the corresponding emissions associated with the production of NiCd batteries which are already quite low, as previously shown. These results, normalized to grams of cadmium emissions per kilowatt-hour of battery energy and indicating ranges for different types of NiCd EV batteries, are summarized in Table V. Thus, it is fairly clear that recycling is environmentally beneficial in both the production and disposal of cadmium-containing products.

RECYCLING OF CADMIUM CONTAINING PRODUCTS

There are four classes of cadmium-containing products which can be and have been recycled on relatively sizable scales. These include nickel-cadmium batteries, both the large industrial and small consumer types, cadmium coatings, cadmium-containing alloys, and cadmium telluride (CdTe) solar cells. In addition, the process wastes from the production of virtually all cadmium products may also generally be recycled, and often are because of the high costs of hazardous waste disposal. For example, sludges, filter cakes, spent anodes and outputs from pollution control devices often may be recycled to recover valuable metals. These so-called manufacturing wastes are recovered from NiCd battery, pigment, coatings, stabilizer, alloy and solar cell production operations and may be recovered either on the manufacturing site or at a separate facility. As previously shown in Table I and Figure 5, nickel-cadmium batteries command the largest share of the cadmium market and they also are, on the average, the cadmium-containing product with the highest cadmium content. Therefore, NiCd batteries are logically the most attractive of the cadmium products for recycling, and they are, in fact, the product which is recycled most today. However, cadmium coatings, cadmium pigments, cadmium alloys and cadmium telluride solar cells are also all recyclable and have been recycled to varying degrees.

The processes available today for the recycling of cadmium-containing products may be conveniently divided into two types – pyrometallurgical processes which are based on high temperature treatments and hydrometallurgical processes which are based on chemical or electrochemical reactions occurring in solutions. In the pyrometallurgical processes, cadmium containing products are often mechanically broken apart and the cadmium exposed either to vacuum or reducing atmospheres at high temperature where cadmium is present as a vapor. At these temperatures, cadmium oxides or hydroxides are reduced back to elemental cadmium which then condenses in cooler parts of the treatment furnaces and then collected. In the hydrometallurgical processes, the cadmium-containing products may also be mechanically attrited and then dissolved in either strong acids or strong bases. A series of ion exchange or precipitation steps are subsequently employed to remove various impurities and create relatively pure solutions of cadmium salts which may be sold as is or used as the solution from which cadmium metal is obtained by electrolytic processes.

Since most of the cadmium product recycling carried out in the world today concentrates on NiCd batteries, this paper will focus mainly on NiCd battery recycling plants and processes. It is generally considered that there are four types of cadmium recycling plants in use today:

- Dedicated Nickel-Cadmium Battery Recyclers
- Stainless Steel Recycling Plants
- Zinc/Cadmium Refineries
- Hydrometallurgical Nonferrous Metals Recycling Plants

A listing of the world's major cadmium recycling plants is presented in Table VI. The dedicated NiCd battery recycling plants treat only NiCd batteries, although some are now recycling NiMH batteries as well. SNAM in France, SAFT in Sweden, ACCUREC in Germany and Hanil Metal Recycle Company in Korea are examples of dedicated NiCd battery recyclers. The SNAM process in France will subsequently be described in more detail as an example of a dedicated NiCd battery recycling process. INMETCO in the United States is a stainless steel recycler whose chief business is recycling stainless steel scrap. As

Table VI – World's Major Cadmium Recycling Plants

Company	Location	Type	Capacity(mt)
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	5,400
ACCUREC	Germany	NiCd Recycler	1,000
TNO/Esdex/Leto*	Netherlands	Hydrometallurgical	200
Uniniquel, S.A	Spain	Hydrometallurgical	Unknown

a service to their NiCd battery customers, INMETCO, which is a subsidiary of INCO, accepts NiCd and NiMH batteries, and recovers both the cadmium and the nickel and iron which are fed into their stainless steel recovery circuits. The INMETCO processes will subsequently be described in more detail as an example of this category. Mitsui Mining & Smelting and Toho Zinc are major zinc/cadmium refineries which also have integrated NiCd battery recycling into their cadmium production circuits. The Toho Zinc process will subsequently be described in more detail. Finally, Hydrometal, TNO and Uniniquel are all example of hydrometallurgical processes which are capable of recycling cadmium containing processes. However, these processes have generally not been applied on major commercial scales to cadmium products, and only limited information is specifically available on the cadmium recovery schemes in hydrometallurgical processes. The TNO/Esdex/Leto process will subsequently be described in more detail. Processes for the recovery of cadmium from silver-cadmium oxide electrical contact alloys and from cadmium telluride solar cells will also be reviewed.

