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# Health, Safety and Environmental Issues Relating to Cadmium Usage in Photovoltaic Energy Systems

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## ABSTRACT

This paper discusses the current technology base and hazards associated with two promising thin-film photovoltaic cells that contain cadmium compounds - cadmium telluride (CdTe) and copper indium diselenide (CuInSe<sub>2</sub>). More specifically, this paper summarizes the toxicological information on cadmium (Cd) compounds; evaluates potential health, safety and environmental hazards associated with cadmium usage in the photovoltaics industry; describes regulatory requirements associated with the use, handling and disposal of cadmium compounds; and lists management options to permit the safe and continued use of these materials. Handling of cadmium in photovoltaic production can present hazards to health, safety and the environment. Prior recognition of these hazards can allow device manufacturers and regulators to implement appropriate and readily available hazard management strategies. Hazards associated with product use (i.e., array fires) and disposal remain controversial and partially unresolved. The most likely effects that could be expected would be those associated with chronic low-level exposures to cadmium wastes. Because of the general immobility of the cadmium present in these devices and availability of environmental and biomonitoring protocols, chronic hazards can be monitored, and remediated if necessary. Nevertheless, concern about cadmium hazards should continue to be emphasized to ensure that health, safety and environmental issues are properly managed. At the same time, the potential role that these systems can play in ameliorating some important health and environmental hazards related to other energy systems should not be ignored.

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## 1.0 INTRODUCTION

Photovoltaic energy systems can play a role in ameliorating some important health (e.g., radiation induced effects of nuclear waste disposal) and environmental (e.g., atmospheric pollution and global climate change) hazards related to energy production. Production, use and disposal of photovoltaic systems, however, are not without risk. In this context, this paper:

- (1) Discusses the current technology base for two promising thin-film options - cadmium telluride (CdTe) and copper indium diselenide (CuInSe<sub>2</sub>).
- (2) Summarizes the toxicological information on cadmium (Cd) compounds.
- (3) Evaluates potential health, safety and environmental hazards associated with cadmium usage in the photovoltaics industry.
- (4) Describes regulatory requirements associated with the use, handling and disposal of cadmium compounds.
- (5) Lists management options to permit the safe and continued use of these materials.

Since the CdTe and CuInSe<sub>2</sub> options are rapidly nearing commercial use, early identification of these issues is important so that effective remediation efforts, where necessary, can be implemented.

## 2.0 CELL FABRICATION

A variety of cadmium-containing photovoltaic devices are now under development; the most prominent are thin-film CdTe and CuInSe<sub>2</sub>. Great interest has focused on these materials because of their high efficiencies achieved in thin-film devices. Heterojunction cells made of CdS/CdTe have achieved 12.3% efficiency, and modules have reached 7.3% (Albright and Ackerman, 1989). Meanwhile, CdS/CuInSe<sub>2</sub> cells and modules have reached 14.3%, and 11.1%, respectively (Mitchell et al., 1988). These are among the highest efficiencies achieved by any

thin-film material so far and are major steps towards producing low cost photovoltaic systems (U.S. Department of Energy - DOE, 1987). In addition, CuInSe<sub>2</sub> modules supplied by ARCO Solar have been tested outdoors at the Solar Energy Research Institute for almost a year without any degradation; the best stability that has been demonstrated among the thin-films. Both CdTe and CuInSe<sub>2</sub> are nearing practical use as demonstrated by the award of two contracts for the first 20 kW systems. These awards were given by PVUSA to ARCO Solar (CuInSe<sub>2</sub>) and Photon Energy (CdTe) for systems to be in-place in 1990.

## 2.1 Cell Characteristics

Cadmium is used in the production of CdS/CdTe and CdS/CuInSe<sub>2</sub> devices.<sup>(1)</sup> The estimated quantities of cadmium used in the production of these devices vary as a function of material density, layer thickness, and material utilization efficiency. In Table 1, densities for single crystal materials are given. These represent the upper limits for materials found in thin-film cells because polycrystalline materials are generally less dense.<sup>(2)</sup>

Material	Density (g/cm <sup>3</sup> )	Cd wt%	Cd or
CdTe	5.9	46.8%	2.75
CdS	4.8	78	3.73

In each type of device, layer thickness may vary. CdTe layers made by Ametek Inc. are 2 microns thick (Meyers, 1988), while those made by Photon Energy are 6 microns (Albright

1 Cadmium as a constituent of CdTe is a necessary part of the device. In CuInSe<sub>2</sub> devices cadmium is present because CdS is usually chosen as an n-type heterojunction partner.

2 Because a layer that is 1 micron thick and 1 m<sup>2</sup> in area contains 1 cm<sup>3</sup>, the estimates given in the last column of Table 1 can be used to calculate the amount of Cd per m<sup>2</sup> for each micron of layer thickness; thus, a 1 micron layer of CdTe contains 2.75 g of Cd/m<sup>2</sup>, and a 6 micron layer contains 16.5 g Cd/m<sup>2</sup>.

and Ackerman, 1989). Similarly, CdS layers made by ARCO Solar for CuInSe<sub>2</sub> devices are 0.03 microns (Mitchell et al., 1988), while those made by Photon Energy are about 0.25 - 3 microns (Albright and Ackerman, 1989).

In the deposition of these layers, some materials are lost for various reasons including unwanted deposition on reactor walls. The ratio of material deposited on the final product to material supplied (feedstock) to the process is known as the utilization efficiency. Utilization efficiency can vary widely among different processing options. In Figures 1 and 2, feedstock required for CdTe and CdS layers of various thickness and various utilization efficiencies are shown. In general, processing options may be considered to be more mature when the cadmium-based layer is  $\leq 2$  microns and the material utilization efficiency exceeds 70%. Thus, the likely range of demands for CdS/CdTe and CdS/CuInSe<sub>2</sub> technologies are 1.8-13 g Cd/m<sup>2</sup> and 0.15 g Cd/m<sup>2</sup>, respectively. The low estimate presented for CdS/CuInSe<sub>2</sub> is appropriate because very thin CdS layers (300 angstroms) are already produced, and no technological improvements are needed to reach the 0.15 g Cd/m<sup>2</sup>. In contrast, technological improvements are still needed to produce thin CdTe cells.

