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INFORMAL REPORT

UNDERSTANDING AND MANAGING HEALTH AND ENVIRONMENTAL RISKS OF CIS, CGS, AND CdTe PHOTOVOLTAIC MODULE PRODUCTION AND USE: A WORKSHOP

Editors:

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ABSTRACT

Environmental, health and safety (EH&S) risks presented by CIS, CGS and CdTe photovoltaic module production, use and decommissioning have been reviewed and discussed by several authors. Several EH&S concerns exit. The estimated EH&S risks are based on extrapolations of toxicity, environmental mobility, and bioavailability data for other related inorganic compounds. Sparse data, however, are available for CIS, CGS or CdTe. In response to the increased interest in these materials, Brookhaven National Laboratory (BNL) has been engaged in a cooperative research program with the National Renewable Energy Laboratory (NREL), the Fraunhofer Institute for Solid State Technology (IFT), the Institute of Ecotoxicity of the GSF Forschungszentrum für Umwelt und Gesundheit, and the National Institute of Environmental Health Sciences (NIEHS) to develop fundamental toxicological and environmental data for these three compounds. This workshop report describes the results of these studies and describes their potential implications with respect to the EH&S risks presented by CIS, CGS, and CdTe module production, use and decommissioning.

ACKNOWLEDGMENTS

Support for the preparation of the information presented in this report was provided by the U.S. Department of Energy, the National Institute of Environmental Health Sciences, and the German Bunderministerium für Forschung und Technologie. We thank the agencies for the technical interest and financial support they have provided for these efforts. We are especially indebted to the authors who presented materials at this workshop and to the participants who actively participated in the discussions following each presentation.

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1. INTRODUCTION

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DOE'S GOALS AND OBJECTIVES

- Construct leading edge experiments and user facilities on schedule, within budget and in an environmentally and fiscally responsible manner.
- Facilitate the application of knowledge and technology.
- Reduce uncertainties, prioritize risk, and eliminate imminent threats of our activities to improve environmental quality.
- Reduce adverse environmental impacts associated with energy production, delivery and use.
- Help industry shift from waste management to resource efficiency and pollution prevention.

WHAT IS THE BIOMEDICAL & ENVIRONMENTAL ASSESSMENT GROUP?

- Characterize environmental, safety and health hazards and risks of complex technologies and risk management options.
- Support DOE, EPA, industry and others to ensure the efficient, safe, and reliable development or operation of existing or new facilities and products.
- Program established in 1970; photovoltaic program established in 1979.

BNL PRODUCTS

- Technical Reports
- Workshops
- Industrial Hygiene/Environmental Audits

- NEPA/Regulatory Analyses

- Accident Investigations

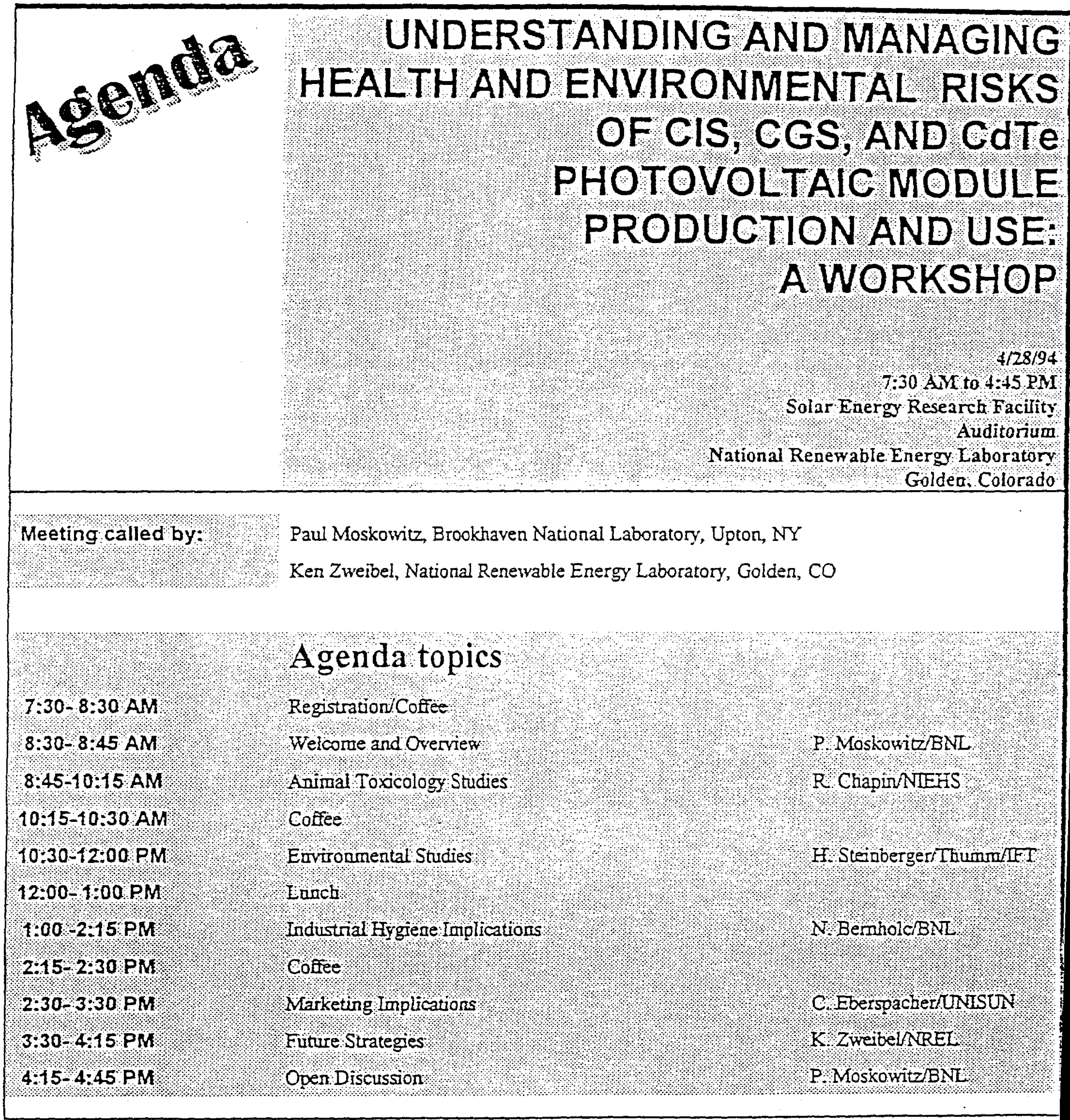
- Interagency/Interindustry Coordination

- EH&S Electronic Bulletin Board Service

WORKSHOP HISTORY

- About three years ago, Brookhaven National Laboratory and Siemens Solar, Inc., petitioned the National Institute of Environmental Health Sciences to start a program to evaluate the toxicity to animals of three compounds (CIS, CGS, and CdTe) of interest to the photovoltaics community.

- The Fraunhofer Institute for Solid State Technology in Munich, Germany responding to guidance from the BMFT began a parallel set of studies to evaluate the environmental mobility and toxicity of CIS and CdTe.



Agenda

UNDERSTANDING AND MANAGING HEALTH AND ENVIRONMENTAL RISKS OF CIS, CGS, AND CdTe PHOTOVOLTAIC MODULE PRODUCTION AND USE: A WORKSHOP

4/28/94
7:30 AM to 4:45 PM
Solar Energy Research Facility
Auditorium
National Renewable Energy Laboratory
Golden, Colorado

Meeting called by:

Paul Moskowitz, Brookhaven National Laboratory, Upton, NY
Ken Zweibel, National Renewable Energy Laboratory, Golden, CO

Agenda topics

7:30- 8:30 AM	Registration/Coffee	
8:30- 8:45 AM	Welcome and Overview	P. Moskowitz/BNL
8:45-10:15 AM	Animal Toxicology Studies	R. Chapin/NIEHS
10:15-10:30 AM	Coffee	
10:30-12:00 PM	Environmental Studies	H. Steinberger/Thumm/IFT
12:00- 1:00 PM	Lunch	
1:00 -2:15 PM	Industrial Hygiene Implications	N. Bernholc/BNL
2:15- 2:30 PM	Coffee	
2:30- 3:30 PM	Marketing Implications	C. Eberspacher/UNISUN
3:30- 4:15 PM	Future Strategies	K. Zweibel/NREL
4:15- 4:45 PM	Open Discussion	P. Moskowitz/BNL

Figure 1-1. Worshop agenda.

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2. THE SYSTEMIC AND REPRODUCTIVE TOXICITIES OF COPPER INDIUM DISELENIDE, COPPER GALLIUM DISELENIDE, AND CADMIUM TELLURIDE IN RATS

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Ralph E. Wilson[1], Barbara J. Davis[1], Bradley J. Collins[2], and Ann C. Lockhart[3]

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INTRODUCTION

A request from Brookhaven National Laboratories and Siemens Solar Corporation to the National Toxicology Program to develop some initial toxicity data on Copper Indium Diselenide (CIS), Copper Gallium Diselenide (CGS), and Cadmium Telluride (CdTe) resulted in a series of studies that are summarized here. The data for each compound are being prepared for publication in the reviewed scientific literature; what follows is a summary of the biological effects, and a brief guide to their interpretation.

STUDY DESIGN AND METHODS

In all cases, the compounds were suspended in 0.5% hemimethylcellulose and administered to adult male and female Sprague-Dawley rats daily by oral gavage. For each compound, a 28-day dose-range-finding (DRF) study was conducted to set doses for the main study. This DRF study involved no mating, just dosing to group-housed adult rats. Because of the lack of any preliminary toxicity data, doses for these DRF studies were 1000, 500, 250, 100, and 0 mg/kg/d. The endpoints used were body weight, clinical signs, food and water consumption, hematology, clinical chemistries and selected organ histopathology at sacrifice.

We used these preliminary data to set doses for the main study with the aim that the top dose would be expected to reduce body weight gain to some degree. The rationale for this is that if no body weight reduction and no adverse effects were seen, we could only conclude that not enough of the compound was given, and the data from such a study would be of limited use. The lack of toxic effects in the presence of reduced body weight (or reduced weight gain, for a short-term study) is more reassuring, for it means that we were already giving as much compound as the animal could reasonably tolerate; some degree of reduced body weight or body weight gain increases our confidence in a negative study (a negative study is one that finds no toxic effects other than weight reduction).

The design for the main study is adapted from Harris et al. (1992), extended by a week (Figure 2-1). The design looks at "systemic" toxicity in male rats: hematology (red and white blood cells), clinical chemistry (enzymes and proteins in the blood, used as circulating markers of tissue damage), histopathology of liver, kidney, spleen (to identify structural changes in those vital organs, which are some of the known target organs for these compounds). Systemic toxicity is evaluated only in males, because the pregnancy status of the females may be altered by exposure to the compound, and both pregnancy and treatment affect these systemic endpoints, making interpretation of systemic toxicity in females very difficult.

The design also evaluates any effects of exposure on:

1) both the function (breeding) and structure of the male reproductive system. In addition, we evaluate sperm number in the epididymis and testis, sperm motility, and the structure of the testis and epididymis. This is done in Group 1, the males.

2) the ability of the compound to affect female fertility (Group 2). Female fertility is separated, in this design, from fetal development, and is defined as the ability to become pregnant and initiate fetal development. This includes the ability to ovulate, fertilize the ovum, implant the conceptus and begin development.

3) the ability of the compound to affect fetal development, birth, and the initiation of lactation (in Group 3). This is accomplished by dosing the females during the period of major fetal organogenesis. This has been thought to be the most sensitive period of fetal development, and is a practice widely accepted in teratology. The animals are dosed from gestation days 6 - 15, and then dosing is stopped, and the dams are allowed to deliver their litters. We then monitor fetal number and weight gain for the first 4 postnatal days. Even though the animals are maintained without dosing for the last third of gestation and parturition and lactation, in previous studies we have seen chemical-related effects in treated animals in these undosed later periods.

THE RESULTS

CIS

Doses for the main study were set at 50, 100, and 250 mg/kg/d.

Group 1 - Males (Table 2-1)

CIS did not affect food consumption, body weight, or clinical chemistry values in males dosed continuously for 28 days. Liver weight was slightly increased, and there were small, not biologically significant changes in red cell production and monocyte (a type of white cell) numbers. There were no effects on any reproductive endpoints in males.

Group 2 - Continuously -Exposed Females (Table 2-2)

CIS reduced female food consumption and weight gain at the top dose, but did not alter either the number of live or dead uterine implants (fetuses) in these females, or the number of corpora lutea, showing that CIS had no effect on ovulation or early fetal development over this time frame.

Group 3 - Gestational Exposure (Table 2-3)

CIS reduced body weight gain during treatment, but not food consumption. There was a significant (25%) reduction in the number of live pups delivered in the high dose group (250 mg/kg), but these pups each were, on average, heavier than their controls, indicating that their intrauterine development was not stunted. Normally, when there are fewer pups per litter, we expect each of them to be heavier. If there are fewer pups per litter and each is lighter than controls, the weight change indicates an adverse effect on fetal development, and the reduced pup number indicates an adverse effect on parental fertility.

Collectively, these data show that sufficient CIS was given so that body weight gain was reduced, both with and without a change in food consumption (groups 2 and 3, respectively). Weight and pup effects in the absence of changes in food consumption (seen in Group 3), and in the presence of a bulky metal suspension, suggested the possibility that some nutritional inadequacies might account for the reduced litter size. A pair-feeding study was conducted to test the possibility that the CIS effect on pup number was due primarily to impaired nutrition (Table 2-4). This study consisted of a group of untreated, control pregnant females, a group treated with 250 mg CIS/kg, and a group that received, each day, only as much food as that consumed by the CIS group. If the "CIS effects" were due to deficient nutrition, then the pair-fed group should also have reduced litter size. We found, surprisingly, that all three groups had the same sized litters; CIS did <u>not</u> reduce the number of pups/litter, nor was pup number reduced in the pair-fed group. This shows not only that there was no adverse effect of reduced food consumption, but also that the CIS "effect" is a relatively small one, in that it cannot be repeated consistently.

Based on the weight of these data, we conclude that CIS, at doses sufficient to reduce weight gain and overall body weight in treated females, has relatively mild systemic toxicity. The fact that the pup number decrease was not seen again when the gestational dosing was repeated in the pair-feeding study also suggests that CIS has no consistent reproductive toxicity over this relatively abbreviated exposure period.

CGS

Doses for the main study were set at 30, 100, and 250 mg CGS/kg body wt./day

Group 1 - Males (Table 2-5)

CGS did not reduce body weight gain or food consumption in males, but liver weights (both absolute and relative to body weight) were increased in the middle and high dose groups at necropsy. There was a dose-related (but probably biologically meaningless) decrease in basophils (a kind of white blood cell) that reached significance at the high dose. There was also a dose-related decrease (which reached significance at the top dose, 23% reduced) in the weight of the cauda epididymis (which stores sperm) and a similar decrease in epididymal sperm count (33% at the top dose). Although this might suggest a decrease in sperm production by the testis, testis histopathology was normal. Reduced sperm storage could be due to either a reduced output of sperm by the testis or an increased efflux of sperm from the epididymis. There was no evidence of the former, and no reasonable precedent for the latter, leaving us uncertain about the cause of this decline.

Group 2 - Continuously-Exposed Females (Table 2-6)

There was a strong dose-related decrease in body weight gain in this group of females. This was probably correlated with pregnancy status and food consumption: most of the controls were pregnant, while most of the high-dose animals were not, and the high dose animals ate less than the controls (possibly due both to treatment effects and to pregnancy status differences, i.e., they may have felt bad and eaten less, and non-pregnant animals eat less than pregnant animals). None of the high dose animals had any live implants, and they also had fewer corpora lutea, indicating that they had ovulated fewer ova. The middle dose group had significantly fewer (by 15%) live implants than the controls. These data indicate that this level of CGS clearly reduced the ability of females to become pregnant and carry their litter.

Group 3 - Gestational Exposure (Table 2-7)

CGS exposure during fetal organogenesis reduced maternal food consumption by 30% at the top dose; these animals also had significantly reduced body weights during and after treatment. Despite this, there was no significant increase in fetal loss before or after birth, and no significant difference in pup weight.

Although these data identify female fertility in Group 2 as a likely target process, the interpretation is complicated. The fertility effects were seen at the same doses that reduced both body weight and survival. Having said that, we should also point out that weight reductions similar to those seen in the middle dose group with CGS (which had significantly fewer implants) were <u>not</u> associated with reduced fertility with the other compounds, suggesting that the effects seen here with CGS are probably <u>not</u> simply secondary to body weight effects. Future studies clearly should focus on female fertility, and should include efforts to repeat these findings.

CdTe

Doses for the main study were set at 10, 30, and 100 mg CdTe/kg/day

Group 1 - Males (Table 2-8)

There was a dose-related decrease in body weight gain, with the high dose animals <u>losing</u> weight during the study. Food consumption was reduced during the first 11 days of exposure in the high dose group only. There were no effects of CdTe exposure on organ weights, sperm parameters, or fertility. Eosinophils (a white blood cell) were reduced at the high dose group. Serum enzymes indicative of liver damage were <u>slightly</u> increased in the high dose group. Serum albumin levels were increased slightly, probably secondary to dehydration and body weight loss. There were no changes in the structure of the kidneys or livers of these animals (known target organs of cadmium toxicity). Additionally, there was no increase in urinary cadmium or protein levels, indices of cadmium exposure and renal glomerulus toxicity, respectively.

Group 2 - Continuously-Exposed Females (Table 2-9)

Animals in the top dose group consumed slightly less food than controls, and gained less than half the weight that controls gained over the course of the study. Nonetheless, there was no change in any fertility endpoint (number of live implants, number of dead implants, number of resorptions, number of corpora lutea), showing both that oral CdTe had no effect on these endpoints, and that apparently this difference in body weight gain was not adverse for reproduction over this period.

Group 3 - Gestational Exposure (Table 2-10)

Females dosed during fetal organogenesis with the high dose level consumed less food than controls, and animals in the middle dose group consumed less food from gestational day 8 - 12. There was a dose-related inhibition of weight gain that started at the lowest dose group, and animals in both middle and high dose groups gained significantly less weight during the experiment, and finished lighter than controls. Despite these body weight effects, there were no effects on the pups: there was no increase in fetal loss before or after birth, and no adverse effect on birth weight or weight gain of the pups after birth.