The capacities reported in Table VI above are capacities for treating metric tonnes (mt) of nickel-cadmium batteries and manufacturing wastes, and do not refer to cadmium production capacities. Depending upon the mix of feedstocks into the recycling process, the cadmium production levels may vary considerably. In addition, not all of the presently available recycling capacity for cadmium products is being utilized presently, which is a result of deficiencies in collection programs and not recycling plants. At present, it is estimated that at least 2,000 metric tonnes of recycled cadmium are produced annually. Primary cadmium production from zinc mining, smelting and refining has average about 18,000 metric tonnes in recent years meaning that at least 10 % of all cadmium production is derived from recycling. This amount is expected to grow in the years ahead with the growth of NiCd battery recycling programs around the world.

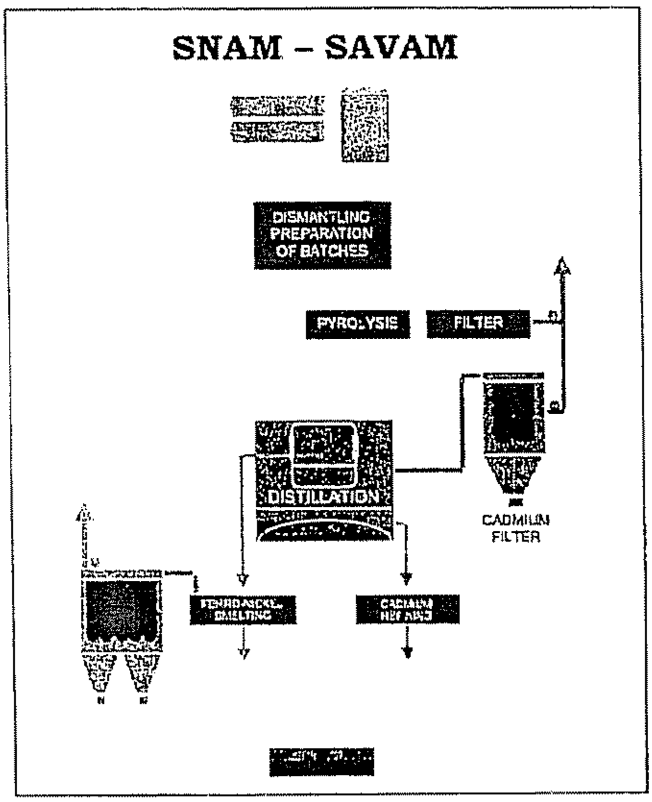

Figure 11 – Schematic Diagram of the SNAM Dedicated NiCd Battery Recycling Process

DEDICATED NICKEL-CADMIUM BATTERY RECYCLING PLANTS

As an example of a dedicated NiCd battery recycling plant, the process employed by SNAM at two plants in France (St. Quentin Fallavier and Viviez) is shown schematically in Figure 11. In the SNAM-SAVAM

Process, both small consumer and large industrial NiCd batteries are recycled. The small consumer cells are first

