BNL 47787
Informal Report

RECYCLING OF CADMIUM AND SELENIUM FROM PHOTOVOLTAIC MODULES AND MANUFACTURING WASTES:

BNL--47787

DE93 002115

A WORKSHOP REPORT

P.D. Moskowitz and K. Zweibel, Editors

March 11-12, 1992

Golden, Colorado

Sponsored by:

U.S. Department of Energy, National Renewable Energy Laboratory, Electric Power Research Institute, The Cadmium Council Inc., and Brookhaven National Laboratory

Biomedical and Environmental Assessment Group
Analytical Sciences Division
Brookhaven National Laboratory
Upton, NY, 11973

This research was performed under the auspices of the United States Department of Energy under Contract No. DE-AC02-76CH00016

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes:
Printed Copy: A06; Microfiche Copy: A01

ABSTRACT

Since the development of the first silicon based photovoltaic cell in the 1950's, large advances have been made in photovoltaic material and processing options. At present there is growing interest in the commercial potential of cadmium telluride (CdTe) and copper indium diselenide (CIS) photovoltaic modules. As the commercial potential of these technologies becomes more apparent, interest in the environmental, health and safety issues associated with their production, use and disposal has also increased because of the continuing regulatory focus on cadmium and selenium. In the future, the recycling of spent or broken CdTe and CIS modules and manufacturing wastes may be needed for environmental, economic or political reasons. To assist industry to identify recycling options early in the commercialization process, a Workshop was convened. At this Workshop, representatives from the photovoltaic, electric utility, and nonferrous metals industries met to explore technical and institutional options for the recycling of spent CdTe and CIS modules and manufacturing wastes. This report summarizes the results of the Workshop. This report includes: 1) A discussion of the Resource Conservation and Recovery Act regulations and their potential implications to the photovoltaic industry; 2) an assessment of the needs of the photovoltaic industry from the perspective of module manufacturers and consumers; 3) an overview of recycling technologies now employed by other industries for similar types of materials; and, 4) a list of recommendations for the various stakeholder groups, that if adopted will help ensure the commercial viability of these technologies.

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1. INTRODUCTION

Since the development of the first silicon based photovoltaic cell in the 1950's, large advances have been made in photovoltaic material and processing options. Now, there is growing interest in the commercial potential of cadmium telluride (CdTe) and copper indium diselenide (CIS) photovoltaic modules. These modules have demonstrated good performance, can be produced by various methods, appear to be environmentally stable, and are well matched to the solar spectrum. Thus, there are large efforts underway in the U.S., and elsewhere to further develop the processes needed for module fabrication and to begin commercialization efforts. As the commercial potential of these technologies becomes more apparent, interest in the environmental, health and safety issues associated with their production, use and disposal has also increased for three reasons. First, many governmental organizations, industry groups and private citizens have been placing greater emphasis on the need to ensure that new energy producing technologies will not endanger environment, health or safety. Second, cadmium (Cd) and selenium (Se, are metals which continue to receive large regulatory [e.g., the Resource Conservation and Recovery Act (RCRA)] scrutiny because of their toxicological properties. Third, programs are already being established to reduce and/or recycle these materials in other industries.

In the future, the recycling of spent or broken CdTe and CIS modules and manufacturing wastes may be needed for environmental, economic or political reasons; however, neither the institutional mechanisms nor the technologies for recycling have been fully established. In response to this need, this report presents the results of a Workshop jointly sponsored by the U.S. Department of Energy (DOE) - National Renewable Energy Laboratory (NREL) and Brookhaven National Laboratory (BNL), the Electric Power Research Institute (EPRI), and The Cadmium Council Inc. to explore technical and institutional options for the recycling of Cd and Se from spent CdTe and CIS modules and related manufacturing wastes.

2. WORKSHOP STRATEGY

The objective of the Workshop was to bring together non-ferrous metal suppliers/recyclers, module manufacturers, and consumers (i.e., utility representatives) to identify and discuss potential technical and institutional options available to the photovoltaic industry for managing spent/broken modules and manufacturing wastes containing Cd and Se. The Workshop Participants and the Agenda are shown in Tables 1 and 2; complete mailing addresses are given in Appendix A. On the morning of the first day, prepared background discussions from each of the stakeholder groups were presented. This was then followed by the formation of two break-out groups; one for Cd and one for Se. Each group was tasked to prepare background position papers and need statements to be used to form recommendations to the stakeholder groups and governing agencies. In the following sections, the background information presented, and recommendations developed are summarized. Viewgraphs used in these presentations are shown in Appendices B-G.

Table 1. List of Participants.

Name	Affiliation
Joseph Armstrong	Martin Marietta
Rajeewa Arya	Solarex Thin Film Division
Mike Benson	Noranda Technology
Dieter Bonnet	Battelle Institut e.V.
Mark Caffarey	Metallurgie Hoboken Overpelt S.A.
Murray Cook	Cadmium Association
David Corbus	National Renewable Energy Laboratory
Vasilis Fthenakis	Brookhaven National Laboratory
Lloyd Herwig	U.S. DOE
Steve Johnson	Golden Technologies
Michael King	ASARCO
Bruce Lanning	Martin Marietta
Taie Li	ASARCO
Peter Meyers	Solar Cells, Inc.
J.M. Morabito	BTL
Hugh Morrow	Cadmium Council
Paul Moskowitz	Brookhaven National Laboratory
Terry Peterson	Solar Power Program, EPRI
Robert D. Putnam	Putnam Environmental Services
Billy Stanbery	Boeing Aerospace and Electronics
Becky Taniel	Siemens Solar
William Tolley	U.S. Department of the Interior
Harin S. Ullal	National Renewable Energy Laboratory
Ken Zweibel	National Renewable Energy Laboratory

Table 2. Workshop Agenda.

	March 11	
8.30 - 8:45	Welcome	Conference Coordinators
8:45 - 9:15	CdTe and CIS PV Thin Films	K. Zweibel/NREL
9:15 - 9:35	CdTe PV Mfg. Needs	P. Meyers/Solar Cells
9:35 - 9:55	CIS PV Mfg. Needs	B. Taniel/Siemens Solar
9:55 - 10:15	Consumer Perspective	T. Peterson/EPRI
10:15 - 10:30	Coffee	
10:30 - 11:00	Cd Industry	H. Morrow/Cd Council
11:00 - 11:30	Se Industry	M. King/ASARCO
11:30 - 11:40	European Perspective	D. Bonnet/Battelle
11:40 - 12:00	Charge to Participants	P. Moskowitz/BNL
12:00 - 13:00	Lunch	
13:00 - 16:30	Cd and Se Breakout Groups	
16:30 - 17:00	Progress Reports	B. Taniel/P. Meyers
	March 12	
8:30 - 10:15	Cd and Se Breakout Groups	
10:15 - 10:30	Coffee	
10:30 - 11:15	Presentation of Findings	B. Taniel/P. Meyers
11:15 - 12:00	Action Items	P. Moskowitz

3. RESOURCE CONSERVATION AND RECOVERY ACT

3.1 Statutory Requirements

Disposal of modules and manufacturing wastes containing Cd and Se may be regulated by Federal and State statutes, regulations and guidelines; a potpourri of controls exist. Of these, RCRA is probably the most important because it is the key regulatory program of the Federal government which focuses on the management of hazardous wastes. More specifically, RCRA is a Federal statute designed to provide "cradle-to-grave" control of hazardous waste by imposing management requirements on generators and transporters of hazardous wastes as well as owners and operators of treatment, storage and disposal (TSD) facilities. The policy goals and objectives of RCRA are to reduce or eliminate as expeditiously as possible, the generation of hazardous wastes. Under RCRA, land disposal is the least favored method for managing hazardous wastes. In addition, all waste that is generated must be handled so as to minimize the present and future threat to human health and the environment. The three major parts of RCRA are Subtitle C, D, and I. Subtitle C regulates hazardous waste, Subtitle D regulates non-hazardous solid waste, and Subtitle I regulates underground storage tanks that hold hazardous substances and petroleum products. This discussion will focus on Subtitle C, the Hazardous Waste Management Program (HWM).

In order for a waste to be subject to HWM regulations, it must be classified as a hazardous waste. A hazardous waste is a solid waste (as defined in Subtitle D), that is not specifically excluded by the U.S. Environmental Protection Agency (EPA) and is either specifically listed as a hazardous waste in Subpart D of part 261 (a "Listed Waste") or exhibits any one of the four characteristics (a "Characteristic Waste") of a hazardous waste (i.e., ignitability, corrosivity, reactivity, and/or toxicity).

If a substance is specifically listed based on the criteria set forth in 40 CFR 261.11, it is presumed to be hazardous regardless of the concentration. Listed Wastes are separated into the following categories: 1) Wastes from non-specific sources (F codes); 2) wastes from specific sources (K codes); and, 3) wastes from commercial chemical products, including off-specification species, containers and spill residues. This category is divided into two sublists (i.e., "P" and "U"). "P" listed wastes are chemicals deemed acutely hazardous when discarded and are subject to more rigorous management requirements. "U" listed chemicals are deemed toxic and therefore considered and regulated as hazardous wastes when discarded. A company may file with the EPA a delisting petition requesting the removal of a waste, generated at their facility, from the RCRA hazardous waste lists. The company must demonstrate that the waste does not contain the hazardous constituents for which the EPA has listed the waste, or any other constituents that cause the waste to be hazardous.

Neither the processes used in the manufacture of CIS or CdTe modules, nor the materials themselves are listed by EPA as hazardous. Thus, module and manufacturing wastes would not be classified as hazardous under these subsections of RCRA. They may, however, be listed as characteristic wastes (see Section 3.2).

3.2 Waste Characteristics

In order to identify characteristics of hazardous wastes that are different from the Listed Wastes, EPA has established testing protocols to measure the ignitability, corrosivity, reactivity and toxicity of the waste. If a waste exhibits any one of these characteristics, it would then be classified as hazardous under RCRA guidelines.

A waste is deemed to have the characteristic of ignitability if it exhibits one of the following four descriptions: 1) It is a liquid of other than an aqueous solution containing less than 24 percent alcohol by volume with a flash point of less than 140^{o} F.; 2) it is a non liquid that which under normal conditions can cause fire through friction, absorption of moisture, or spontaneous chemical change; 3) it is an ignitable compressed gas; and, 4) it is an oxidizer as defined by DOT regulations.

Wastes that have the potential to corrode metal, escape their containers, and liberate other wastes are considered to have characteristics of corrosivity. These wastes are either aqueous and have a pH of <2.0 or >12; or a liquid that corrodes steel at a regular rate greater than 6.35 millimeters per year under specific test procedures.

Wastes that are extremely unstable and have a tendency to easily react or explode exhibit characteristics of reactivity. Suitable test protocols are unavailable for testing reactivity. EPA, however, has promulgated various criteria to assist a manager in judging this characteristic.

Finally, EPA has established the use of the toxicity characteristic leaching procedure test (TCLP) to identify wastes likely to leach hazardous constituents into ground water. There are prescribed TCLP limits for 25 organic chemicals, 8 inorganics and 6 insecticides/herbicides. The TCLP limit for metals are given in Table 3.

Table 3. TLCP Limits for Metals.

Compound	TCLP Limit (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

3.3 Administrative Implications

RCRA divides administrative responsibilities into two categories: Generators, and Transporters. Since the photovoltaic community may be generating materials that could be considered hazardous due to their toxicity (i.e., a characteristic waste), this discussion focuses on regulations set forth for generators of hazardous waste. Some shipping and transport documentation requirements are also relevant and they are listed below.

Generators are defined as any person, by site, whose act or process produces hazardous waste or whose act first causes hazardous waste to become subject to regulation. There are three categories of hazardous waste generators based on the amount of waste generated: 1) Small quantity generators (< 100 kg/month); 2) medium-quantity generators (between 100 and 1000 kg/month); and, 3) large quantity generators (> 1000 kg/month). It is a generator's responsibility to fulfill the following requirements: 1) Determine if the solid waste is hazardous; 2) notify the EPA and obtain an identification number; 3) identify and classify waste according to DOT's Hazardous materials tables; 4) comply with all packaging, marking and labeling requirements; 5) determine whether additional shipping requirements are applicable; 6) complete the uniform Hazardous Waste Manifest, a control and transport document that accompanies the hazardous waste at all times; 7) provide appropriate placards to transporter; and, 8) comply with record keeping and reporting requirements.

Small quantity generators are conditionally exempt from RCRA requirements. Medium and large quantity generators must comply with all RCRA imposed requirements and certify on each waste manifest that a program is in place to reduce the quantity and/or toxicity of the hazardous waste at the site. The generator also must describe the waste minimization program that is in place, and the results achieved by that program. Table 4 lists the elements that should be included within an effective waste minimization program.

The status of these efforts must be included in a biennial report submitted to the EPA by March 1 of each even-numbered year. This report must also contain the EPA numbers for the generator, transporters and designated facility where hazardous waste was sent as well as a description and accounting of the quantity of hazardous waste generated.

Each generator must establish a training program for appropriate facility personnel. The purpose of the training requirements is to reduce the potential for errors that might threaten human health or the environment by ensuring that facility personnel acquire expertise in areas to which they are assigned. The program must also include training for personnel to ensure facility compliance with all applicable regulations.

RCRA also requires each facility to be operated and maintained in a manner that will minimize the possibility of fire, explosion or unplanned sudden or non-sudden release.

Further, each facility must have a contingency plan, as outlined in Subpart D of part 265, that is designated to minimize hazards in the case of an emergency. The plan must include a description of actions that will be undertaken by facility personnel, a detailed list of emergency equipment with locations, and evacuation procedures.

Table 4. Elements Needed for an Effective Waste Minimization Program.

Top Management Support
- Waste minimization as compliance policy.
- Specific goals for waste minimization.
- Commitment to recommendations.
- Designated waste minimization coordinator.
- Employee training.

Characterization of Waste Generation

Periodic Waste Minimization Assessments
- Comprehensive audits of entire waste process to ensure effective minimization.
- Comprehensive analysis.

Technology Transfer Program

Program Evaluation

3.4 Economic Implications

If a waste is classified as hazardous, then it must be disposed of in a RCRA controlled landfill. The current cost for such disposal is in the range of $100 to $400 per 55 gallon drum.

3.5 Applicability to the Photovoltaics Industry

The different photovoltaic market segments will vary in their recycling needs, as well as in the urgency with which they must be addressed. Based upon immediate need, the manufacturing, and utility (remote and grid connected) power markets would need to be initially addressed, while the development of recycling options for the consumer market can be delayed.

The principal short-term concern will focus on the disposal or re-processing of manufacturing wastes. At the present time, it is an open question, whether or not rejected thin film CIS or CdTe modules and manufacturing wastes will be classified as a hazardous material under RCRA. Recycling of these materials, however, may still be desirable for political and social reasons.

Due to their long useful lives, large-scale disposal of spent photovoltaic devices will not occur until 20 to 30 years after their initial installation. Here, RCRA will be of most concern to processes/module designs which give rise to products failing the TCLP test. Preliminary analyses on a very small number of samples suggest that some CdTe modules may fail the TCLP test, and so a longer term concern may be the large-scale disposal of these devices.

The ability to maintain institutional control over photovoltaic modules supplied to the marketplace will depend on the nature of the products and consumers. Photovoltaic products may range from small scale battery rechargers (several watts), to moderate scale residential or commercial arrays (1-100 kW_p), to large-scale central-station utility applications (MW_p). Consumers may include individuals, small businesses and large corporations (e.g., regulated utilities). The ability to maintain institutional controls closely follows these groupings. That is, maintaining institutional control over small products sold to individual consumers will be very difficult. The best method for these groups may be to provide incentives (e.g., rebates on new products, deposits, and rewards) for the return of retired devices. For this to occur, the products must include clear identification of who the product should be returned to and what will be provided in return (e.g., money). Utilities retiring large quantities of modules are clearly identifiable and responsible organizations. There must be benefits to these organizations as well. This could include, return of deposits, and perhaps more importantly compliance with RCRA, if the modules are classified as hazardous. The middle-sized group, may present the largest problem with respect to recycling because of the larger quantities of modules that they may be discarding, yet this group may have a smaller level of awareness and compliance with regulations than that of the utilities because they may have limited technical resources. Clearly, a common thread, across all three groups, is the need for the establishment of incentives, and an educational program to inform customers that such incentives exist.

3.6 Perspective

The quantities of hazardous materials contained in photovoltaic modules are very small (e.g., 5-14 g of Cd or Se per m^2 of module or about 1 g of Cd or Se per MWh of electricity produced) in absolute measures and extremely small in relative measures when compared with overall inputs of such materials to waste streams from all other sources. Most of the Cd found in municipal solid waste, for example, is from Ni-Cd battery disposal. Thus, the marginal contribution of Cd from the photovoltaic modules, in comparison with the Cd from all other sources, will be very small. Further, the actual flux to the environment of Cd from CdTe modules will probably not be large for two important reasons: First, the CdTe will be sandwiched between two layers of glass and reasonably isolated from the environment; and, second, CdTe is insoluble in water and would, therefore, exhibit only limited mobility in the soil environment found beneath landfills. Finally, it is now clear that solid deposits of Cd to landfill sites are only a minor contributor to the presence of the metal in the food chain. Air emissions of Cd from municipal incinerators are the primary focal point of environmental attention. Recent studies, however, have shown that these emissions can be adequately controlled (Chandler, 1992). There is less information available for Se, although it is present in the ash from coal-fired power plants, and is found in the leachate beneath municipal waste landfills.

4. PHOTOVOLTAIC INDUSTRY NEEDS

4.1 Module Manufacturers

The "cradle-to-cradle" recycling of Cd and Se based photovoltaic modules and production process by-products would generate a number of different waste streams which include waste generated by the manufacturer during the production process and customers' spent modules. The actual quantities and types of "wastes" generated by each manufacturer will be specific to the material and method of manufacture. Without going into detail, these wastes may include, but are not limited to:

1. Solids including CdS, CdTe, $CuInSe_2$ and various non-stoichiometric mixtures containing Cd, Te, Se, and Zn. These deposits may have to be scrapped off the walls of the deposition chambers or apparatus, they may include sand (from a bead blaster), and

particles from the objects being cleaned. Additional wastes could be cleaning rags coated with acids and dust collected on particle filters.