It is known that only 5-8% of orally administered cadmium passes through the lining of the gut to be absorbed by the body (rev. in Goyer, 1986) so this lack of measurable urinary Cd is not terribly surprising. As absorption increases, Cd levels are known to rise in the liver and kidney, and then Cd starts to appear in the urine. Since we used the same relatively insensitive biomarker that is used to monitor human Cd exposure (urinary Cd), it's possible that there was some renal or hepatic absorption and storage that we wouldn't have seen, i.e., that was not reflected in the urinary levels. However, what is more informative is that no change in fertility was seen at this degree of body weight reduction. This increases the likelihood that the changes seen in the CGS study (reduced female fertility) are not simply secondary to the reduced weight gain, but are more likely a toxic effect of CGS *per se*.

DISCUSSION

These data are an important first step in the determination of the hazards posed by these compounds, but they are a relatively small first step. These studies have a number of serious limitations when it comes to their use in risk assessment (the process of predicting the risk to human health based on animal studies):

1) They used oral exposure. These compounds were administered by oral gavage into the stomach. This is accepted practice in toxicology, but it does not

fully mimic the most likely route of human exposure during manufacturing (which is inhalation). This difference will be critical for several of the compounds: CdTe, because Cd is so poorly absorbed across the gut epithelium, but is more efficiently absorbed across the pulmonary epithelium, and CIS, because inhaled indium not only may be absorbed, but has been shown to produce lung damage in rats (Blazka et al., 1994). Studies on these three compounds are ongoing at NIEHS, and these will document the degree of chemical absorption through the lungs.

2) They were short-term. These studies are much shorter than most studies used to characterize the toxicity of a compound. The benefit of the current approach is that highly toxic compounds can be identified quickly. The drawback is that if a compound shows no toxicity in these studies, it might still be toxic over longer exposures, or by other routes. This length of study also precludes making any sort of conclusion about the possible carcinogenicity of these compounds. Longer studies will doubtless be conducted on 1 or 2 high-priority compounds.

3) We don't know absorption. This can be remedied relatively easily (by measuring tissue levels of the appropriate elements in treated animals). Tissues to address this issue have been collected and are awaiting analysis. Clearly, if the compound is not absorbed through the gut and is not present in the bloodstream, then the issue of appropriate route becomes critical, and another study, using the human route of exposure, must be performed.

4) There are no genetic toxicity data. This, too, can be remedied relatively easily. Genetic toxicity (damage to the DNA in either regular cells in the body, or to the sperm or eggs) may increase the chances of producing cancer or miscarriages/heritable damage in the offspring, respectively. Based on the structure of these compounds, we do not predict that this is likely, but it must be addressed at some point.

5) They provide only limited general toxicity data. Although the clinical chemistry, hematology, and histopathology data are sound, they could be expanded in the next study, especially the histopathology (more organs could be evaluated). This would increase our confidence in the findings.

6) Finally, there are no data on lung effects of the compounds themselves. This should be evaluated, as the lungs are the probable route of human exposure. This is likely to be most important for indium (Blazka et al., 1994), but may be relevant for other elements as well.

Despite their limitations, these studies can give us some idea of the processes that are likely to be most sensitive if the compounds do get into the bloodstream. And we know that this design is able to identify chemicals that, with longer exposures, do cause significant toxicity (Harris et al., 1992). That predictability suggests that more work should be done with CGS, if it appears to be commercially viable and is likely to move into production.

Nevertheless, based on what is known about the toxicity of the individual elements, these data suggest that at least CIS and CdTe, over this limited time frame, are not significantly more toxic than the individual elements. The female reproductive toxicity of CGS demands more investigation to compare the effects against the toxicity of the individual elements.

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Goyer, R.A. Toxic Effects of Metals. in Casarett and Doull's Toxicology, ed. by C.D. Klassen, M.O. Amdur, and J Doull, Macmillan Publ. Co., New York, 1986, pp. 582-635.

Table 2-1

GROUP 1

Male Sprague Dawley Rats

	COPPER INDIUM DISELENIDE (mg/kg/day)				
	0	50	100	250	Trend
FERTILITY AND NECROPSY DATA					
n Treated	9	9	9	9	
BW Terminal (g)	479.9 ± 7.3[a]	474.3 ± 20.8	475.1 ± 6.7	488.0 ± 7.2	p=0.4631
BW Change (g)	1.6 ± 0.9	-7.6 ± 9.3	2.0 ± 1.0	7.9 ± 1.2	p=0.3664
n Fertile Prior to Exposure	9	9	9	9	—
n Fertile During Exposure	9	8	8[b]	6	p=0.0810
Liver Weight (g)	17.2 ± 0.6	17.7 ± 0.5	17.7 ± 0.4	18.8 ± 0.3*	p=0.0146
Liver Weight (%)	3.60 ± 0.09	3.80 ± 0.17	3.72 ± 0.08	3.80 ± 0.03*	p=0.0019
Kidney Weight (g)	1.59 ± 0.03	1.69 ± 0.04	1.59 ± 0.03	1.70 ± 0.06	p=0.2195
Kidney Weight (%)	0.33 ± 0.01	0.36 ± 0.02	0.33 ± 0.01	0.35 ± 0.01	p=0.2589
Spleen Weight (g)	0.79 ± 0.04	0.77 ± 0.06	0.84 ± 0.02	0.80 ± 0.03	p=0.6927
Spleen Weight (%)	0.17 ± 0.01	0.16 ± 0.01	0.18 ± 0.004	0.16 ± 0.004	p=0.6516
Testes Weight (g)	1.88 ± 0.08	1.88 ± 0.06	1.81 ± 0.12	1.94 ± 0.05	p=0.7777
Right Epididymis Weight (g)	0.63 ± 0.02	0.65 ± 0.03	0.66 ± 0.02	0.66 ± 0.02	p=0.5723
Left Cauda Weight (g)	0.16 ± 0.01	0.17 ± 0.01	0.18 ± 0.01	0.16 ± 0.01	p=0.7995
Sperm/g Cauda (x 10^6)	734.7 ± 63.0	617.2 ± 76.1	718.5 ± 29.9	677.6 ± 38.9	p=0.9325
% Sperm Motility	80.0 ± 3.1	72.0 ± 8.7	79.4 ± 7.6	80.8 ± 1.9	p=0.9101
FOOD CONSUMPTION					
n Treated	9	9	9	9	
Grams per day					
SD 3-7	17.8 ± 1.0[a]	21.7 ± 0.7	18.7 ± 0.5	18.9 ± 0.6	p=0.5162
SD 7-11	19.3 ± 0.8	18.9 ± 1.3	18.1 ± 0.7	19.0 ± 0.9	p=0.5629
SD 11-19	22.1 ± 0.6	21.6 ± 1.8	22.2 ± 0.9	23.2 ± 0.8	p=0.5627
SD 19-23	22.7 ± 0.4	21.6 ± 1.8	22.2 ± 0.9	23.2 ± 0.8	p=0.5627
SD 23-28	23.0 ± 0.6	21.4 ± 1.4	22.7 ± 0.5	23.8 ± 0.6	p=0.2772
HEMATOLOGY DATA					
RBC (10^6/µl)	8.9 ± 0.1	8.7 ± 0.3	8.7 ± 0.1	8.9 ± 0.1	p=0.9765
Hemoglobin (g/dl)	15.9 ± 0.2	15.3 ± 0.6	15.7 ± 0.2	15.9 ± 0.2	p=0.9527
Hematocrit (%)	49.3 ± 0.9	47.7 ± 2.0	48.9 ± 0.7	49.8 ± 0.7	p=0.6268
MCV (fl)	56.0 ± 0.7	54.7 ± 1.0	56.4 ± 0.4	56.0 ± 0.6	p=0.3448
MCH (pg)	17.9 ± 0.1	17.6 ± 0.2	18.0 ± 0.2	17.9 ± 0.3	p=0.9764
MCHC (g/dl)	31.9 ± 0.3	32.2 ± 0.3	32.0 ± 0.4	32.0 ± 0.3	p=0.4007
Reticulocytes[c]	0.11 ± 0.007	0.14 ± 0.01	0.15 ± 0.01*	0.16 ± 0.01*	p=0.0104
Platelets (1000/µl)	611.0 ± 54.6	804.6 ± 86.4	737.1 ± 45.3	821.6 ± 20.2*	p=0.0010
WBC (1000/µl)	8.7 ± 0.8[a]	6.0 ± 0.6	7.6 ± 0.7	8.0 ± 0.6	p=0.8023
Seg. Neutrophils[c]	1.1 ± 0.2	1.0 ± 0.2	1.1 ± 0.2	1.1 ± 0.1	p=0.6063
Lymphocytes[c]	6.8 ± 0.7	4.4 ± 0.5*	6.0 ± 0.6	6.3 ± 0.5	p=0.6695
Monocytes[c]	0.46 ± 0.10	0.22 ± 0.03*	0.21 ± 0.3*	0.25 ± 0.02*	p=0.1366
Eosinophils[c]	0.13 ± 0.03	0.13 ± 0.03	0.14 ± 0.02	0.15 ± 0.03	p=0.5453
Basophils[c]	0.03 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	p=0.0745
LUCs[c]	0.21 ± 0.03	0.21 ± 0.08	0.15 ± 0.03	0.19 ± 0.06	p=0.5453

[a] Mean ± SEM

[b] Only eight females available

[c] Expressed as absolute values

*$p<0.05$ compared to controls

Table 2-2

GROUP 2
Continuous Exposure
Female Sprague Dawley Rats

	COPPER INDIUM DISELENIDE (mg/kg/day)				
	0	50	100	250	**Trend**
FERTILITY AND NECROPSY DATA					
n Treated	9	9	8	9	
BW Change SD 0-28 (g)	72.6 ± 4.7[a]	68.1 ± 7.2	65.6 ± 6.7	37.3 ± 11.3*	p=0.0028
Pregnant/Treated	9/9	7/9	7/8	6/9	p=0.0810
n Live Implants	11.3 ± 0.7	10.6 ± 2.0	10.2 ± 1.8	6.2 ± 2.1	p=0.2395
n Dead Implants	0	0	0	0	—
Early Resorptions	0.56 ± 0.30	0.22 ± 0.10	0.25 ± 0.25	0.56 ± 0.34	p=0.8776
Late Resorptions	0	0.11 ± 0.11	0	0.22 ± 0.22	p=0.3516
Total Implants	11.9 ± 0.9	10.9 ± 2.1	10.5 ± 1.9	7.0 ± 2.1	p=0.1811
Corpora Lutea	14.4 ± 0.4	14.1 ± 0.9	15.0 ± 0.5	13.2 ± 0.7	p=0.3703
FOOD CONSUMPTION					
n Treated	9	9	8	9	
Grams per day					
SD 0-4	15.5 ± 0.4[a]	13.0 ± 0.8*	12.9 ± 2.3*	11.2 ± 0.9*	p=0.0028
SD 4-8	14.8 ± 0.8	14.9 ± 0.5	14.0 ± 0.5	12.4 ± 0.9	p=0.0100
SD 8-12	14.1 ± 0.6	14.5 ± 0.3	13.2 ± 1.3	11.4 ± 1.1*	p=0.0086
SD 17-20	19.0 ± 0.5	18.9 ± 0.6	18.7 ± 0.8	14.5 ± 0.9*	p=0.0014
SD 20-24	18.8 ± 0.4	18.7 ± 0.6	18.7 ± 0.8	16.2 ± 1.4	p=0.0636
SD 24-28	19.6 ± 0.4	18.8 ± 0.9	19.2 ± 0.8	14.6 ± 1.2*	p=0.0018

[a] Mean ± SEM

*p<0.05 compared to controls

Table 2-3

GROUP 3

Gestational Exposure

Female Sprague Dawley Rats

	COPPER INDIUM DISELENIDE (mg/kg/day)				
	0	50	100	250	Trend
FERTILITY AND NECROPSY DATA					
Females					
Pregnant/Treated	10/10	10/10	8/10	9/10	
BW Change (g)					
GD 6-15	46.4 ± 1.7[a]	53.2 ± 10.1	39.0 ± 3.0*	39.1 ± 1.8*	p=0.0059
GD 0-15	72.1 ± 2.2	68.9 ± 1.8	64.2 ± 4.0	66.8 ± 2.4	p=0.0651
BW PND 1 (g)	295.2 ± 5.5	292.1 ± 3.5	289.7 ± 5.1	295.6 ± 4.3	p=0.7551
BW PND 4 (g)	291.5 ± 5.7	291.9 ± 2.5	286.1 ± 6.2	298.7 ± 4.3	p=0.6545
Neonates					
PND 0					
n Live	14.8 ± 0.7	12.7 ± 0.9	12.9 ± 0.9	11.2 ± 1.1*	p=0.0031
n Dead	0	0.3 ± 0.3	0	0.2 ± 0.2	p=0.3617
PND 1					
n Live	14.8 ± 0.7	12.7 ± 0.9	12.9 ± 0.9	11.2 ± 1.1*	p=0.0031
n Dead	0	0	0	0	—
PND 4					
n Live	14.7 ± 0.7	12.6 ± 0.9	12.9 ± 0.9	11.1 ± 1.0*	p=0.0042
n Dead	0.1 ± 0.1	0.1 ± 0.1	0	0	p=1.0000
Mean Body Weight (g)					
PND 1	6.6 ± 0.1	6.9 ± 0.2	7.0 ± 0.1*	7.3 ± 0.2*	p=0.0020
PND 4	8.9 ± 0.3	10.3 ± 0.5	9.7 ± 0.4	10.2 ± 0.5	p=0.0651
n Implantation Sites	15.4 ± 0.7	14.4 ± 0.9	14.0 ± 1.0	13.4 ± 1.1	p=0.0941
FOOD CONSUMPTION					
n Treated	10	10	8	9	
Grams per day					
GD 6-8	20.1 ± 1.3[a]	20.1 ± 0.9	20.9 ± 1.2	17.9 ± 0.9	p=0.2720
GD 8-10	19.5 ± 0.7	19.8 ± 0.7	19.4 ± 1.2	19.3 ± 1.1	p=0.9244
GD 10-12	22.9 ± 0.6	20.7 ± 0.7	21.7 ± 0.9	20.8 ± 0.5	p=0.0980
GD 12-14	22.0 ± 0.6	21.8 ± 0.7	21.8 ± 1.5	22.6 ± 0.6	p=0.3288

[a] Mean ± SEM

*p<0.05 compared to controls

Table 2-4

PAIR FEEDING STUDY

Female Sprague Dawley Rats

	COPPER INDIUM DISELENIDE (mg/kg/day)			
	0 *Ad Lib*	250 *Ad Lib*	0 *Restricted*	**Trend**
FERTILITY AND NECROPSY DATA				
Females				
n Treated	11	12	12	
n Pregnant	11	10	10	
BW Change (g)				
GD 6-15	51.1 ± 1.5[a]	36.2 ± 3.4*	22.5 ± 3.1*	p=0.00008
GD 15-21	86.7 ± 2.6	86.3 ± 3.5	100.1 ± 7.7*	p=0.0085
BW PND 1 (g)	266.6 ± 3.1	258.1 ± 5.2	257.7 ± 3.4	p=0.0208
BW PND 4 (g)	272.3 ± 1.8	267.7 ± 4.7	269.7 ± 3.3	NS
Neonates				
PND 0				
n Live	12.5 ± 0.6	11.8 ± 0.7	11.3 ± 1.2	NS
n Dead	0.2 ± 0.1	0.1 ± 0.1	0	NS
PND 1				
n Live	12.6 ± 0.6	11.6 ± 0.6	11.2 ± 1.1	NS
n Dead	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	p=0.0313
PND 4				
n Live	12.2 ± 0.6	11.6 ± 0.6	11.4 ± 1.2	NS
n Dead	0.1 ± 0.1	0	0	NS
Mean Body Weight (g)				
PND 1	7.2 ± 0.2	7.0 ± 0.1	7.5 ± 0.2	p=0.0170
PND 4	10.6 ± 0.6	9.6 ± 0.3	10.3 ± 0.3	p=0.0175
n Implantation Sites	13.8 ± 0.5	12.8 ± 0.5	12.2 ± 1.0	p=0.0315

[a] Mean ± SEM

*$p<0.01$ compared to controls (ad lib)