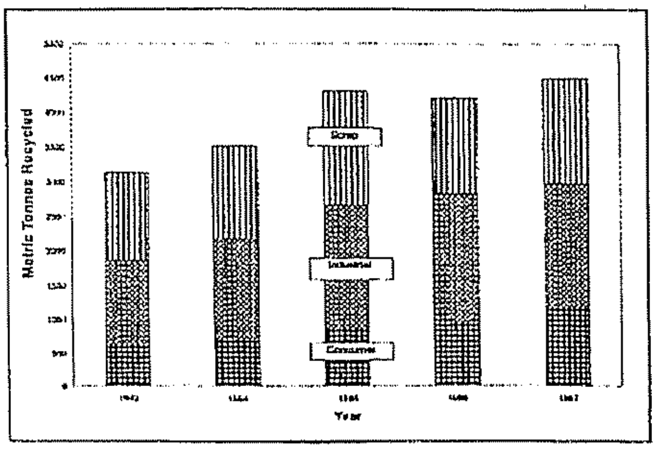

Figure 12 – NiCd Batteries and Manufacturing Scrap Recycled at SNAM – France

crushed in a hammer mill, while the large industrial cells are dismantled by removing the tops and draining the potassium hydroxide electrolyte. A low temperature pyrolysis process is also carried out on the small consumer cells to remove moisture and organic materials. The nickel plates are separated from the cadmium plates in large industrial batteries, and the scrap nickel sold directly to the stainless steel scrap industry. Small consumer NiCd batteries are generally of the spiral wound construction so that nickel and cadmium plates cannot be separated directly from one another as they can for the large industrial batteries. Thus, the pyrolysized small consumer cells and the cadmium plates from the large industrial materials plus any cadmium containing NiCd battery manufacturing wastes are the materials which are next fed into the high temperature distillation furnace. Because of the marked separation in melting and vaporization temperatures between cadmium on the one hand and iron and nickel on the other, relatively pure cadmium is quickly and easily separated from other metals and subsequently recondenses in the cooling zones of the furnace. The cadmium produced by this process is generally in the 99.99 % purity range, is fully utilizable for the production of new NiCd batteries, and may be recycled in this manner an unlimited number of times.

The amounts of industrial and consumer NiCd batteries as well as the tonnage of NiCd battery manufacturing scrap recycled at SNAM in recent years in shown in Figure 12. As is the case with most NiCd recycling facilities around the world, the tonnages of NiCd batteries and manufacturing scrap have increased steadily during the 1990s. Eventually, the consumer battery recycling portion will be the largest component of recycled materials since the consumer battery sector accounts for about 80 % of the NiCd battery market today. Today in Europe, North America and Japan, industrial NiCd batteries are recycled at fairly high rates, approximately 80 % to 85 %, while consumer NiCd batteries generally are recycled in the 25 % to 35 % range. The recycling rate for industrial scrap is quite high since regulations do not allow even minute quantities to be emitted or discarded.

The SAFT recycling plant in Oskarshamn, Sweden is also a dedicated NiCd battery recycling plant which has been operating in conjunction with SAFT's industrial NiCd battery production facility at the same location since the 1970s. Industrial NiCds are returned by SAFT customers to their plant for credit towards the purchase of new batteries, and the cadmium recycled from old batteries can almost immediately be incorporated into new NiCd batteries. The Hanil Metal Recycle Company facility in

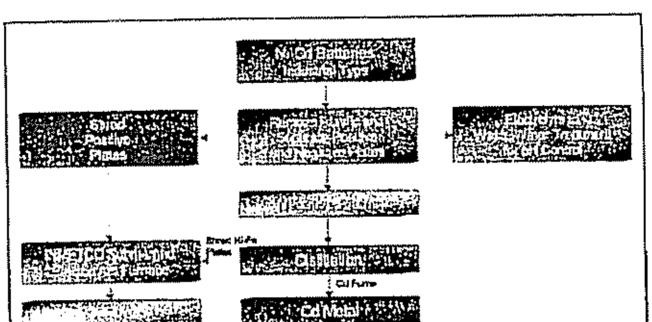

Figure 13 - Schematic Diagram of INMETCO Process for Recycling Industrial NiCd Batteries

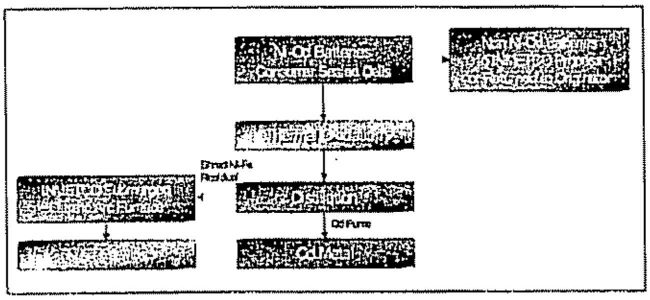

Figure 14 - Schematic Diagram of INMETCO Process for Recycling Consumer NiCd Batteries