2. Liquids including water and alcohols containing Cd and Se compounds. In the electrodeposition of CdTe from an aqueous bath, the solutions are either acidic or basic, containing dissolved Cd salts and TeO_2. As these components are depleted from solution during electrodeposition, they are continuously added to solution. If the deposition bath becomes contaminated, disposal and recycling of Te and Cd would be needed.

3. Modules rejected during manufacturing for various reasons and in various stages of manufacture.

4.2 Consumers

In the U.S., the largest potential user of photovoltaic modules is the electric utility industry. This industry has a well deserved reputation for conservatism, so one might expect it to resist adopting any new technology containing hazardous substances. But, utility companies are quite experienced in handling very large quantities of potentially hazardous materials; they annually dispose of 70 million tons of coal ash and 12 million tons of scrubber by-products at a cost of over a billion dollars. These wastes are composed of various materials including arsenic, cadmium, selenium and tellurium. Moreover, the burden of these large volume waste streams is growing, because present landfills are nearing capacity, new ones are harder to site, and the industry faces increasingly stringent environmental regulations.

On the other hand, using renewable energy generation technologies as a substitute for coal-fired capacity presents the possibility of reducing the magnitude of these wastes. In particular, photovoltaic bulk power generation (even using modules containing CdTe or CIS) promises orders-of-magnitude reduction in the utilities' waste handling problems. Thus, the hazards posed by Cd or Se containing photovoltaic modules, represent to the utility industry not a new problem, but rather a great opportunity for diminishing a large existing one.

5. OPTIONS FOR THE RECYCLING OF PHOTOVOLTAIC MODULES

Many options exist for the recycling of spent modules and manufacturing wastes. These can be divided into two broad classes: Centralized and Decentralized. Implementation of the centralized technologies implies that wastes will be shipped from manufacturing and consumer locations (e.g., an electric utility) to large facilities engaged in the collection and recycling of wastes. Decentralized opuions are more focused on the management of wastes at module production facilities. Thus, the decentralized options are smaller in scale and more focused on manufacturing wastes.

5.1 Centralized Strategies

It may be possible to incorporate the recycling of photovoltaic materials containing Cd into facilities recycling other Cd-containing products. Numerous commercial operations exist in North America, Europe and Japan for recycling Cd bearing wastes. These include both non-ferrous smelters and recyclers which handle such wastes as spent Ni-Cd batteries, electroplating sludge, electric arc furnace dust and Cd process wastes from the battery, pigments, stabilizers and various other industries. The treatment employed to recover Cd may be pyrometallurgical, generally involving heating to temperatures from 400 to 1200^{o} C, either in vacuum, air, or in a reducing atmosphere; or hydrometallurgical which involve chemical or electrochemical recovery from solutions. Depending on the nature of the waste being treated and the by-process employed to recover Cd, various products including Cd, CdO, CdS, $CdSO_4$, or $CdCl_2$ may be produced. These recycled products are then generally sent to final Cd refining processes to obtain the high purity Cd product which can be used in the industry.

Facilities that recycle used Ni-Cd batteries are of special interest because of their rapid growth in capacity. A variety of metallurgical processes are available for Ni-Cd battery recycling. There are of either pyrometallurgical or hydrometallurgical type and have been extensively described elsewhere (Oda 1992, David 1992, van Deelen and van Erkel, 1990).

Recycling of Se together with Te, from drums of "Xerox" photocopiers has been practiced in the copier industry. Information on the commercial scale of such recycling is proprietary, but some insight of what may be a commercial process, appears in two U.S. patents by S.S. Badesha of Xerox Corporation. The Xerox Corporation used to recycle Se from photoconductive scrap including Se, As, and Te, but it is no longer practiced since their photocopiers contain much less Se than in the past. Currently, users of Se (e.g., Xerox) sell their scrap to Se suppliers who introduce the wastes into their process streams and combine recycling with manufacturing. It appears that the energy involved in recycling such a metal is much less than the energy involved in mining the primary material. Such Se producers/recyclers include the Canadian Copper Recovery (CCR), the Swedish company Boliden, and the German company Retorte, which reclaims all heavy metals.

The method used by CCR is a combination of the "wet" Badesha method and a thermal method to obtain solid Se. Thus, it appears that the technology of reclamation for Se exists, and is in fact practiced in several countries when the market forces are favorable. With the current cost of Se of about $20/lb, such recovery is economical even without including the avoided cost of environmentally safe disposal. The Badesha method has an associated cost of about $10/lb or less; this estimate includes paying $2/lb to the suppliers of the scrap.

One problem which may affect the economics of any given method for the photovoltaic industry, is the relatively high amount of glass or plastic in photovoltaic panels. These materials may need to be separated before the recycling of Cd or Se is accomplished. The low density of Cd or Se in these products adds to the collection and processing costs. Glass and plastic can be separated by various methods including physical (e.g., sand blasting, pyrolysis or other temperature differentiation methods, vacuum, flotation), or chemical methods (e.g., in solution solvents). At present, we do not have estimates of the cost of such separation.

The experience available on recycling lead-acid batteries could be quite useful in assessing the feasibility and costs of a similar effort in photovoltaic reclamation. There is an established recycling mechanism for lead-acid batteries in the U.S., which works quite well (Dodds and Goldsberry, 1986). Virtually all large, industrial lead-acid batteries (approximately 75% of all lead-acid batteries), are recycled. Also, a significant amount (e.g., 500 tons in 1991) of industrial Ni-Cd batteries are recycled by ANMETCO, Pittsburgh, PA; as well as additional quantities being shipped abroad for recycling. Dry small cell and small batteries are not recycled in the U.S. at present. Most dry small batteries are disposed of by the individual consumer in the same way as other municipal waste, although this is not likely to continue. Separation of the plastic from the metals and photovoltaic material may be attained the same way that plastic is separated in commercial facilities recycling lead-acid batteries. The process in these facilities is as follows (Dodds & Goldsberry, 1986). The batteries are either cut into parts with a hammer mill or the top carefully removed to reuse the plastic case. In the first method the batteries are decased and the parts are hit against a striker bar which allows the plates, separators and acid to fall onto a vibrating conveyor feeding into a storage bin. Acid drains off and is neutralized with ammonia. The rest of the battery is fed to a crusher and then fed to a separator where the plastic casing material is separated from the plates, and connectors; the scrap is then smelted to form lead. The plastic casing is also reused totally or partially depending on the material. Organic polymeric materials may undergo molecular changes during reprocessing which limit the number of times a polymeric material can be reprocessed. The plastic can be used as a fuel since it contains about 20,000 Btu/lb.

The non-ferrous metals industry, particularly the Cu industry, uses large amounts of silica as a fluxing agent ($>500,000$ tons/year in the U.S. alone) in their smelting processes. Smelters are allowed to accept materials, even if they are "Listed" or "Characteristic" wastes, which are effective substitutes for feedstocks in their processes, and the silica used in photovoltaic modules would qualify as such a material for fluxing. The other elements present in photovoltaic modules, for example Cu, In, Se, Cd, Te, Zn, and Mo are already present in various quantities in the smelting process. An open question is whether these modules would have to be stripped of plastic or crushed to a suitable size. Several vendors sell relatively inexpensive equipment that can crush/shred full 1 ft x 4 ft modules to a suitable size for high-density transport and easy reclamation processing. The resulting pieces look like the < 2 in diameter chunks left when tempered glass is broken.

Other feed materials to non-ferrous pyrometallurgical and hydrometallurgical operations include Cd, CdO, $Cd(OH)_2$, $CdCl_2$, $CdSO_4$, CdS, Te, TeO_2, Se and SeO_2. These materials could substitute for other feedstocks and be treated at the smelter without the need for additional permitting.

The above wastes are those which can be accepted by primary metal smelters. Subtitle C of RCRA requires that hazardous materials (e.g., those that fail TCLP) must be disposed of in a facility with a RCRA permit. However, RCRA permits are not needed by non-ferrous smelters if they wish to receive unmanifested materials, which fail TCLP, as effective substitutes for feedstocks or commercial chemicals used in their process. Various other wastes which having failed TCLP testing and are classified as hazardous wastes, cannot be classified as substitutes for raw material feedstocks and would have to be subjected to a different recycling route. The economic and technical feasibility of the recycling of, for example, mixed Cd and Te wastes, is confirmed. Recycling companies exist that accept and process Cd-bearing liquid wastes. Hydrometal (Engis, Belgium), TNO (The Netherlands), Toho Zinc (Japan), and Encycle (Corpus Christi, TX) are companies established to recycle liquids containing non-ferrous metals such as Cd, Te, and Se. An alternative solution would be to develop a transportable process that could travel from one photovoltaic manufacturer to another. This transportable process would convert the waste into a solid form that could be accepted by primary producers as legitimate feed materials. Such a process has been developed by the U.S. Bureau of Mines and tested on CdTe manufacturing scrap (Tolley and Palmer, 1991). To implement such an alternative process, however, would require more complete knowledge of compositions of photovoltaic manufacturing waste. This would require close cooperation between manufacturers and recyclers. The efficiency of these processes can be greatly enhanced by developing in-house procedures for treatment of process wastes into forms more amenable to primary producers and recyclers.

5.2 Decentralized Recycling Strategies

Useful parallels can be drawn from the treatment of metal-containing liquid wastes by other metal consuming industries. Closed-loop Cd electroplating processes have been operating for a number of years, and several other Cd using industries are able to reintroduce process wastes into earlier process stages. There are three main methods of treating metal-containing effluent:

1. Traditional method of precipitating metal as an hydroxide, sedimenting it as a sludge and dumping it in a hazardous waste site or perhaps sending it to a pyrometallurgical smelting plant. Any metal recovered is fortuitous and the method is considered cheap.

2. Methods for concentrating metal in solution and recycling a process solution within the plant. The unit processes of recycling include ion exchange, reverse osmosis, dialysis, solvent extraction, etc. Ion exchange may also be used for removing last traces of metal after a less than optimal precipitation stage.

3. Methods for recovering metal directly by reduction, typically electrowinning or cementation.

Hydroxide precipitation can be achieved at alkaline pH values for most metals. As a general practice, all metal wastes arising from a plant are often mixed together. However, it is clear that to attain the levels of residual metal demanded by EPA-style regulations some separation is vital. Furthermore, the optimal pH for each metal varies and is a very sensitive parameter in respect of residual metal composition. This is illustrated in Figure 1 for four common electroplating metals. While Cu and Cr have similar optimum pH values, Ni and Cd have markedly higher values and at the former critical pH value of pH=9, Cd is substantially soluble.

A frequently used alkali is lime which is cheap and appears to promote hydroxide flocculation very effectively, but it has a pH value of 9.5 at saturation. Consequently lime is adequate for Cu and Cr, but inadequate for Cd. In practice the EPA residual limit can therefore only be achieved by individual precipitation of each metal at optimum pH using an appropriate alkali agent (lime, soda ash, sodium hydroxide, etc.).

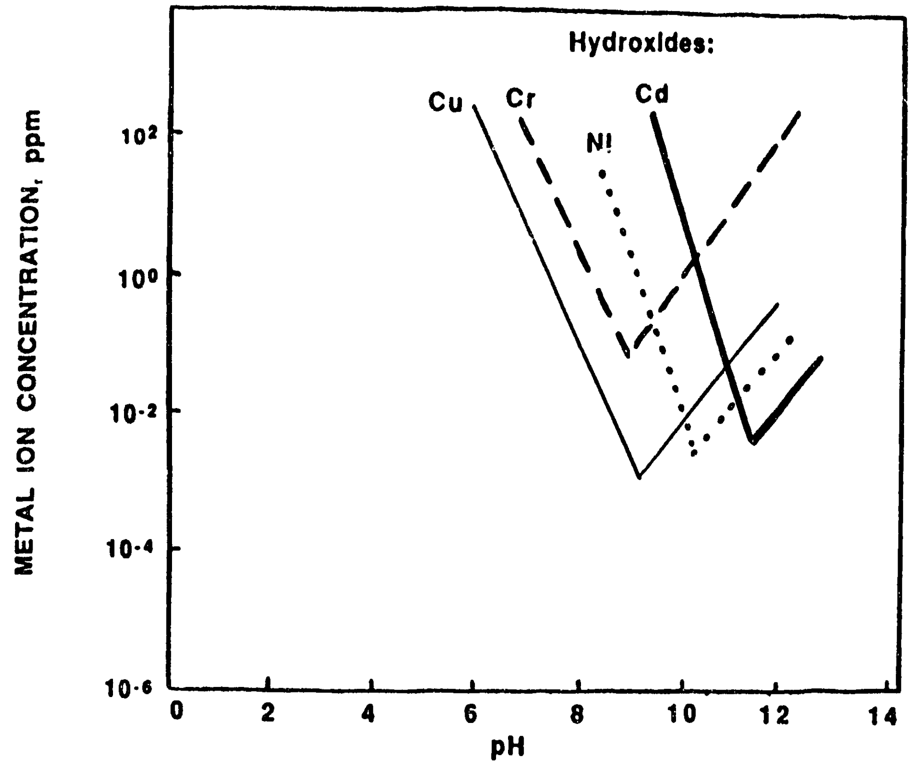

Figure 1. Metal Ion Concentration vs. pH for Precipitation of Metal Hydroxides.

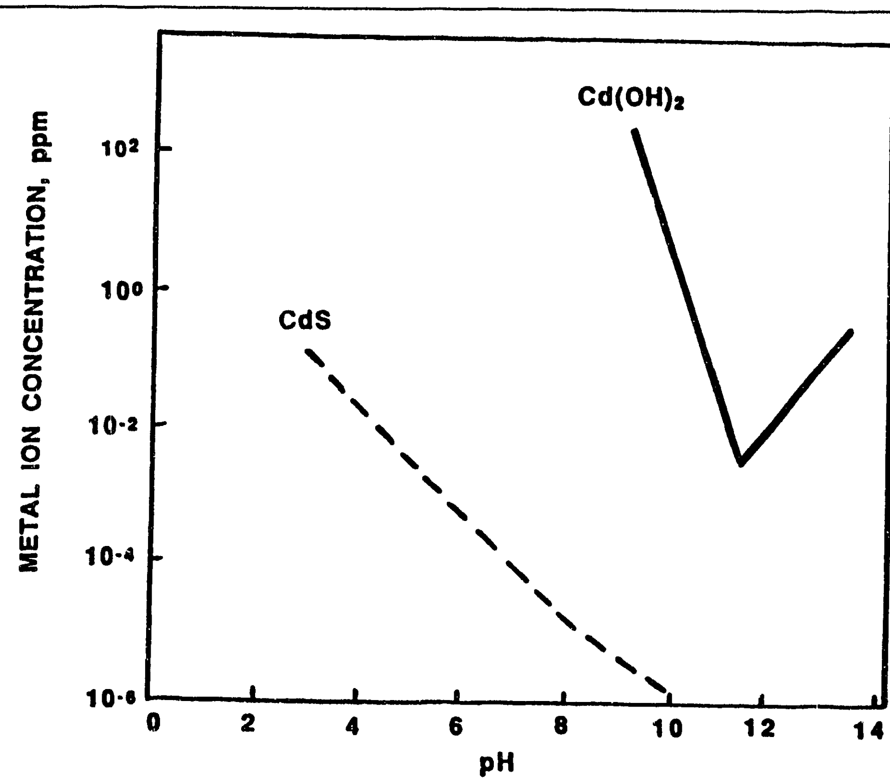

Figure 2. Metal Ion Concentration vs. pH for Cadmium Sulfide and Hydroxide.

If a lower residual limit is set, alternative precipitation reactions must be examined and several options can be considered. The use of sulfide precipitation is well-known using hydrogen sulfide gas or sodium sulfide, and enables residual metal concentrations to be decreased by more than 1000 fold, depending on the pH (see Figure 2). Another precipitating agent is dimethyldithiocarbamate which has the virtue of producing a very small volume of sludge.

Amongst the methods of concentrating metals in solution, Ion Exchange is widely practiced and can be very effective. However, it nas not been used extensively for Cd. Similarly, electrowinning is occasionally practiced for Cd but it is not a normal practice. Nevertheless, data exist for Cd recovery in several types of cells, for example, for conventional cyanide electroplating rinses and dragging out the 'Chemelec' cell has been found to be very effective in the concentration range 200 to 1 ppm yielding 95% recovery (Tyson 1984) after which ion exchange may be used to produce a zero Cd discharge.

Recovery and separation has been reported for a mixed acid Cd-Zn solution (Gabe and Walsh, 1986) using a rotating cylinder electrode reactor, and for a cyanide waste water system using a high surface area cathode reactor (Shaulys and Rovinelli, 1991). In the latter case Cd levels in dragout tanks rose to 25 ppm over 12 hrs, but an electrowinning circuit could hold it at 1-4 ppm. In a batch operation, Cd was reduced from 36.3 ppm to 0.23 ppm over 9.5 hrs using 30A at 4V; over 97% was in fact recovered. The performance represented classical exponential metal recovery (Figure 3).

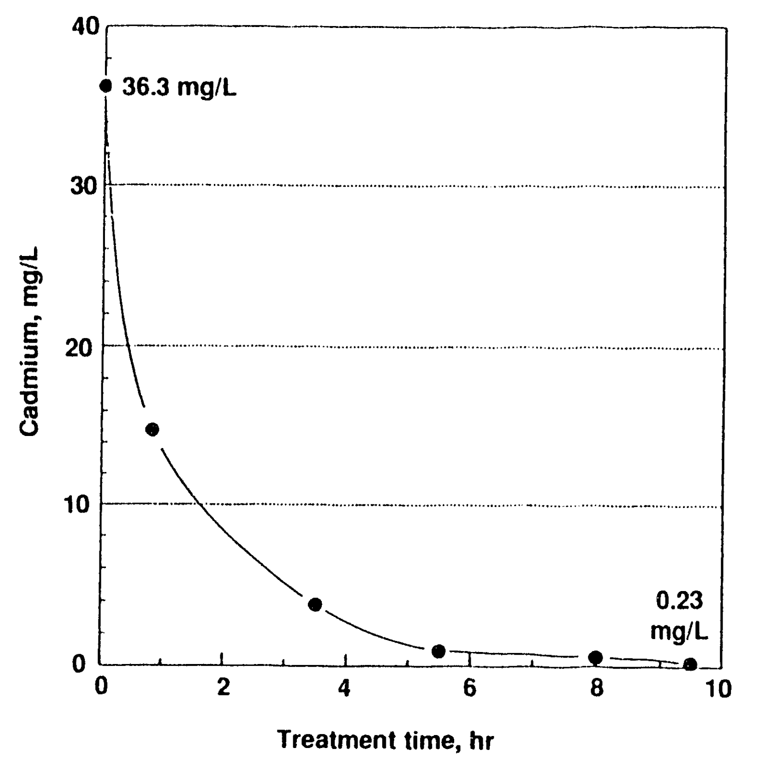

Figure 3. Reduction of Cadmium from Rinse Waters Using Electrowinning.