Table 2-5

GROUP 1

Male Sprague Dawley Rats

	COPPER GALLIUM DISELENIDE (mg/kg/day)				
	0	30	100	250	*Trend*
FERTILITY AND NECROPSY DATA					
n Treated	10	10	10	10	
BW Terminal (g)	393.5 ± 6.9[a]	389.6 ± 7.4	392.1 ± 5.6	387.4 ± 10.5	p=0.7537
BW Change (g)	15.5 ± 3.5	15.5 ± 2.2	15.4 ± 2.5	6.1 ± 5.1	p=0.1765
n Fertile Prior to Exposure	9/10	9/10	10/10	10/10	—
n Fertile During Exposure	10/10	6/10	8/9[b]	1/7[b]	p=0.0020
Liver Weight (g)	13.5 ± 0.3	13.7 ± 0.3	14.8 ± 0.3*	15.4 ± 0.6*	p=0.0002
Liver Weight (%)	3.42 ± 0.04	3.52 ± 0.04	3.79 ± 0.06*	3.98 ± 0.06*	p=0.0000
Kidney Weight (g)	1.25 ± 0.05	1.27 ± 0.03	1.31 ± 0.06	1.33 ± 0.05	p=0.1476
Kidney Weight (%)	0.32 ± 0.02	0.33 ± 0.01	0.33 ± 0.12	0.34 ± 0.01	p=0.0337
Spleen Weight (g)	0.69 ± 0.02	0.71 ± 0.02	0.67 ± 0.03	0.71 ± 0.03	p=0.6122
Spleen Weight (%)	0.17 ± 0.005	0.18 ± 0.004	0.17 ± 0.005	0.18 ± 0.006	p=0.4915
Testes Weight (g)	1.62 ± 0.12	1.70 ± 0.05	1.77 ± 0.05	1.70 ± 0.04	p=0.8186
Right Epididymis Weight (g)	0.60 ± 0.01	0.59 ± 0.02	0.58 ± 0.02	0.53 ± 0.03	p=0.6837
Left Cauda Weight (g)	0.22 ± 0.01	0.21 ± 0.01	0.19 ± 0.01	0.17 ± 0.01*	p=0.0006
Sperm/g Cauda (x 10^6)	775.0 ± 40.9	726.1 ± 31.3	824.8 ± 65.1	686.3 ± 76.5	p=0.6465
Total Sperm Count (x 10^6)	33.5 ± 2.2	30.5 ± 1.7	31.4 ± 2.6	22.9 ± 3.0*	p=0.0263
% Sperm Motility	82.7 ± 3.5	75.2 ± 3.9	70.5 ± 5.1	72.1 ± 5.9	p=0.4050
FOOD CONSUMPTION					
n Treated	10	10	10	10	
Grams per day					
SD 3-7	17.8 ± 0.6[a]	16.4 ± 0.5	16.3 ± 0.5	15.5 ± 0.7	p=0.0631
SD 7-11	20.2 ± 0.6	19.5 ± 0.4	19.2 ± 0.9	18.1 ± 0.6*	p=0.0280
SD 19-23	20.6 ± 0.5	20.6 ± 0.5	21.3 ± 0.4	20.6 ± 0.5	p=0.5953
SD 23-28	20.8 ± 0.5	21.0 ± 0.5	21.3 ± 0.4	21.0 ± 0.3	p=0.3652
BW Change (g)					
SD 3-28	15.5 ± 3.5	15.2 ± 2.2	15.4 ± 2.5	6.1 ± 5.1	p=0.1765
HEMATOLOGY DATA					
RBC (10^6/µl)	8.4 ± 0.05[a]	8.3 ± 0.1	8.3 ± 0.05	8.3 ± 0.1	p=0.1885
Hemoglobin (g/dl)	15.2 ± 0.1	15.2 ± 0.2	15.1 ± 0.2	14.9 ± 0.2	p=0.2565
Hematocrit (%)	46.1 ± 0.3	46.4 ± 0.6	45.5 ± 0.5	45.5 ± 0.8	p=0.3726
MCV (fl)	55.0 ± 0.6	55.7 ± 0.6	55.0 ± 0.7	54.9 ± 0.3	p=0.4957
MCH (pg)	18.0 ± 0.2	18.3 ± 0.2	18.3 ± 0.3	18.0 ± 0.1	p=0.7550
MCHC (g/dl)	32.9 ± 0.2	32.9 ± 0.2	33.2 ± 0.2	32.8 ± 0.2	p=1.0000
Reticulocytes[c]	0.12 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	0.14 ± 0.01	p=0.1763
Platelets (1000/µl)	675 ± 35	630 ± 47	708 ± 33	717 ± 72	p=0.4536
WBC (1000/µl)	10.6 ± 0.5	10.5 ± 0.8	9.2 ± 0.9	10.4 ± 0.9	p=0.3958
Seg. Neutrophils[c]	0.93 ± 0.05	1.18 ± 0.18	1.04 ± 0.16	1.17 ± 0.14	p=0.2463
Lymphocytes[c]	8.83 ± 0.50	8.38 ± 0.78	7.48 ± 0.60	8.33 ± 0.69	p=0.3116
Monocytes[c]	0.30 ± 0.02	0.35 ± 0.04	0.23 ± 0.02	0.40 ± 0.07	p=0.9549
Eosinophils[c]	0.19 ± 0.03	0.29 ± 0.06	0.23 ± 0.05	0.18 ± 0.04	p=0.4042
Basophils[c]	0.10 ± 0.01	0.08 ± 0.01	0.11 ± 0.03	0.05 ± 0.01*	p=0.0219
LUCs[c]	0.26 ± 0.04	0.19 ± 0.03	0.21 ± 0.06	0.24 ± 0.03	p=0.6612
CLINICAL CHEMISTRY DATA					
ALT	108.8 ± 15.2[a]	70.2 ± 11.6*	142.1 ± 43.9	125.5 ± 14.6	p=0.0188[†]
Sorbital Dehydrogenase	30.7 ± 5.1	19.6 ± 3.1	43.5 ± 14.6	41.2 ± 5.7	p=0.0261[†]
5' Nucleotidase	24.4 ± 1.0	22.9 ± 0.6	24.9 ± 1.2	26.3 ± 1.0	p=0.1139
Alkaline Phosphatase	115.2 ± 5.5	121.1 ± 8.0	124.0 ± 7.0	143.5 ± 6.1*	p=0.0095
Total Bile Acids	40.5 ± 5.3	34.4 ± 4.6	42.3 ± 4.9	43.7 ± 3.8	p=0.3718
Urea Nitrogen	19.9 ± 0.9	20.1 ± 0.7	19.1 ± 0.9	19.0 ± 0.7	p=0.2936
Total Protein	7.1 ± 0.1	7.1 ± 0.2	7.0 ± 0.1	7.1 ± 0.1	p=0.5667
Albumin	3.6 ± 0.1	3.5 ± 0.1	3.5 ± 0.1	3.6 ± 0.1	p=0.7778

[a] Mean ± SEM

[b] Female(s) died prior to mating

[c] Differentials expressed as absolute values

* *$p<0.05$ compared to controls*

[†] Kruskal-Wallis Test p-value

Table 2-6

GROUP 2

Continuous Exposure

Female Sprague Dawley Rats

	COPPER GALLIUM DISELENIDE (mg/kg/day)				
	0	30	100	250	Trend
FERTILITY AND NECROPSY DATA					
n Treated	10	10	10	10	
BW Change SD 0-28 (g)	73.3 ± 3.8[a]	61.3 ± 7.2	53.2 ± 3.4*	8.9 ± 9.7*	p=0.00002
Pregnant/Treated	10/10	6/10	8/9[b]	1/7[b]	p=0.0020
n Live Implants	13.2 ± 0.6	13.0 ± 0.9	11.2 ± 0.5*	0	p=0.0095
Early Resorptions	0.4 ± 0.2	2.0 ± 0.9*	0.1 ± 0.1	4	p=0.0106[†]
Late Resorptions	0	0	0	0	—
Total Implants	13.6 ± 0.6	15.0 ± 1.0	11.4 ± 0.6*	4	p=0.0206
Corpora Lutea	15.6 ± 0.9	15.5 ± 1.3	14.7 ± 0.4	7.1 ± 2.0*	p=0.0049
FOOD CONSUMPTION					
n Treated	10	10	9	9	
Grams per day					
SD 0-4	15.9 ± 0.8[a]	14.3 ± 0.5	14.6 ± 1.4	11.8 ± 1.3*	p=0.0008
SD 4-8	15.8 ± 0.5	14.9 ± 1.1	14.0 ± 1.2	9.1 ± 0.5*	p=0.00004
SD 8-12	15.7 ± 0.5	17.1 ± 1.0	15.6 ± 1.1	9.4 ± 0.8*	p=0.0012
SD 17-20	17.9 ± 0.6	17.7 ± 0.5	20.5 ± 1.1*	14.0 ± 1.5*	p=0.0015[†]
SD 20-24	19.4 ± 0.5	18.4 ± 0.7	18.6 ± 0.3	13.3 ± 1.0*	p=0.0001
SD 24-28	19.9 ± 0.5	18.2 ± 0.8	19.3 ± 0.5	13.6 ± 1.0*	p=0.0012
BW Change (g)					
SD 0-28	73.3 ± 3.8	61.3 ± 7.2	53.2 ± 3.4*	8.9 ± 9.7*	p=0.00002

[a] Mean ± SEM

[b] Female(s) died during exposure

* p<0.05 compared to controls

[†] Kruskal-Wallis Test *p*-value

Table 2-7

GROUP 3

Gestational Exposure

Female Sprague Dawley Rats

	COPPER GALLIUM DISELENIDE (mg/kg/day)				
	0	30	100	250	Trend
FERTILITY AND NECROPSY DATA					
Females					
Pregnant/Treated	7/11	8/12	10/12	10/12	
BW Change (g)					
GD 6-15	39.9 ± 2.7[a]	32.3 ± 2.8	39.7 ± 3.0	-2.3 ± 4.2*	p=0.0004
GD 0-15	66.2 ± 3.8	57.6 ± 3.5	64.9 ± 2.6	23.9 ± 4.4*	p=0.0002
BW PND 1 (g)	272.5 ± 7.4	257.6 ± 7.1	257.7 ± 6.9	217.9 ± 11.1*	p=0.0008
BW PND 4 (g)	280.3 ± 8.9	264.7 ± 4.7	271.2 ± 8.8	225.9 ± 8.1*	p=0.0003
BW Change (g)					
PND 1-4	7.8 ± 4.8	7.1 ± 2.2	13.5 ± 2.7	8.6 ± 2.8	p=0.4508
Neonates					
PND 0					
n Live	13.9 ± 0.9	10.6 ± 1.6	12.8 ± 0.6	9.4 ± 1.4	p=0.0598
n Dead	0.1 ± 0.1	0.2 ± 0.2	0	0.7 ± 0.3	p=0.1584
PND 1					
n Live	13.7 ± 0.8	10.6 ± 1.6	12.7 ± 0.6	9.1 ± 1.4	p=0.0521
n Dead	0.1 ± 0.1	0	0.1 ± 0.1	0.3 ± 0.3	p=0.8697
PND 4					
n Live	13.6 ± 0.8	10.6 ± 1.6	12.7 ± 0.6	8.8 ± 1.5	p=0.0510
n Dead	0.1 ± 0.1	0	0	0.3 ± 0.2	p=0.4658
Mean Body Weight (g)					
PND 1	6.5 ± 0.04	7.2 ± 0.2*	7.1 ± 0.2	5.6 ± 0.3	p=0.0016[†]
PND 4	9.5 ± 0.1	10.3 ± 0.3*	9.8 ± 0.4	8.1 ± 0.5	p=0.0180[†]
n Implantation Sites	14.7 ± 0.9	11.9 ± 1.5	15.1 ± 0.7	14.0 ± 0.6	p=0.8079
FOOD CONSUMPTION					
n Treated	11	12	12	12	
Grams per day					
GD 6-8	18.3 ± 1.0[a]	15.8 ± 0.8	17.3 ± 0.9	13.6 ± 0.8*	p=0.0051
GD 8-10	18.7 ± 1.0	17.4 ± 1.0	18.4 ± 0.7	11.8 ± 1.1*	p=0.0001
GD 10-12	19.3 ± 0.8	17.6 ± 0.9	18.9 ± 1.0	12.1 ± 1.2*	p=0.0003
GD 12-14	18.9 ± 1.1	17.8 ± 1.0	17.9 ± 1.0	12.4 ± 1.3*	p=0.0013
BW Change (g)					
GD 6-15	39.9 ± 2.7	32.3 ± 2.8	39.7 ± 3.0	-2.3 ± 4.2*	p=0.0004

[a] Mean ± SEM

*p<0.05 compared to controls

[†] Kruskal-Wallis Test p-value

GROUP 1

Table 2-8

Male Sprague Dawley Rats

	CADMIUM TELLURIDE (mg/kg/day)				
	0	10	30	100	**Trend**
FERTILITY AND NECROPSY DATA					
n Treated	10	10	9[a]	10	
BW Terminal (g)	429.6 ± 9.8[b]	432.1 ± 5.0	421.2 ± 9.6	400.8 ± 7.4*	p=0.0079
BW Change (g)	6.0 ± 0.8	2.3 ± 3.6	-0.5 ± 2.0*	-23.2 ± 4.9*	p=0.000004
n Fertile Prior to Exposure	10/10	10/10	10/10	10/10	—
n Fertile During Exposure	8/10	7/9[c]	9/9	5/8[c]	p=0.4100
Liver Weight (g)	14.6 ± 0.7	15.0 ± 0.4	15.5 ± 0.3	14.7 ± 0.3	p=0.3283
Liver Weight (%)	3.38 ± 0.10	3.47 ± 0.10	3.69 ± 0.05*	3.67 ± 0.05*	p=0.0024
Kidney Weight (g)	1.47 ± 0.10	1.60 ± 0.05	1.54 ± 0.05	1.57 ± 0.95	p=0.2811
Kidney Weight (%)	0.34 ± 0.01	0.37 ± 0.01	0.37 ± 0.01	0.39 ± 0.01*	p=0.0010
Spleen Weight (g)	0.69 ± 0.02	0.70 ± 0.02	0.70 ± 0.03	0.69 ± 0.01	p=0.7069
Spleen Weight (%)	0.16 ± 0.005	0.16 ± 0.004	0.17 ± 0.006	0.17 ± 0.003	p=0.0711
Testes Weight (g)	1.82 ± 0.06	1.90 ± 0.05	1.87 ± 0.03	1.86 ± 0.03	p=0.9301
Right Epididymis Weight (g)	0.59 ± 0.03	0.64 ± 0.02	0.63 ± 0.02	0.61 ± 0.02	p=0.9700
Left Cauda Weight (g)	0.20 ± 0.01	0.21 ± 0.01	0.19 ± 0.01	0.20 ± 0.01	p=0.7069
Sperm/g Cauda (x 10^6)	155.8 ± 18.5	162.8 ± 88.4	124.1 ± 10.7	149.3 ± 12.9	p=0.6700
% Sperm Motility	61.8 ± 3.1	55.1 ± 2.1	54.3 ± 6.5	61.2 ± 3.5	p=0.9301
FOOD CONSUMPTION					
n Treated	10	10	9	10	
Grams per day					
SD 3-7	19.3 ± 0.5[b]	19.0 ± 0.5	17.9 ± 0.7	16.4 ± 0.4*	p=0.0003
SD 7-11	18.3 ± 1.2	19.9 ± 0.4	18.3 ± 0.4	16.7 ± 0.5*	p=0.0007
SD 17-19	20.4 ± 0.6	20.8 ± 0.3	19.3 ± 0.7	19.8 ± 0.7	p=0.2645
SD 19-23	21.0 ± 0.7	21.2 ± 0.2	20.0 ± 0.5	19.1 ± 0.6	p=0.0073
SD 23-28	21.9 ± 0.7	22.0 ± 0.3	21.4 ± 0.6	21.0 ± 0.4	p=0.1202
BW Change (g)					
SD 3-28	6.0 ± 0.9	2.3 ± 3.6	-0.5 ± 2.0*	-23.2 ± 4.9*	p=0.000004
HEMATOLOGY DATA					
RBC (10^6/µl)	8.8 ± 0.1	8.7 ± 0.1	8.4 ± 0.1*	9.0 ± 0.2	p=0.0397[†]
Hemoglobin (g/dl)	15.6 ± 0.2	15.4 ± 0.2	15.2 ± 0.3	15.7 ± 0.3	p=0.9600
Hematocrit (%)	48.1 ± 0.7	47.2 ± 0.7	46.7 ± 1.0	48.5 ± 0.9	p=0.8903
MCV (fl)	54.4 ± 0.6	54.2 ± 0.8	55.9 ± 0.8	53.9 ± 0.5	p=0.9595
MCH (pg)	17.7 ± 0.1	17.1 ± 0.2	18.1 ± 0.3	17.5 ± 0.2	p=0.6970
MCHC (g/dl)	32.5 ± 0.1	32.7 ± 0.2	32.5 ± 0.2	32.4 ± 0.1	p=0.6154
Reticulocytes[d]	0.12 ± 0.01	0.13 ± 0.01	0.14 ± 0.01	0.12 ± 0.01	p=0.8887
Platelets (1000/µl)	675 ± 39	668 ± 36	544 ± 77	707 ± 35	p=0.9700
WBC (1000/µl)	10.2 ± 1.0[b]	10.3 ± 0.8	9.8 ± 1.5	19.0 ± 10.7	p=0.2336
Seg. Neutrophils[d]	1.0 ± 0.1	1.0 ± 0.1	1.3 ± 0.3	1.3 ± 0.1	p=0.0882
Lymphocytes[d]	8.4 ± 0.9	8.5 ± 0.7	7.6 ± 1.0	7.0 ± 1.0	p=0.1294
Monocytes[d]	0.28 ± 0.03	0.38 ± 0.06	0.41 ± 0.08	0.36 ± 0.04	p=0.2695
Eosinophils[d]	0.17 ± 0.03	0.13 ± 0.03	0.18 ± 0.08	0.08 ± 0.03*	p=0.0336
Basophils[d]	0.01 ± 0.01	0	0	0.01 ± 0.01	p=0.4715
LUCs[d]	0.34 ± 0.09	0.31 ± 0.05	0.28 ± 0.06	0.24 ± 0.04	p=0.4747
CLINICAL CHEMISTRY DATA					
ALT	73.8 ± 16.7[b]	109.7 ± 36.0	78.7 ± 8.5	94.9 ± 12.7*	p=0.0331
Sorbital Dehydrogenase	17.6 ± 4.2	28.2 ± 9.6	20.1 ± 2.2*	21.0 ± 2.3*	p=0.0260
5' Nucleotidase	23.6 ± 1.1	24.2 ± 1.2	23.1 ± 0.8	22.4 ± 0.83	p=0.3767
Alkaline Phosphatase	88.2 ± 4.5	87.2 ± 4.6	84.6 ± 1.8	78.3 ± 4.0	p=0.1030
Total Bile Acids	40.3 ± 5.9	53.3 ± 7.4	47.5 ± 5.4	51.2 ± 7.5	p=0.3537
Urea Nitrogen	17.3 ± 0.8	15.5 ± 0.6	15.2 ± 0.7	17.9 ± 0.7	p=0.0447[†]
Total Protein	7.45 ± 0.12	7.21 ± 0.1	7.28 ± 0.1	7.31 ± 0.1	p=0.6771
Albumin	3.48 ± 0.05	3.54 ± 0.1	3.46 ± 0.1	3.71 ± 0.05*	p=0.0306[†]
Urinary Creatinine	159.9 ± 12.1	177.9 ± 9.1	171.1 ± 9.1	156.6 ± 13.4	p=0.9648
Cd/mg Creatinine/ml Urine	0.078 ± 0.02	0.073 ± 0.02	0.085 ± 0.05	0.088 ± 0.03	—