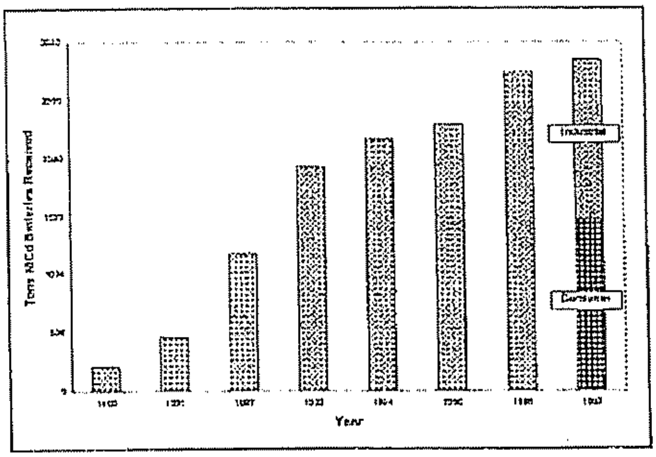

Figure 15 - Nickel-Cadmium Batteries Recycled at INMETCO, 1990 - 1997

Changwon City, Korea is one of several companies who recycle the NiCd batteries collected under the program organized by the Battery Association of Japan. ACCUREC GmbH in Mulheim, Germany utilizes a partial vacuum distillation process rather than a high temperature reduction process, and recycles NiCd batteries collected under various European collection programs.

STAINLESS STEEL RECYCLING PLANTS

The International Metals Reclamation Company, Inc (INMETCO), a subsidiary of INCO Limited located in Ellwood City, Pennsylvania, USA, operates a stainless steel recycling plant capable of processing approximately 60,000 tons of nickel-chromium-iron bearing materials annually. Their principal product is an Fe-Ni-Cr master alloy which is utilized by the stainless steel industry in the production of new stainless steel. Although the vast majority of their input materials is stainless steel scrap, such as turnings, swarf, pickle liquor, plating sludges and other materials high in nickel, they process NiCd, NiFe and NiMH batteries for their nickel and iron values. Several years ago they installed a cadmium distillation plant similar in design to the system employed by SAFT in Sweden. The cadmium separation is accomplished in a manner similar to that previously indicated for the dedicated NiCd battery recyclers, but the iron and nickel residues from the cadmium distillation step are subsequently fed into their high temperature metal recovery (HTMR) unit and blended with their other iron-nickel-chromium materials. Schematic diagrams of the

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INMETCO processes for recycling industrial and consumer NiCd batteries are shown in Figures 13 and 14.

INMETCO serves both as a collection point in the Rechargeable Battery Recycling Corporation's (RBRC) rechargeable battery collection program in the United States, and as the recycling plant for the RBRC collection programs in both the United States and Canada. The tonnage of NiCd batteries and manufacturing wastes which have been recycled at INMETCO has grown steadily during the 1990s as shown by the data in Figure 15. Until recently, only total tonnage was recorded, but beginning in 1997, separate figures were maintained for industrial and consumer NiCd batteries. One interesting advantage of the stainless steel NiCd battery processing operation is that integration with a stainless recycling facility allows for certain economies of scale not available to other processes and ensures that the nickel recovered from spent NiCd batteries is promptly moved into the recycling loop.

PRIMARY ZINC/CADMIUM REFINERIES

Both NiCd battery manufacturing wastes and spent nickel-cadmium batteries may also be recycled in primary zinc/cadmium refineries. Since Japan is the largest NiCd battery producing country in the world, considerable amounts of NiCd battery manufacturing wastes are generated. Japan is also the world's largest producer of cadmium, and the Japanese NiCd battery producers are the Japanese cadmium producers' largest customers. In addition, Japan has one of the highest use rates of rechargeable batteries per capita in the world, much higher than in Europe or North America. Thus, it is not unexpected that Japanese industry has developed a sophisticated collection and recycling system for its NiCd batteries and manufacturing wastes, and that it has already begun to integrate cadmium and cadmium oxide production with nickel-cadmium battery recycling. Two of the largest primary zinc/cadmium producers in Japan, Mitsui Mining & Smelting Co., Ltd. and Toho Zinc Co., Ltd. have modified their cadmium production circuits so that feedstock from NiCd battery manufacturing wastes and spent NiCd batteries, both consumer and industrial, may be incorporated into their processes.