It is clear that both precipitation and electrowinning techniques are adequate to enable Cd to be used safely in electroplating operations, but given the residual limits imposed by environmental agencies, these techniques must be optimized by not allowing mixing with other metals and by using Cd-dedicated operations.

In the long term, two other considerations must be kept in mind. Firstly, the need to minimize the volume of precipitate produced as dumping becomes more restrictive; and, secondly, the trend towards zero discharge plants. To meet these requirements, a combination of processes are preferred, typically a first stage of electrowinning to recover >90% metal followed by a refining stage of ion exchange or precipitation which will remove the remaining contaminants.

5.3 Overview

Although many waste materials from the CdTe/CIS industry may require special handling, a number of wastes can simply be treated as non-hazardous. For instance, clean glass that is broken during handling or cleaning can be disposed of without special treatment. Other materials such as tin oxide or tin oxide-coated glass can also be disposed of without special treatment according to the RCRA. An effort must be made to understand the nature of all the wastes in order to segregate and treat in simplified ways those that are not hazardous.

The various waste streams generated by photovoltaic manufacturing processes can be categorized into at least four groups for which different options for recycling are available. First, modules rejected during manufacturing and customers spent modules can be recycled. Pyrometallurgical processes currently used in non-ferrous smelting can be used for recycling. Further information is needed to determine whether treatment such as the removal of plastics or pottants would be required prior to shipment for smelting. Alternatives which may be more cost-effective need to be further investigated. These might include stripping and recovery of the highest value metals such as In, Se, Te and Mo, followed by normal glass recycling mechanisms, or even recycling of the spent module through established glass recycling channels.

Second, some waste streams will consist of materials in completely different forms than the initial raw materials, but still in very concentrated form. Examples of this are chemical bath solutions and deposition system residues. The most appropriate and cost-effective option for recycling these materials will vary with their specific nature. Treatment of these materials prior to recycling may be advantageous; however, this may result in additional regulatory requirements and hence costs.

Third, some wastes may be in their original form and purity. An example of this is spent molybdenum sputtering targets, which can usually be returned to the vendor for credit.

A fourth category of wastes specific to CdTe modules is mixed wastes which, according to current regulations, cannot be accepted by primary producers. Liquid wastes such as those generated during electrodeposition fit into this category. Barriers to recycling do not appear to be technical. Recycling companies exist that accept and process Cd-bearing liquid wastes. An alternative solution would be to develop a transportable process that could travel from one photovoltaic manufacturer to another. This transportable process would convert the Cd into a solid form that could be accepted by primary producers as legitimate substitute feed materials. To implement such an alternative process, however, would require more complete knowledge of compositions of photovoltaic manufacturing waste and close cooperation between manufacturers and recyclers.

6. RECOMMENDATIONS

As a follow-up to the discussions held at the Workshop, lists of recommendations to various stakeholder groups were prepared. These are presented below.

6.1 To the Photovoltaics Industry

6.1.1 Environmentally Conscious Manufacturing (ECM) and Design for the Environment (DFE)

ECM and DFE contain all aspects associated with the design process (i.e., product and manufacturing) which minimize the environmental impact of manufacture, use, and eventual disposal of the finished product. This step is part of the overall Product Realization Process (PRP). It also means that recyclability must be designed into both the manufacturing process and the product; that is, wastes and environmental hazards are minimized from the start.

The photovoltaic industry should continue to take a proactive stance with regard to industrial ecology and regulatory issues. This means that the industry should:

- Design modules that can be easily disassembled by recyclers and also contain materials which can be recycled. In this way the environmentally sound image of the industry can be sustained and economic advantages will be realized.
- Reduce generated waste throughout the process.
- Reduce quantity of rejected modules through quality control.
- Reduce quantity of broken final products through quality control and improvements in shipping packages.
- Focus R&D on process efficiency to improve material utilization.
- Use less material by improving the physical and electrical properties of the cell and decreasing the cell thickness.

6.1.2 Total Quality Management

A total quality management approach needs to be developed for the recycling of photovoltaic process wastes and modules. The key elements that should be addressed include:

- Systems for tracking of all materials from suppliers to finished products.
- Design for waste minimization with recyclability as an objective (i.e., DFE).
- Alleviating customer concerns and addressing misconceptions through appropriate testing and education.
- Minimizing exposure to legal liabilities through proactive implementation of regulatory requirements; that is, moving beyond today's standards.

6.1.3 Waste Classification

It is an open question, whether thin film CIS and CdTe modules will be classified as hazardous materials under RCRA. In the U.S., materials are defined as hazardous if they are "listed" or "characteristic." Neither CdTe or CIS are listed wastes. Although the few CIS thin film modules tested have passed the TCLP test and the few CdTe modules tested have failed the TCLP, these sample sizes were very small and it is uncertain how other modules will fair with respect to the TCLP test. This issue bears significantly on all aspects of future module recycling and disposal. Hence, modules from all possible photovoltaic suppliers should be tested by TCLP. Of more immediate concern are manufacturing wastes. Because of the diversity of wastes, manufacturers should independently characterize their manufacturing wastes with respect to the TCLP test. It is important to note that failure of the TCLP test only designates a module/waste as hazardous for landfill, not as a generic classification in all aspects of its use.

If photovoltaic manufacturing wastes are to be re-processed to generate feedstock materials suitable for processing by non-ferrous smelters or other off-site recycling facilities, the photovoltaic plant may be required to comply with RCRA regulations dealing with the treatment, storage, and disposal of hazardous wastes. Therefore, an analysis should be prepared of how a facility would be impacted under RCRA if manufacturing wastes are re-processed on site.

6.1.4 Improved Visibility to SEIA

A third critical recommendation to the photovoltaic industry is to improve its visibility to vital resources, such as the Solar Energy Industry Association (SEIA), to assist in regulatory issues. At present, the majority of member industries are concerned with existing and near-term crystalline silicon technologies. SEIA should be used as a resource to facilitate a proper regulatory climate for CIS and CdTe.

One issue which requires support from SEIA is to establish that photovoltaic modules are a "green" product. For example, while preliminary data on CIS modules support the passing of TCLP tests, localized governmental regulations may prove restrictive. Similarly, for CdTe clear control strategies (even if CdTe passes the TCLP tests) would be helpful to ameliorate public concerns. SEIA's role may be to support member companies in securing appropriate green labels for their products, and encouraging innovative recovery and recycling schemes.

Tax credits and/or tax incentives may be needed to enhance recycling. SEIA's role, as well as the DOE's, would be to champion possible incentives to improve the position of the photovoltaic community.

6.1.5 Industry Cooperation

Increased cooperation in the area of environment, health and safety is needed. This can be encouraged via meetings and other means of interaction such as the photovoltaic safety bulletin board hosted at BNL. Participation with other industry groups [e.g., Selenium Tellurium Development Association (STDA), Semiconductor Safety Association (SSA), American Institute of Chemical Engineers (AIChE), The Cadmium Council Inc.], should also be explored. Industry's continued proactive support of safety, health and environmental activities at NREL, BNL, EPRI and other research organizations, form a strong foundation for such progress.

6.2 To the Non-ferrous Metals Industry

A listing of the range of recycling processes available for spent CdTe and CIS modules is needed. Options listed should include both hydrometallurgical and pyrometallurgical processes, non-ferrous metal suppliers and Cd recyclers. The report should include consideration of pre-processing of spent modules by manufacturers into forms which are more economically or technically favorable to recycling by smelters or recyclers. Other issues which should also be considered would include economics of collection, transportation, storage, reclamation and disposal of residual products. Initial analysis by the industry, for example, indicates that spent CdTe modules can readily be incorporated into existing non-ferrous smelters or Cd recycling plants, at costs which are not prohibitive.

Information should be supplied to the photovoltaics industry on the handling and usage of Cd and Se products (e.g., use the STDA/The Cadmium Council Inc. mailing list); the environmental outlook on Cd and Se; and forums for the photovoltaic industry to interact with other Cd and Se users (i.e., International Symposium on Se and Te usage, May 1994 in Belgium). Photovoltaic manufacturers should be invited to take associate membership of metal industry trade associations.

6.3 To the Utility Industry

The electric utilities, as one of the largest potential customers for photovoltaics, should actively participate in developing strategies to recycle both hazardous and non-hazardous materials in photovoltaic modules. The utilities also should clearly publicize their needs in regards to toxic materials handling, as well as other photovoltaic-related requirements. Additionally, the utility industry could aid photovoltaic development by quantifying the value to itself of hazardous waste stream reductions that switching to photovoltaics could offer. For example, some part of the $1 billion expended annually on coal wastes is one component of such a potential savings.

6.4 To DOE

Establish forums (i.e., mechanism of communication) between photovoltaic industry and other DOE laboratories (e.g., Argonne National Laboratory and Sandia) to investigate waste minimization and recycling activities. This would supplement existing core cooperation between NREL and BNL. DOE can assist in cost/benefit analyses of cradle-to-grave photovoltaic modules vs. waste from conventional power sources.

It is also recommended that an investigation be made of the methods used by, for example, the electroplating industry for minimization of metal-containing wastes. This is a logical step before addressing the external treatment/reprocessing of process wastes. Such an approach is likely to prove more economic than external treatment and would be consistent with the waste minimization objectives of RCRA. The different process routes would have differing suitability for in-house treatment; liquid wastes containing $CdSO_4$, $CdCl_2$, etc., would be particularly suited to such treatment.

6.5 To EPA

Thin film photovoltaic modules are designed to operate in harsh environments for periods of 10 years or more. The nature of the materials used in CIS and CdTe modules are such that they should be environmentally stable against acidic dissolution and thin film modules constructed from them are mechanically stable.

On this basis, it is recommended that the EPA should consider CIS modules as non-hazardous at the end of their useful life on the basis of the existing TCLP testing procedure. This same strategy must be revisited for CdTe in the future as the modules are redesigned for Cd minimization to pass the TCLP.

7. CONCLUSIONS

1. Manufacture of CIS and CdTe modules will result in the production of several wastes, some of which could be recycled.

2. Physical state, chemical composition and quantity of these wastes are not yet fully characterized, but could range from concentrated metals to modules and liquids containing very small quantities of metals.

3. It is not yet clear which, if any, wastes will be classified as hazardous under Federal or state statutes. Even those wastes characterized as hazardous can be handled by existing recycling technologies since they are safely generated and routinely handled in larger quantities by the non-ferrous metal industry.

4. Principles of ECM and DFE should be incorporated early in the design and manufacture of these devices. These strategies can reduce the cost and quantity of material that must be disposed of and can facilitate recycling.

5. Various recycling options exist. They vary depending on size (e.g., small on-site vs. large off-site smelters) and the composition of the wastes (e.g., liquids vs. modules) that can be accommodated.

6. There is sufficient capacity in smelters to accommodate all wastes produced by CIS and CdTe manufacturers for at least the next ten to twenty years.

7. The cost to the photovoltaic industry of recycling is not clear, but is not expected to be a burden to commercialization of these photovoltaic technologies. However, it should be recognized that if such costs reach a level whereupon the cost benefit that thin film technologies offer over traditional crystalline silicon becomes eroded, then commercialization of these thin film technologies could be affected.

8. Large scale recycling may be encouraged by the following:

- compliance with RCRA
- possible tax credits for manufacturers and consumers
- manufacturer buy-backs

9. Recycling will likely be implemented in stages, beginning with manufacturing wastes, extending to large-scale utility arrays, and finally to other product lines. The near-term need is the handling of manufacturing wastes.

10. A cooperative approach should be developed between the smelter, the metal producer and the photovoltaic module manufacturer.

11. The utility industry is not likely to be deterred by the presence of Cd and Se in modules. Appropriate methods for recycling or disposal will, however, be required.

12. Proactive efforts of the photovoltaic industry to meet recycling needs may be useful, to assist the commercial success of all photovoltaic technologies.

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APPENDIX A. PARTICIPANT MAILING LIST

Joseph Armstrong
Martin Marietta
P.O. Box 179
Denver, CO 80201
Tel: (303) 971-9399
Fax: (303) 971-9421

Rajeewa Arya
Solarex - Thin Film Division
826 Newtown-Yardley Road
Newtown, PA 18940
Tel: (215) 860-0902
Fax: (215) 860-2986

Mike Benson
Noranda Technology
240 Hymus Blvd.
Pointe Claire Quebec
CANADA H9R1G5
Tel: (514) 630-9473
Fax: (514) 630-9379

Dieter Bonnet
Battelle Institut e.V.
Am Römerhof 35
D-6000 Frankfurt 90
GERMANY
Tel: 011496979082631
Fax: 0114969790882

Mark Caffarey
Metallurgie Hoboken Overpelt S.A.
14 A. Greinerstraat
2660 Hoboken
BELGIUM
Tel: 32-3-829-7111
Fax: 32-3-829-6949

Murray Cook
Cadmium Association
42 Weymouth St.
London WIN 3LQ
UNITED KINGDOM
Tel: 44 71499 8425
Fax: 44 71 493 1555

David Corbus
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80215
Tel: (303) 231-1364
Fax: (303) 231 1199

Vasilis Fthenakis
Brookhaven National Laboratory
Bldg. 475
Upton, NY 11973
Tel: (516) 282-2830
Fax: (516) 282-7867

Lloyd Herwig
U.S. DOE
PV DIV CE-131
1000 Independence Ave.
Washington, DC 20585
Tel: (202) 586-5538
Fax: (202) 586-7114

Steve Johnson
Golden Technologies
P.O. Box 4040
Golden, CO 80402
Tel: (303) 239-7744
Fax: (303) 239-7719

Bruce Lanning
Martin Marietta
P.O. Box 178 MS 3085
Denver, CO 80201
Tel: (303) 971-9551
Fax: (303) 971-9421

Taie Li
ASARCO Inc.
495 East 51st Avenue
Denver, CO 80216
Tel: (303) 296-5936

Peter Meyers
Solar Cells, Inc.
2650 North Reynolds Road
Toledo, OH 43615
Tel: (419) 534-3377
Fax: (419) 534-2794

J.M. Morabito
BTL
1236 Moffit Ave.
Bethlehem, PA 18018
Tel: (215) 691-6329
Fax: (215) 882-9603

Hugh Morrow
Cadmium Council
P.O. Box 2664
Greenwich, CT 06836
Tel: (203) 625-0911
Fax: (203) 625-0918

Paul Moskowitz
Brookhaven National Laboratory
Upton, NY 11973
Tel: (516) 282-2017
Fax: (516) 282-7867

Terry Peterson
Solar Power Program, EPRI
3412 Hillview Ave. Box 10412
Palo Alto, CA 94303
Tel: (415) 855-2594
Fax: (415) 855-2954

Robert D. Putnam
Putnam Environmental Services
2525 Meridian Parkway
P.O. Box 12763
Research Triangle Park, NC 27709
Tel: (919) 361-4657
Fax: (919) 361-2571

Billy Stanbery
The Boeing Company
Box 3999 MS 9E-XX
Seattle, WA 98124-2499
Tel: (206) 657-6964
Fax: (206) 657-9336

Becky Taniel
Siemens Solar
4650 Adohr Lane
Camarillo, CA 93011
Tel: (805) 388-6571
Fax: (805) 388-6557

William Tolley
U.S. Department of the Interior
Bureau of Mines
Salt Lake City Research Center
729 Arapeen Drive
Salt Lake City, UT 84108-1283
Tel: (801) 524-6150, FTS-588-6150
Fax: (801) 524-6119, FTS-588-6119

Harin S. Ullal
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401
Tel: (303) 231-1486
Fax: (303) 231-1030

Ken Zweibel
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80215
Tel: (303) 231-7141
Fax: (303) 231-1030

APPENDIX B. CdTe AND CIS PV THIN FILMS (K. ZWEIBEL)

The Potential of PV

- PV resource is about 10,000 times existing energy demand and is not geographically limited
- PV technology is progressing rapidly and should become cost-competitive c. year 2000.
- PV without storage can provide 10% of our electricity
- PV with storage can provide energy for almost any energy requirement, including vehicles

P5-G0665012

State of Photovoltaics

'Cottage Industry'

- Markets small (50 MW worldwide) and dispersed
- Production too small for economies-of-scale
- System costs high (about \$10/W_p or 40 c/kWh); all components too costly, but dominated by module costs
- Module technologies key
  - Many module technologies, none mature
  - Rapid progress, especially in some new module technologies (CIS, CdTe)
- Today's modules: crystalline and amorphous silicon
- International competition