[a] One male died during dosing

[b] Mean ± SEM

[c] Females died prior to mating

[d] Differentials expressed as absolute values

* p<0.05 compared to controls

[†] Kruskal-Wallis Test p-value

Table 2-9

GROUP 2

Continuous Exposure

Female Sprague Dawley Rats

	CADMIUM TELLURIDE (mg/kg/day)				
	0	10	30	100	Trend
FERTILITY AND NECROPSY DATA					
n Treated	10	10	10	10	
BW Change SD 0-28 (g)	76.9 ± 8.1[a]	55.4 ± 7.2	56.5 ± 5.4	33.8 ± 4.4*	p=0.0018
Pregnant/Treated	8/10	7/9	9/9[b]	5/8[c]	p=0.4100
n Live Implants	10.5 ± 1.8	11.7 ± 1.5	13.2 ± 1.1	11.0 ± 0.6	p=0.8509
Early Resorptions	0.5 ± 0.3	0.1 ± 0.1	0.2 ± 0.1	1.0 ± 0.3	p=0.2705
Late Resorptions	0	0	0	0	—
Total Implants	11.0 ± 1.8	11.9 ± 1.6	13.4 ± 1.1	12.0 ± 0.4	p=0.7644
Corpora Lutea	13.9 ± 0.8	15.4 ± 0.8	15.8 ± 0.4	14.5 ± 0.8	p=0.5803
FOOD CONSUMPTION					
n Treated	10	9	10	10[c]	
Grams per day					
SD 0-4	12.9 ± 0.4[a]	11.9 ± 1.1	12.3 ± 0.4	10.7 ± 0.5*	p=0.0117
SD 4-8	14.9 ± 0.5	14.3 ± 0.4	14.7 ± 0.4	12.4 ± 0.7*	p=0.0104
SD 8-12	15.2 ± 0.3	14.8 ± 0.5	14.6 ± 0.2	12.8 ± 0.6*	p=0.0023
SD 17-20	19.5 ± 0.6	18.4 ± 0.6	19.0 ± 0.3	16.0 ± 0.4*	p=0.0089
SD 20-24	18.7 ± 0.6	17.7 ± 0.7	17.2 ± 0.4	15.9 ± 0.4*	p=0.0046
SD 24-28	21.0 ± 0.6	18.8 ± 0.8*	19.5 ± 0.4*	18.2 ± 0.3*	p=0.0122
BW Change (g)					
SD 0-28	76.9 ± 8.1	55.4 ± 7.2	56.5 ± 5.4	33.8 ± 4.4*	p=0.0018

[a] Mean ± SEM
[b] One male died prior to mating
[c] Two females died during exposure
*p<0.05 compared to controls

Table 2-10

GROUP 3

Gestational Exposure

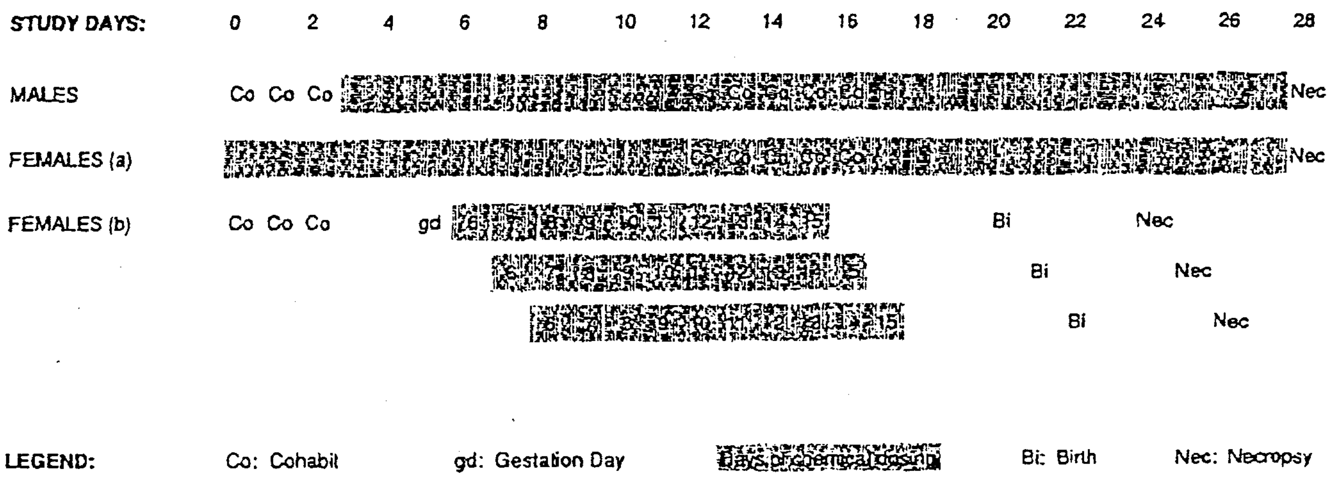
Female Sprague Dawley Rats

	CADMIUM TELLURIDE (mg/kg/day)				
	0	10	30	100	Trend
FERTILITY AND NECROPSY DATA					
Females					
Pregnant/Treated	12/13	10/11	12/12	10/10	
BW Change (g)					
GD 6-15	42.3 ± 2.7[a]	28.7 ± 8.5	33.4 ± 1.1*	19.2 ± 3.9*	p=0.000009
GD 0-15	66.6 ± 2.7	54.1 ± 7.5	56.4 ± 2.5*	42.3 ± 6.0*	p=0.00004
BW PND 1 (g)	273.2 ± 6.6	266.5 ± 5.3	250.4 ± 4.3*	232.0 ± 6.9*	p=0.00002
BW PND 4 (g)	284.5 ± 6.0	275.4 ± 5.7	260.6 ± 6.2*	249.9 ± 7.2*	p=0.0002
BW Change (g)					
PND 1-4	13.9 ± 2.0	10.8 ± 2.1	10.2 ± 4.1	17.9 ± 3.6	p=0.4695
Neonates					
PND 0					
n Live	12.8 ± 0.7	10.6 ± 1.0	11.8 ± 0.9	12.3 ± 0.6	p=0.6161
n Dead	0.3 ± 0.2	0.1 ± 0.1	0.6 ± 0.3	1.0 ± 0.6	p=0.3116
PND 1					
n Live	12.7 ± 0.7	10.6 ± 1.0	11.6 ± 0.9	12.1 ± 0.6	p=0.5520
n Dead	0.1 ± 0.1	0	0.2 ± 0.1	0.2 ± 0.1	p=0.3945
PND 4					
n Live	12.7 ± 0.7	10.5 ± 0.9	11.5 ± 0.9	12.0 ± 0.6	p=0.4998
n Dead	0	0	0.1 ± 0.1	0.1 ± 0.1	p=0.2905
Mean Body Weight (g)					
PND 1	6.8 ± 0.2	7.1 ± 0.2	7.0 ± 0.2	6.5 ± 0.2	p=0.5362
PND 4	10.0 ± 0.4	10.5 ± 0.3	10.2 ± 0.5	9.1 ± 0.4	p=0.2468
n Implantation Sites	13.9 ± 0.8	13.3 ± 0.6	13.9 ± 0.6	14.0 ± 0.3	p=0.9113
FOOD CONSUMPTION					
n Treated	13	11	12	10	
Grams per day					
GD 6-8	19.9 ± 0.9[a]	19.1 ± 1.4	19.1 ± 0.8	16.6 ± 0.9*	p=0.0246
GD 8-10	20.0 ± 0.3	19.5 ± 1.1	18.6 ± 0.6*	17.3 ± 0.8*	p=0.0039
GD 10-12	21.1 ± 0.5	19.3 ± 1.0	18.9 ± 0.8*	17.0 ± 0.5*	p=0.0001
GD 12-14	20.2 ± 1.1	18.7 ± 1.1	20.4 ± 0.8	15.4 ± 1.2*	p=0.0045
BW Change (g)					
GD 6-15	42.3 ± 5.2	28.7 ± 8.5	33.4 ± 1.1*	19.2 ± 3.9*	p=0.00001

[a] Mean ± SEM

*p<0.05 compared to controls

SUBCHRONIC TOXICITY SCREEN INCLUDING OBSERVATIONS FOR REPRODUCTIVE AND DEVELOPMENTAL TOXICITY



OBSERVATIONS:

MALES	Subchronic toxicity and male fertility (3 dose levels plus control, n=10/group); bw days 3, 7, 11, 15, 19, 23, 28; modified *functional observational battery; gross necropsy; histopathy on liver, kidney, testis; hematology on blood at termination;* fertility before and during chemical administration, epididymal sperm motility and total epididymal sperm count.
FEMALES (a)	Subchronic toxicity and female fertility (3 dose levels plus control, n=10/group) bw days 0, 4, 8, 12, 16, 20, 24, 28; % pregnant, number of implants, and number of corpora lutea.
FEMALES (b)	Development toxicity (3 dose levels plus control, n=10 smear-positive females/group). Confirm mating by vaginal smear or plug during cohabitation; dose females on gd 6 through 15; bw on gd 0, 6, 10, 15, and pnds 1 and 4; number and weight of pups at pnd 1, 4; uterine implantation sites at nec, pnd 4.

Figure 2-1. This figure schematizes the design used to evaluate the toxicity of CIS, CGS, and CdTe. For the first three days of the study, males (Group 1) are co-habited with a group of females (Group 3). At the end of cohabitation, the animals are separated, and the females housed until they are dosed from gestation day 6 - 15. They are allowed to give birth, and rear their young until postnatal day 4. Meanwhile, the males are dosed from study day (SD) 3 until SD27. These males are mated with another group of females (Group 2) from SD12-SD16, during which time both sexes are being treated with the compound. Food consumption and body weights are measured for all animals. Additional endpoints are: for Group 1, clinical chemistries, hematology, organ weights and pathology, and sperm measures (count and motility). For Group 2, additional endpoints are the number of pregnant females, the number of uterine implants, and the number of corpora lutea. For Group 3, endpoints are the number and weight of pups on postnatal days 0, 1, and 4, and number of maternal uterine implantation sites.

3. ENVIRONMENTAL AND HEALTH ASPECTS OF COPPER-INDIUM-DISELENIDE AND CADMIUM-TELLURIDE THIN-FILM PHOTOVOLTAIC MODULES

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ABSTRACT

Copper-indium-diselenide (CIS) and cadmium-telluride (CdTe) are semiconductor compounds that can be used to produce thin-film photovoltaic modules. There is ongoing research being conducted by various federal agencies and private industries to demonstrate the commercial viability of this materials. Because these are new technologies, and because scant information about the health and environmental hazards associated with the use of this materials is available, studies have been initiated to characterize the environmental mobility and environmental toxicology of this compounds. The objective of these studies is to identify the environmental and health hazards associated with the production, use, and disposal of CIS and CdTe thin-film photovoltaic modules. The program includes both theoretical and experimental components and is funded by the German Bundesministerium für Forschung und Technologie (BMFT). Theoretical studies are being undertaken from the Fraunhofer Institute of Solid State Technology to estimate material flows through the environment for a range of production options as well as use and disposal scenarios. The experimental programs are carried out by the Institute of Ecotoxicology of the GSF Forschungszentrum für Umwelt und Gesundheit (GSF-IÖC) and characterize physical and chemical parameters e.g. leachability and biological parameters e.g. EC_{50} in daphnia and algae. In parallel, the U.S. Department of Energy (DOE) and the National Institute of Environmental Health Sciences (NIEHS) funded an experimental program on biological systems, e.g. feeding studies in rats.

LIFE CYCLE OF SOLAR MODULES

The complete lifecycle of almost all products includes:

- the starting material
- the manufacturing
- the installation, operation and use
- the recycling and disposal.

Today, nearly any type of marketing concept is based on a linear product path starting with the raw material and ending after usage with the disposal of the product. However, most product life cycles can be closed by a recycling strategy based either on the product or material level.

In order to characterize all materials and material-paths into air, water and soil in the life cycle of our selected products for the thin-film modules we define the areas of investigations according to the following:

In the production of starting materials for the thin-film modules, solids, liquids, gaseous materials (elements and compounds) and prefabricated components must be considered. Solar module manufacturing uses these materials including the substrate, thin-films, laminates, cover glass, junction boxes, cables and frame materials. For the installation, operation or use we have restricted the photovoltaic (PV) modules to power application products like solar power plants or solar houses or to public accessible products like solar powered emergency call boxes on highways. Normal operation and accidents must be examined. Disposal including landfilling and incineration are issues to be investigated with their contribution of the material and material-flows of the products and byproducts into the environment e.g. drain-water, decomposition gas, slag or electro-filter dust and exhaust fume.

The entire lifecycle of a photovoltaic module shows outputs of rejected matter in every stage of the linear product line, e.g. of the incoming and outgoing materials at the spezification control, of the final product after manufacturing or at the usage, when reduced power occurs. Inputs of reusable materials to the product line are possible at the refining processes of starting materials or somewhere at the module manufacturing. Inputs of systems, components or subsystems are fed back into the product line at manufacturing or before disposal (Fig. 1).

This investigation concentrates on the materials and paths of materials during the lifecycle of a solar module, but excludes all materials for solar module mounting systems, batteries, converters, and grid connections. It also excludes the energy consumption of module or material production processes.

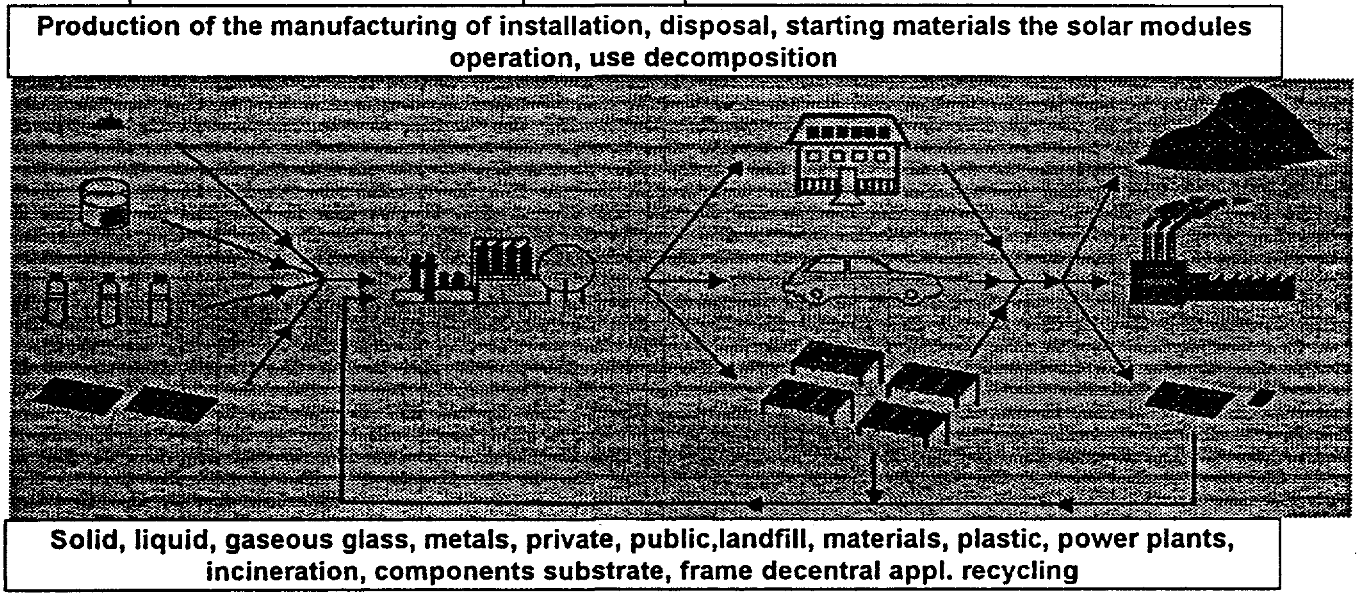

Figure 3-1. Lifecycle of a solar module

The principal material flow of input, output and auxiliary substances in a single processing step is shown in Figure 2. Input materials are all materials partly or totally transformed into the product. Auxiliary materials are all materials taking part in the processing but not remaining in the product. Output materials are the rejected input materials or the rejected auxiliary materials.

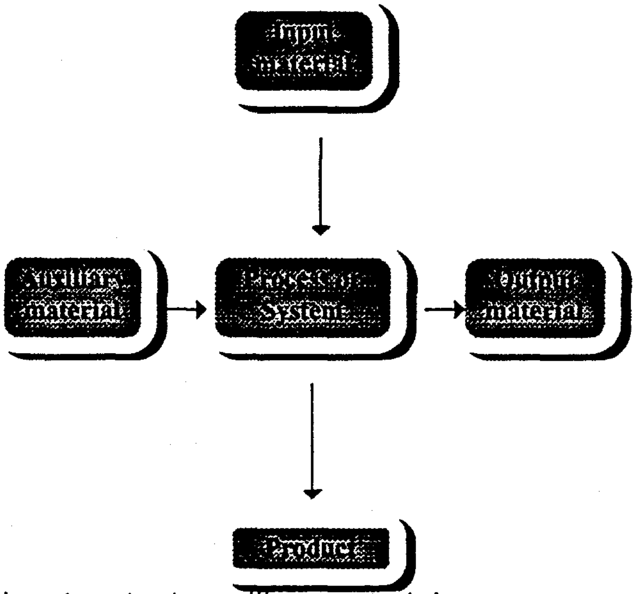

Figure 3-2. Definition of input, output, auxiliary materials

STARTING MATERIALS

The weight ratio of the element within the uppermost shell of the earth is called the total abundance. In order to identify the highest need for the conservation of resources, Table 1 compares the total material abundance, the annual production rate, and the minimum material consumption of important materials needed to produce 1 GW_e of solar modules. This roughly correlates to a 10 km^2 module area. Based on this analysis, it seems that tellurium (Te), indium (In) and selenium (Se) will be the bottleneck materials in future.

Table 3-1. Abundance, Production and Material Consumption of Important Elements for Thin-Film Module Fabrication

Material	Abundance	Production t/a	Consuption t/GW CdTe	Consumption t/GW CIS
copper	$1 \cdot 10^{-4}$	$9.30 \cdot 10^{6}$		$1.1 \cdot 10^{3}$
indium	$1 \cdot 10^{-7}$	$1.34 \cdot 10^{2}$		30
selenium	$8 \cdot 10^{-7}$	$1.50 \cdot 10^{3}$		41
molyb-denum	$1 \cdot 10^{-5}$	$1.17 \cdot 10^{5}$		76
cadmium	$3 \cdot 10^{-5}$	$1.80 \cdot 10^{4}$	62	3
tellurium	$1 \cdot 10^{-8}$	$3.50 \cdot 10^{2}$	89	
soda lime glass	$1 \cdot 10^{-1}$	$2.10 \cdot 10^{7}$	$1.25 \cdot 10^{5}$	$1.25 \cdot 10^{5}$

Copper (Cu) mining is the most important source of Se. As Se is found on the lower most right side of the periodic table, it shows a quasi-noble behavior and, therefore, is enriched like gold (Au) or silver (Ag) in the anode mud of the electrolytic refining method of Cu. Copper ores are found in many places in the world, but presently they are very diluted. Ores with a Cu content of more than 0.5 % are mineable. This means that 1,000 t of stones or rocks must be mined to be cracked and leached to produce 1 t of technically pure Cu.