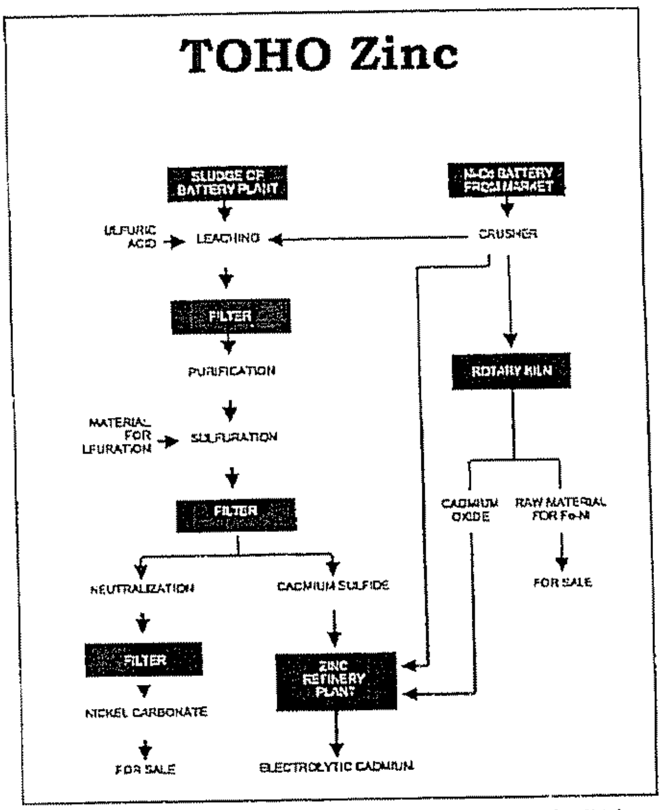

Figure 16 - Schematic Diagram of Toho Zinc Co., Ltd. NiCd Battery and Waste Recycling Processes

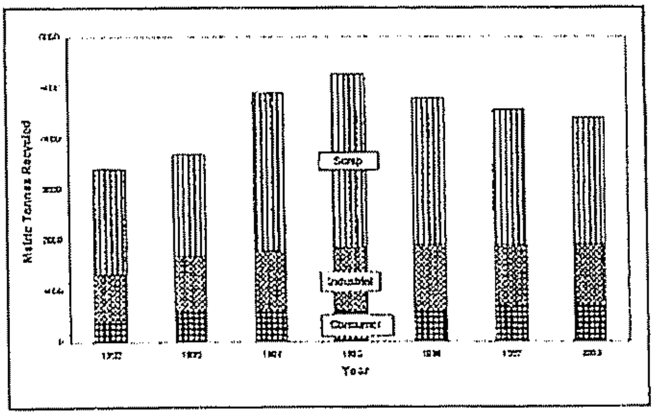

Figure 17 - NiCd Batteries and Manufacturing Wastes Recycled in Japan, 1992 - 1998

A schematic diagram of the process employed at Toho Zinc Co., Ltd is shown in Figure 16. Essentially, the manufacturing wastes are recycled by a hydrometallurgical process which involves dissolution in a sulfuric acid solution, filtration, purification and sulfuration to form a cadmium sulfide precipitate which is then fed into the zinc refinery. Spent batteries, on the other hand, are processed by a pyrometallurgical process whereby cadmium is separated from nickel and iron by volitalization and once again then fed into the zinc refineries. Thus, by placing some preliminary steps before the zinc refininery operations, the Toho Zinc process is able to accept a broader range of feddstocks, including NiCd batteries and manufacturing wastes.

The NiCd batteries recycled at both Toho Zinc and Mitsui Mining & Smelting are collected as part of the long standing collection program currently operated by the Battery Association of Japan (BAJ), formerly known as the Japan Storage Battery Association (JSBA). All of the major battery producers in Japan, both rechargeable and non-rechargeable, support this program. The other major recyclers who process NiCd batteries and NiCd battery manufacturing wastes include Kansai Catalysts and Hanil Metal Recycle Co., Ltd. in Korea which operates in conjunction with the Japan Recycle Center, Ltd in Japan. This collection and recycling effort has gathered and recycled large tonnages of batteries and manufacturing wastes for many years now, well back into the 1980s, and has realized the largest tonnages in the world of total NiCd-related materials recycled. The large amounts of NiCd battery manufacturing wastes recycled in the Japanese program is reflective of the large amount of NiCd batteries produced in Japan. This material is normally recycled fairly promptly, within the same year as it is utilized for the production of batteries. Spent batteries, of course, enter the recycling loop many years after their manufacture, depending upon application, service lives, collection systems, and many other factors. Estimates have been made that show that it is not unreasonable to assume that consumer NiCds will be recycled approximately 15 years after manufacture, and that industrial NiCds will be recycled approximately 25 years after manufacture. The amounts of NiCd batteries and manufacturing wastes recycled in the BAJ program for the period from 1992 through 1998 are summarized in Figure 17.