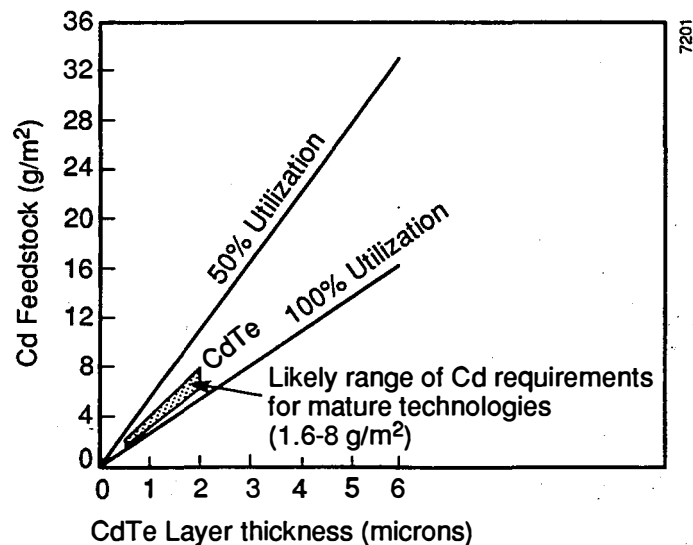


Figure 1. Quantity of cadmium feedstock material needed to make CdTe layers of differing thickness.



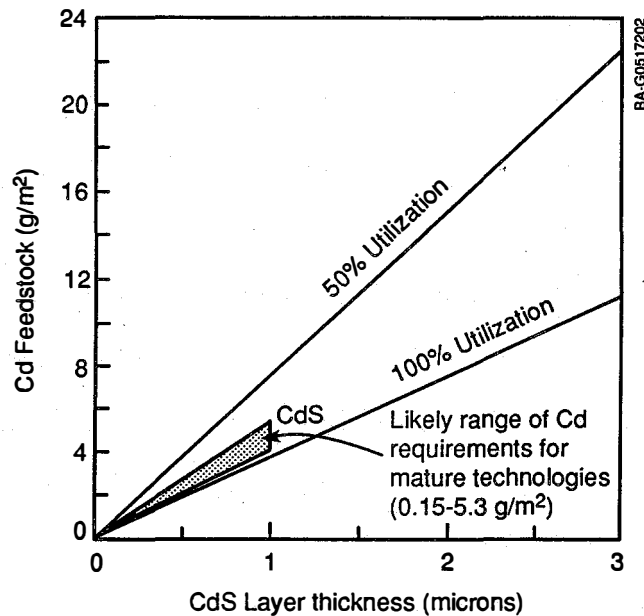


Figure 2. Quantity of cadmium feedstock material needed to make CdS layers of differing thickness.

## 2.2 Fabrication

Table 2 shows selected processing options used for cadmium telluride or cadmium sulfide deposition. Three commercially important options are electrodeposition, spraying and dip coating.

In electrodeposition, CdTe is deposited on substrates as the cathode of an electrolytic bath. The overall efficiency of this process is almost 90%. Depleted ions are replenished continuously by sacrificial anodes. The electrolyte is stable indefinitely, but losses due to leakage, spillage, or evaporation must be made up by periodically adding solution to the bath. The temperature of the solution is about 80°C, at which the vapor pressure of the feedstock materials is very low.

Spraying is a process in which a liquid containing the desired materials is atomized and deposited on a suitable substrate. The starter materials may be elemental Cd, CdTe, or CdS in suspension, or it may be a more complex chemical feedstock that reacts on contact with the substrate, as in spray pyrolysis. Spraying usually requires feedstock preparation steps, including CdTe or CdS synthesis, or the synthesis of their chemical precursors. It is considered to be a

low cost process because of its potential for continuous processing, high throughput, and low capital costs. In systems used for making large areas, a utilization efficiency approaching 90% should be possible.

Table 2. Selected Methods of CdS and CdTe		
Method	Materials	Status
Electrodeposition	CdTe	Near Commercial
	CdS	Near Commercial
Spraying (All Forms)	CdTe	Commercial
	CdS	Commercial
Screen Printing (Sintering)	CdTe	Commercial
	CdS	Commercial
Dip Coating	CdS	Near Commercial
Close Spaced Sublimation	CdTe	Experimental
Evaporation	CdTe	Experimental
	CdS	Near Commercial
Chemical Vapor Deposition	CdTe	Experimental
	CdS	Experimental

In the process chosen for this analysis - spray pyrolysis - compound formation occurs on the substrate. Chemicals carrying the desired materials, e.g., cadmium and sulfur, are sprayed onto a heated substrate. Spray pyrolysis has been used for the deposition of the CdS in CdS heterojunction and CdS/CdTe/ZnTe n-i-p photovoltaic cells (Meyers 1988). In these cell types, CdS is deposited from a solution of CdCl<sub>2</sub> and thiourea (H<sub>2</sub>NCSNH<sub>2</sub>). Since the efficiency of spray pyrolysis is very low (e.g., 5% - 10%), the commercial viability of this option is questionable.

Dip coating is an electroless chemical precipitation process in which CdS is deposited from a saturated solution. It can be used to make very uniform and thin (0.03 micron) CdS layers. It is considered low cost because of its simplicity and low capital costs. Although there

have been problems with this process due to unwanted deposition of CdS on exposed surfaces other than the substrate, recent work at the University of South Florida (Prof. Ting Chu, personal communication) suggests that utilization rates exceeding 75% could be attained in commercially mature systems.

### 2.3 Perspective on Cadmium Usage

To gain perspective on the potential use of cadmium in the photovoltaic industry, it is useful to examine the consumption of cadmium by other industries. In 1986, U.S. cadmium consumption for all uses amounted to approximately 4385 metric tons (See Figure 3). Its primary uses included: corrosion protection on steel products; yellow and red pigments; vinyl plastics; television tubes; and nickel cadmium batteries. Current cadmium usage in the photovoltaics industry is negligible. If annual CdS/CdTe production amounted to 10, 100 and 1000 MWp (assuming 10% electrical conversion efficiency for modules and  $13 \text{ g Cd/m}^2$ ), demand for cadmium would be 1.3, 13, and 130 metric tons, respectively. Thus, even at high production rates, the photovoltaic industry would still represent only a small fraction of the total U.S. consumption.

Another perspective can be obtained by comparing the quantity of cadmium present in these devices with that emitted by conventional energy systems. On a per energy-unit basis, over its operating lifetime, a photovoltaic module containing 1 g of cadmium will produce about 1 MWh of electricity. This is approximately equal to the quantity of cadmium released to the atmosphere by a coal-fired electricity generating plant producing 1 MWh of energy (U.S. DOE, 1989). In addition, the coal-fired facility will also release other hazardous materials including about 120 g As/MWh. Put in this context, the cadmium issue associated with these photovoltaic devices again seems rather small.