Zinc (Zn) production is the main source of In; about 7 million t are produced every year. Like Cu, about 10^6 t of stones must be processed for each ton of In produced. Since In is noble and, in addition, shows a low melting point, but a high boiling point, it can be extracted from Zn by destilling. Electrolysis of In-rich Zn is done, too, in order to get technically pure In.

The Se production which is associated with the Cu production follows the mining rates of copper ores. About 10^6 t of stones must be moved for one ton of Se.

Molybdenum (Mo) is mostly associated with Cu in Cu-mines and can be extracted from ores by mechanical flotation, chemical oxidation and reduction. Because of the high Mo-content in most sulfidic ores, only $40 \cdot 10^3$ t stones contribute to the manufacuring of one t pure Mo.

Zn ores and production again are the main sources for the Cadmium (Cd) production. Electrolysis is one of the most efficient technique applied to the concentrate of the Zn mud, but oxidation, destillation and floating is a practisized alternative in the world. Sphalerit (ZnS) ores contain ca. 67 % Zn and 0.1 to 0.4 % Cd. Therefore about $15 \cdot 10^3$ t are needed for 1 t Cd.

Tellurium (Te) has also been won in the Cu production although various Te minerals are known. Approximately 95 % of the Te production comes from the electrolytical extraction in the Cu manufacturing. Te has a very low abundance and no special enrichment in ores are observed besides of that in manganium (Mn) nodes. It therefore points to the highest material movement efforts of $40 \cdot 10^6$ t for one ton of pure Te.

MANUFACTURING

The structure of a CIS-cell and a CdTe-module can be seen in Figure 3a and 3b. Various thin-films are deposited on a glass substrate and covered by the front glass. In the homogeneous layers mechanical or laser structuring techniques form monolythically integrated parallel cells. The whole set of photoactive devices is called a module.

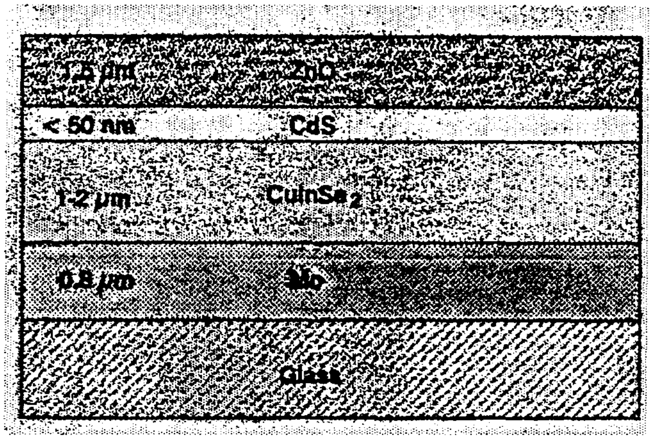

Figure 3-3a. Cross section of a typical CIS solar cell (Siemens Solar Industries 1994)

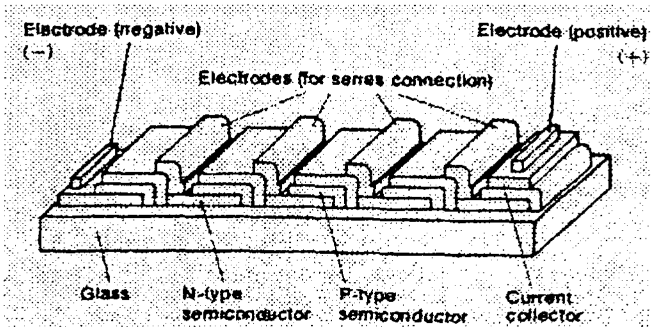

Figure 3-3b. Schematic of a typical CdTe solar module (Panasonic product catalogue 1993)

For two different types of modules, CIS and CdTe, the total material input of the critical element Cd is calculated for a 1 m^2 module area and a 1 μm layer thickness. CIS consumes roughly 1 $g/m^2/\mu m$ Cd for the cadmium-sulfide (CdS) layer formation as the total input material. In comparison CdTe uses 10 to 550 $g/m^2/\mu m$ Cd for the CdTe and CdS layer formation depending on the deposition technique.

The ratio of the deposited material and the input material is defined as the process efficiency according to material utilization. Thus the wide range of Cd consumption in the CdTe technology reflects the variation in the layer thicknesses and, in addition, far more the variation in the process efficiencies e.g. 90% to 10% range for screen printing to spray pyrolysis or chemical bath deposition.

INSTALLATION, OPERATION, USE

In the literature there is no reference to accidents or incidents during storage, but a few to transporting. Problems are known in the installation phase of silicon photovoltaic modules due to the malfunction of the electrical insulation, of the mechanical structure or the cabling along with broken glasses (van der Weiden 1991, Schaffrin 1991, Chianese 1991).

Breaks in cables, modules destroyed by snow storms, bubbles between the laminated glasses caused by temperature rises, mechanical impact on modules and stone throwing onto the modules are some of the problems externally created and reported in the literature during use and operation of silicon modules. Penetrating water in an aggressive environment near the sea or salt from highways in wintertime and elevated temperatures have created short-circuits and corrosion. Sparks of thunder storms have destroyed many modules and entire systems in Germany, Greece and Italy. Electric short-circuits have been generated by servicing personal during installation or maintenance. In some cases melting of the cover glasses as a consequence of the high temperature in and around the sparks are reported. O'Riordan (O'Riordan 1991) has investigated the system in Ireland on the Fota Islands. Table 2 shows the different effects on the modules.

Table 3-2. Effects and Problems of Silicon Solar Modules on the Fota Islands in Ireland

Reason for the problems	Numbers	% Ratio
Broken front glasses	22	28
Oxidation of front contacts	16	20
Color change of the substrate	15	19
Penetration of water	11	14
Broken substrate glasses	10	13
Broken ends	4	5
Laminate	1	1
In total for 2,772 modules	79	100

DISPOSAL

Different options for waste disposal are under discussion in Europe. Waste incineration is gaining more political interest and was indirectly implemented by the new legislative initiative in 1993 in Germany defining the "technical regulations for municipal waste". These new regulations do not allow wastes to be disposed at a regular landfill (Class 1 or 2) when metallic elements in an eluate or organic compounds in the ash of incinerated materials of a typical product exceed given limits. The content of metallic elements in the eluate has to be proved following the German leaching test DEV S4. The remaining organic compounds in the ash also have to be verified according to the German ashing standard tests. Since modern products mostly contain plastic materials, their ashes exceed the 3 % or 5 % organic limits for Class 1 or Class 2 landfill deposition, respectively. Therefore they fail the municipal landfill regulations and have to be placed in hazardous waste landfills or pretreated by waste incineration.

Slag and filter dust of a municipal waste incineration facility have to be tested in the same way (for metals and organics) before disposing in landfills. In case they exceed the limits for Class 1 or 2 landfills, they must be disposed in landfills for hazardous materials.

On the basis of an one year averaged distribution of input and output materials for a German municipal waste incineration facility (Nottrodt, 1975), we have estimated the total released material in slag, filter dust and pure gas dust assuming a 1 kW module input of CIS-technology, see Figure 4a, and a 1 kW module input of CdTe-technology, see Figure 4b.

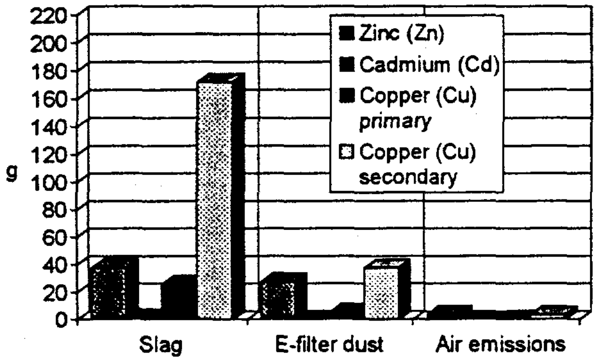

Figure 3-4a. Output material distribution of a 1 kW CIS-module input into a municipal waste incineration facility in Germany

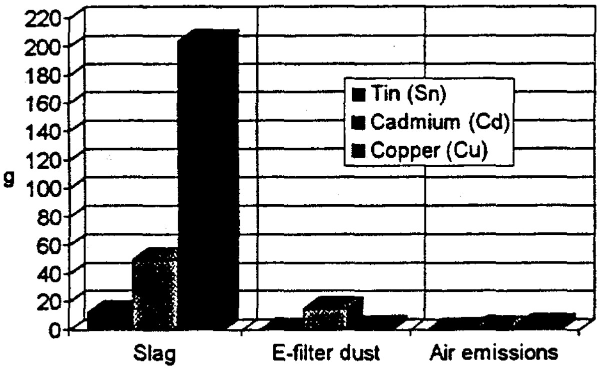

Figure 3-4b. Output material distribution of a 1 kW CdTe-module input into a municipal waste incineration facility in Germany

These estimations again take into consideration the materials both from the thin-film layers on the substrate (primary) and the frame materials (secondary). The main contribution in the case of CIS is Cu in the slag of around 200 g in total, of 43 g in filter dust and 4 g in the released gas dust. Cadmium is represented in slag as 1.5 g, as 0.5 g in the filter dust, and around 0.05 g in the released gas dust.

For the CdTe-module example, Cu is about as high as for CIS-modules 200 g in slag and 4 g in the released gas dust. Cadmium is in slag 50 g, in filter dust 15 g, and 2 g in the gas dust.

RECYCLING

Preexperiments on commercially available CdTe-modules for recycling have been carried out using liquid nitrogen, sand blasting techniques and HCl etching. Liquid nitrogen has peeled off large areas of thin-film layers. The remaining residues on the surface of the glass substrate were then etched back by HCl, which left a clean transparent glass substrate showing small reflecting zones along the removed structuring lines. Sand blasting with two different sand particle sizes (50 mm glassbeads and 70 mm corundum) seems also possible for recycling, if the working speed can be controlled in the correct processing window to avoid surface cracks or holes of the glass substrate. Similar studies are being prepared for CIS modules.

CONCLUSION

The theoretical investigation showed few relevant materials released as output materials in a linear product line along the life cycle of a CIS- or CdTe-module.

Mining has $1 \cdot 10^6$ t material output from mines for 1 t technically pure In- or Se-material production and $40 \cdot 10^6$ t for pure Mo-material production. Cd is consumed as total input material in the PV-manufacturing area of about 1 g/m²/µm for the CIS-technology and 10 to 550 g/m²/µm for the CdTe-technology and, both with respect to different process efficiencies and material utilization. Following our model, Cu, Zn, or Cd could be found at detectable concentrations in waste incineration facilities. Preexperiments on recycling with CdTe modules seem to be transformable to CIS modules and are now taken into consideration.

Thus, all life cycle steps of PV modules seem controllable in the qualitative and quantitative effects of materials running along paths in and out of processes or systems.

ACKNOWLEDGMENT

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4. ENVIRONMENTAL STUDIES

EXPERIMENTAL APPROACH TO ASSESS ENVIRONMENTAL RISKS OF THE USE AND DISPOSAL OF THIN-FILM SOLAR CELLS

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ABSTRACT

Thin-film solar cell technology is a new one and the most promising compounds in this technology are copper-indium-diselenide (CIS) and cadmiumtelluride (CdTe). Since there is scant information available about health and environmental hazards, studies have been initiated to characterize the environmental mobility and environmental toxicology of these compounds and materials. The objective of this study is to characterize the environmental hazards associated with the use, and disposal of CIS and CdTe thin-film photovoltaic modules. This study is funded by the Bundesministerium für Forschung und Technologie (BMFT). It is a collaboration with Fraunhofer Institute for Solid State Technology and Brookhaven National Laboratories.

Here we report the strategy and experimental work to assess environmental aspects associated with the use and disposal of modules. For qualitative and quantitative estimation of a potential burden to the environment different areas of use and the disposal of solar cells and modules are looked at. These informations are obtained from literature and data provided by developers of this new technology. These more theoretical studies are the backing for the experimental work where entry into and pathway through the environment of used substances is simulated by physical and chemical experiments in the laboratory, (e.g., solubility,) K_d-values in soil and leachability are determined. In biological experiments the possible impact on living matter is established. These experiments comprise toxicity (e.g., EC_{50} in daphnia and bacteria) as well as mutagenicity tests (e.g., Ames-test).

INTRODUCTION

New industrial production processes for innovative products which will be produced in high numbers with newly developed materials demand a very distinctive and precise evaluation of health and environmental aspects. To keep potential hazards as low as possible the development of new technics for the assessment of toxicological and ecotoxicological risks is necessary. A complete judgement of the potential of materials or combinations of materials endangering man or the environment is a complex procedure that can only be performed by knowledge of the physical, chemical, toxicological and ecotoxicological parameters.

The aim of our study is to assess the risks for environment and health arising during the life-cycle of thin-film solar cells. Since the sunlight is directly converted into electric energy photovoltaics is considered to be a non-polluting technology. However, experiences with the environmental behaviour of solar cells in reality are scarce, especially when new problems arise from high numbers and long-term operation or the invention of a new technology.

At the moment much research is being conducted by various public research institutions and private industry to demonstrate the commercial viability of so-called thin-film solar cells. The active layer of these consists of newly developed semiconductor compounds of which copper indium diselenide and cadmium telluride are the most promising. They are supposed to come to the market-place at a convenient price. For this type of solar cells all the criteria for new technologies mentioned above are valid.

During production the amount of materials used is much greater than in the rest of a products life-cycle. However, this part is covered by regulations for handling, transport, safety etc. to a great extent and risks should be at a minimum. For this reason our study mainly focusses on the use and disposal of solar cells.

RATIONALE OF THE DESIGN OF EXPERIMENTS

In general the same chemical and physical properties, the same physical transport phenomena and biological mechanisms playing a role in material cycles in nature determine the environmental behaviour and the effects of critical materials. Important factors for an assessment of potential consequences arising from the invention of new technologies is on one hand the knowledge of the path along which a certain material is distributed and on the other hand the potential impact on environment. In Fig. 4-1 a simple scheme of possible paths into different compartments of the environment is given.

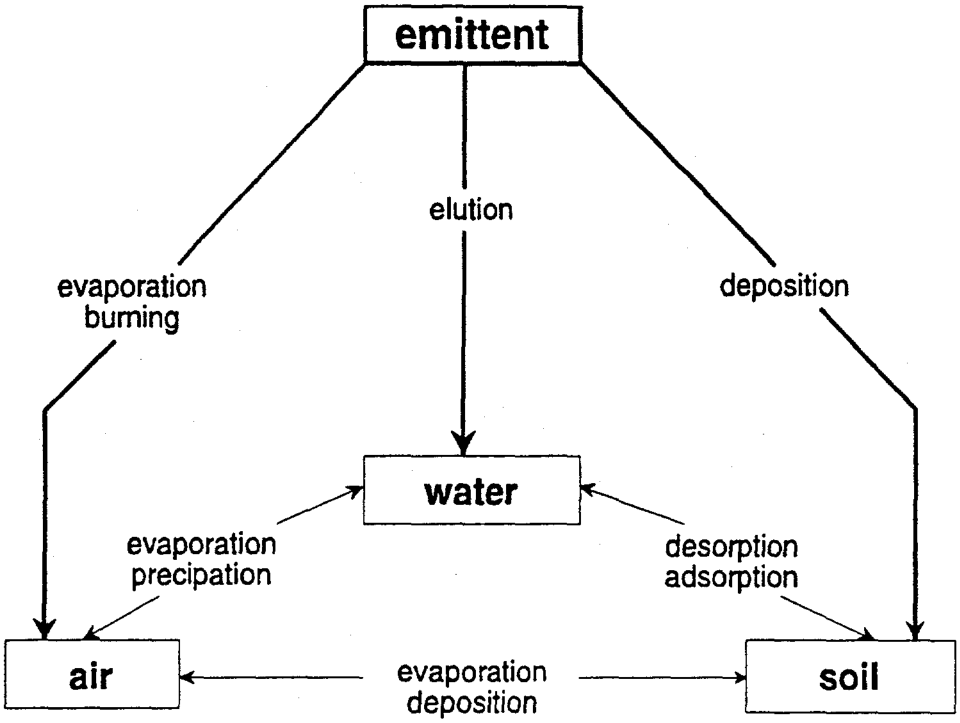


Figure 4-1. Pathway of substances in the environment.

Besides the physico-chemical characterization of materials and the detection of the material load in different compartments of the environment studies in respect of the ecotoxicological impact of emitted chemicals on organisms are essential. Ecotoxicology is commonly defined as the science of chemical and physiological stress to living organisms, populations and communities. To perform an ecotoxicological evaluation and a risk assessment of materials emitted to the environment the following parameters are necessary:

- Input (/output) into the environment
- Tendency of dispersion
- Persistency
- Accumulation
- Toxic effect

By knowledge of these parameters the strategy of assessing ecotoxicity shown in Fig. 4-2 can be followed.