The amounts of manufacturing scraps have begun to decline after 1995, indicating the decline in the production of NiCd batteries in Japan and a shift to other manufacturing areas. The relative amounts of industrial NiCd batteries collected and recycled has been rather steady while the tonnages of consumer NiCd batteries collected and recycled has continued to increase. Because of the explosive growth in the consumer NiCd market in the mid to late 1980s, it is expected that it will be the consumer NiCd battery recycling sector which will grow the most in the years ahead. This trend was also noted in the collection programs in Europe and North America previously discussed.

HYDROMETALLURGICAL CADMIUM PRODUCT RECYCLING PLANTS

In principle, nickel-cadmium batteries and a number of other cadmium-containing products, as well as wastes and scraps from product manufacturing processes, may be recycled by hydrometallurgical techniques. In these processes, the wastes and/or scraps are generally

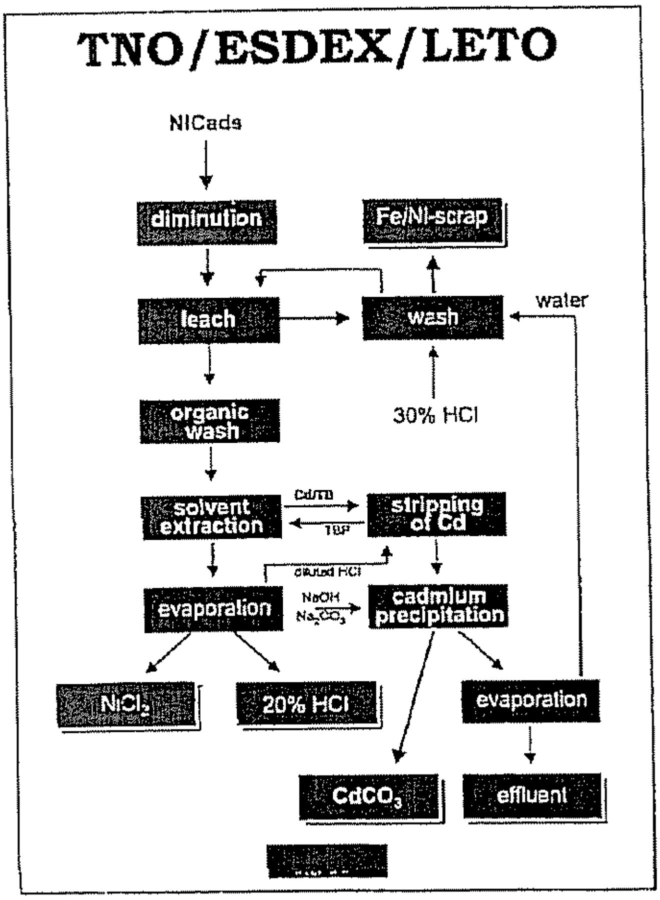

Figure 18 - Schematic Diagram of TNO/Esdex/Leto Hydrometallurgical Process for Recycling NiCds