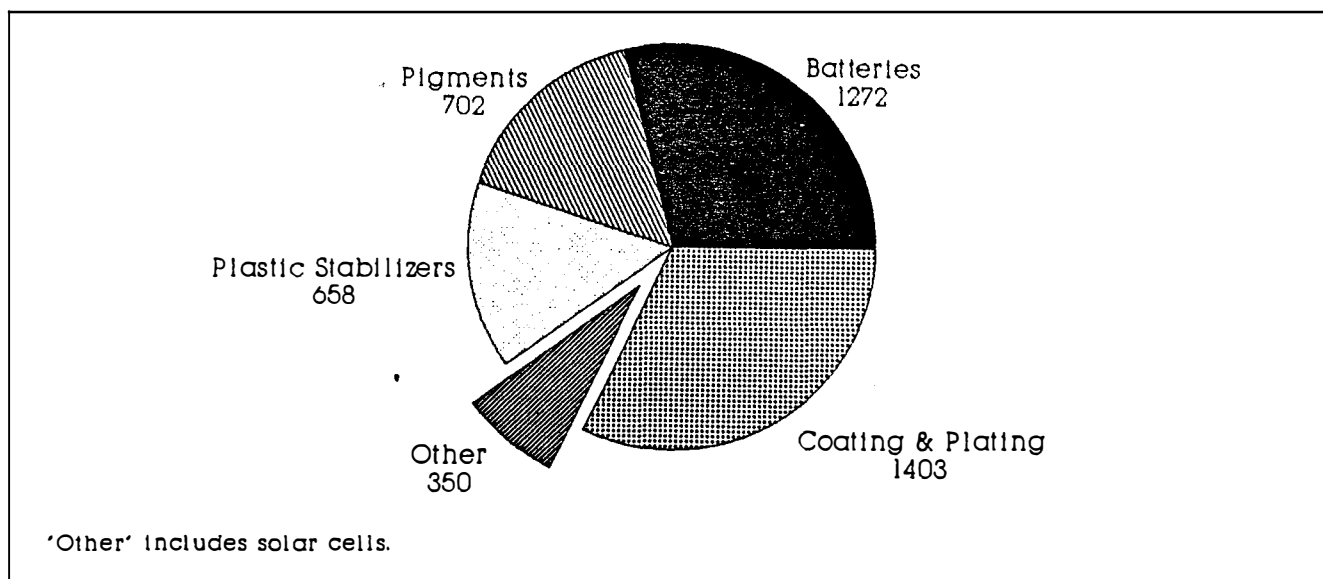


Figure 3. U.S. consumption of cadmium by product type in 1986.

Finally, it is important to note that there are other larger environmental sources of cadmium. They include: cadmium-containing phosphate fertilizers, Ni/Cd batteries (which contain more chemically mobile cadmium compounds), and direct and fugitive emissions from primary and secondary metal smelters.

### 3.0 HEALTH AND SAFETY ISSUES

Health, safety and environmental concerns from use of cadmium may arise during cell/module manufacturing, module use, and module disposal. The issues that exist include:

- (1) Inherent biological hazards associated with cadmium exposure.
- (2) Health and safety of workers at manufacturing facilities.
- (3) Health and safety of the public who could be exposed to waste products emitted from manufacturing facilities and to by-products associated with fires at consumer locations.
- (4) Environmental hazards arising from the disposal of waste by-products from manufacturing and module decommissioning.

The projected impacts of cadmium usage in the photovoltaics industry should be based on analyses of mature, rather than current or emerging, technologies. The history of thin-film development has repeatedly shown that cell and processing options mature as they near commercialization. But, to give full breadth to this analysis, process and layer thickness that are more characteristic of current technologies are examined. Thus, these discussions give a "worst" case perspective on the hazards. They are based on electrodeposition and spray pyrolysis plants manufacturing 10 MWp of CdTe photovoltaic cells per year.<sup>(3)</sup> These options represent extremes in cadmium usage because of their differences in deposition efficiency and assumed cell layer thickness. Similarly, because of the nature of the production process, they also span the range of potential health hazards associated with the use of cadmium compounds. Much of the information presented in these discussions is drawn from background papers prepared by Moskowitz et al. (1985), Moskowitz et al. (1989), and Moskowitz and Fthenakis (in preparation).

### 3.1 Cadmium Toxicology

Details on the pharmacology and toxicology of inorganic cadmium compounds are reviewed in documents prepared by international [e.g., World Health Organization (WHO), 1984; Commission of European Communities 1978], national [e.g., U.S. Environmental Protection Agency (EPA - 1984a, 1984b; Occupational Safety and Health (OSHA - 1988)], and trade (e.g., Leone et al., 1986; Lauwerys and Malcom, 1985) agencies and organizations. Numerous reviews have also been published in the technical literature (e.g., Friberg et al., 1985; Friberg et al., 1986). Potential health effects of both acute-short term and chronic long-term exposures to inorganic cadmium compounds are summarized below; the information presented is extracted from the aforementioned reviews. In theory, the toxicology and hazards from different cadmium compounds (e.g., cadmium chloride, cadmium sulfide, cadmium telluride, cadmium sulfide) will differ due to physical (e.g., solubility) and pharmacokinetic (e.g., absorption across

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3 Based on a total cell area of 110,000 m<sup>2</sup>, 10% solar to electric efficiency, 10% loss of active area due to cell separation and metal interconnects, and AM1 conditions.

the gastrointestinal tract) factors. However, due to the general lack of compound specific information, the toxicology summaries presented below are for all inorganic cadmium compounds. Potential variations in health consequences by compound are now being examined.

Short-term inhalation of cadmium dusts and fumes at concentrations ranging from 200-500  $\mu\text{g}/\text{m}^3$  may cause symptoms of metal fume fever. More intense exposure (40 to 50  $\text{mg}/\text{m}^3$  for 1 hour, 9  $\text{mg}/\text{m}^3$  for 5 hours, and 5  $\text{mg}/\text{m}^3$  for 8 hours) may lead, after a latent interval of several hours, to more serious effects resulting from severe bronchial and pulmonary irritation. Death may result within 7 to 10 days after exposure. Persons who survive such acute exposure episodes may recover without permanent damage, but it is possible that repeated episodes of acute or subacute pneumonia may favor the development of lung emphysema.

Acute oral intoxication may arise from ingestion of cadmium by workers who eat, smoke, or bite their fingernails in the work place. Symptoms are those of gastrointestinal tract irritation including nausea, vomiting, abdominal cramps and diarrhea. These symptoms may occur 15-30 minutes after exposure to a dose of 15 - 30 mg. A single oral dose exceeding 300 mg may be fatal.