Context of $CuInSe_2$ (CIS) and CdTe

Low Cost Thin Films

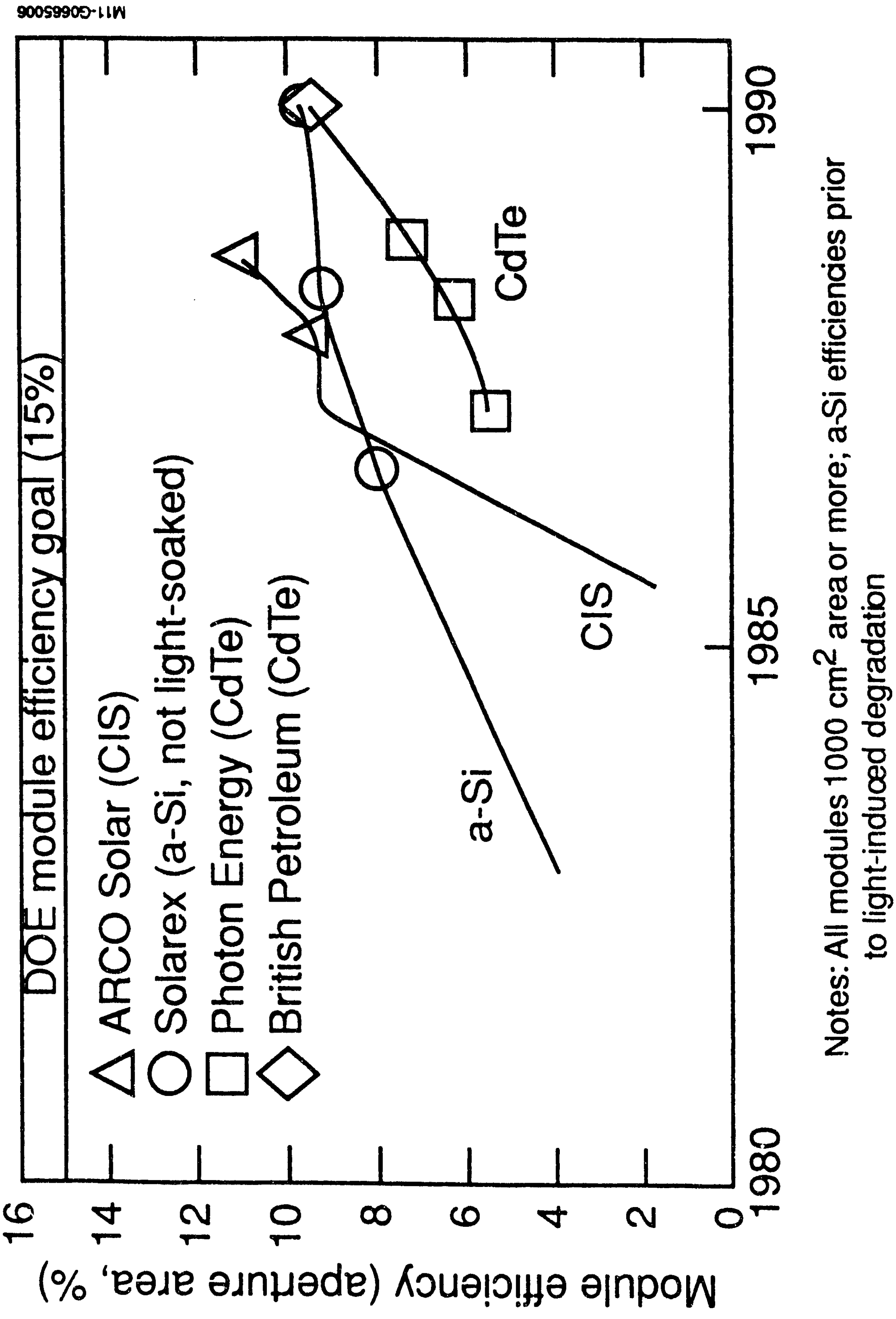
- Thin films have potential to reduce module costs by about 75% versus today's crystalline silicon
  - Less material and reduced energy input
  - Large-area coating processes

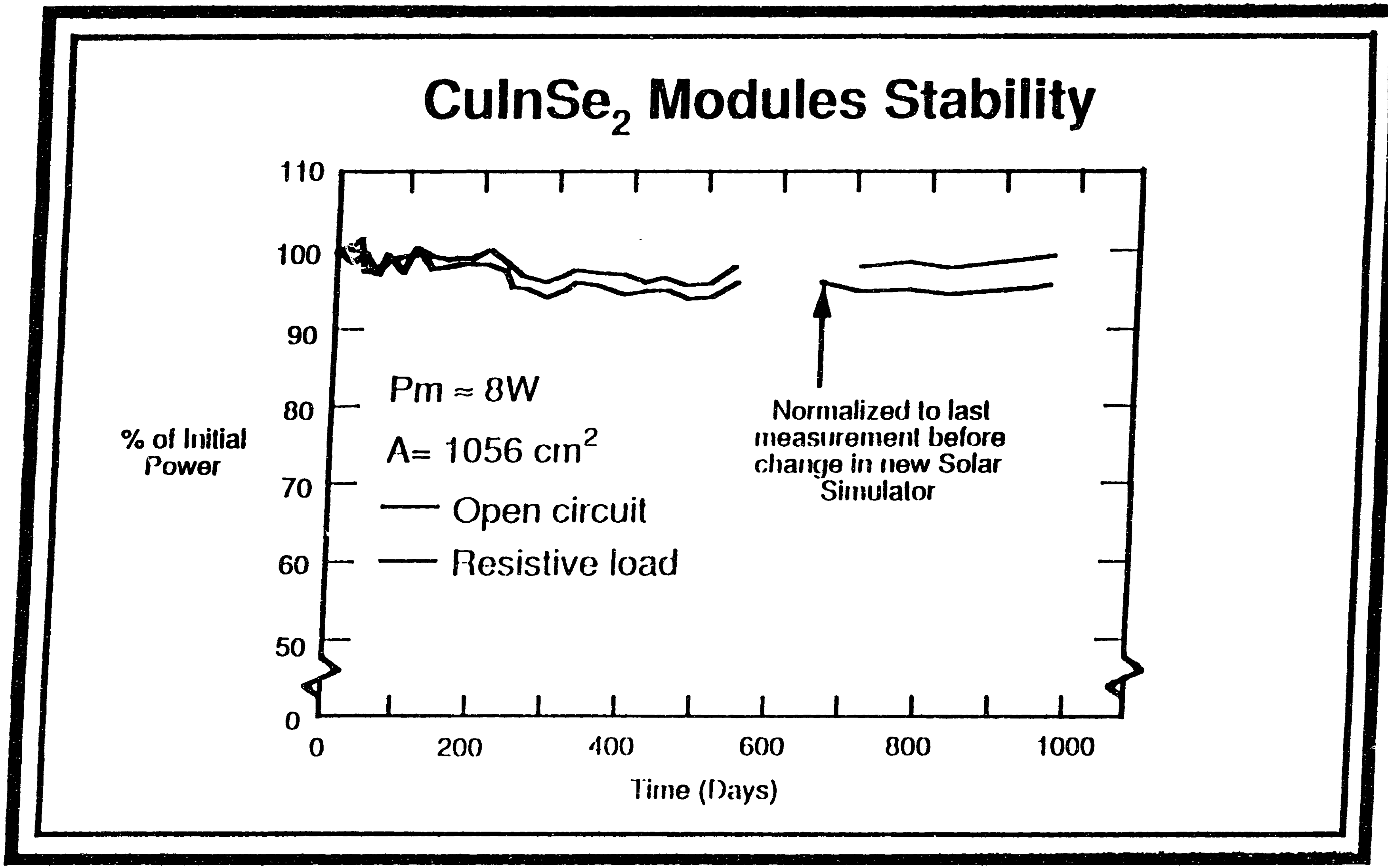
- Amorphous silicon is a thin film (with low cost potential) but it has poor PV characteristics: low efficiency and inadequate stability

- CIS and CdTe have excellent laboratory efficiencies, good potential for low cost, and promising outdoor reliability; Now considered by many to be 'most likely to succeed'

- Practical potential: 15% modules, $50/m² costs*, 30-year outdoor life imply systems under $1/W_p$ (6 c/kWh)

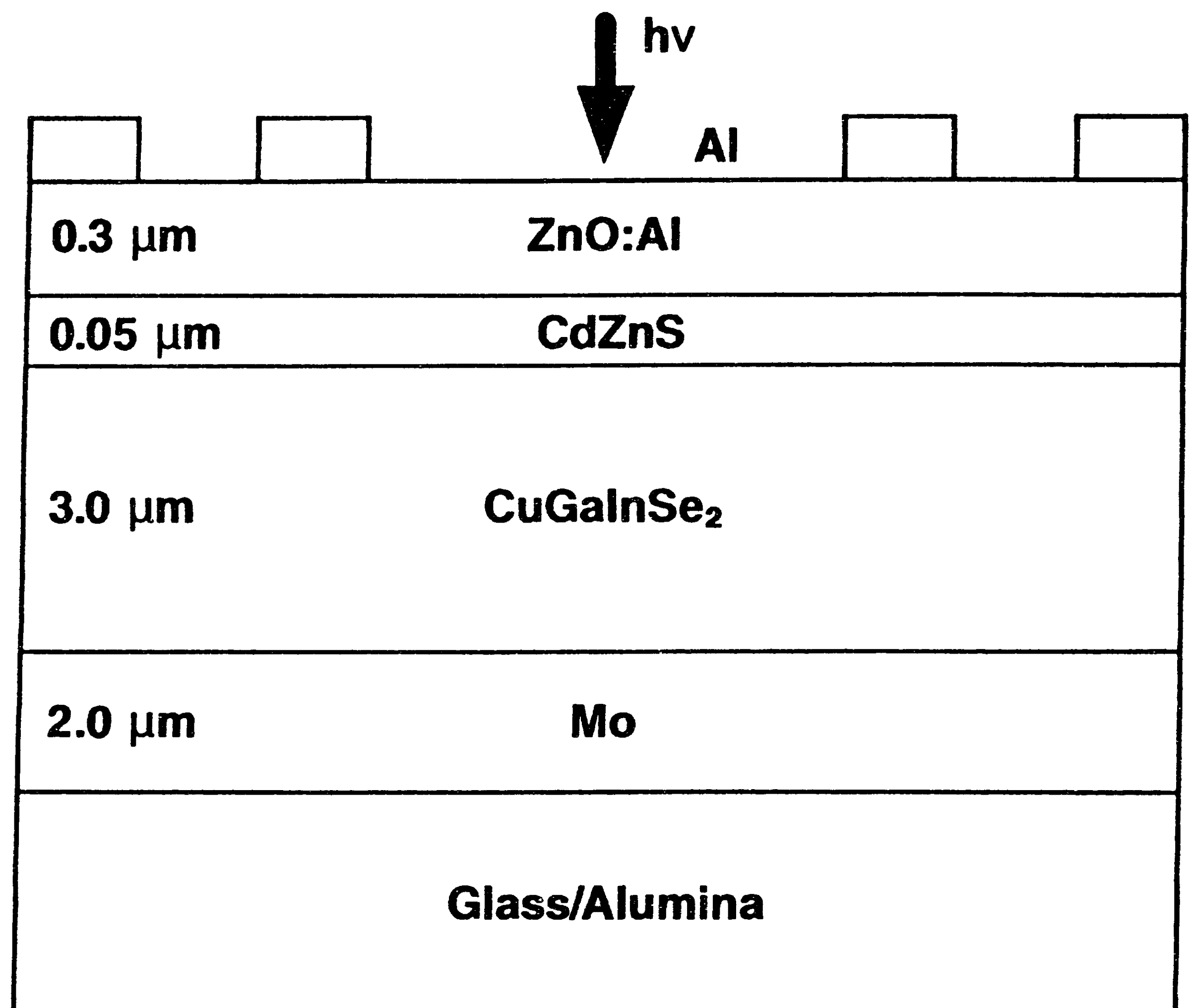
*For mature industry with large markets


M11-G0665006
Module efficiency (aperture area, %)
16
14
12
10
8
6
4
2
0
1980
1985
1990
DOE module efficiency goal (15%)
ARCO Solar (CIS)
Solarex (a-Si, not light-soaked)
Photon Energy (CdTe)
British Petroleum (CdTe)
a-Si
CIS
CdTe
Notes: All modules 1000 cm² area or more; a-Si efficiencies prior
to light-induced degradation

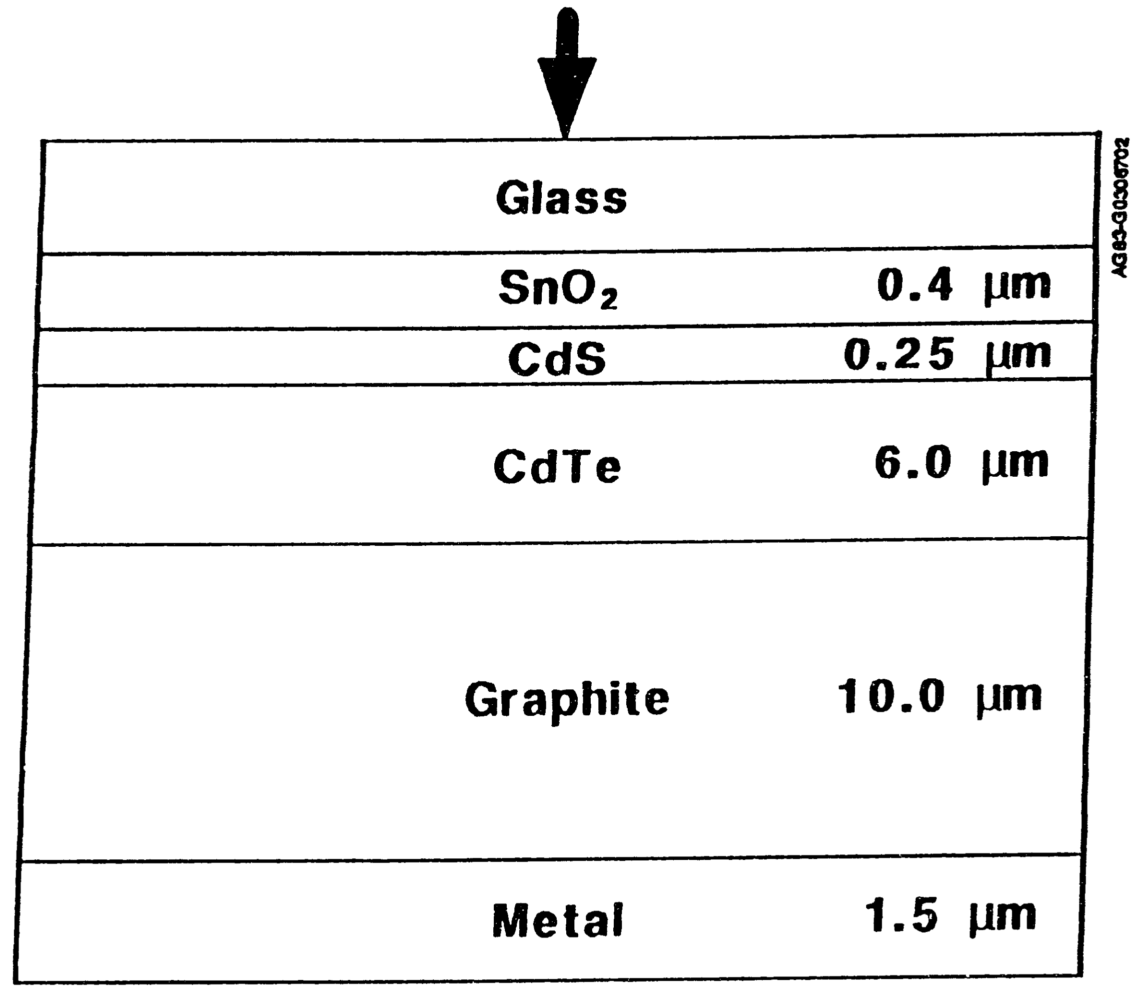


P56 G0833002

Solar Cell Structure



Solar Cell Structure



CIS and CdTe Corporate Participants

Company	Material	Status
Siemens Solar (US)	CIS	Prototype Production; 10%, 4 ft2*
ISET	CIS	First ft2 modules
Boeing, Solarex, EPV	CIS	Good Cells
Martin Marietta. Iowa Thin Films	CIS	Start up
Photon Energy	CdTe	Prototype production; 7% 4 ft2*
BP Solar (UK)	CdTe	Prototype production; 10% 1 ft2*
Solar Cells Inc	CdTe	Pre-prototype Production
Matsushita (Japan)	CdTe	Sells cells; 8% 1ft2*
Martin Marietta	CdTe	Start up

*Best large module

Example Industrial Processes

Material	Process	Comments
CIS	sputtering/selenization	sputter metals (Cu,In); selenize with H2Se or Se
	co-evaporation of elements	control issues
CdTe	spraying	
	electrodeposition	slow; liquid waste; high utilization
	close spaced sublimation	high rate
	screen printing	
CdS	spray pyrolysis	waste
	CSS	
	electrodeposition	slow; liquid waste
	solution growth	liquid waste; CdS losses

Impacts of Some Hazardous Materials From PV and Coal

Material	From PV	From Coal
Cadmium	1 kg/GWh	1 kg/GWh
Selenium	1 kg/GWh	16 kg/GWh
Tellurium	1 kg/GWh	0.2-0.5 kg/GWh
Arsenic	0.5 kg/Gwh	120 kg/GWh

Sequestered Amounts of Cd and Se in Photovoltaic Modules

Layer	Typical Thickness	Typical Amounts per square meter	Amount per MW (10% eff)	Amount per GW (10% eff)	Sequestered* (30 yr life)
CuInSe2	2 microns	Se: 4 g	40 kg	40 MT	1200 MT/GW
CdTe	2-5 microns	Cd: 5.5-14 g	55-140 kg	55-140 MT	1650-4200 MT/GW
CdS	0.02-0.2 microns	Cd: 0.07-0.7 g	0.7-7 kg	0.7-7 MT	21-210 MT/GW
CdS/CdTe	2.2-5.2 microns	Cd: 6.2-14.7 g	62-147 kg	62-147 MT	1860-4410 MT/GW

*Sequestered amounts are per gigawatt of annual production

APPENDIX C. CdTe PV MFG. NEEDS (P. MEYERS)

Environmental Concerns Regarding Manufacturing and Disposal of Thin Film CdTe PV Modules

Peter V. Meyers

Solar Cells, Inc.