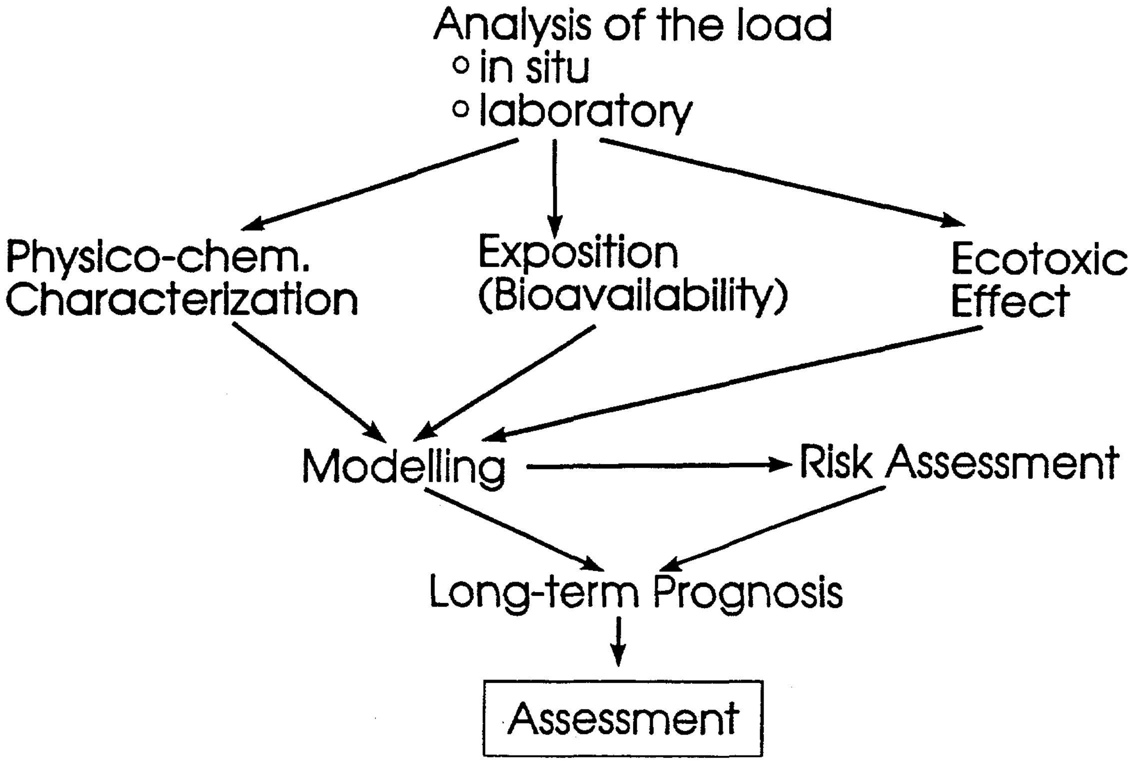


Figure 4-2. Strategy of an assessment.

REALIZATION OF AN ASSESSMENT

As mentioned before the realization of a risk assessment demands a great number of physico-chemical and ecotoxicological data. Only some of these data are available from literature. For many materials and elements especially if they are used in future technologies there is a total lack of data. The potential entry into and the effect in the environment has to be simulated in laboratory experiments. In Fig. 4-3 a scheme of the procedure how the environmental behaviour of used substances is characterized in experiments is illustrated. Data gained can be used in analysis of problems and future concepts.

The item physico-chemical experiments deals with the emission into different compartments of the environment. The emission to water to surface water as well as to groundwater can in reality occur by leaching of defect solar cells with rainwater or in landfills by seepage water. These possibilities are simulated in laboratory and outdoor experiments. Volatile products and residues that may be generated in the case of fire on house-roofs or in waste incinerations are detected with the aid of modern thermoanalytical methods. The behaviour of materials and compounds in soil transported via air or water, especially the interaction between compounds and soil is a very complex process. In addition there is no such thing like the "soil" but a great variety of soils with different composition. This problem with different soils is solved by the use of a selection of representative components in adsorption-desorption experiments. The results have to be extrapolated to longer time periods.

In toxicological-ecotoxicological investigations the effects of critical substances to environmental organisms are detected. The toxicity tests carried out with aquatic organisms show acute and chronic effects. The chronic effects are less spectacular than acute effects but changes of populations as a consequence of sublethal effects take place more often in reality.

Accumulation tests indicate unwanted uptake and enrichment of noxious substances in living organisms. These investigations also permit conclusions in respect to long-term effects.

In mutagenicity tests possible effects on the whole biosphere are covered which may happen at concentrations far below those exhibiting toxic effects.

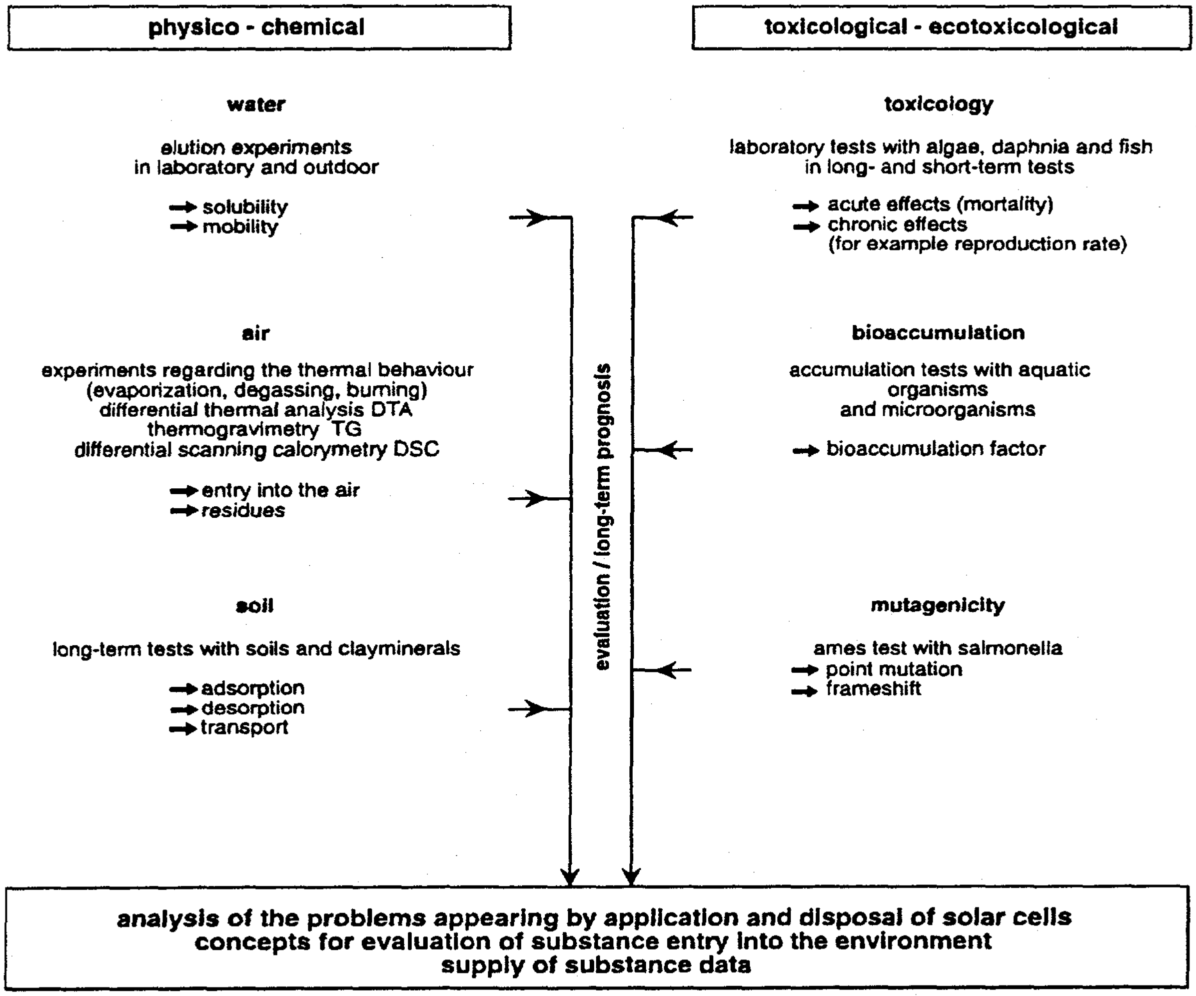


Figure 4-3. Characterization of used substances and materials.

EXPERIMENTS AND RESULTS

The physico-chemical part of our work was started with elution tests. A part of these tests is performed outdoors. There solar cell panels and fragments (in order to simulate accidents) are exposed to natural weather conditions. The eluates are sampled at convenient time periods and analyzed. These experiments will endure more than two years.

The situation in landfills is simulated by nationally and internationally approved elution tests. Four different methods are used, the German DEV S4, the TCLP, the Swiss test and an elution test developed at the University of Wisconsin for EPA. They have in common that the samples are rotated end over end for 24 hours with an eluent. In reality seepage water shows an aggressive behaviour which is simulated by acidification of percolating waters or addition of complexing agents.

Zinc, molybdenum and selenium are the elements eluted in the highest amounts from fragmented solar cells. In Fig. 4-4 a comparison is shown between the different tests and the concentrations found in the eluates. Zinc is eluted in the highest amounts at low pH and high complexing agent content whereas molybdenum and selenium are eluted better at higher pH. They are supposed to elute as anionic species and this may explain their behaviour.

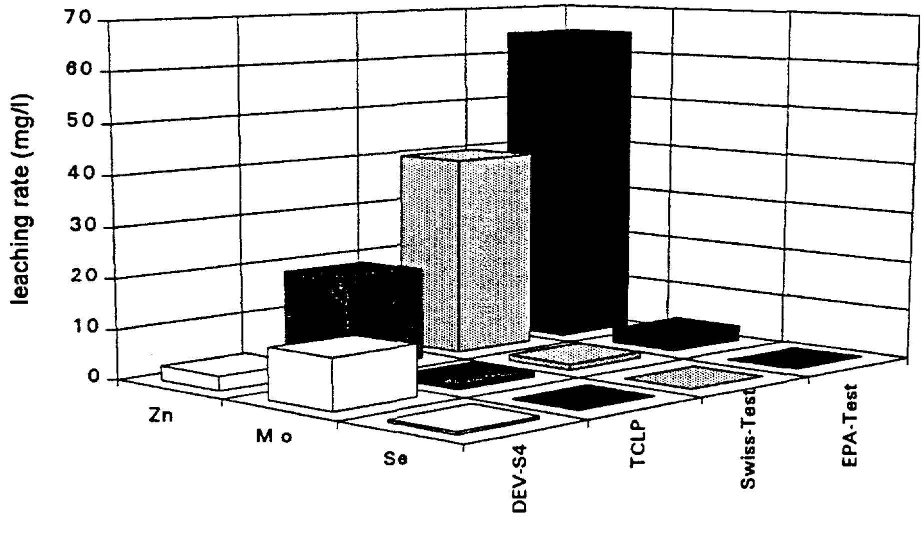
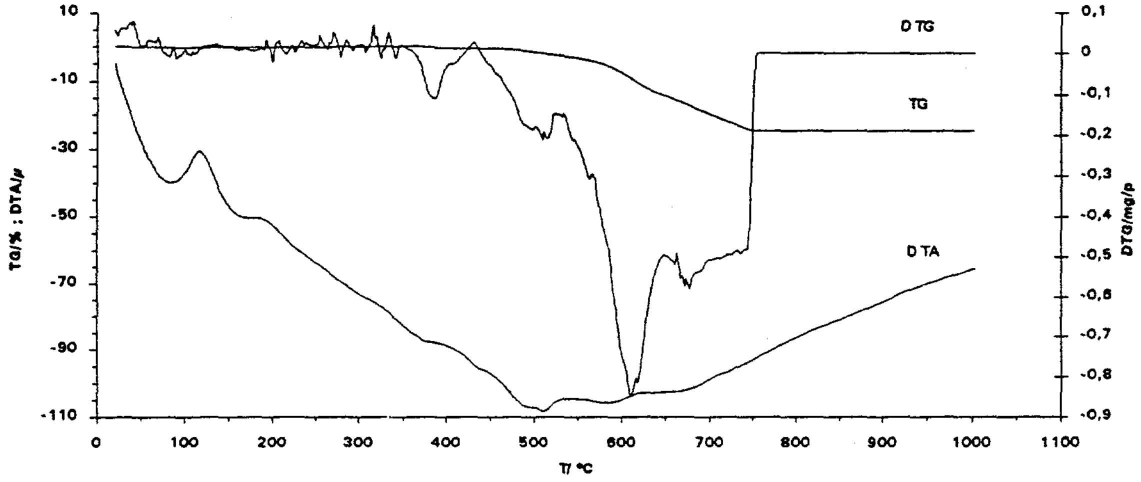


Figure 4-4. Different elution tests.

Fig. 4-5 shows the results of a differential thermal analysis. Samples of pure CIS and CdTe material were heated in air. Important information can be deduced from the thermogravimetry curve. For CIS a weight loss of about 20% is found starting at around 600°C. As proved by other experimental methods this corresponds to the loss of one selenium atom per $CuInSe_2$. For CdTe a small increase of the weight between approximately 750 - 800°C must be due to oxidation. Around 1000°C evaporation of the material starts, finally there is no material left in the measuring cups.


DTA of CIS

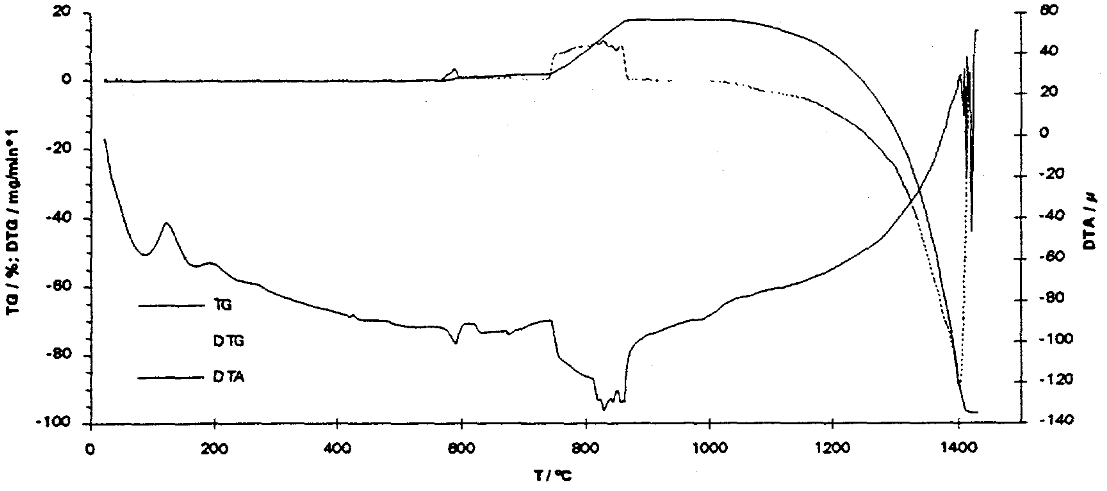

DTA of CdTe

Figure 4-5. Differential thermal analysis of CIS and CdTe.

In sorption experiments with soils and clay minerals usually a strong sorption is found for cationic species whereas the sorption for anionic species like molybdate is rather faint. This is illustrated by Fig. 4-6. For selenium in its two possible anionic species the situation becomes more difficult because selenite is a strong adsorbent in contrast to selenate which usually is a weak one.

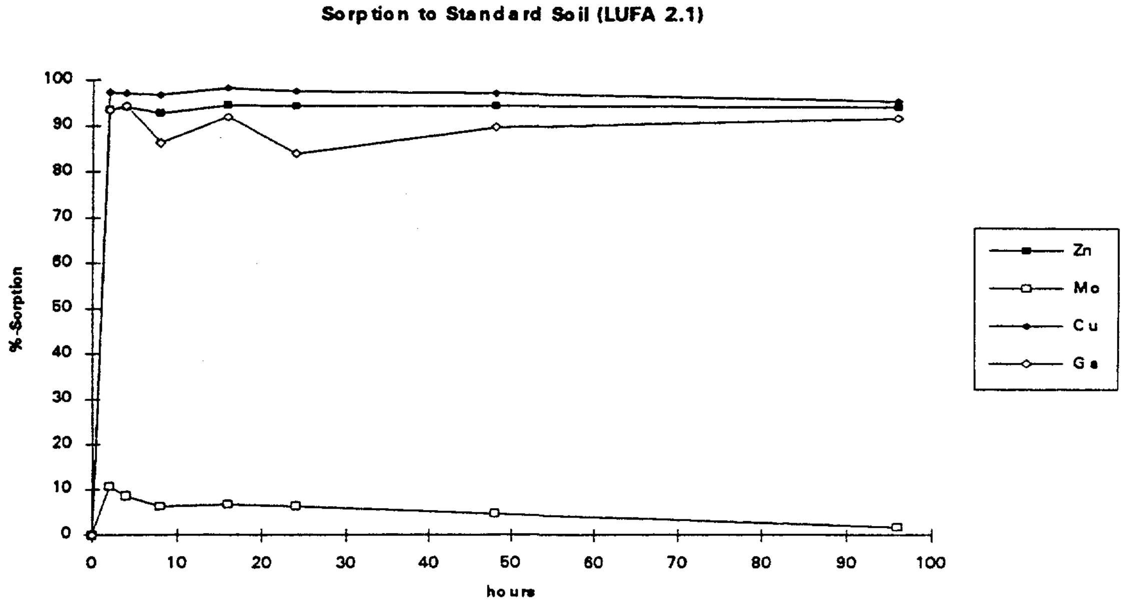


Figure 4-6. Sorption of a mixture of metal compounds to a standard soil.

In toxicity tests the effects found were dependent on the speciation of the single elements tested. That means the oxidation state as well as the counterions influence toxicity. This effect is demonstrated in Table 4-1 for toxicity tests with Daphnia magna (waterflea) for selenium. The same effect can be watched in other toxicity tests. In further experiments combinatory effects of compounds that may come into existence from solar cells have to be taken into account.

Table 4-1. *Daphnia magna* Acute Toxicity (24h-Test)

Test Substance		EC$_{50}$ (in mg/L of Element)
$K_2Cr_2O_7$	0,2	Cr
Na_2SeO_4	2,2	Se
Na_2SeO_3	3,7	Se
$ZnSO_4$	1,7	Zn
K_2TeO_3	5,6	Te

Fig. 4-7 shows the result of an acute toxicity test with algae for sodium selenate. Selenium in its different speciations shows a non-classical behaviour in some toxicity tests; at rather low concentrations no toxic action can be detected but a small stimulating effect can be observed.