The principal effects of continued exposure to low levels of cadmium are on the kidneys, lungs and bones. In the body, cadmium accumulates in the renal cortex where it is effectively retained. The renal cortex is generally accepted to be the critical organ for cadmium accumulation, and proteinuria (abnormal excretion of low molecular weight proteins) to be one of the classical effects of cadmium poisoning. The evolution of measured renal proteinuria to more severe renal dysfunction is usually slow. The latent period before the clinical observation of excessive proteinuria, depends on the intensity of exposure, but in general exceeds 10 to 20 years of exposure. The level of cadmium in the kidney cortex associated with the increased urinary excretion of specific indicator proteins (e.g., immunoglobulin, and  $\text{B}_2$ -microglobulin) in approximately 10% of the population is about 200  $\mu\text{g}$  Cd per g wet weight of the kidney cortex. The health significance of increased urinary excretion of specific proteins in the absence of other evidence of kidney dysfunction is not well defined.

Absorption of cadmium by the body is about ten times greater from inhalation than through ingestion. WHO has calculated that a person ingesting 248 ug/day (or by analog inhaling 24.8 ug Cd/day)<sup>(4)</sup> would achieve a critical kidney concentration of 200 ug/g at age 50. With daily ingestion intake limited to a range of 57-71 ug or daily inhalation (assuming no cadmium ingestion) limited to 5.7-7.1 ug Cd/day<sup>(5)</sup>, the renal cortex would receive only about a quarter of the critical concentration.

Various types of lung disturbances including emphysema, obstructive lung disease, pulmonary fibrosis, and lung cancer, have been found in workers chronically exposed to cadmium dust and fume. Measured exposure levels between 0.5 and 5 mg Cd/m<sup>3</sup> have been associated with increased mortality from respiratory disease among Swedish battery and U.K. cadmium workers. EPA has concluded that inhaled inorganic cadmium compounds are probable human carcinogens. This determination was based on limited evidence from human epidemiologic studies and "sufficient" evidence of carcinogenicity in rats and mice. In this context, EPA has estimated that lifetime exposure to  $6 \times 10^{-4}$  ug Cd/m<sup>3</sup> would result in a lifetime cancer risk of  $1 \times 10^{-6}$ ; the parallel estimate prepared by OSHA is  $4.3 \times 10^{-4}$  ug Cd/m<sup>3</sup>. At present, there are no human clinical or animal experimental data to indicate that ingestion of cadmium results in cancer.

Chronic exposure to excessive cadmium levels may also cause bone disease characterized by softening, bending and reduction in bone size. Excessively exposed individuals may complain of pain in the back and extremities, and difficulties in walking. It is generally thought, however, that the bone changes are secondary to renal dysfunction. Such pronounced effects were observed in Japan, where there was an outbreak of Itai-Itai bone disease associated with unusually large exposure levels; estimated dietary intake ranged from 300-600 ug Cd/day. In this case, the disease affected some women in their sixth decade who had borne several children. Although the etiology of the disease is not yet fully understood, it is thought that

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4 Breathing air containing 1.2 ug Cd/m<sup>3</sup> for 24 hours/day would result in an intake of 24.8 ug Cd/day.

5 Breathing air containing ~0.3 ug Cd/m<sup>3</sup> for 24 hours/day would result in an intake of 6 ug Cd/day.

cadmium exposure due to environmental pollution in the area, in association with various nutritional deficiencies, may have been an important contributing factor.

Other possible effects include hypertension, nausea and nasal irritation. In some workers exposed to cadmium, loss of sense of smell has also been observed.

### 3.2 Occupational Health

Hazards to worker (as well as public) health presented by cadmium compounds in various processing steps vary as a function of compound specific toxicity, exposure mode and physical state of the compound. Differences in toxicity among various cadmium compound were highlighted in the previous section. Possible exposure pathways include inhalation, ingestion and dermal absorption. In production facilities, workers may be routinely or accidentally exposed to cadmium compounds through the air they breathe, as well as by ingestion from hand-to-mouth contact. Of these two pathways, inhalation is probably the most important because of the larger exposure potential, and higher absorption efficiency of cadmium compounds through the lung than the gastrointestinal tract. In general, absorption through the skin is not recognized to be a large source of exposure to cadmium compounds. The physical state in which the cadmium compound is used and/or released to the external environment is another determinant of risk. Processing options in which cadmium compounds are used or produced in the form of fine fumes or particles, especially those  $\leq 5$  microns diameter in size which are readily inhalable and penetrate deep into the lung, present larger hazards to health. Similarly, processing options which use/produce volatile or soluble cadmium compounds also must be more closely scrutinized (note that neither cadmium sulfide nor cadmium telluride are soluble as pure compounds in water). Sources of possible exposures, and background information of the processes themselves, are given below.

In electrodeposition, the principal cadmium-related health hazards to workers are from dust generated during feedstock preparation, and from fine particles proximate to the



electrolytic baths. Although this is a potential hazard, biological monitoring data (as described in Section 5.1) collected at Ametek, where electrodeposition is currently used, show that these types of exposures can be maintained at levels which should not present risks to workers. Accidental release of the liquid from a bath and subsequent cleanup may also present hazards to worker health.

In spray pyrolysis a large quantity of by-products including fine particles will be generated since it has a very low utilization efficiency (e.g., 5% - 10%). Some of these materials will deposit on the reactor wall, requiring periodic scraping or chemical removal and cleaning. The large remaining fraction will be contained in the exhaust gas. In this type of process, hazards to workers may arise from feedstock preparation, fume/vapor leaks, and maintenance type operations (e.g., scraping and cleaning). Because of the acute health hazard associated with cadmium fumes that could be accidentally released from a spray pyrolysis unit, special precautions are needed to protect worker health.

### 3.3 Public Health

Public health may be affected principally from chronic exposure to cadmium compounds released to the environment as a by-product of different manufacturing steps or as a waste from the uncontrolled disposal of spent photovoltaic modules at the end of their useful life. In addition to potential chronic low-level exposures, concern has also been expressed about hazards associated with the release of cadmium compounds during the accidental combustion of a CdTe array during a building fire. Potential exposure pathways of interest include food, water and air. As discussed in the previous sections, the actual hazard presented by these activities will also vary by compound. Again, those that are more physically and biologically mobile will tend to present greater hazards.

Alternate fabrication options may affect the environment in different ways. Electrodeposition is a very efficient process; the technical literature suggests a process efficiency

of approximately 90%; the remaining 10% is lost during rinsing or from product defects. Thus, of the 590 kg of  $\text{CdSO}_4$  and 450 kg of  $\text{TeO}_2$ <sup>(6)</sup> required annually, only a routine maximum of 11 kg/yr of Cd and 12 kg/yr of Te, mostly as ions in solution, must be recycled or directly disposed. If the electrodeposition batch becomes contaminated, or if a spill occurs, then additional materials may need to be treated. Effluent limitations for this industry will probably be similar to those promulgated by EPA under authorities of the Clean Water Act (CWA - see Section 4.2) for cadmium battery manufacturing (EPA, 1984c) or electroplating of common metals (EPA, 1984d). EPA CWA effluent limitations for new cadmium battery manufacturing (specific to anode electrodeposition) limit the industry to a maximum peak discharge of 7.03 mg Cd/kg of cadmium processed per day for direct discharges into surface waters and of 40 mg Cd/kg for discharge into publicly owned sewage treatment plants. Monthly average limits are 2.81 mg Cd/kg of cadmium processed per day for surface water discharges and 16 mg Cd/kg for treatment plant disposal. If effluent concentrations from the electrodeposition process option exceeds these limits, they will need to be treated prior to discharge. These effluents could be treated in an on-site  $\text{Cd}^{++}$  treatment station similar to the one in which effluents from CdS spray pyrolysis could be routinely treated (see below).