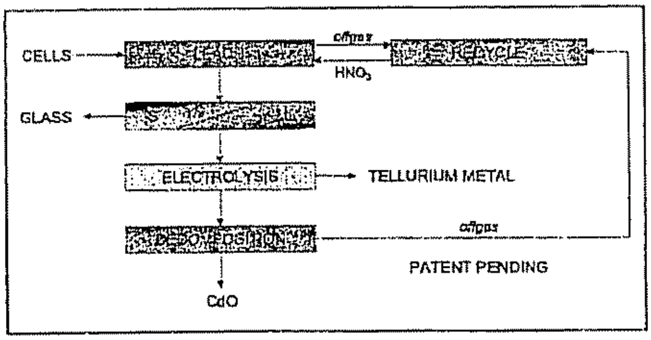

Figure 19 - Schematic Diagram of Drinkard Metallox of Recycling CdTe Solar Cells

dissolved in either strong acids or strong bases and then subjected to a series of chemical or electrochemical steps to successively remove various other constituents. Hydrometallurgical recycling operations are ordinarily well adapted to handle manufacturing wastes in liquid form such as spent plating solutions or sludges from water pollution control systems. The drawback to hydrometallurgical processes is that they are relative expensive compared to pyrometallurgical processes, and must be justified by the recovery of economically more valuable metals. With cadmium and nickel prices both at record low prices in recent years, NiCd battery recycling by hydrometallurgical means has not been as favorable as utilization of pyrometallurgical systems. Nonetheless, there are some systems and circumstances under which hydrometallurgical techniques may be the only available method, and hydrometallurgical recycling is often capable of recovering many different metals whereas a pyrometallurgical plant might only recover a few.

An example of a pilot type hydrometallurgical recycling plant designed for the recovery of nickel and cadmium from NiCd batteries is shown in Figure 18. This pilot was originally designed by TNO in The Netherlands, and later modified by Esdex and Leto, also in The Netherlands. It was never operated on a full commercial scale, its maximum throughput being about 200 metric tonnes per year. Nonetheless, it was always considered a technical success if not an economic or commercial one. Hydrometal in Belgium, on the other hand, processes a wide variety of nonferrous materials by a hydrometallurgical process, but relies on recycling of more commercially viable materials than on NiCd batteries. Uniniquel S.A. in Spain had also developed a hydrometallurgical process for recycling NiCd battery manufacturing wastes, but that process also never achieved full commercial operation.

Another interesting variation on the hydrometallurgical process is one specifically developed by Drinkard Metallox in the United States for the recovery of cadmium tellurium from Cadmium Telluride (CdTe) solar cells. CdTe solar cells contain very thin layers of both cadmium telluride and cadmium sulfide (CdS) on glass substrates. The first step in the Drinkard Metallox process is leaching of the CdS and CdTe from the glass by dissolution in strong nitric acid solutions. Tellurium is removed from the acid solution by electrolytic means, leaving an impure cadmium salt solution from which cadmium oxide is removed by decomposition. The cadmium oxide so produced is presumably pure enough so that it may be fed into a cadmium oxide production plant for use in the production of NiCd batteries. The exact details of this

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process are proprietary. Similar processes for recycling CdTe solar cells have also been developed by First Solar LLC in the United States and BP Solarex in the United Kingdom and United States. Ordinarily, these recycling processes would not be cost effective except that solar cells employ very high purity and therefore higher cost raw materials. Furthermore, cadmium, even high purity cadmium, may not be enormously expensive, but tellurium is. Thus, the economics of the CdTe solar cell recycling processes are driven by three factors - the cost of tellurium, the low cost of solar cell raw materials compared to the overall cost of the solar cell system, and the widespread adoption of recycling policies by the CdTe solar cell industry to ensure proper disposal of manufacturing wastes and spent products. A schematic and very simplified diagram of the Drinkard Metallox process is shown in Figure 19.

SILVER – CADMIUM OXIDE (AG – CDO) ELECTRICAL CONTACT ALLOYS RECYCLING PROCESS

One of the minor uses for cadmium is in electrical contact alloys where cadmium oxide (CdO) is employed to give strength, reduce arcing and prevent erosion in silver-based electrical contact alloys utilized in switches. Unlike many other materials which could be used in this application, cadmium will improve strength, arcing and erosion characteristics without diminishing the conductivity of the contact alloy. Because of the high silver content of these alloys, they are valuable and are recycled to recover as much silver as possible. In this case, the cadmium is recycled because silver is recycled, but simultaneous recovery of cadmium also simplifies subsequent production of new Ag-CdO electrical contact alloy. Essentially, this process appears to be a loop of alloying, internal oxidation, formation of mill products, and recycling of scrap by reduction at high temperatures to form AgCd alloy which is then fed back into the original alloying process.