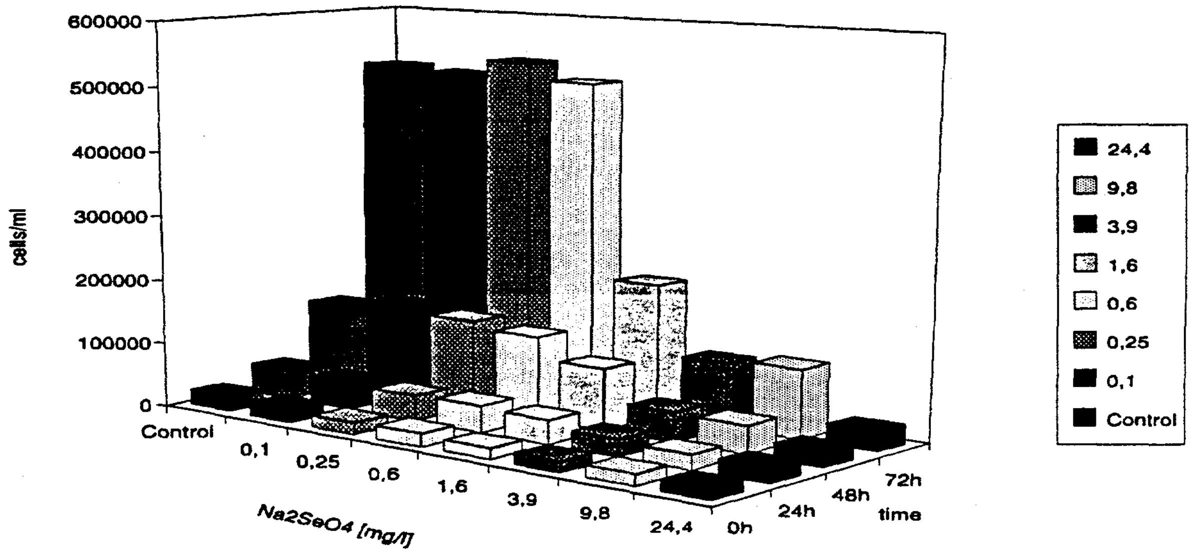


Figure 4-7. Selenate toxicity on algae.

CONCLUSION

For our experimental work it will be necessary to focus more on the speciation of the elements that are able to enter environment because the impact and the effect of these elements on compartments of the environment greatly depends on their speciation.

These data gained in laboratory and outdoor experiments in respect of materials and their apparent risks shall flow into an analysis of the problems appearing by operation and disposal of solar cells. The knowledge of possible risks to man and environment shall make the development of a minimizing strategy possible.

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5. INDUSTRIAL HYGIENE IMPLICATIONS

COPPER INDIUM DISELENIDE

N. M. Bernholc, P. Moskowitz, R. Chapin and M. Harris

ABSTRACT

Copper Indium Diselenide (CIS) is one of the new materials being used by the photovoltaic industry. This paper summarizes the toxicology data for CIS and its precursor compounds, reviews the established control processes, and describes the components that comprise an effective industrial hygiene program to control exposures to CIS in the photovoltaic processes. The limited information on toxicity, showed that at low dose levels there were no adverse reproductive effects in animals. The toxicity of the precursor compounds (i.e., copper, indium, and selenium) was not demonstrated. The results of monitoring industrial exposures indicate that in photovoltaic research and development operations, exposures are well controlled by using traditional engineering controls, personal protective equipment, work practices, and monitoring. Each of these components is discussed. Because of the toxicity of the parent compounds, an ongoing effective industrial hygiene program is needed to ensure that workers' health is not compromised.

INTRODUCTION

The photovoltaic industry is developing new materials that will improve the efficiency of thin-film solar cells and reduce production costs. For many of these new chemical compounds, such as copper indium diselenide (CIS), there is limited information on toxicity. In light of new findings, this paper presents recent animal data, then analyzes and interprets the information in combination with exiting data on related compounds to provide a more coherent overview for managers of CIS research and development, and production facilities. Specifically, this paper: 1) summarizes the existing literature on the toxicity of CIS and related compounds; 2) compares CIS toxicity with other chemicals commonly used in photovoltaic production; and, 3) reviews work practices and procedures for safely handling CIS.

CHEMICAL AND PHYSICAL PROPERTIES OF CIS

Copper indium diselenide (CIS), also known as copper indium selenide, is a gray powdery solid at room temperature and pressure (Budavari 1989). It has a relatively high molecular weight of 336.3. In pure form, it reportedly has a slight garlic-like odor which is probably due to the selenium constituent. Table 5-1 summarizes the chemical and physical properties of CIS.

TOXICOLOGICAL PROPERTIES OF CIS

The only toxicological data for CIS comes from Harris et al. (1994), who evaluate the systemic and reproductive toxicity of CIS. Their studies were designed to provide a rapid, relatively inexpensive, short-term toxicity evaluation of CIS in a common laboratory animal. Their short, 28-day study design made the selection of dose levels critical because dosages that would ordinarily kill an animal in a typical 13-week study often can be tolerated for 4 weeks. Therefore, inhibition of weight gain as well as other clinical parameters, were used as indicators for the toxicity of CIS.

Range Finding Study

Harris et al. (1994) conducted a non-mating, 28 day range finding study of CIS with adult male and female Sprague-Dawley rats. Groups of eight animals of each sex received CIS suspended in 0.5% methyl cellulose (aqueous) by gavage at levels of 0 (control), 100, 250, 500, or 1000 mg/kg/day. Animals had *ad libitum* access to rat chow during the study. After 28 days, the rats were killed and clinical signs, in-life body weights, terminal body and organ weights, histology, clinical chemistry, and hematology were evaluated. Six of the eight female rats survived administration of 1000 mg/kg/day of CIS, while all of the female rats at lower dosages survived to the end of the experiment. With the exception of one death in the 250 mg/kg male cohort, all male rats survived for the 28 days.

Treated animals, regardless of sex, gained less weight than controls. This was statistically significant at or above doses of 250 mg/kg/day. At 250 mg/kg/day, males gained 40% less weight than controls and females gained 97% less weight than their respective controls. At doses of 500 and 1000 mg/kg/day, the animals actually lost weight; this effect was more pronounced in female rats than in the males.

Female rats showed a statistically significant increase in relative spleen weight at the 1000 mg/kg/day dose level, suggesting an increase in turnover of blood cells. Hematological results confirmed that there was a shift towards the proliferation of immature forms of blood cells. In female rats at or above doses of 250 mg/kg/day, serum albumin decreased, serum bile acids tripled, and serum alkaline phosphatase levels increased. These results suggest that CIS causes mild changes in liver function and possibly problems with nutrient absorption. Male rats treated with doses at or above 250 mg/kg/day showed an increase in relative liver weights. However, only at doses of 1000 mg/kg/day were statistically significant increases in relative kidney and testis weights seen. These increases appear to reflect to the overall decrease in body weight.

Developmental and Reproductive Toxicity of CIS

To identify whether CIS had any effects on reproduction and development, Harris et al. (1994) administered aqueous suspensions of CIS in 0.3% methyl cellulose by gavage to groups of sexually mature male and female Sprague-Dawley rats. Based upon data from the range-finding study, dosages were set at 50, 100, and 250 mg/kg/day.

CIS produced small hematological changes but had no effects on the reproductive system (neither organ structure nor fertility) in male rats. Furthermore, there were no differences in body weight or patterns of food consumption at any dosage. While statistically significant increases in liver weight occurred in animals dosed at 250 mg/kg/day, clinical chemistry measurements did not indicate any hepatic changes. Hematological data showed mild regenerative anemia and a decrease in monocytes in animals dosed at 100 and 250 mg/kg/day.

Female rats exposed during gestation, (days 6-15 only), at dosages at 100 and 250 mg/kg/day gained 15% less weight than their respective controls. Although there was no increase in post-natal deaths, there was a slight dose-related decrease in litter size and a corresponding increase in offspring weight. Post-partum maintenance and the growth rates of the offspring were not affected. Females who were continuously exposed females (dosed from day 1-28), at the highest dose level (250 mg/kg/day) gained half as much weight as controls. However, these females also consumed less food than their respective controls. As no effect was observed in the numbers of corpora lutea total or in the number of live implants, the authors concluded that CIS had no observable effect on ovulation, fertilization, or embryo implantation. Nevertheless, the slight dose-related decrease in litter size and increase in offspring weight suggests some possible early toxicity, even though their later maintenance and growth were unaffected. These effects could not be duplicated during a subsequent paired-feeding study suggesting that the effects may be explained entirely by the females reduced food consumption and loss of body weight.

Discussion

Based on the work of Harris et al. (1994), CIS did not consistently cause adverse effects at the dosage levels evaluated. The chemical does not appear to produce effects similar to those of any of its parent compounds, (i.e., hydrogen selenide, copper indium). Since most occupational exposures generally occur through inhalation or dermal absorption, not ingestion, good work practices and procedures should minimize these routes of exposure. However, because this study was conducted in laboratory rats under oral administration, caution must be exercised in extrapolating the toxicity data to occupational exposures. These studies also indicate that, at the levels tested, CIS does not produce reproductive toxicity. Although high-dose, gestationally-exposed females produced 25% fewer pups than controls, this effect was not reproducible and could be explained largely by the decrease in food consumption in treated animals. Similarly, CIS did not show developmental toxicity.

COMPARATIVE TOXICITY OF CIS PRECURSORS

No clinical information is available on the potential human health effects from CIS. As a surrogate, instead we will review the known effects of copper, indium, selenium, and other compounds that are used to produce CIS photovoltaic modules. This information is summarized in Tables 5-2 and 5-3.

Copper

Copper is a reddish-brown metal with an atomic weight of 63.55, with high melting (1083°C) and boiling (2567°C) points. It is soluble in nitric and hot sulfuric acid; it is insoluble in water in the metal form but many copper salts are soluble in water (Budavari 1989). Industrial uses include the manufacture of bronze, brass, and other copper alloys, pigments, fungicides, electrical conductors, and in electroplating (ACGIH 1993; Budavari 1989). Industrial exposures to metal primarily occur from copper fumes in welding (ACGIH 1993). Occupational heath effects from copper fume include upper respiratory tract irritation accompanied by a metallic or sweet taste, nausea, metal fume fever, and in some cases, discoloration of the hair and skin (ACGIH 1993). Allergic contact dermatitis also has been reported. Chronic exposure to dusts and mists containing copper salts can result in irritation and ulceration of nasal mucosal membranes. Ingested copper can act as an irritant and produce salivation, nausea, vomiting, gastric pain, hemorrhagic gastritis, and diarrhea (Stokinger 1981). Individuals with Wilson's disease, (a rare heridatry disease), may experience hepatic cirrhosis, brain damage, nerve cell demyelination, kidney effects, corneal copper deposition, and may die (Amdur et al. 1991).

Indium

Indium is a silver-white, shiny, ductile metallic element with an atomic weight of 114.82. It has a relatively low melting point of 156.6°C. It is soluble in acids, slightly soluble in sodium hydroxide, but insoluble in water (Budavari 1989). Indium and its compounds are used in bearings for automobiles and aircrafts, solder, low-temperature melting alloys, nuclear reactor control rods, and in semiconductor devices.

Radioisotopes of indium are used in cancer treatment and diagnostic imaging of body organs. Soluble indium salts can be highly toxic when introduced intraperitoneally or intravenously (McCord et al. 1942). Toxicity is related to the chemical form and it is moderately irritating when ingested. Indium trichloride can cause severe lung damage and can lead to the development of fibrotic tissue (Blazka et al. 1994). The biological half-life of indium ranges from 2-14 days. Intravenous administration of indium chloride in mice produces renal toxicity and liver necrosis accompanied by an increase in microsomal enzyme activity and a reduction in heme-synthesizing enzymes. Hydrated indium oxide produces damage to phagocytic cells in the liver and the reticuloendothelial system. Indium sesquioxide (In_2O_3) produces edema and slow-healing lung lesions, but no fibrosis. There is limited evidence that intravenous injection of indium nitrate is a teratogen in hamsters and is empbryopathic at doses above 1 mg/kg (ACGIH 1993).

Selenium

Selenium exists in several allotropic forms, including a red to bluish-black amorphous solid, or a dark red, gray or bluish-black crystal or a brownish-red liquid (ACGIH 1993). It has a high boiling point (685°C). The liquid is soluble in aqueous solutions of dilute caustic alkali, potassium cyanide, and potassium sulfite (Budavari 1989). It burns in air with a bright blue flame forming selenium dioxide and emits a characteristic odor resembling rotten horseradish (Budavari 1989). The amorphous forms are soluble in carbon disulfide, methylene iodide, benzene, or quinoline, while the gray or metallic form is the most stable, and is soluble in carbon disulfide or ether but insoluble in water or alcohol. In the amorphous form it reacts with water to form selenious acid and hydrogen. Selenium may form selenium dioxide, which dissolves on contact with water into selenious acid (Budavari 1989). Odor thresholds for selenium and compounds are not documented. Selenium itself does not have an odor threshold; however, hydrogen selenide has an odor threshold of 0.3 ppm (AIHA 1989).

Three forms of selenium poisoning have been described: Acute selenosis; subacute selenosis; and, chronic selenosis. In animals, acute exposures may cause imbalances in walking, cyanosis of the mucous membranes, labored breathing, and death. Pathologic findings include congestion of the liver, endocarditis and myocarditis, degeneration of the smooth musculature of the gastrointestinal tract, gallbladder and bladder, and erosion of the long bones. Subacute selenosis occurs from exposure to large doses of selenium over a long period resulting in neurological dysfunction (impaired vision, ataxia, disorientation) and respiratory distress. Selenium also has been reported to retard growth, decrease fertility, and to show embryotoxicity, fetotoxicity and teratogenicity in animals. For subchronic exposures, organic forms of selenium are more toxic than inorganic selenium compounds (ACGIH 1993). In humans, besides a garlic odor in the breath, sweat, and urine, chronic exposure to selenium can cause dermatitis, sore throat, fatigue, anorexia, gastroenteritis, hepatic degeneration, and an enlarged spleen. An increased incidence of dental carries also have been reported. Selenium can be detected in the hair, nails, and blood.

Interestingly, selenium is an essential element in the human diet where daily intakes of 500-860 µg as selenium can be tolerated for long periods (Piscator 1989). When in the form of hydrogen selenide, it is a flammable, highly toxic gas with an immediately dangerous to life and health (IDLH) value of only 2 ppm. The hazards from acute exposure to hydrogen selenide are similar to those of other selenium compounds; however, pulmonary edema also can occur.

AIRBORNE EXPOSURES IN THE WORKPLACE

Copper is known to cause discoloration of skin, hair and teeth, as well as metal-fume fever (Hamilton et al., 1983). Hypersensitivity skin reactions, as well as ulcerated nose lesions also have been reported. Concentrations of 1-3 mg/m^3 can alter taste. While metal fume fever has been reported from concentrations as low as 0.1 mg/m^3, other sources report no ill effects at concentrations up to 0.4 mg/m^3 (ACGIH 1993).

Information on the consequences of workers' exposure to indium is limited. Indium production workers complain of tooth decay, joint and bone pain, nervous and gastrointestinal disorders, heart pains, and general debility. No air concentrations or durations of exposure were reported (ACGIH 1993).

Selenium grinding operations, with air concentration of 0.2 to 3.6 mg/m^3, produced symptoms of garlic breath, skin rashes, gastrointestinal distress, metallic taste, and psychological effects (ACGIH 1993). Urinary values were between 0.25 and 0.43 mg/L. At a selenium rectifier production operation, headaches were the most commonly reported symptom in 35 of 62 workers exposed to airborne concentrations of 0.007-0.05 mg/m^3. Conjunctivitis, and tracheobronchitis were found in nine workers. Biological samples gave higher values than would be expected from the air values, indicating inhalation was not the only route of exposure (ACGIH 1993). Inhalation of less than 0.2 ppm of hydrogen selenide caused nausea, vomiting, metallic taste in the mouth, garlic breath odor, and extreme lassitude and fatigue. An extensive health surveillance study was conducted in a selenium production facility (Robin 1984, 1989; Vaillancourt et al. 1994). Twenty selenium production workers were compared to control workers. Results from a questionnaire revealed no specific medical problems and there was no garlic odor of the breath on selenium workers. Burns were caused from contact with selenium dioxide. Selenium concentrations were below the TLV under normal working conditions, and an average concentrations of 135 µg/L in the urine were seen. Workers who demonstrated abnormally high urine selenium levels (224-875 µg/L) were removed from their job. No individuals reported selenium intoxication, and all blood counts, and kidney and liver function tests were normal. Air concentration corresponded to 0.05-0.89 µg/m^3. Selenium was rapidly eliminated from the body; urine levels fell from 800 to 78 µg/L in two days. The authors concluded that short- term exposures to as high as 4.5 times the TLV, will not have adverse effects. They developed an optimal internal guideline for urinary selenium of 150 µg/L, and set the maximal levels at 250 µg/L. Also, they reported that red cell glutathione peroxidase was significantly higher in exposed workers than in controls, and that this increased activity may be protective against cancer and cardiovascular disease. A follow-up study (Vailliancourt, et al. 1994) reporting 13 years of medical surveillance of workers exposed to selenium and its compounds, found no toxicity from airborne levels ranging from non-detectable to several times the TLV. Hence, they revised their internal guidelines to an optimum urine level of 200 µg/L, with a maximum level of 475 µg/L. An average urinary of selenium was reported as 102 µg/L. Except for metallic taste, workers with urinary levels as high as 1268 µg/L showed no signs of toxicity and normal renal and hepatic functions. Concentrations of 5 mg/m^3 (1.5 ppm) hydrogen selenide produce intolerable eye and nasal irritation (ACGIH 1993). Contact dermatitis lesions may occur with selenium dioxide selenium fumes, red selenium and sodium selenite (WHO 1987). If uticaria occurs, the employee have no further contact with selenium whatsoever (Friberg et al. 1979).

STANDARDS

The Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) have set exposure limits for copper, indium, selenium and hydrogen selenide (Table 4). Both the OSHA permissible exposure limit (PEL) and the ACGIH threshold limit value (TLV) are 8-hr, time-weighted average exposure concentrations to which nearly all workers can be exposed for a normal 8-hour work-day and a 40-hour work week, without adverse effect. For copper, the 8-hr PEL is 0.1 mg/m^3 as a fume, 1 mg/m^3 as a dust or mist. The ACGIH set a higher TLV for copper fume, 0.2 mg/m^3, based on information that showed no adverse effects to copper fume levels of 0.4 mg/m^3. This level was set to protect workers from irritation and systemic effects. The dust and mist values are the same. The indium PEL and TLV of 0.1 mg/m^3, were based on the data associated with severe pulmonary toxicity from indium salts (ACGIH 1993). The selenium TLV and PEL of 0.2 mg/m^3 as selenium were set to prevent systemic toxicity and to minimize the potential of ocular and upper respiratory tract irritation. Hydrogen selenide has an 8-hr TLV of 0.05 mg/m^3 to prevent irritation and prevent the onset of chronic hydrogen selenide-related disease.