Because of the low efficiency in spray pyrolysis, large quantities of cadmium-containing wastes may be produced: assuming a 10% utilization efficiency, about 950 kg of  $\text{CdCl}_2$ ,  $\text{CdO}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and thiourea by-products (e.g.,  $\text{SO}_2$ , urea) would be generated. Some of this material will be deposited on the reactor walls, but most of it will be in a gaseous form in the exhaust stream. Under these assumptions, an 8 hr/day operation for 250 days a year, would produce emission flow rates up to 0.45 kg/hr. According to the New York State Department of Environmental Conservation Guidelines (1987), these emissions would need to be reduced by at least 60% to 0.2 kg/hr to meet the discharge limitations imposed by the state.<sup>(7)</sup>

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6 The annual material use for a 10 MWp electrodeposition process is about 590 kg  $\text{CdSO}_4$  and 450 kg of  $\text{TeO}_2$  (assuming 90% process efficiency, 2  $\mu\text{m}$  CdTe layer), and for pyrolysis is about 680 kg of  $\text{CdCl}_2$  and 280 kg of thiourea (assuming a 10% deposition efficiency and 0.1  $\mu\text{m}$  CdS layer).

7 There are no federal atmospheric emission standards for cadmium compounds.

Large-scale disposal of spent photovoltaic devices will occur ~20 to 30 years after their initial installation. In the decommissioning of these devices, the principal concern will be associated with the presence of cadmium in the solid wastes. Although most of the solid waste would be nonhazardous and could be placed simply at modest cost in a municipal landfill, the presence of more than 100 kg of cadmium in these devices could trigger requirements under the Resource Conservation and Recovery Act (RCRA - see Section 4.3) which would require disposal in a controlled hazardous waste landfill at much larger cost. In principal, such triggering would occur only for disposal from a large, central-station application or from a repository of utility-controlled decentralized units. In the case of disposal in a municipal waste-stream, hazards to the public could arise from combustion and mobilization of cadmium compounds to the atmosphere or from leaching of landfilled waste and mobilization of cadmium compounds into ground and surface waters and possibly terrestrial foodchains. Although these hazards are probably not large, they require further analysis.

Public health hazards associated with the release of cadmium from a CdTe/CdS module during a fire have aroused great interest. This question has recently been examined in some detail by Moskowitz and Fthenakis (in preparation). In their analyses they evaluated the release, atmospheric transport and risk associated with the mobilization to the atmosphere of cadmium present in CdTe modules. Fire scenarios involving a residential array of 5 kW<sub>p</sub>, a commercial roof-top array of 100 kW<sub>p</sub>, and a 500 kW<sub>p</sub> ground-mounted sub-station were examined. Of these scenarios, the first two are the most likely since residential and commercial buildings are often involved in fire related incidents; the third is highly improbable since it is difficult to conceptualize a mechanism leading to the complete combustion of a large ground-based array field. Nevertheless, as a "worst case" exercise, all three scenarios were evaluated by defining the source term, examining dispersion of emitted materials in the atmosphere, and estimating health risks associated with exposure to emitted compounds.

Two different assumptions were made to estimate the quantity of material released: (1) 100% of CdTe material present in the photovoltaic array fields is released to the atmosphere as

dust and fumes; and, (2) 10% of CdTe is liberated to the atmosphere. The latter is more likely because of the high melting point of CdTe (1041°C).

To estimate the ground-level ambient atmospheric concentrations from these releases, a standard Gaussian atmospheric dispersion model was used. In the modeling efforts the following major assumptions were made: Vapor and fume densities are approximately equal to the CdO density; releases for all scenarios last about 5 min; and, "worst" meteorological conditions are represented by a Pasquill stability class F and a constant wind velocity of 1 m/s.

If photovoltaic material is released in the form of either fume or vapor, this release will last only a few minutes and, consequently, outdoor human exposures, if any, will be of about the same duration. Given the short duration of the predicted exposures, the OSHA/NIOSH Immediately Dangerous to Life or Health (IDLH) level (referring to 30 min exposures) is best used as a measure of hazard for comparison with the calculated ground-level ambient concentrations. The IDLH level for cadmium compounds (e.g., CdO fumes) is 40 mg/m<sup>3</sup>.

Results of the modeling exercises are presented in Figures 4 and 5. As shown, releases of fumes during fires in residential buildings equipped with 5 kW<sub>p</sub> arrays will not result in hazardous ground-level concentrations. Releases of CdTe from the larger systems may produce a plume which could present health hazards to the public in the immediate vicinity of the system, if more than 10% of the CdTe is liberated. However, because of the high melting point of this compound, this is unlikely.