Workshop on
Recycling Cd and Se
Bearing Photovoltaic
Modules,
NREL
11 -12 March 1992

Outline

Quantities
- Arrays
- Manufacturing

Issues
- Customer Perception
- Political vs Scientific
- Landfill vs Recycle

Objectives
- Rational Solutions
- Interim Procedures

Quantities

Ultimate Problem - Arrays

Assumptions:

Module efficiency	7%
CdTe thickness	2 um
Glass thickness	5 mm
Array packing density	50%

Working numbers:

MODULES

Mass Cd/m^2	5.8 g
Mass % Cd in module	0.1%
Volume % CdTe in module	0.04%
Mass Cd per kW	83 g/kW

ARRAYS

Power area density	140 kW/Acre
Cd area density	12 kg/Acre
Value of Cd at $30/lb	$780/Acre
Te area density	13 kg/Acre
Value of Te at $60/lb	$1700/Acre

Quantities

Current Concern - Manufacturing

Assumption: Material utilization is 50%

Working numbers:

Plant Capacity

10 MW/yr	100 mW/yr	
140 thousand m^2/yr	1.4 million m^2/yr	modules
830 kg Cd/yr	8.3 metric tons Cd/yr	modules
830 kg Cd/yr	8.3 metric tons Cd/yr	waste
940 kg Te/yr	9.4 metric tons Te/yr	waste

Issues

Political vs Scientific: How real is the problem?

Environmental Damage	-	what could happen?
	-	what is likely to happen?
	-	how can we find out?
Regulatory Restrictions	-	are they reasonable now?
	-	what are they likely to be in the future?
	-	are the present and anticipated standards achievable?
	-	can we distinguish between Cd and CdS or CdTe?

Issues

Landfill vs Recycling

Economics

Too much for landfill?
Too little to recover?

Recycling Procedures

What are the mechanics of recycling?
What can be done now?

Issues

Customer Perception - what can be done to reassure our customers?

Scientific studies?

Realistic regulatory environment?

Remove cusomer's Cradle-to-Grave responsibility?

Manufacturer maintains responsibility?

Recycler maintains responsibility?

Objectives

Rational Solutions

- Strategy should include
  - Scientific Studies
  - Political Factors
  - Customer Education

Interim Procedures - next two years

- Links with suppliers and recyclers

APPENDIX D. CIS PV MFG. NEEDS (B. TANIEL)

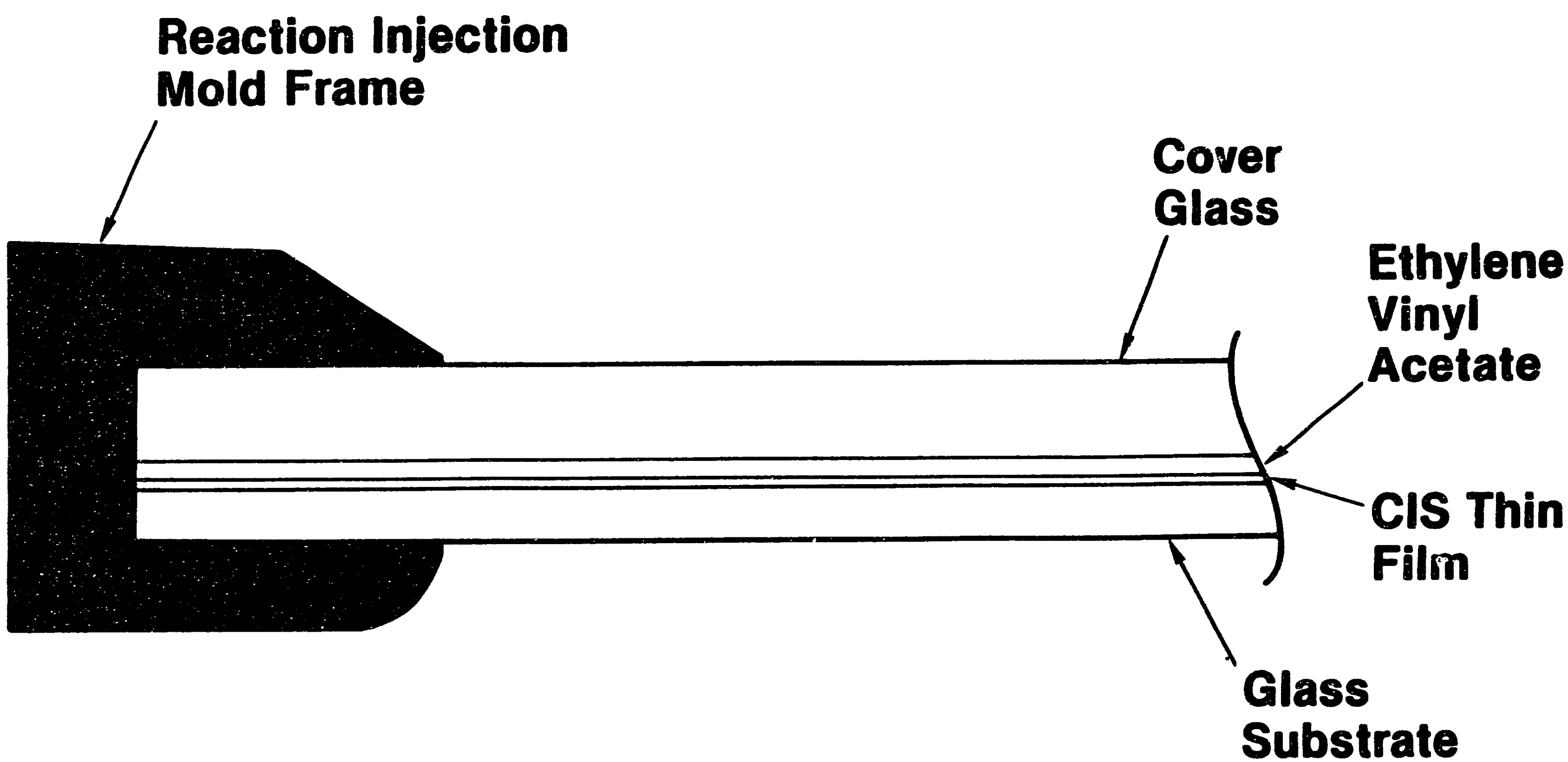
CIS
(Copper Indium Diselenide)
RECYCLING OPTIONS

C. Eberspacher
R. Taniei

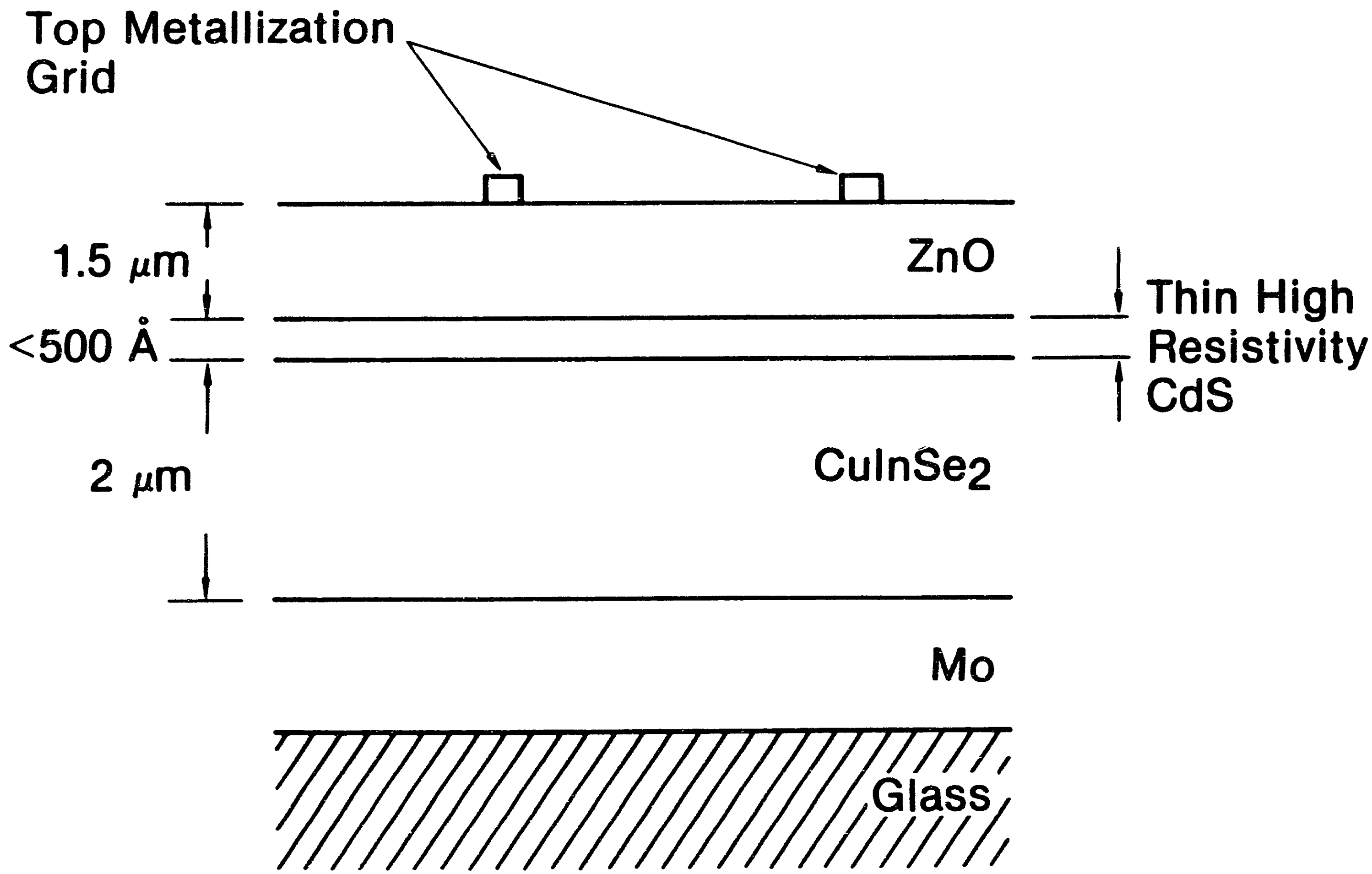
Siemens Solar Industries
Camarillo, California

March 11, 1992

CIS MODULE
Laminated, Framed



$CuInSe_2$ SOLAR CELL CROSS SECTION



Environmentally conscious manufacturing:

- Manufacture
- Shipment
- Useful Life
- Disposal

Manufacture:

Process Inputs

- **Hazardous** (e.g., gases)
- **Non-Hazardous** (e.g., glass)

Process Outputs

- **Hazardous** (e.g., dusts, contaminated solvents)
- **Non-Hazardous** (e.g, glass)

Is CIS hazardous or non-hazardous?

National Institute of Environmental Health Studies (NIEHS)

- Study of $CuInSe_2$, $CuGaSe_2$, and CdTe toxicology
- Animal testing for basic toxicity
- Further testing for toxic effects, lethal thresholds, and carcinogenicity as appropriate from initial results

Is the product hazardous or non-hazardous in its life and at the end of its life?

Fraunhofer/GSF/Brookhaven study of CIS environmental and materials safety:

- Full spectrum evaluation of life cycle of CIS modules, including manufacturing, use, disposal, and recycling

Brookhaven study of EPA classification of CIS module plates:

- CIS plates passed the EPA's "TCLP" test for solubility in acidic solutions. Thus, CIS plates are not hazardous by U.S. Federal standards.

Is the product hazardous or non-hazardous in its life and at the end of its life?

(continued)

California waste classification testing of CIS modules:

- Most fine-grain metal compounds "fail" by definition under California's strict waste laws.

- Extensive testing shows that Siemens Solar Industries' CIS module materials are environmentally stable against acidic dissolution and that thin film modules are mechanically durable. Other manufacturers should do their own testing.

Recycling:

- Saves energy

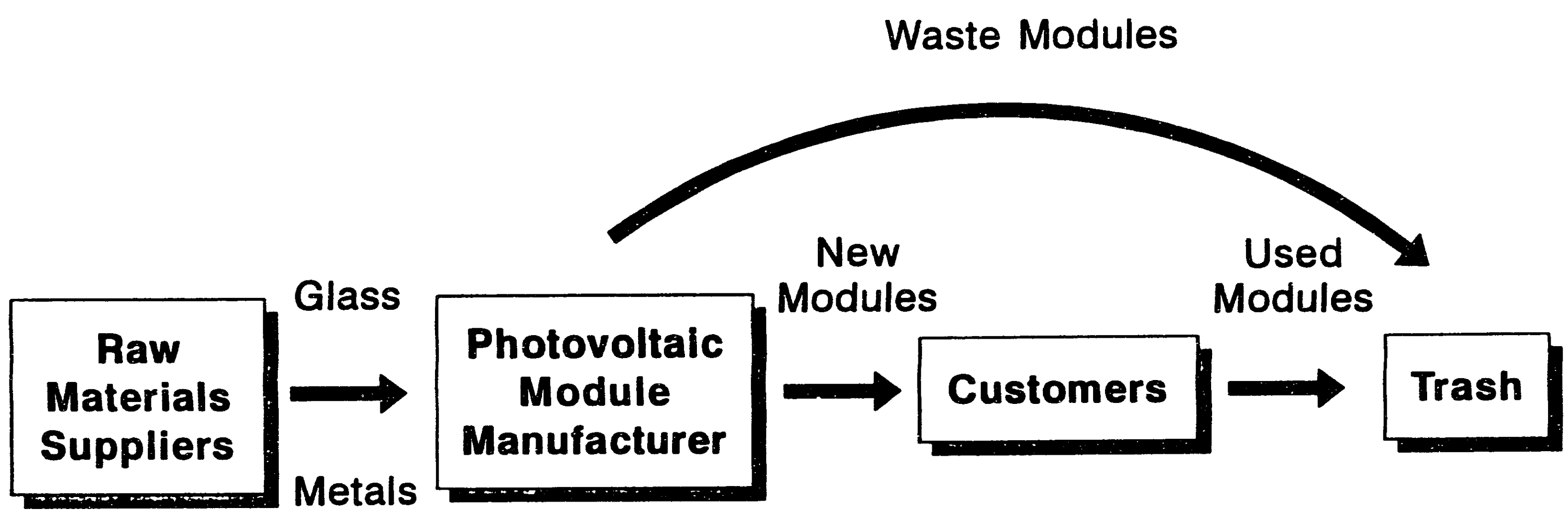
  In particular, energy required for manufacturing glass and for primary metals extraction

- Saves air, water, and landfill space

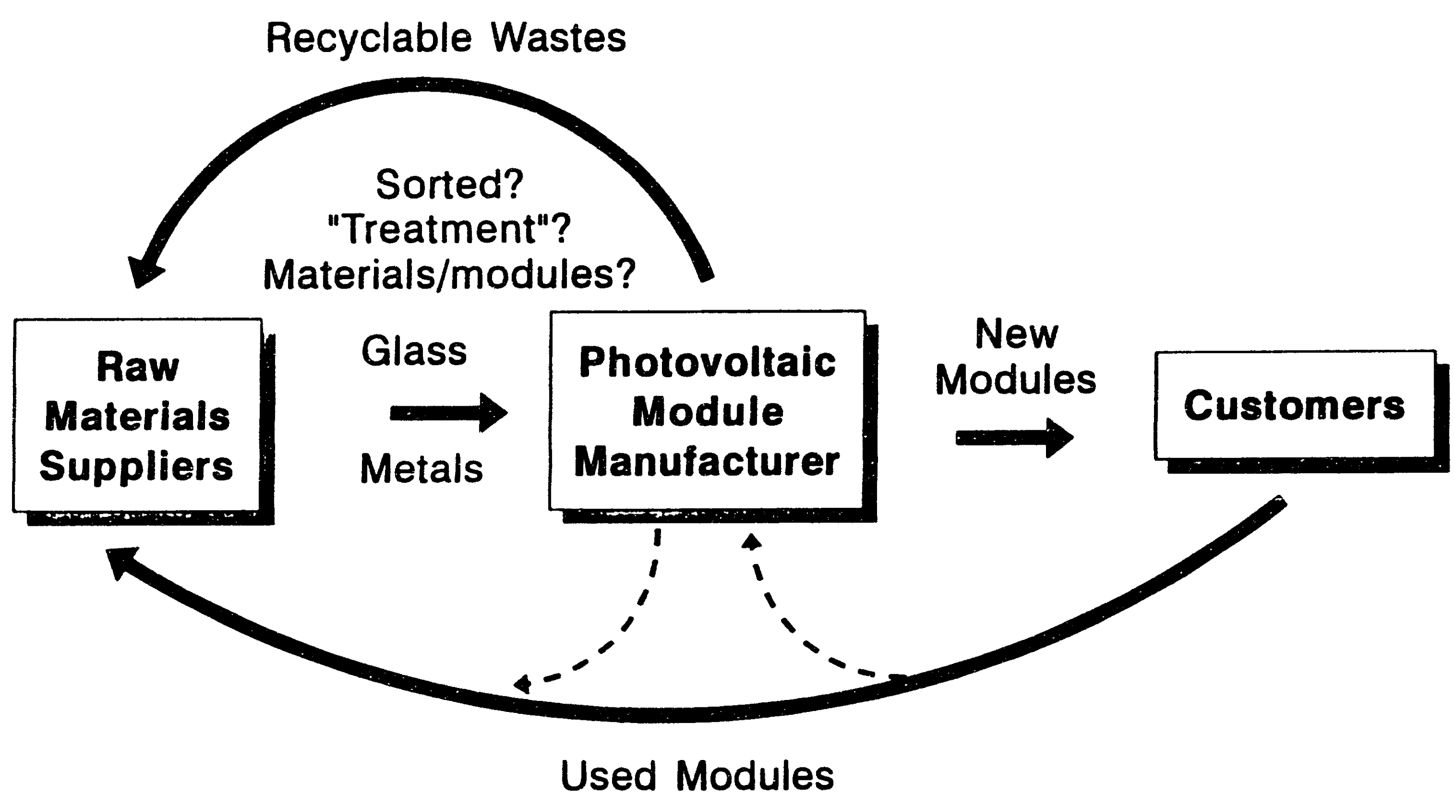
  For example, limited landfill space for glass disposal

- Saves money

Wasteful strategy to be avoided:



Desirable strategies:



Conclusions:

- Environmentally conscious manufacturing
- Hazardous and non-hazardous inputs and outputs
- Studies of CIS module manufacturing, use, disposal, and recycling
- Preliminary studies indicate CIS modules are non-hazardous
- Recycling issues:

  - Customer → (PV manufacturer?) → raw material suppliers
  - Waste sorting and/or "treatment"
- Recycling facilitation and support

APPENDIX E. CONSUMER PERSPECTIVE (T. PETERSON)

ELECTRIC UTILITY HIGH-VOLUME WASTE MANAGEMENT

- 70 million tons of coal ash and 12 million tons of scrubber products produced per year--and expected to increase
- Coal ash and flue-gas desulfurization by-product disposal presently costs over $1 billion per year
- Landfills are nearing capacity and becoming harder to site
- About 18% of utility fly ash is sold for use by others-- mostly as substitute for cement

RESOURCE RECOVERY (RECYCLING)

- Markets exist for strategic metals, alumina, magnetite, and other components
- Hydrochloric acid leaching is under investigation
- EPRI Waste & Water Management Program tools
  - Ash and FGD by-product disposal manuals
  - ASHDAL, SLUDGE-COST computer codes

EFFLUENT TREATMENT

- Reference manual for treatment/disposal of low-volume wastes
- Penn P&L case study mentions selenium
- Iron coprecipitation studied for trace heavy-metal removal

APPENDIX F. Cd INDUSTRY PERSPECTIVE (H. MORROW)

Chart 4

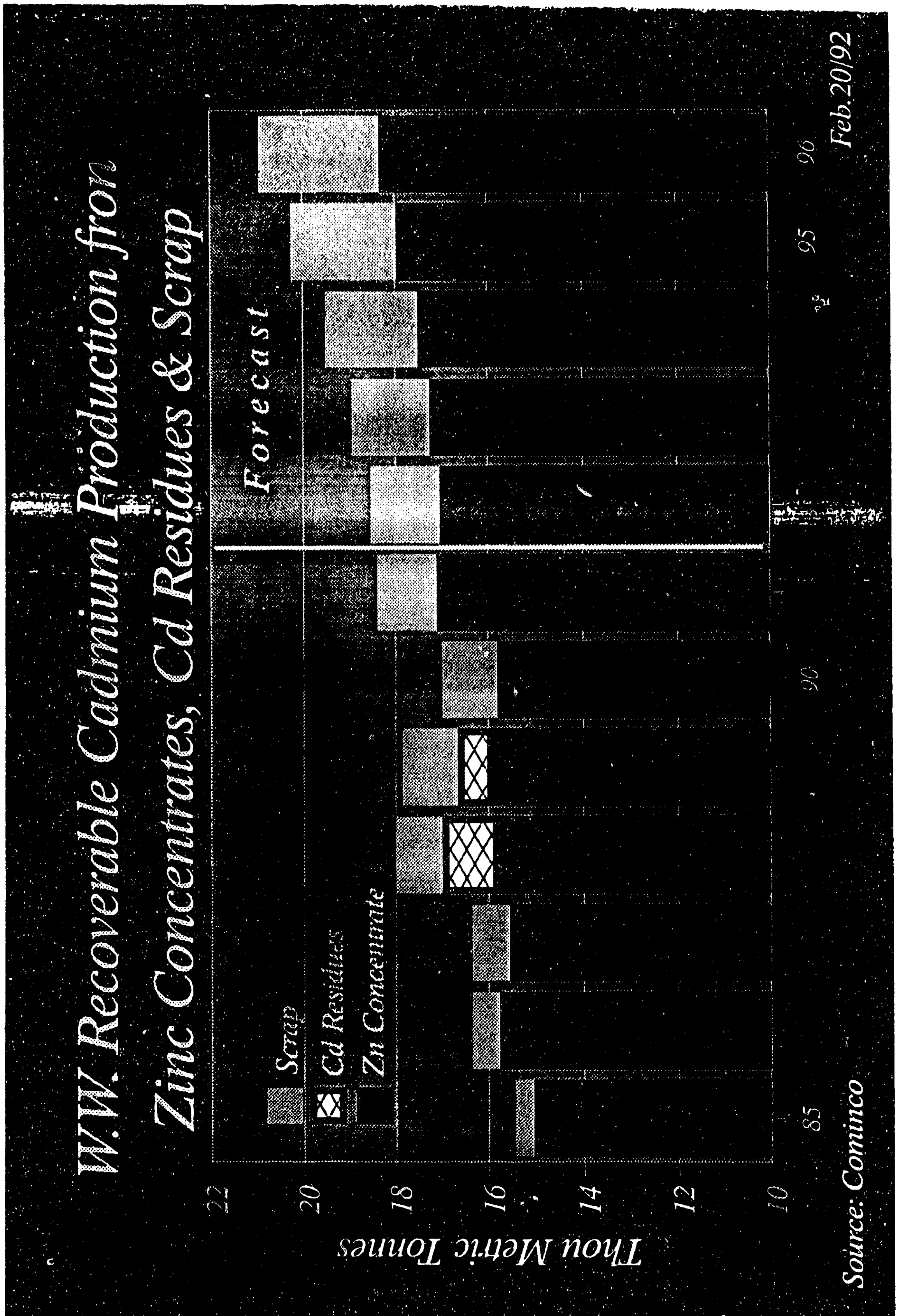
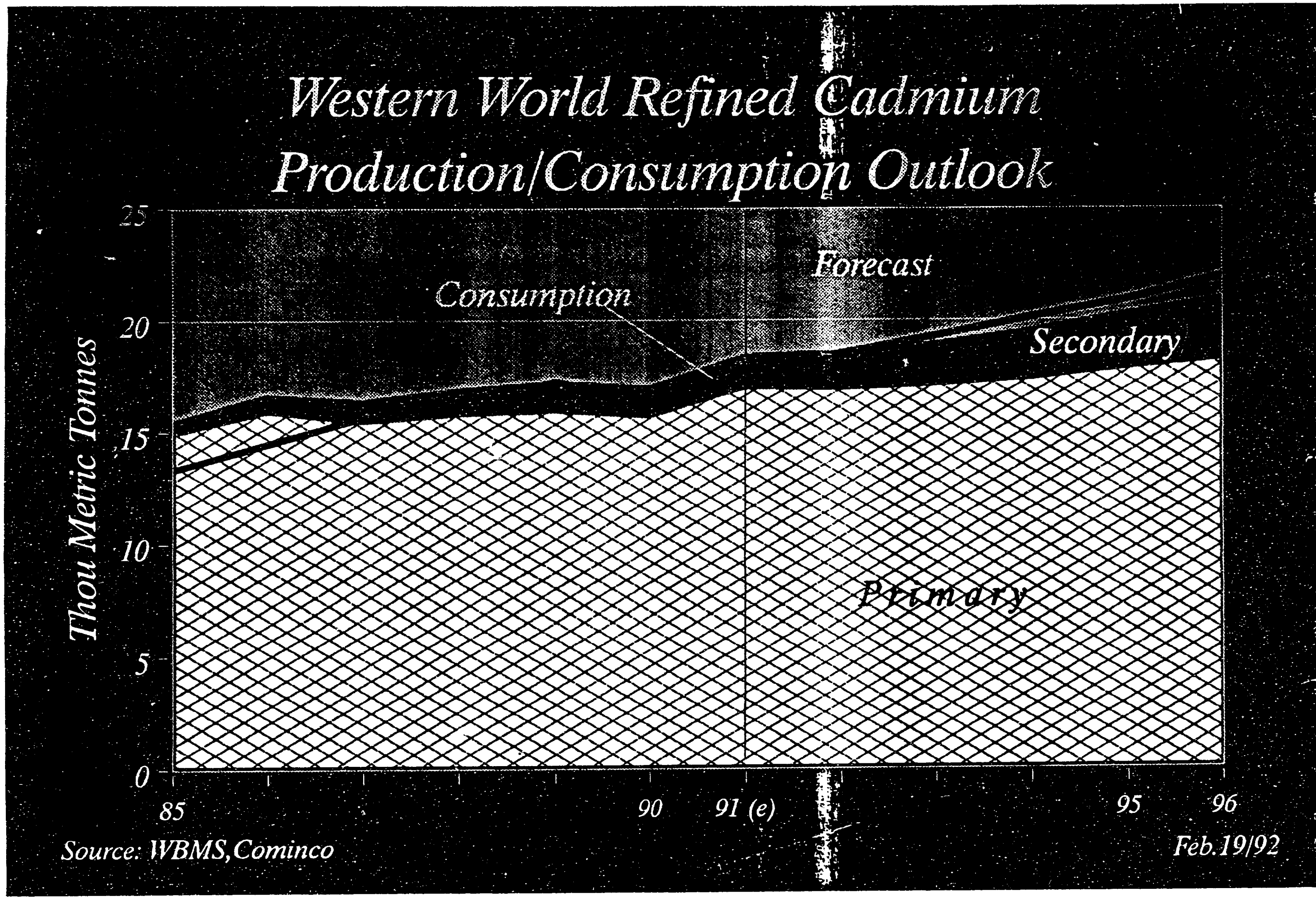

W.W. Recoverable Cadmium Production fro
Zinc Concentrates, Cd Residues & Scrap
Scrap
Cd Residues
Zn Concentrate
Forecast
Thou Metric Tonnes
22
20
18
16
14
12
10
85
90
95
96
Source: Cominco
Feb.20/92

Chart 12


Western World Refined Cadmium
Production/Consumption Outlook
Thou Metric Tonnes
25
20
15
10
5
0
Consumption
Forecast
Secondary
Primary
85
90
91 (e)
95
96
Source: WBMS,Cominco
Feb.19/92

CADMIUM USES

- BATTERY ELECTRODES
- PLASTICS ADDITIVES
- CORROSION COATINGS
- MINOR ALLOYING ELEMENT

CADMIUM RECYCLING

- NICKEL-CADMIUM BATTERIES
- ELECTROPLATING SLUDGES
- ELECTRIC ARC FURNACE DUST
- PROCESS WASTE

RECYCLING PROCESSES

- **PYROMETALLURGICAL**
  - Distillation
  - Oxidation
- **HYDROMETALLURGICAL**
  - Chemical
  - Electrochemical

NONFERROUS SMELTERS

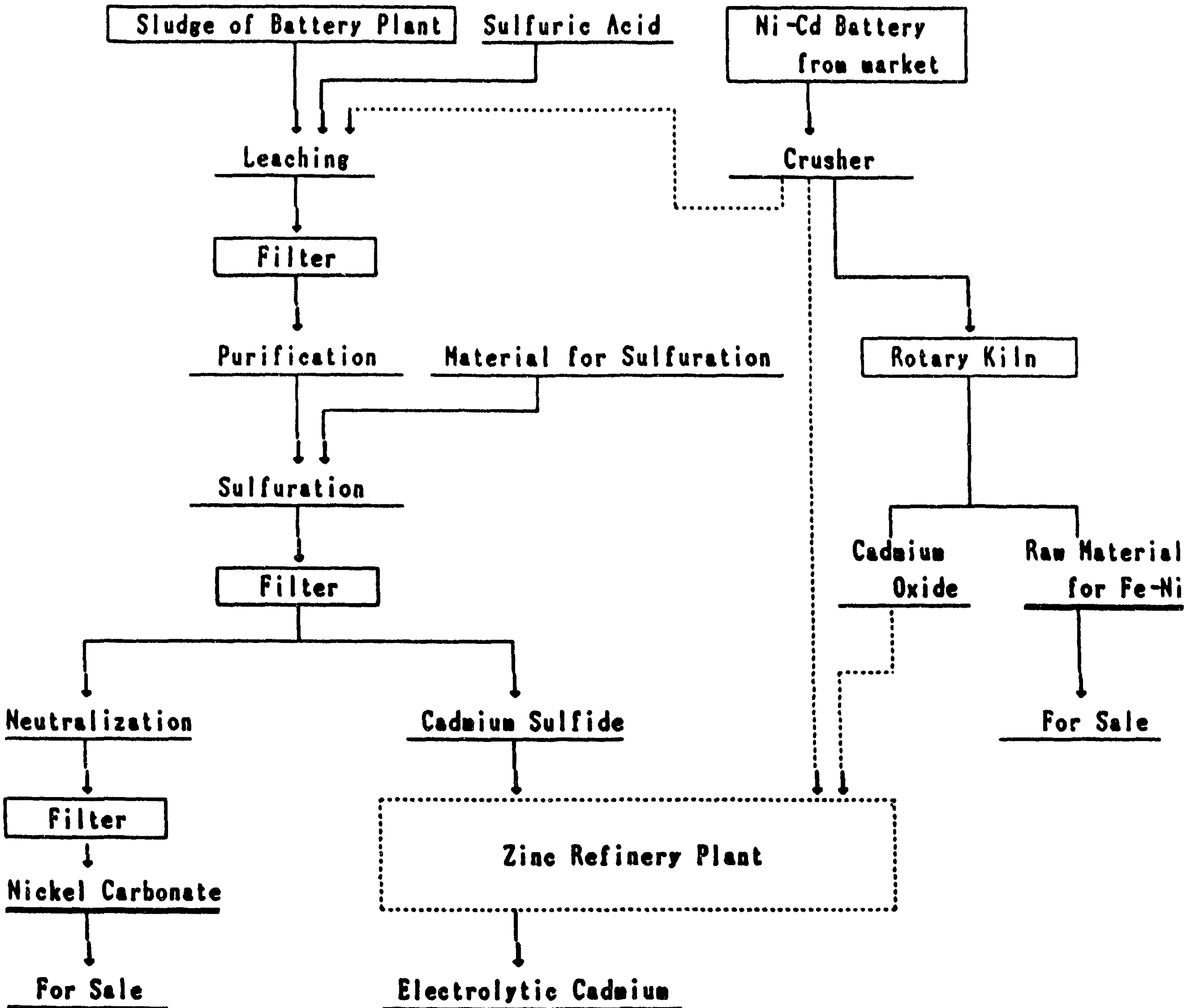
- ASARCO INC. (USA)
- BERZELIUS (GERMANY)
- BIG RIVER ZINC (USA)
- NUOVA SAMIN (ITALY)
- TOHO ZINC (JAPAN)

PYROMETALLURGICAL PLANTS

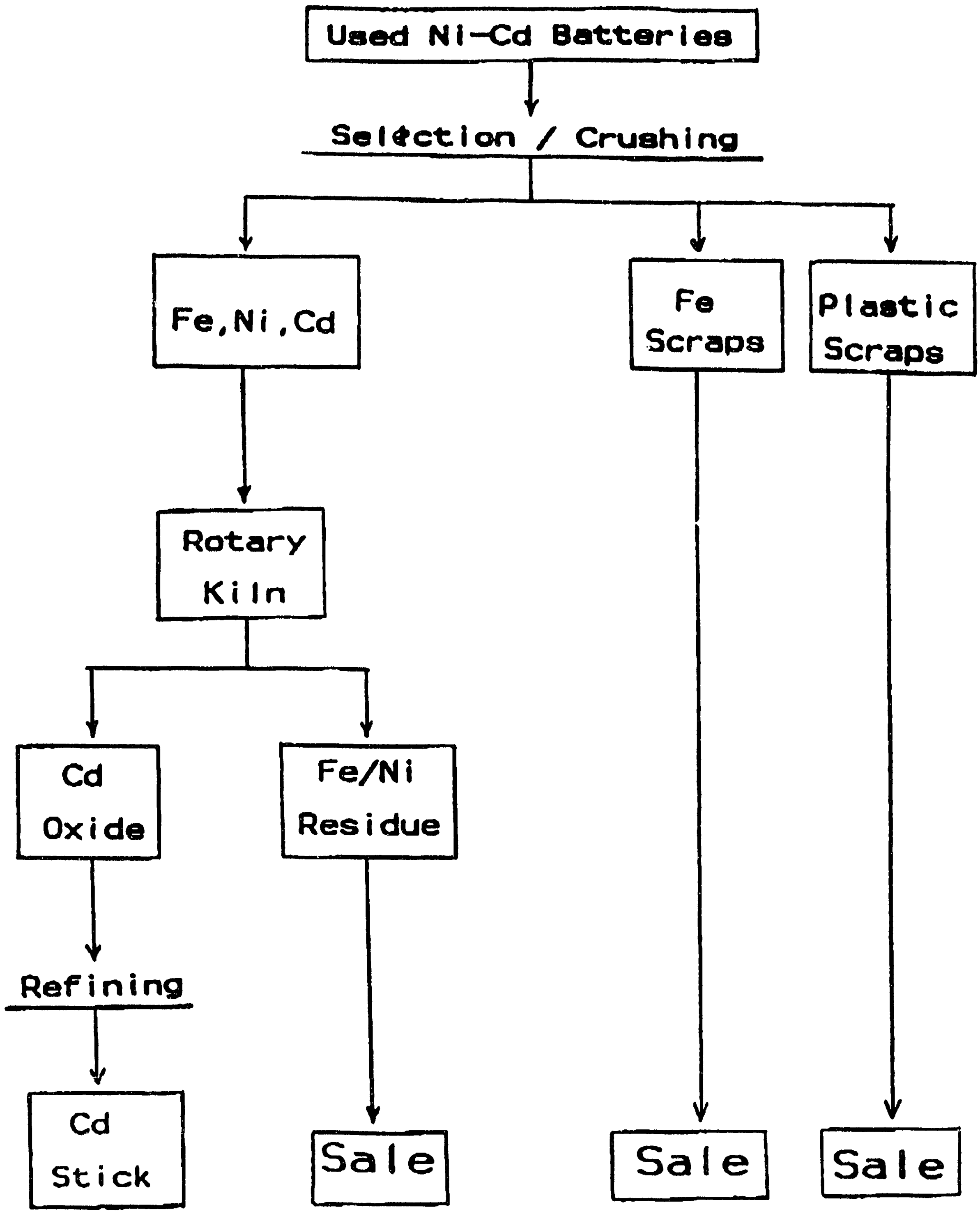
- JAPAN RECYCLE CENTER
- KANSAI SHOKUBAI
- TOHO ZINC COMPANY
- S.N.A.M. (FRANCE)
- S.A.V.A.M. (FRANCE)
- SAFT NIFE (SWEDEN)