The development of such a recycling process is important in that many cadmium-containing brazing and soldering alloys have been replaced with cadmium-free alternatives, but it has been very difficult to find adequate substitutes for the Ag-CdO electrical contact alloys. Cadmium-containing brazing and soldering alloys are one application in which inhalation exposures of cadmium fumes at high levels might be expected, and are therefore

Table VII – Estimated Recycling Rates for Cadmium-Containing Products

Product	Type	Area	Estimated Recycling Rate
NiCd Batteries	Industrial	Western World	85 %
	Consumer	Western World	15 %
	All Types	USA	23 %
	All Types	Japan	20 %
	All Types	Europe	25 %
Cadmium Coatings		Western World	30 %
Alloys		Western World	35 %

Sources: Borst 1995, Mukunoki and Fujimoto 1996, Morrow 1995

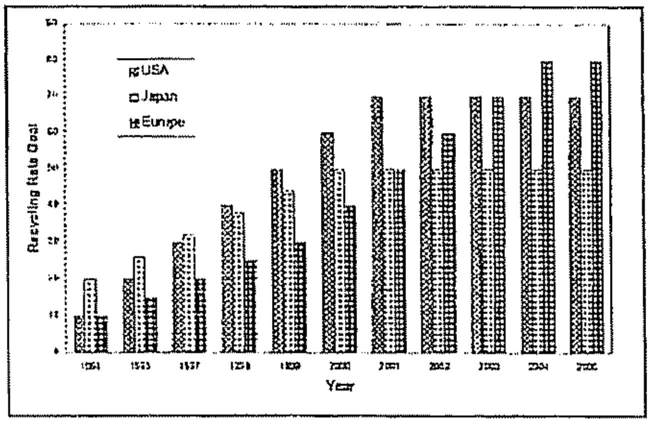

Figure 20 – NiCd Battery Recycling Goals for North American, Japanese and European Programs

an application where substitution should be encouraged as much as possible. If such substitution is not possible, then adequate respiratory protection must be provided for workers handling cadmium-containing brazing and soldering alloys. Silver-cadmium oxide electrical contact alloys, on the other hand, do not generate high exposures of cadmium fumes, and concerns with these alloys would be with their disposal and not their use. The Ag-CdO recycling process, fortunately, can obviate much of that concern.

RECYCLING RATES AND RECYCLING GOALS FOR CADMIUM PRODUCTS

Nickel-cadmium batteries contain the highest average cadmium content of any of the cadmium-containing products and represent the largest share of the cadmium consumption market. They are, therefore, the most logical target upon which to concentrate the most efforts to collect and recycle cadmium products. At present, estimates of NiCd battery recycling rates vary widely from country, particularly since there is no one widely accepted definition on how to properly calculate recycling rates. It is relatively easy to determine how much material is collected and recycled. It is extremely difficult to establish what the amount recycled should be compared against to yield a recycling rate. Most systems up to the present have compared the amount recycled against the amount sold into the market at some point in the past which is meant to represent the lag between the time batteries are manufactured and the time that they become available for collection and recycling. A more recent technique simply measures the amount of NiCd batteries recycled and compares that amount to the amount in municipal solid waste in any given year. Both methods essentially compare the amount of batteries recycled to the amount of batteries available for recycling during a given year.

Some of the estimates for the recycling rates associated with nickel-cadmium batteries and other cadmium products made about 4 to 5 years ago are summarized in Table VII. While everyone believes that these rates are increasing, there is little agreement on the present actual recycling rates.

There are ambitious programs for collection and recycling of NiCd batteries in North America, Europe and Japan, and more recntly the Organization for Economic

Cooperation and Development (OECD) has worked on coordinating programs in such a way as to improve and facilitate NiCd collection and recycling. For example, an OECD website is now available which lists the NiCd collection programs in OECD nations and how to access them through the internet, phone, fax or mail, and, most importantly, where to take spent NiCd batteries for collection. The address of the OECD NiCd collection website is: www.oecd.org/ehs/NiCd/index.htm

In addition to the Rechargeable Battery Recycling Corporation (RBRC) program in the United States and Canada and the Battery Association of Japan (BAJ) program in Japan, a new program, designated "Collect NICad", has just been formed in Europe and promises to achieve high recycling rates in the very near future. It is obvious that the NiCd battery manufacturers, users, raw materials suppliers and recyclers around the world have all made a big commitment to the recycling of NiCd batteries, and that considerable financing and sustained effort will be required to achieve the levels of recycling rates expected by the regulators and promised by the industry. Achievements of some of these recycling levels which are shown in Figure 20 will be a formidible job, but one which holds the promise of greatly reduced air emissions from cadmium products and eventually recycling levels comparable to those enjoyed by the lead acid battery industry

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