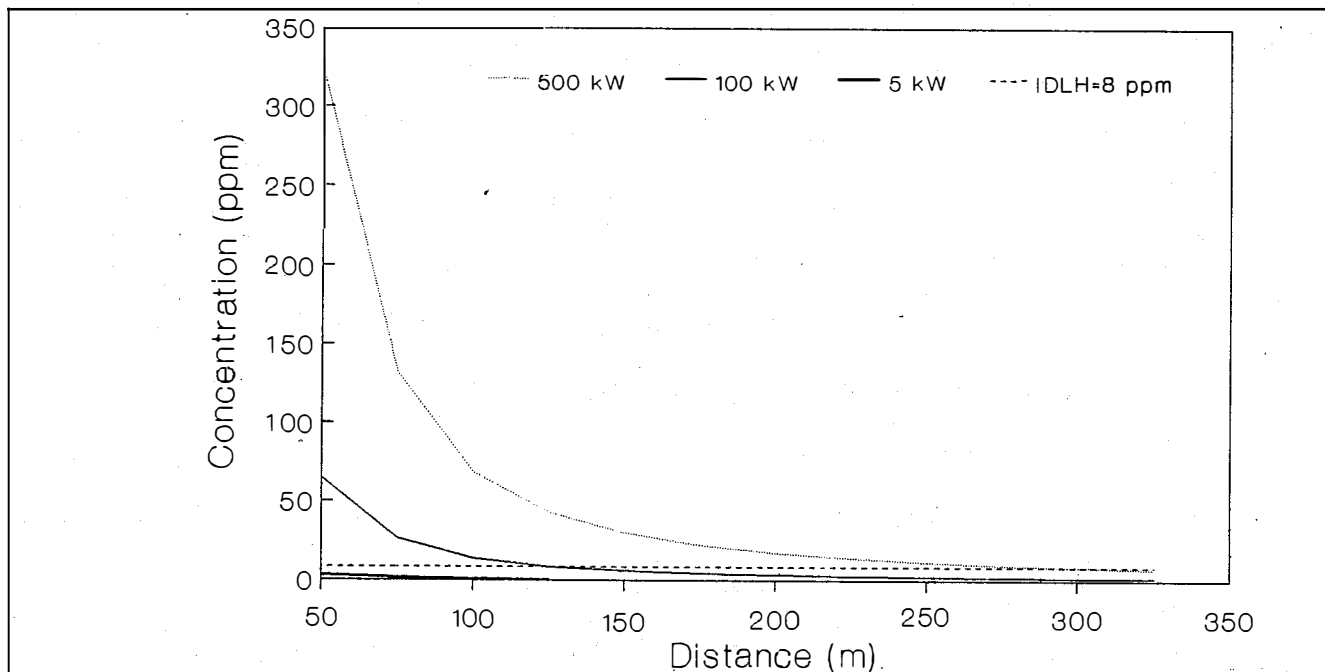


Figure 4. Estimated ground-level concentrations of cadmium from a fire consuming CdTe modules of different sizes - 10% release.

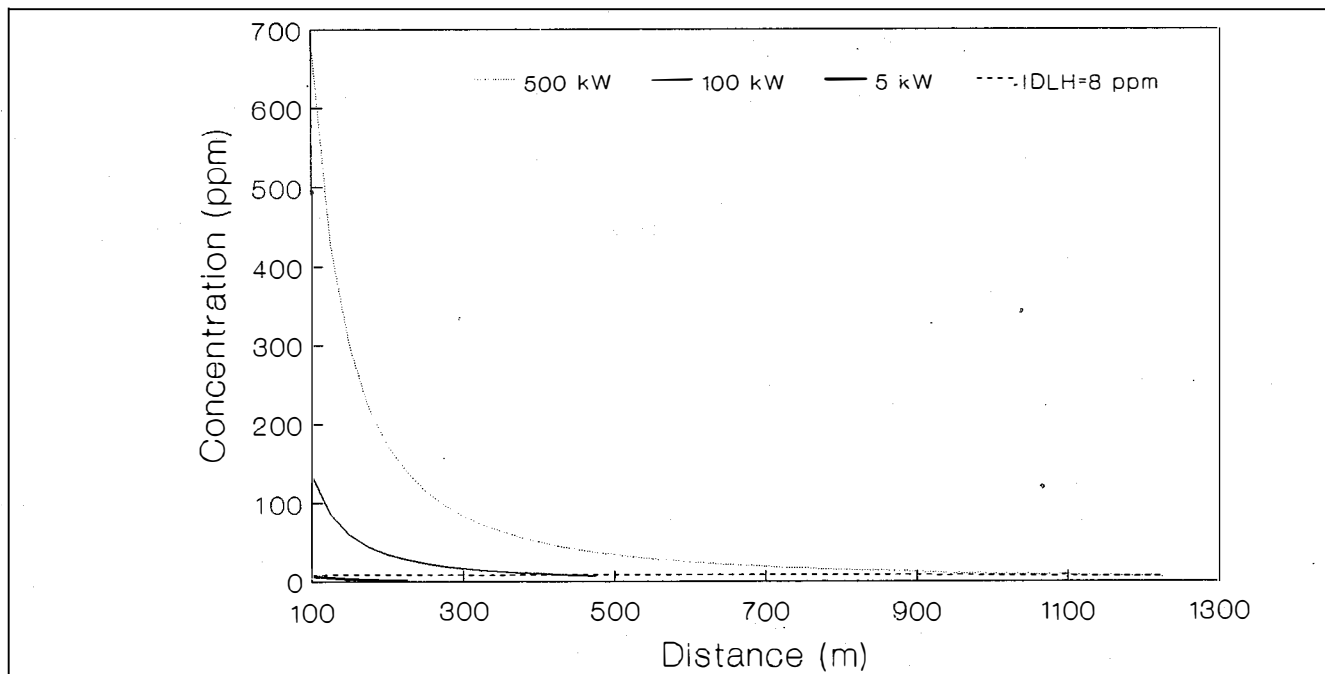


Figure 5. Estimated ground-level concentrations of cadmium from a fire consuming CdTe modules of different sizes - 100% release.

## 4.0 Federal Statutes and Regulations

Federal statutes and regulations protect health by controlling environmental releases of liquid, solid and gaseous materials to the environment and by controlling work practices and worker exposures to toxic and hazardous materials. Cadmium-specific environmental, health and safety requirements of importance to the photovoltaics industry are summarized below.

### 4.1 Clean Air Act

The Clean Air Acts of 1970 and 1977 charged EPA with the regulatory responsibility to develop air quality criteria and standards and to establish national emission standards - called New Source Performance Standards - for air pollutant discharges from many industrial categories. It also provided the Agency the authority to control discharges - called Hazardous Air Pollutants - that presented significant risk to human health . In this context, EPA is considering the need to establish National Emissions Standards for Hazardous Pollutants (NESHAP) for cadmium compounds (EPA, 1985a). If such standards are promulgated, however, they would likely apply only to large sources such as glass smelters and should not be directly applicable to the photovoltaics industry.

### 4.2 Clean Water Act

The Clean Water Act of 1977 (CWA) authorized EPA to control industrial liquid discharges. To implement the Act, EPA has developed ambient water quality criteria and standards, and has established emission limitations for liquid pollutant discharges from many different industries. In addition, the Act authorizes EPA to prescribe "best management practices" to prevent the release of toxic and hazardous pollutants from manufacturing or

treatment processes and the "best available technology economically achievable" to control the discharges of toxic pollutants (EPA, 1983). Regulations developed for the semiconductor and photovoltaic industries include control requirements for pH, fluoride, and toxic organics, but fail to mention standards for cadmium. Effluent and pretreatment standards have also been developed for battery manufacturing, and electrodeposition industries (EPA, 1984c; 1984d). These were discussed in Section 3.4.

