HEALTH AND SAFETY ISSUES RELATED TO THE PRODUCTION, USE AND DISPOSAL OF CADMIUM-BASED PHOTOVOLTAIC MODULES

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ABSTRACT

This paper discusses environmental, health and safety issues associated with the use of cadmium in thin-film cadmium telluride photovoltaic modules. Cadmium-related environmental, public health and occupational health hazards may arise during the manufacturing, use, and disposal of spent devices. In this context, photovoltaic processing technology, statutory/regulatory limits, toxicology, and health hazards associated with two processing alternatives (electrodeposition and spray pyrolysis) nearing commercialization are reviewed. To ensure the continued viability of this material alternative, control options to permit the safe use of cadmium are discussed.

INTRODUCTION

This paper discusses environmental, health and safety issues associated with the use of cadmium in thin-film cadmium telluride photovoltaic modules. Cadmium-related environmental, public health and occupational health hazards may arise during the manufacturing, use, and disposal of spent devices. In this context, photovoltaic processing technology, statutory/regulatory limits, toxicology, and health hazards associated with two processing alternatives (electrodeposition and spray pyrolysis) nearing commercialization are reviewed. To ensure the continued viability of this material alternative, control options to permit the continued safe use of cadmium are discussed. This conference paper summarizes the results of a more detailed report published elsewhere (1).

TECHNOLOGY CHARACTERIZATION

Numerical estimates of quantities of cadmium used and wastes produced are based on electrodeposition and spray pyrolysis plants manufacturing 10 MWp of CdTe photovoltaic modules per year. The annual material use for electrodeposition is about 590 kg $CdSO_4$ and 450 kg of TeO_2 (assuming 90% deposition efficiency, 2 μm CdTe layer), and for pyrolysis is about 680 kg of $CdCl_2$ and 280 kg of thiourea (assuming a 10% deposition efficiency and 0.1 μm CdS layer). These two options because of their differences in deposition efficiency and cell layer thickness represent low and high limits of cadmium demands imposed by this material option. 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. Other process options may differ in scale, but not necessarily in type of hazard present.

TOXICOLOGY

The toxicology of inorganic cadmium compounds is reviewed in detail in documents prepared by international [e.g., World Health Organization - WHO (2); Commission of European Communities (3)], national [e.g, U.S. Environmental Protection Agency - EPA (4,5); Occupational Safety and Health - OSHA (6)], and trade [e.g., (7,8)] agencies and organizations. Several reviews have also been published in the technical literature (e.g., 9, 10). The principal effects of continued exposure to low levels of cadmium are on the kidneys (proteinuria), lungs (cancer) and bones (osteomalacia).

OCCUPATIONAL HEALTH

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. In electrodeposition, the principal cadmium-related health hazards to workers are from dust generated during feedstock preparation, and from cadmium vapors and fine particles proximate to the electrolytic bath. Accidental release of the liquid from an electrodepostion bath and subsequent cleanup may also present hazards to worker health. In spray pyrolysis, 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 which could be accidentally released from a spray pyrolysis unit, special precautions may be needed to protect worker health. In this context, OSHA has recently proposed (11) to amend its existing regulation for occupational exposure to cadmium. The proposed standards would lower the 8-hour time weighted permissible exposure limits to 5 or 1 micrograms of cadmium per cubic meter of air ($\mu g/m^3$). This represents a 20 to 100-fold reduction in the permissible exposure limit to cadmium fumes.

PUBLIC HEALTH

Public health may be affected by these manufacturing options principally from chronic exposure to cadmium compounds released to the environment. Potential exposure pathways of interest include food, water and air. 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. Each of these issues is discussed below.

Manufacturing

Electrodeposition is a very efficient process; the technical literature suggests a process efficiency of approximately 90%; the remaining 10% will be lost during rinsing or from product defects. Thus, of the 590 kg of $CdSO_4$ and 450 kg of TeO_2 required annually, only a maximum of 11 kg of cadmium and 12 kg of tellurium, mostly as ions in solution, must be directly disposed during routine operations. If the 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 for cadmium battery manufacturing or electroplating of common metals. Federal effluent limitations for new cadmium battery manufacturing 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. If this situation occurs, these effluents could be treated in the same on-site Cd^{++} treatment station where the effluents from CdS spray pyrolysis would be routinely treated.

Because of the low efficiency of spray pyrolysis (~10% efficiency), large quantities of cadmium containing wastes may be produced: about 900 kg of $CdCl_2$, CdO, HCl, H_2S and thiourea by-products (e.g., SO_2, urea). 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. Assuming, conservatively, an 8 hr/day operation for 250 days a year, emission flow rates up to 0.4 kg/hr could be generated. These emissions would need to be reduced to 0.2 kg/hr to meet state implemented discharge limitations.

Use

Public health hazards associated with the release of cadmium from a CdTe/CdS module during a fire have aroused great interest. To estimate the quantity of material released during a fire, two different scenarios were evaluated for three different sized array fields (a 5 kW_p residential, a commercial roof-top arrays of 100 kW_p, and a 500 kW_p ground-mounted sub-station). The first assumed that 100% of CdTe material present in the different sized array fields is released to the atmosphere as dust and fumes. The second assumed that only 10% of CdTe is liberated to the atmosphere. The latter is more likely because of the high melting point of CdTe (1041^{o}C). To estimate the ground-level concentrations from these releases, an atmospheric dispersion model was used. 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. Therefore, the OSHA/NIOSH Immediately Dangerous to Life or Health (IDLH) level (referring to 30 min exposures), was used for comparison with the calculated ground-level ambient concentrations. The IDLH level for cadmium compounds (e.g., CdO fumes) is 40 mg/m^3.

Results of the modeling exercises show that releases of fumes during fires in residential buildings equipped with 5 kW_p solar 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.

Decommissioning

Large-scale disposal of spent photovoltaic devices should 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 will 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 modules (~10^4 m^2 of modules or about 1 MW_p) could trigger Federal requirements which will then require disposal at much larger cost in a controlled hazardous waste landfill. Although these hazards are probably not large, they require further analysis.

MANAGEMENT OPTIONS

A mix of administrative, engineering, and personal controls may be needed to protect worker and public health from the hazards associated with the use of cadmium.

Administrative controls include, but are not limited to:

- Development and implementation of material tracking and control systems to increase accountability associated with the use and disposal of chemicals.
- 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 of a workplace air monitoring and medical surveillance 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). Similarly, a medical surveillance (including individual case histories, biannual chest x-rays, urinary cadmium measurements, and determination of forced vital capacity and forced expiratory volume) should be implemented to establish 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.
- Compliance with federal statutes and regulations designed to 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 requirements are

included in the Clean Air Act, Clean Water Act, Resource Conservation and Recovery Act, Toxic Substance Control Act, CERCLA, Occupational Safety and Health Administration Act.

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 providing 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. The acidic atmospheric effluent stream from a spray pyrolysis station can be treated by chemical precipitation, sedimentation and filtration.

Personal controls relate to actions and options 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. 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.

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