TOHO ZINC

- Zinc and Lead Smelter
- Treat Ni-Cd Process Sludges
  - Wet Chemical Methods
  - Produce $NiCO_3$ and CdS
  - CdS Refined to Electrolytic Cd
- Recycle Spent Ni-Cd Batteries
  - Batteries Crushed
  - Rotary Kiln at 1000°C
  - Produce CdO and (Fe,Ni)O
  - CdO Refined to Electrolytic Cd
- 1,700 mt Cadmium per year

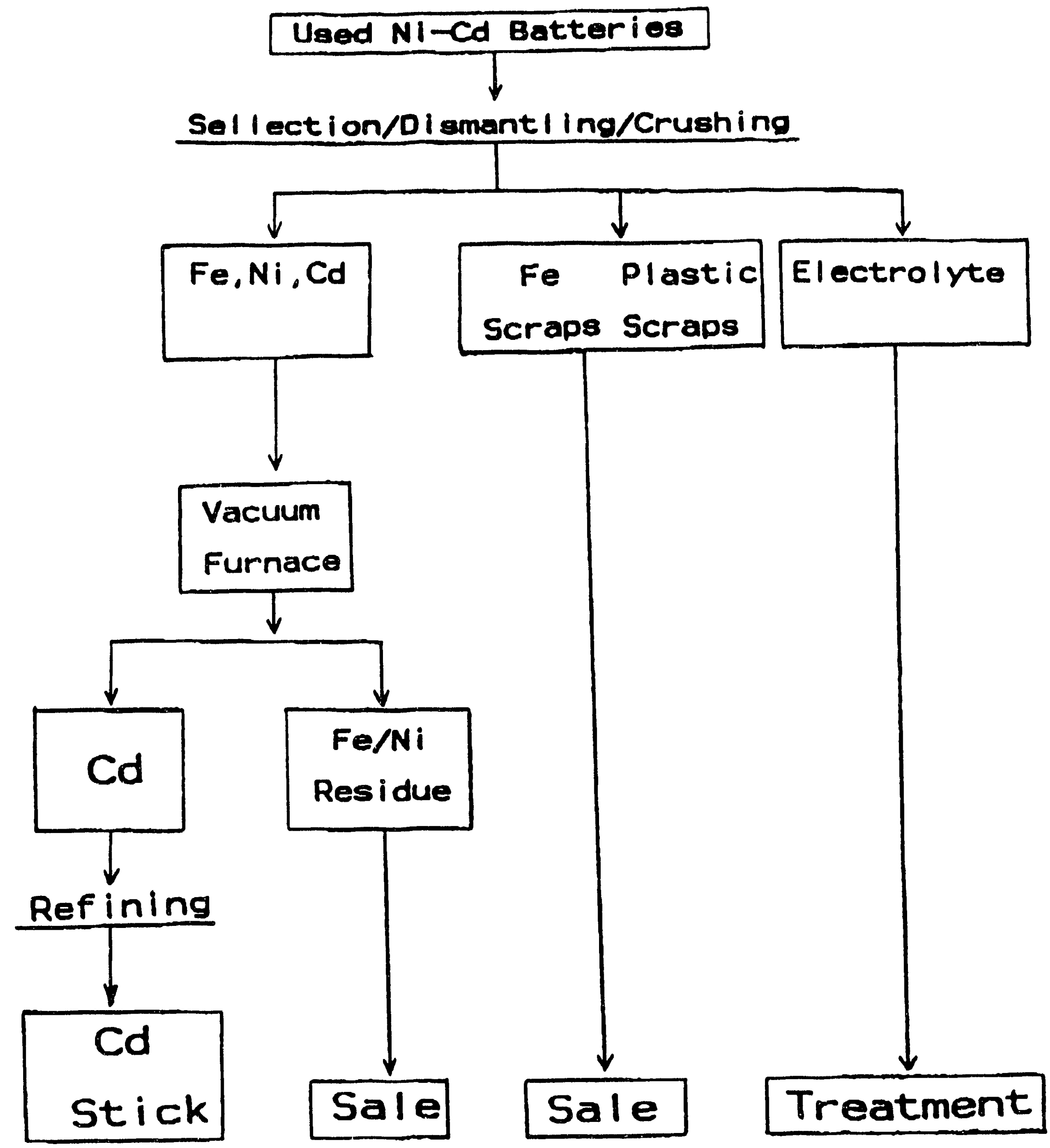

Sludge of Battery Plant
Sulfuric Acid
Ni-Cd Battery from market
Leaching
Crusher
Filter
Purification
Material for Sulfuration
Rotary Kiln
Sulfuration
Cadmium Oxide
Raw Material for Fe-Ni
Filter
Neutralization
Cadmium Sulfide
For Sale
Filter
Zinc Refinery Plant
Nickel Carbonate
For Sale
Electrolytic Cadmium

TOHO ZINC



Used Ni-Cd Batteries
Selection / Crushing
Fe,Ni,Cd
Fe
Scraps
Plastic
Scraps
Rotary
Kiln
Cd
Oxide
Fe/Ni
Residue
Refining
Cd
Stick
Sale
Sale
Sale

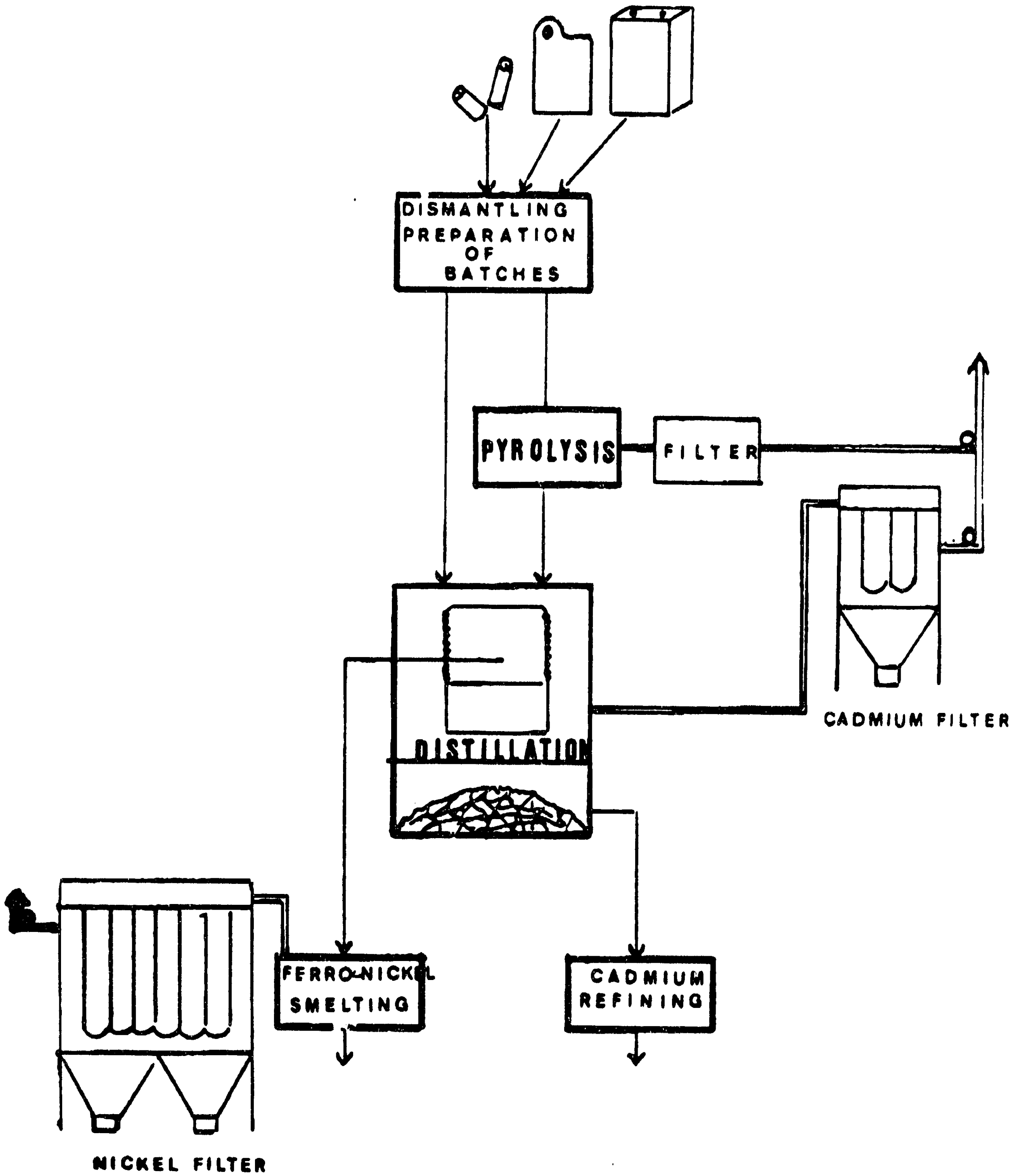
TOHO ZINC



JAPAN RECYCLING CENTER

SNAM - SAVAM

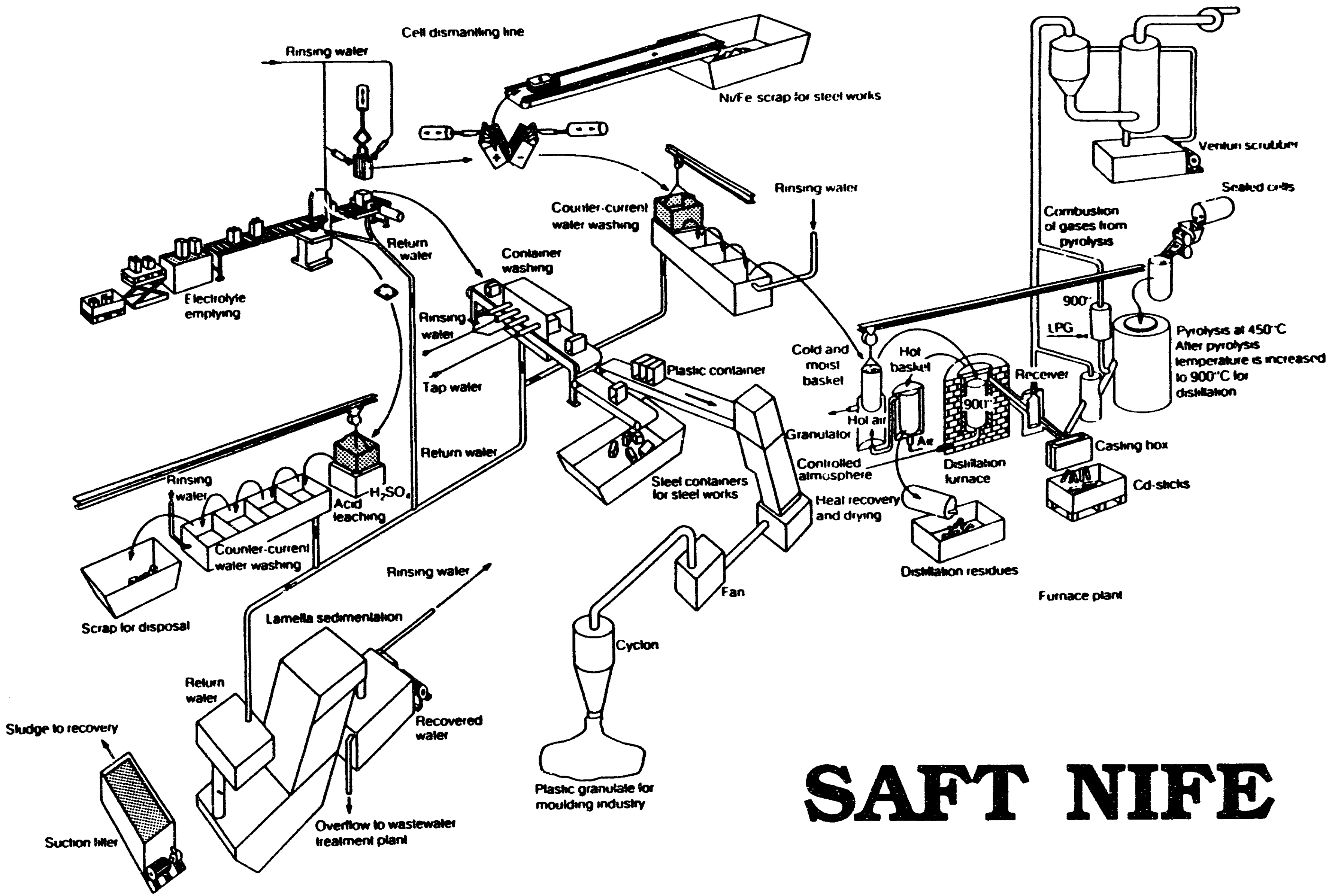
- Recycle Ni-Cd Batteries
- Batteries Dismantled
  - Positive Electrodes (Fe, Ni)
  - Casings & Separators (Plastic)
  - Negative Electrodes (Cd)
- Pyrolytic Treatment at 400°C
- Cadmium Distillation (99.95%)
- Refining or CdO Conversion
- 1200 mt Cd per year (SNAM)
  2200 mt Cd per year (SAVAM)


DISMANTLING
PREPARATION
OF
BATCHES
PYROLYSIS
FILTER
DISTILLATION
CADMIUM FILTER
FERRO-NICKEL
SMELTING
CADMIUM
REFINING
NICKEL FILTER

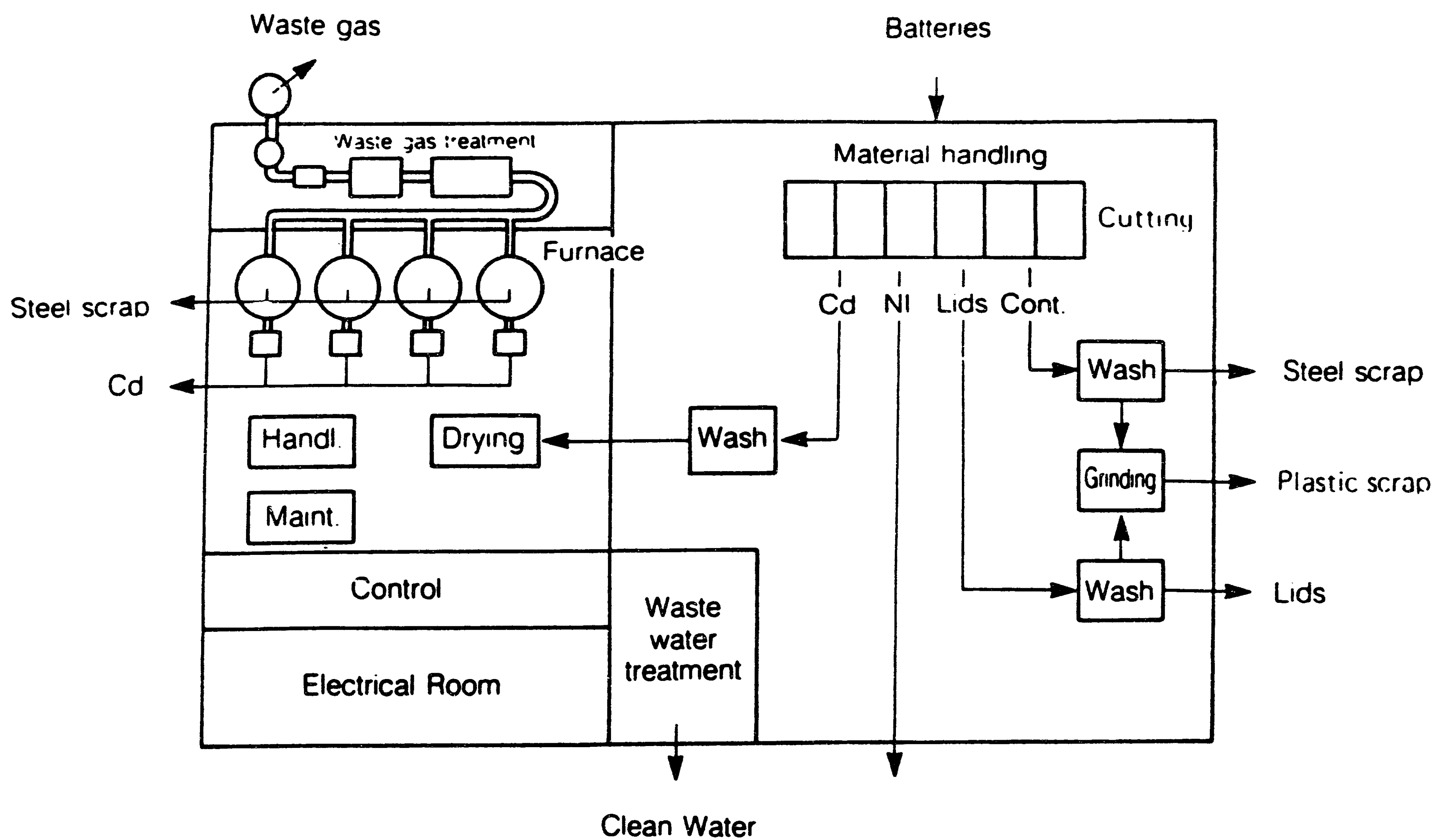
SNAM - SAVAM

SAFT NIFE

- **Recycle Ni-Cd Batteries**
- **Batteries Dismantled**
  - **Positive Electrodes (18% Ni)**
  - **Containers & Separators (Plastic)**
  - **Negative Electrodes (10-25% Cd)**
- **Sealed Cells Decomposed at 400°C**
- **Cadmium & Coke Heated to 900°C**
- **Cadmium Reduced, Distilled & Cast**
- **Electrolytically Refined**
- **200 mt Cadmium per year**


Cell dismantling line
Rinsing water
Ni/Fe scrap for steel works
Venturi scrubber
Sealed cells
Counter-current water washing
Rinsing water
Return water
Container washing
Combustion of gases from pyrolysis
Electrolyte emptying
Rinsing water
Tap water
900°
LPG
Pyrolysis at 450°C After pyrolysis temperature is increased to 900°C for distillation
Plastic container
Cold and moist basket
Hot basket
Receiver
Hot air
Granulator
Air
Casing box
Return water
Controlled atmosphere
Distillation furnace
Rinsing water
Acid leaching
H_2SO_4
Steel containers for steel works
Heat recovery and drying
Cd-sticks
Counter-current water washing
Distillation residues
Rinsing water
Fan
Furnace plant
Scrap for disposal
Lamella sedimentation
Cyclon
Return water
Sludge to recovery
Recovered water
Plastic granulate for moulding industry
Overflow to wastewater treatment plant
Suction filter