#### 4.3 Resource Conservation and Recovery Act

EPA regulates the disposal of solid and hazardous wastes under the authority of the Resource Conservation and Recovery Act (RCRA) of 1976. RCRA provides guidelines for the protection of ground water, surface water, and ambient air from hazardous solid waste contamination. Under RCRA, EPA has established the Hazardous Waste Management (HWM) program to regulate the control of hazardous wastes from the point of generation through transportation, storage, and ultimate disposal. Under the HWM program, EPA has established special management requirements for handling hazardous wastes. Strict standards for specific materials have been set for proper record keeping, labeling, packaging, and transportation, as well as for facility siting, inspection, personnel training, and emergency planning (EPA, 1986a). Inorganic cadmium compounds have been listed by EPA under authorities of this act as hazardous. A generator may be conditionally exempt from these regulations if no more than 100 kg per month of cadmium containing waste is produced. An exemption may also be granted if the generator can show through EPA toxicity testing procedures that the liquid extract from processed waste is not hazardous (i.e., the liquid extract does not contain more than 1 mg Cd/l) (EPA, 1986b).

#### 4.4 Toxic Substances Control Act

Prior to enactment of the Toxic Substances Control Act (TSCA) of 1981, existing environmental legislation e.g., Clean Air Act, Federal Water Pollution Control Act, etc., provided for regulatory control of potentially toxic materials only after their discharge into the environment. As awareness of the scope and severity of hazards associated with toxic pollutants increased, the need for screening and/or testing of chemicals before they are used on a production scale was realized by Congress and became the major motivation for passage of TSCA. TSCA empowered EPA with two major regulatory obligations: (i) acquisition of information on existing chemical substances to identify and evaluate potential hazards; and (ii) regulation of production, use, distribution, and disposal of such substances, where necessary. These objectives are met through implementation of TSCA provisions including: an inventory list, pre-manufacturing notice (PMN), significant new use regulations (SNUR), reporting/record-keeping requirements, and testing criteria. Because of their past usage by industry and listing by EPA, the following cadmium compounds are exempt from these requirements: Cd, CdCl, CdS, and CdTe.

#### 4.5 Comprehensive Environmental Response, Compensation, and Liability Act

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA, also known as the Superfund Act) and the Superfund Amendments and Reauthorization Act of 1986 were enacted by Congress to respond to releases of hazardous substances to the environment either through accidental spills or chronic releases, e.g., malfunctioning or abandoned dump sites. By mandating authority over the cleanup of hazardous waste contamination, CERCLA complements earlier legislation by providing "cradle to grave" oversight of materials which potentially threaten human health and safety and the environment. Much of CERCLA focuses on remedial action issues specifically relating to the



cleanup of existing toxic waste sites. These issues pertain to generators of toxic substances only in as much as the law may hold them partially responsible for the costs incurred in cleaning waste sites. Of more direct consequence to photovoltaic manufacturers are those sections of CERCLA which deal with accidental releases of toxic materials. In this regard, the Act requires anyone in charge of a facility where hazardous substances are released in quantities greater than or equal to those determined pursuant to Section 102 to immediately notify the National Response Center. The CERCLA reportable quantity for cadmium for any single event is 4.5 kg (EPA, 1985b).

#### 4.6 Occupational Safety and Health Administration Act

Under the Occupational Safety and Health Act of 1970, the Occupational Safety and Health Administration (OSHA) was empowered to set workplace air contaminant standards to protect worker health. The current OSHA eight hour per day time weighted average (TWA) exposure limit is  $0.1 \text{ mg/m}^3$  for fumes and  $0.2 \text{ mg/m}^3$  for dust. The 15 minute short-term exposure limits (STEL) or "ceiling" levels for fume and dust are  $0.3 \text{ mg/m}^3$  and  $0.6 \text{ mg/m}^3$ , respectively (OSHA, 1988). Under the same act, the National Institute for Occupational Safety and Health (NIOSH) develops and periodically revises recommendations for limits of exposure to potentially hazardous substances or conditions in the workplace. In such a review NIOSH (1984) recommended that cadmium and its compounds be considered as potential occupational carcinogens and that occupational exposure levels be reduced to the lowest feasible level.<sup>(8)</sup> Similarly, OSHA has recently issued a directive to alert employers and employees of the inadequacy of OSHA's own exposure standards and of the need to reduce exposures to the American Conference of Governmental and Industrial Hygienists standards for cadmium dust

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8 "Potential occupational carcinogens" means any substance or mixture of substance which causes an increased incidence of benign and or malignant neoplasms, or a substantial decrease in the latency period between exposure and onset of neoplasms in humans or in one or more experimental mammalian species as the result of any oral, respiratory or dermal exposure, or any other exposure which results in the induction of tumors at a site other than the site of administration.

and salts of  $50 \text{ ug/m}^3$  for an 8-hour TWA (vs. the OSHA standard of  $200 \text{ ug/m}^3$ ); and for cadmium oxide fume,  $50 \text{ ug/m}^3$  as a 15 minute ceiling (vs. the OSHA standard of  $300 \text{ ug/m}^3$ ) (OSHA, 1988).

## 5.0 MANAGEMENT OPTIONS

A mix of administrative, engineering, and personal controls may be needed to protect worker and public health from hazards associated with the use of cadmium. These are discussed below. Most of these discussions focus on occupational controls. In many instances these options may also be useful in protecting public health.

### 5.1 Administrative

Administrative controls refer to management options implemented at a facility to reduce occupational exposures to toxic materials like cadmium. Such controls include, but are not limited to:

- \* Firm commitment of management to ensure that all reasonable measures are taken to protect the health and safety of their employees and the public.
- \* Development and implementation of management schemes to ensure that no work proceeds without the health and safety ramifications of that work being considered.
- \* Development and implementation of management safety committees to review all new equipment purchases, and major modifications to ensure and certify that health and safety issues and needs have been adequately explored.
- \* Development and implementation of material tracking and control systems to increase accountability associated with the use and disposal of chemicals.

- \* Development and establishment of training and refresher programs, consistent with Worker Right-to-Know Laws, to ensure that workers understand the hazards, engineering controls and responsibilities associated with handling of human carcinogens.
- \* Establishment of cadmium-specific directives instructing employees to wash their hands and face prior to eating, smoking or drinking; use of company-supplied uniforms which should not be brought home; prohibition of eating, drinking and smoking in work areas; and, establishment of good housekeeping principles including use of vacuums with high efficiency filters specific for cadmium dust and wet mopping.
- \* Establishment and posting of areas where cadmium is stored and used, as regulated areas to minimize the number of potentially exposed employees.
- \* Establishment of a workplace air monitoring program to ensure that employee exposures to cadmium are below established thresholds. For air contaminants, area representative samples should be taken from locations where different operations are occurring (e.g., batch mixing, electrodeposition, etching).
- \* Establishment of a medical surveillance (including individual case histories, biannual chest x-rays, urinary cadmium measurements, and determination of forced vital capacity and forced expiratory volume) to compile essential baseline data to measure any change which might be attributable to cadmium exposure. A critical component of this program is pre-placement, continuing (e.g., annually) and departure/termination measurements of urinary cadmium levels. These data will give a reasonable indication of the relative effectiveness of control strategies implemented within the facility and also allow management to identify workers at risk.

In the event of a fire involving an array larger than 100 kW<sub>p</sub>, emergency response personnel should notify the public to stay indoors with all windows closed until the transient

cloud containing the cadmium dust and fume disperses to safe concentrations. Procedures for notifying the public (e.g., sirens) should be planned before the installation of such devices. Furthermore, practice exercises should be conducted routinely.

Because of concerns associated with disposal of spent devices containing cadmium compounds, existing institutional controls as enumerated under RCRA should be followed to ensure that such devices are disposed of in an environmentally sound manner. Institutional mechanisms, however, do not exist for controlling disposal of arrays from small decentralized applications. Although hazards presented by such disposal are probably not large, both control options and hazards should be more carefully evaluated.

## 5.2 Engineering

Engineering controls to protect occupational health from cadmium fumes or dust include process station isolation and work space ventilation options. Process isolation can be done by physically enclosing the station while providing local exhaust, and worker's interface by e.g., "a glove box". Local exhaust ventilation can also be provided without totally enclosing the process station by negative pressure exhaust just above the process station or by "air curtains" where air is forced between the worker and the source of emissions to carry away and subsequently exhaust contaminants. In addition to process station exhaust, adequate ventilation of the whole work space will be required to prevent the accumulation of any residual contaminants. Together, these two options should always keep the concentration of cadmium compounds below the permissible limits. Frequent monitoring may be required for areas with large potential sources of cadmium compounds (e.g., spray pyrolysis area). In other areas, for example laser scribing, less frequent monitoring may suffice.

The acidic atmospheric effluent stream from a spray pyrolysis station can be treated by chemical precipitation, sedimentation and filtration (Doty and Meyers 1988). A possible treatment scheme involves: i) cooling of the effluent stream with water through a heat

exchanger; ii) chemical scrubbing in a multi-baffle spray scrubber utilizing either calcium hypochlorite solution or chlorinated alkali solution, to oxidize such ions as cyanides ( $CN^-$ ) to harmless cyanates ( $CNO^-$ ). In the alkaline chlorination oxidation, excess of chlorine and caustic will further oxidize cyanates to carbon dioxide and nitrogen.  $CdO$  and  $H_2S$  will form in solution  $CdO$  and  $S$  particulates, which can be filtered out and periodically leached in sulfuric to make acid-soluble  $CdSO_4$ . The remaining solution contains cadmium cations that can be finally inactivated in an electrolytic bath where they deposit a cadmium layer on the cathode. It may be possible to use this solution in the electrodeposition of  $CdTe$ .

### 5.3 Personal

Personal controls relate to actions available to the individual to reduce his/her own exposure levels. In this context, proper personal hygiene is extremely important because of the potential for ingesting cadmium. Employees who work in an environment where cadmium dust is present should shower daily and wash their hands and faces prior to eating, smoking and drinking. Employees should also be encouraged to refrain from nail biting and from wiping their faces with the sleeves of their shirts or jackets. While working with cadmium, employees should use personal protective equipment to avoid all potential skin contact, including where appropriate, gloves and a laboratory coat. Similarly, all operations in which cadmium-containing dust or fumes might be generated should be conducted within a properly designed and functioning hood, or other suitable containment device to reduce all inhalation potentials. Maintenance workers tasked with the routine clean-up of reactors and clean-up of accidental spills may be at special risk. During such operations, they should use OSHA-certified respirators or supplied air, as well as other personal protective devices (e.g., gloves). After clean-up operations have been completed, these workers should be required to shower and change their clothing.

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

Handling of cadmium in photovoltaic production can present hazards to health, safety and the environment. As discussed, however, prior recognition of these hazards can allow device manufacturers and administrators to implement appropriate and readily available hazard management strategies. Hazards associated with product use (i.e., array fires) and disposal remain controversial and partially unresolved. The most likely effects would be those associated with chronic low-level exposures to cadmium wastes. Because of the long latency period associated with the manifestation of such effects, and the availability of environmental and biomonitoring protocols, such hazards can be easily and inexpensively monitored, and remediated if necessary. In any event, the relative risk presented by these devices is small for the following important reasons:

(1) Cadmium-containing modules are by design well-sealed from the environment, usually between two sheets of glass. This design should prevent the mobilization of the cadmium compounds from arrays placed in landfills.

(2) CdTe and CdS compounds are thermally and chemically stable. To the extent that the perceived hazards from these activities are important, management strategies can be implemented to reduce them. It is quite possible, for example, that in lieu of disposal, CdTe modules could be recycled for their valuable, high purity cadmium and tellurium. This possibility is now being explored.

(3) Cadmium-containing modules do not present any major new hazard to health or the environment, especially if reasonable management strategies are implemented. Furthermore, as an alternative to existing energy options, which are by themselves far more stressful to health and the environment, cadmium-containing modules could reduce other important energy-related health and environmental hazards.

In conclusion, the cadmium-containing modules examined in this report are among the most promising photovoltaic options. They have a substantial probability of achieving the long-term goals established by DOE for cost, efficiency, and stability. Concern about cadmium hazards should continue to be emphasized to ensure that health, safety and environmental hazards are properly managed. At the same time, the potential benefits in ameliorating some important health (e.g., radiation induced effects of nuclear waste disposal) and environmental (e.g., atmospheric pollution and global climate change) hazards related to energy production from conventional energy sources should not be ignored.

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16. Abstract (Limit: 200 words) This paper discusses the current technology base and hazards associated with two promising thin-film photovoltaic cells that contain cadmium compounds - cadmium telluride (CdTe) and copper indium deselenide (CuInSe <sub>2</sub> ). More specifically, this paper summarized the toxicological information on cadmium (Cd) compounds; evaluates potential health, safety and environmental hazards associated with cadmium usage in the photovoltaics industry; describes regulatory requirements associated with the use, handling and disposal of cadmium compounds; and lists management options to permit the safe and continued use of these materials. Handling of cadmium in photovoltaic production can present hazards to health, safety and the environment. Prior recognition of these hazards can allow device manufacturers and regulators to implement appropriate and readily available hazard management strategies. Hazards associated with product use (i.e., array fires) and disposal remain controversial and partially unresolved. The most likely effects that could be expected would be those associated with chronic low-level exposures to cadmium wastes. Because of the general immobility of the cadmium present in these devices and availability of environmental and biomonitoring protocols, chronic hazards can be monitored, and remediated if necessary.			
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