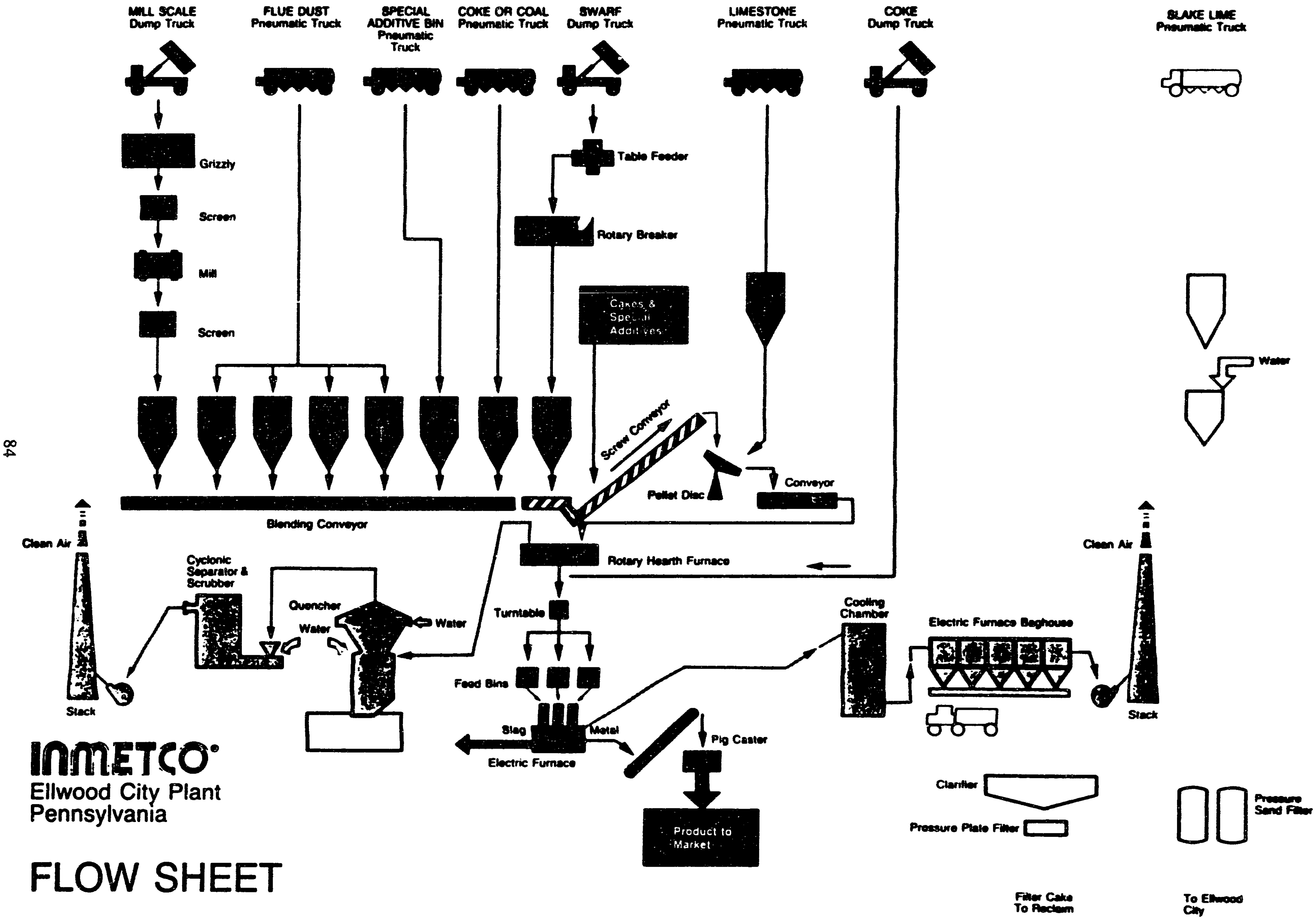
SAFT NIFE


Waste gas
Batteries
Waste gas treatment
Material handling
Cutting
Furnace
Steel scrap
Cd
Cd
Ni
Lids
Cont.
Wash
Steel scrap
Grinding
Plastic scrap
Wash
Lids
Handl.
Drying
Wash
Maint.
Control
Electrical Room
Waste water treatment
Clean Water

SAFT NIFE

INMETCO

- **Stainless Steel Recycler**
- **Residues Treated**
  - **Dusts, Scale and Swarf (Fe, Ni, Cr)**
  - **Spent Catalysts**
  - **Spent Ni-Fe and Ni-Cd Batteries**
  - **Electroplating Sludges**
- **Batteries Drained and Shredded**
- **Heated with Carbon at 1260°C**
- **Cd, Zn, Pb Fumed Off and Collected**
- **Refined by Horsehead Resources**

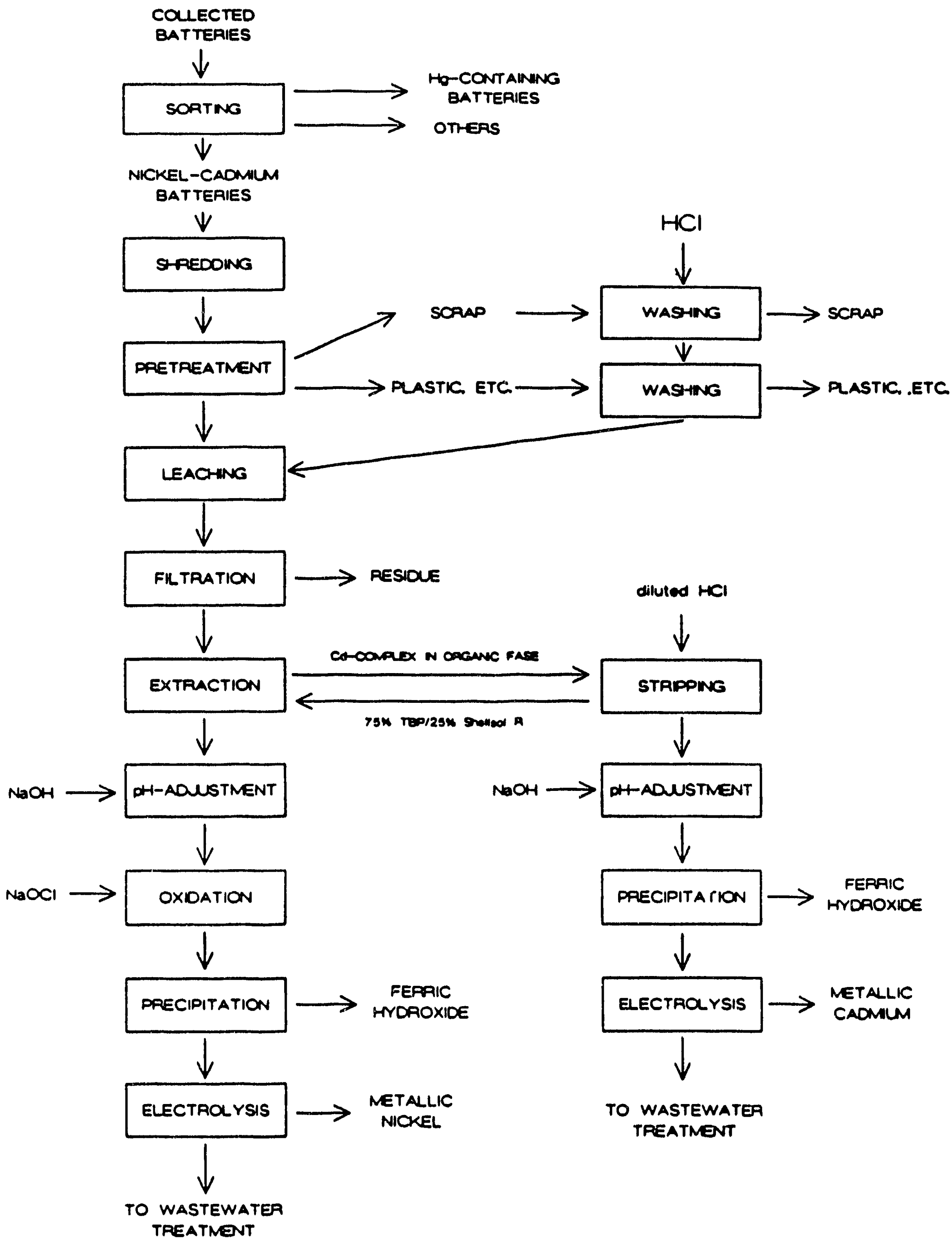

MILL SCALE Dump Truck
FLUE DUST Pneumatic Truck
SPECIAL ADDITIVE BIN Pneumatic Truck
COKE OR COAL Pneumatic Truck
SWARF Dump Truck
LIMESTONE Pneumatic Truck
COKE Dump Truck
SLAKE LIME Pneumatic Truck
Grizzly
Screen
Mill
Screen
Table Feeder
Rotary Breaker
Cakes & Special Additives
Water
Screw Conveyor
Pellet Disc
Conveyor
Blending Conveyor
Rotary Hearth Furnace
Clean Air
Stack
Cyclonic Separator & Scrubber
Quencher
Water
Water
Turntable
Feed Bins
Slag
Metal
Electric Furnace
Pig Caster
Product to Market
Cooling Chamber
Electric Furnace Baghouse
Clean Air
Stack
Clarifier
Pressure Plate Filter
Pressure Sand Filter
Filter Cake To Reclaim
To Ellwood City
INMETCO®
Ellwood City Plant
Pennsylvania
FLOW SHEET

HYDROMETALLURGICAL PLANTS

- T N O (NETHERLANDS)
- HYDROMETAL (BELGIUM)
- TOHO ZINC (JAPAN)

TNO

- Residues Treated
  - Electroplating Wastes
  - Ni-Cd Battery Process Wastes
  - Spent Ni-Cd Batteries
- Ni-Cds Sorted & Separated
- Acid Leaching & Solvent Extraction
- Treated with HCl to $CdCl_2$
- Electrolytically Refined to Cd
- Pilot Plant - 20 mt batteries per year


COLLECTED BATTERIES
SORTING
Hg-CONTAINING BATTERIES
OTHERS
NICKEL-CADMIUM BATTERIES
SHREDDING
HCl
PRETREATMENT
SCRAP
WASHING
SCRAP
PLASTIC, ETC.
WASHING
PLASTIC, ETC.
LEACHING
FILTRATION
RESIDUE
diluted HCl
EXTRACTION
Cd-COMPLEX IN ORGANIC FASE
75% TBP/25% Shellsol R
STRIPPING
NaOH
pH-ADJUSTMENT
NaOH
pH-ADJUSTMENT
NaOCl
OXIDATION
PRECIPITATION
FERRIC HYDROXIDE
PRECIPITATION
FERRIC HYDROXIDE
ELECTROLYSIS
METALLIC CADMIUM
TO WASTEWATER TREATMENT
ELECTROLYSIS
METALLIC NICKEL
TO WASTEWATER TREATMENT

TNO

HYDROMETAL

- Residues Treated
  - Nonferrous (Zn, Cu, Pb, Sn, Cd)
  - Pigments (Cd, Se, S)
  - Battery Sludges (Ni, Cd, Co, Zn)
- Solid / Liquid Separations
- Cost Justified By Major Metals
- Cadmium Sulphate Solution Produced
- Electrolytic Conversion to Cd Metal
- 100 - 200 mt Cadmium per year

APPENDIX G. Se INDUSTRY PERSPECTIVE (M. KING)

THE NON-FERROUS METAL INDUSTRY'S ROLE AS A SUPPLIER AND RECYCLER OF SELENIUM AND TELLURIUM FOR PHOTOVOLTAIC CELLS

MICHAEL G. KING
ASARCO Inc.

for the

SELENIUM-TELLURIUM DEVELOPMENT ASSOCIATION

MARCH 11, 1992

SELENIUM-TELLURIUM DEVELOPMENT ASSOCIATION

Company	Country	Primary Producer		
		Copper	Selenium	Tellurium
Asarco	USA	x	x	x
Centromin	Peru	x	x	x
Inco	Canada	x		
Kennecott	USA	x	x	
M&CP	UK			
Mitsubishi	Japan	x	x	x
MHO	Belgium	x	x	x
Noranda	Canada	x	x	x
Norddeutsche	Germany	x	x	
Outokumpu	Finland	x	x	
Pacific Rare Metals	Phillipines		x	x
Phelps Dodge	USA	x	x	x

WORLD COPPER PRODUCTION*

(SHORT TONS/YEAR)

	Mined	Smelted	Refined
Western Europe	370,000	600,000	1,800,000
Eastern Europe	1,870,000	1,920,000	2,260,000
Asia	610,000	1,540,000	1,650,000
Africa	1,320,000	1,200,000	900,000
USA	1,500,000	1,200,000	2,100,000
Canada/Mexico	1,070,000	690,000	720,000
South America	2,170,000	1,600,000	1,400,000
Australasia	540,000	220,000	280,000
China	400,000	470,000	500,000
TOTALS	9,850,000	9,440,000	11,610,000

* Approximations

COPPER PROCESSING

MINE (ores: 0.5 - 2.0% Cu)

↓

CONCENTRATOR (25-30% Cu)

↓

SMELTER (blister, anodes: 98-99% Cu)

↓

ELECTROREFINERY (cathodes: 99.99% Cu)

THE COPPER - SELENIUM, TELLURIUM RELATIONSHIP

Electrorefining of Copper

Anodes (98-99% Cu) Electrolysis --> Cathodes (99.99% Cu)

(Se,Te,Ag,Au,Ni,)
(As,Sb,Bi,Pb)

+

Mud (Slimes)*

Ag <--------- Separation Processes (Se,Te,Ag,Au) (As,Sb,Bi,Pb)
Au
Se
Te

+ Residues (As,Sb,Bi,Pb)

*COMPOUNDS PRESENT

Cu_2Se	CuAuSe
CuAgSe	Au_2Se
Ag_2Se	AgAuSe
Cu_2Te	CuAuTe
CuAgTe	Au_2Te
Ag_2Te	AgAuTe

USES OF SELENIUM

Annual Free World Production 1500-2000 tons

Application	% of Market
*Electrical	33
Pigments	19
Glass	20
Metallurgy	14
Agricultural/Biological	6

* Principal use is for photoreceptors as As_2Se_3

USES OF TELLURIUM

Annual Free World Production 200-250 tons

Application	% of Market
Metallurgy	55
Chemicals	25
Electrical	15
Others	5

PHOTOVOLTAIC INDUSTRY'S REQUIREMENTS FOR SELENIUM AND TELLURIUM

Assume 2 μm layer is deposited (≈ $10 g/m^2$ of Se, $8 g/m^2$ of Te)

Assume 10% cell efficiency ($100 w/m^2$)

$CuInSe_2$ Devices

Annual Capacity Added	Se Needed Tons/Year)	In Needed Tons/Year)
100 MW	11.1	8.8
1000 MW	111	88*

CdTe Devices

Annual Capacity Added	Te Needed (Tons/year)
100 MW	8.8
1000 MW	88

* World production of Indium is ≈ 100 tons/year

RECYCLING OF PHOTOVOLTAIC CELLS

Are Photovoltaic Cells Hazardous as Defined by TCLP?

	TCLP Limits	$CuInSe_2$	CdTe	
As(ppm)	5	<.1	<.1*	.16**
Ag(ppm)	5	<.05	<.05	<.05
Ba(ppm)	100	<.2	<.2	4.6
Cd(ppm)	1	.15	8.0	9.5
Cr(ppm)	5	.15	.14	.16
Hg(ppb)	200	<.5	<.5	<.5
Pb(ppm)	5	3.8	.13	.26
Se(ppm)	1	<.1	<.1	<.1
		Pass	Fail	Fail

* Large panels

** Small panels

ENVIRONMENTAL REGULATIONS

Subtitle C of RCRA requires that hazardous materials (Fail TCLP) can only be disposed of in a facility with a RCRA permit.

Non-ferrous smelters do not have RCRA permits.

$CuInSe_2$ passes TCLP - is not a hazardous material.

CdTe fails TCLP - classified as a characteristicly hazardous waste.

RCRA permits are not needed by non-ferrous smelters if they wish to receive unmanifested materials which fail TCLP as effective substitutes for feed stock or commercial chemicals used in the process.

Non-ferrous smelters purchase large quantities of silica and lime as fluxing agents.

Photovoltaic cells use glass (silica) substrates.

FLUX REQUIREMENTS OF NON-FERROUS SMELTERS

	Weight %		
	CaO	SiO_2	FeO
Typical copper smelter slag	2	30	45
Typical lead smelter slag	20	25	30

Estimated SiO_2 purchases for US Copper Industry:

400,000 - 500,000 tpy as fine sand.

100,000 - 150,000 tpy as granules (3/4")

TOTALS: 500,000 - 650,000 tpy

[Sodium tolerance (1%) = 5000 - 6500 tpy]

Lead smelters purchase little SiO_2

If panels are shipped out of the USA, the Basel Convention will become a factor.

PROJECTED GLASS RECYCLING BY NON-FERROUS SMELTERS

Typical glass composition:	Na_2O	15%
	CaO	9%
	SiO_2	72%
	MgO	3%
	Al_2O_3	1%

Assume: 800g glass/ft^2

1.6g Te/ft^2 (0.2% wt)

2.0g Se/ft^2 (0.25% wt)

Recycling of 100W of panels/year

Se recycled	11.1 tons		
Te recycled	8.8 tons		
Glass recycled	4400 tons	SiO_2 -	3,200 tons
		Na_2O -	660 tons

Recycling of 1000 MW of panels/year

Se recycled	111 tons		
Te recycled	88 tons		
Glass recycled	44000 tons	SiO_2 -	32,000 tons
		Na_2O -	6,600 tons

END

DATE
FILMED

1 / 13 / 93