EXPOSURE MONITORING FOR PHOTOVOLTAIC MANUFACTURING

There is little published information on the results of employee exposure monitoring in the manufacturing of photovoltaic cells except through personal communication (Gay 1994). Information was collected from mechanical scribing operations on CIS modules and includes data on cadmium sulfide and zinc oxide, which are also used during the production process (Gay 1994). All levels of copper, indium, cadmium, and selenium were below the ACGIH TLVs and OSHA PELs for the respective elements and the analytical detection limits. Local ventilation (HEPA vacuum cleaners) was used to minimize equipment generated dust (Personal

Communication). Area and personal sampling from selenium deposition operations were also below the analytical detection limits (<0.0015-0.0038 mg/m^3).

The literature contains limited information on other semiconductor production processes. Ungers, et al. (1985) determined that arsenic can be released from freshly ion-implanted silicon wafers, manufactured under high vacuum conditions (10^{-6} torr). Although information is available about the behavior of dopant atoms on the crystal lattice of the substrate, there is little data on dopant atoms in the crystal lattice of the substrate, and nothing about the fate of atoms associated with this superficial deposition. The theory that these atoms diffuse out of the wafer and are released to the environment gained support from workers' complaints of odors associated with wafer-handling operations near the ion implanter station. The implication is that there is potential for serious accumulation in any facility where the rooms are poorly ventilated. Odor problems have also been reported in thin-film production work (Donley 1994; Mosier 1994; Gay 1994). One solution has been to evacuate the deposition chamber several times before it is opened (Gay 1994). Hydrogen selenide is generated by the reaction of exscess selenium deposited on steel in an acid oil bath media (WHO 1987). In epitaxial operations, arsine and phosphine were found in the head space of the mechanical pump and as a contaminant in vacuum pump's oil (Mosovsky et al. 1992). Selenium contamination has been similarly reported during thin film production, (Mosier 1994; Gay 1994). Contamination of the headspace of pumps used for chamber purging has been detected. Thus, while chamber purging may effectively control airborne releases of toxicant, the materials may be transferred elsewhere and later pose a maintenance problem.

METHODS OF CONTROL

Occupational exposure to CIS and its precursors may occur during module production, installation, maintenance, and waste disposal. Although preliminary data suggest that CIS poses little acute or sub-chronic toxicity, prudence dictates caution in working with this material, requiring continuous evaluation of the manufacturing process, and identification of key steps that may result in exposure to employees. In general, the hierarchy of control includes engineering controls, personal protective equipment, and work practices. Area and personal monitoring also should be conducted to provide information on the type and extent of employees' exposure, to assist in identifying potential sources of exposure, and to gather data on the effectiveness of control methods.

Monitoring

Air monitoring is a useful industrial hygiene tool for documenting the effectiveness of a control program. Additionally, personal monitoring is required by OSHA for regulated chemicals. Other OSHA requirements, such as training in hazard communication and medical surveillance, also are triggered by monitoring results. Samples must be taken within the employee's breathing zone (i.e., personal samples) and must reflect the employee's exposure over 8 hrs, without regard to the use of respirators, to airborne concentrations of a specific chemical or chemicals. Representative sampling is permitted when there are several of employees performing essentially the same job, with similar duration and level of exposure, under essentially the same conditions. Initial monitoring of workplace exposures is required for regulated chemicals and is a good work practice for other toxic chemicals. Additional monitoring is required whenever processes change that may expose employees to a chemical at or above the action level. Such changes may occur in the production process, raw materials, equipment, personnel, work practices, or finished products. Therefore, monitoring can reflect the effectiveness of control processes. It also may indicate changes in work practices, or failure of equipment. Pump oil maintenance is another job category which requires monitoring. It has been reported that pump oils are contaminated with selenium products (Gay 1994; Mosier 1994). Recently, OSHA determined that monitoring can be discontinued whenever sampling results indicate exposures below the action level. OSHA acknowledges that monitoring can be a time-consuming and expensive endeavor (29 CFR 1910.1027, "Preamble to the Cadmium Standard).

Sampling and analytical methodology should follow either NIOSH- or OSHA-approved procedures. Table 5-5 lists monitoring methodologies for copper, indium, and selenium. These metals can be collected on 0.8 micron mixed cellulose ester filter using a pump with a maximum flow rate of 2 liters/min. For copper, and selenium, OSHA validated analytical methods using atomic absorption spectroscopy. Additionally, an inductively coupled argon plasma procedure was approved for copper. OSHA has not yet validated a methodology for hydrogen selenide.

Quality Control

Air samples should be analyzed in laboratories with demonstrated proficiency for measuring the analyte under study; this is both required by OSHA, as well as a good work practice. It is not unreasonable to require a precision and accuracy of monitoring within the designated action level limits set by OSHA. For example, the OSHA Method ID-189 for cadmium provides analytical precision and accuracy capabilities that are five times lower than the PEL for this compound. Proficiencies for specific types of analyses can be demonstrated by participating in the proficiency accreditation testing programs of NIOSH or AIHA. Where these are unavailable, laboratories should demonstrate proficiency to meet either EPA or state requirements for the specific chemical under examination, because the failure to use a certified laboratory can challenge the credibility of a control program by invalidating the results of sampling.

Biological Monitoring

OSHA does not have requirements on biological exposure monitoring for CIS or its precursors copper, indium, or selenium. However, biological monitoring techniques are available for selenium and copper.

Baselt, (1980) proposed a urine screening test for copper using atomic absorption spectroscopy (AAS). A sensitivity of 2 µg/L in urine was established by this method. Normal urine values are 15-60 µg/ 24 hr volume. Serum copper levels may be used to verify urine levels.

Selenium can be detected in the hair, nails, blood, and urine (Baselt 1980). Urine selenium levels, using AAS, range from non-detectable to 150 µg/L in normal persons. Levels of 22-204 µg/L were found in asymptomatic selenium workers (Baselt 1980). Blood levels of selenium do not correlate well with ingested selenium doses, while urine concentrations of selenium correlate well with dietary intake and air concentrations (Baselt 1980). Furthermore, plasma selenium levels usually are lower than urinary levels, suggesting that exposed workers have an enhanced elimination of plasma selenium (Robin 1984, 1989). While hair will reflect a history of exposure, urine is a preferred for monitoring since it reflects recent exposures. A biological threshold limit value of 100 µg/L urine was proposed which correlates to air selenium concentrations of 0.1 mg/m^3. A minimum detection limit of 2 µg/L can be achieved by AAS. Inductively coupled argon plasma atomic emission spectroscopy also can be used.

Engineering Controls

Three main categories of engineering controls are generally accepted as good industrial hygiene practices: substitution, containment and isolation, and exhaust ventilation (general and local).

Direct chemical substitution is not always possible, especially in industries such as photovoltaic manufacturing that heavily rely upon specific compounds. While substitution often means replacing a more hazardous material with a less hazardous one, another kind of substitution is the exchange of one process for another. For example, changing from a powder to a pellet usually will reduce exposure. Similarly, automation of a process can also significantly reduce the potential hazard to employees. Occupational exposures also can be reduced by either containing the operation or isolating the workers from the operation by placing them in a clean room, a properly ventilated cab, or some distance from the source of exposure.

When other methods of control prove ineffective or infeasible, ventilation is an important engineering control available to the industrial hygienist. Local ventilation is the most effective method of control because it captures contaminants at or near their source and exhausts them outside the workplace. Also, it requires a smaller volume of air and uses a smaller fan and dust collector than general ventilation. General ventilation (or ventilation by dilution) dilutes the concentration of a contaminant by circulating large quantities of air into and out of the workroom. Sheehy and Jones (1993) evaluated three factories producing gallium arsenide for arsenic exposures and control systems. The areas that were evaluated included crystal growing operations (Liquid Encapsulated Czochralski (LEC) and Horizontal Bridgeman (HB)); liquid encapsulated cleaning operations, and ingot grinding/wafer sawing. Only one plant had poor exposure control. All processes at that plant, except epitaxy, averaged arsenic exposures at or above the OSHA action level of 5 $\mu g/m^3$. The problems were attributed to poor ventilation and poor work practices. HEPA filtering of work areas, maintaining work areas under negative pressure, and isolating hazardous operations were effective control techniques. By analogy, similar control processes should be instituted in CIS production areas, such as deposition, scribing, finishing, grinding, and any recovery and equipment cleaning procedures. These operations should be controlled by using local ventilation, and effective work practices and procedures. An additional consideration is control for odors, since CIS can have a smell associated with it. Ventilation effectively controls this problem. An additional operation that may require engineering controls is the mechanization of the oil change process by using quick-disconnect lines attached directly to waste oil drums. While fugitive emissions are still possible, these procedures will minimize the potential for airborne exposure. Exhaust gases and other effluents from photovoltaic cell production may require treatment before release from the facility. Scrubbers, filters, and other air pollution control equipment should be integrated into the engineering control system. Hydrogen selenide can be controlled by resin bed or liquid scrubbers.

Personal Protective Equipment

Personal protective equipment includes, but is not limited to, coveralls, shoe covers, head coverings, and goggles. Protective suits and gloves as well as respirators are to be used when engineering controls do not reduce exposures to acceptable levels. During maintenance operations, such as machine-oil change, oven and deposition chamber maintenance and cleanup, the use of disposable protective outer garments (e.g., Tyvek^{TM} jumpsuits) are generally recommended to prevent personal contamination.

Respirators may be used when engineering and workpractice controls are not technically feasible, when such controls are being installed, when they fail and need to be supplemented, or for emergency situations. They also may be used for operations which require entry into tanks or confined spaces. Selection of respirators should follow the NIOSH/OSHA respirator selection guidelines, and only OSHA/NIOSH approved respirators and cartridges should be used. These selection guidelines are summarized in Tables 5-6 through 5-9. If airborne levels can be effectively controlled, as indicated by airborne and biological monitoring, then no additional respirator protection is required. A review of the limited results of monitoring (see Section 6.0) suggest that in these experimental areas, current routine operations do not require workers to use respirators. Areas where additional protective equipment may be required are during cleaning and maintenance operations, in emergencies, or equipment failure. Respiratory protection is not required for levels at or below the PEL. However, employees may elect to wear respiratory protection, even though sampling show that there is no need for such protection. If respirators are provided by the employer, the requirements for a respiratory protection program must be implemented, outlined in 29 CFR 1910.134 (Respiratory Protection); this standard includes the requirements for a minimal acceptable program.

Impermeable gloves must be used with all compounds. For copper, indium and selenium dust, glove selection is relatively simple since virtually all glove elastomers will adequately protect against solid particles which do not permeate through gloves. If the compounds are in other forms (e.g., acids), then acid-resistant gloves, such as butyl rubber should be used.

For copper, indium, and selenium fumes, protective clothing and foot coverings are necessary to prevent employee's body, street clothing, and shoes from becoming contaminated. If provided and used properly, protective clothing helps to prevent chemical exposure spreading beyond the workplace.

Work Practices

Good work practices include: (1) following the proper procedures to minimize exposures in production and control equipment; (2) not eating, drinking, smoking, chewing tobacco or gum, or applying cosmetics in regulated areas or carrying items associated with these activities into regulated areas; (3) good housekeeping, and (4) using separate washing and changing rooms.

Good housekeeping plays a key role in controlling of occupational health hazards. Accumulations of dust in the workplace on overhead ledges, equipment, and floors, should be removed before some disruption, like traffic or random air currents, re-entrains the dust and makes it airborne again. A regular cleanup schedule using HEPA-filtered vacuum cleaners is an effectively removes dust from the work area. Similarly, immediate cleanup of any toxic spills is a very important control measure.

Periodically inspecting and maintaining process and control equipment, such as ventilation systems, is another important work-practice control. This practice can help detect abnormal conditions so that timely maintenance can be performed. In plants where total containment is used as an engineering control, the failure of the ventilation system can result in hazardous exposures since equipment which is near failure or in disrepair will not perform normally or predictably.

In addition to these work practice controls, workers must know how to carry out their tasks to maximize the effective use of engineering controls. Failure to properly operate engineering controls also may contaminate the work area. Workers can be alerted to safe operating procedures through fact sheets, discussions at safety meetings, and other educational means. Decontamination procedures, such as using sodium hypochlorite (bleach) solutions to decontaminate selenium. This effectively oxidizes any residual selenium compounds to elemental selenium.

Other effective work practices include administrative controls such as scheduling production and/or worker tasks in ways that minimize the employee's exposure (e.g., *scheduling high exposure operations or clean-up* when the fewest number of employees are present). However, rotation of workers is not an acceptable administrative control and should never be used as it increases the number of employees exposed, albeit, hopefully, at lower exposure levels.

CONCLUSIONS

Recent toxicity studies of CIS reported no adverse reproductive effects on animals at dosages of 50, 100 and 250 mg/kg/day. Higher levels showed minimal effects. The study did not show any of the effects produced by the individual elements of copper, indium and selenium. The only effect seen in the CIS study was a mild regenerative anemia. Based on these results, it appears that oral administration of these levels of CIS does not produce toxic effects. However, we still do not have any information on the effects of inhalation exposure. Therefore, manufacturers and researchers should continue to control exposures to CIS. This includes monitoring, engineering controls, the use of personal protective equipment and good work practices. Additionally, while no exposure limits exist for CIS, such limits exist for its precursor compounds and other chemicals used in production.

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Table 5-1. Properties of Copper Indium Diselenide (CIS)

Name	Copper Indium diselenide
Synonym	Copper indium selenide
Chemical Formula	$CuInSe_2$
CAS #	12018-95-0
Molecular Weight	336.28
Appearance	Gray powder/pieces
Odor	Slight garlic-like odor
Boiling Point	Not Available
Vapor Pressure	Not Available
Reactivity with water	Not Available
Solubility	Not Available

Table 5-2. Availability Toxicity Information and Exposure Limits

	COPPER	INDIUM	SELENIUM	HYDROGEN SELENIDE	CIS
Carcinogenicity	--	--	x[1]		
Reproductive/ Developmental Effects	x	x	x	x	x
Pharmacokinetics/ Metabolism	x	x	x	x	-
Human/ Epidemiology studies	-	-	x	x	-
Exposure Limits	x	x	x	x	-

x Available
-- Not Available
1 Some forms

TABLE 5-3. TOXICITY INFORMATION FOR COPPER, INDIUM, AND SELENIUM AND COMPOUNDS FROM RTECS, ACGIH 1993, HSDB^{R}, IRIS, CLAYTON ET AL., AND AMDUR (1991).

	COPPER	**INDIUM**	**SELENIUM**	**HYDROGEN SELENIDE**
Atomic weight	63.55	114.82	78.96	80.98
Specific gravity	8.9	7.3	4.3 (amorphous) 4.3-4.8 (crystals)	2.1
Melting Point	1083°C	156.6°C	170-217°C (crystals)	-65.7°C
Boiling Point	2567°C	2000°C	684.8 or 684.9°C (all forms)	-41.5°C
Solubility	Nitric and hot sulfuric acid; insoluble in water	Acids; slightly soluble in sodium hydroxide; insoluble in water	Depending on form: Amorphous: Carbon disulfide, methylene iodide, benzene, quinoline, or ether; Metal crystal: slightly soluble in carbon disulfide; insoluble in water or alcohol. Liquid: Dilute aqueous caustic solutions potassium sulfite.	Carbon disulfide, carbonyl chloride, and water
Typical Form at Room Temperature	Reddish, lustrous, malleable metal. Becomes coated with green basic carbonate in moist air.	Soft white metal with bluish tinge.	Dark red to bluish-black amorphous solid, dark red, gray or black crystal or brownish-red liquid.	Colorless gas.
Lethal doses	LD_{Lo} 120 ug/kg (Oral)Human	10 mg/kg subcutaneous:Mice: 10 g/kg: Oral: Mice	33 mg/kg/8 hr LD_{50}Rabbit (Selenium) 2.3 mg/kg	300 ppb/8 hr LC_{50} Guinea Pig
Carcinogenicity	No evidence of carcinogenesis	No evidence of carcinogenesis	The National Toxicology Program classifies selenium sulfide as "reasonably anticipated to be a carcinogen.	No evidence of carcinogenesis

TABLE 5-3. TOXICITY INFORMATION FOR COPPER, INDIUM, AND SELENIUM AND COMPOUNDS FROM RTECS, ACGIH 1993, HSDB^R, IRIS, CLAYTON ET AL., AND AMDUR (1991).

Reproductive/ Developmental Effects	Oral exposures caused decreased fertility and increased rate of spontaneous abortions seen in rats (1.21-1.52mg/kg (22-35 weeks)	Indium nitrate by IV caused digital malformations in hamsters and embryopathic effects.	Depends on form and route of exposure. Teratogen in birds, developmental effects in pigs, sheep, mice sheep, reproductive effects in pigs and mice).	
Pharmacokinetics/ Metabolism	Essential part of several enzymes. Transported to albumin and bound to a-ceruloplasmin. Expected by bile and stored in liver and bone marrow (bound to metallothionein.	Intestinal absorption of orally-administered indium is low. Compounds accumulated in the liver.	Inorganic selenium is detoxified *in vivo* via S-adenosylmethionine primarily in the liver, kidney, and lung to dimethylselenide causing the garlic breathe odor in poisoned individuals.	See selenium.
Human/ Epidemiology studies	Inhalation: Irritation of nasal mucous membranes, pharynx, ulceration with perforation of the nasal septum. Skin: Itching eczema, discoloration of skin and hair. Eyes: Conjunctivitis or ulceration and cornea turbidity. Ingestion: Salivation, diarrhea, nausea, vomiting , gastric pain, and hemorrhagic gastritis. Chronic exposures: Anemia.	Tooth decay, joint and bone pain, nervous and gastrointestinal disorders, heart pains, and general debility. Neurological effects (oral).Aches and pain, chills and tremors hepatic effects	Selenium oxychloride: third degree burns of human skin. selenium dioxide: skin burns, dermatitis, and an allergic type reaction of the eyes. Selenium sulfide: dermally absorbed through abrasions. Selenium oxide: bronchial spasms, asphyxiation, chills fever, headache and bronchitis. Pneumonia if untreated. Tachycardia effects	Target organs: respiratory system and eyes. <0.2 ppm nausea, vomiting, metallic taste in mouth, garlic breath odor, extreme lassitude and fatigue. Toxic Effects: Running nose and eyes, coughing, sneezing, slight tightness of the chest, pulmonary edema

Table 5-4. OSHA and ACGIH Exposure Limits for Copper, Indium and Selenium Compounds

	Copper	Indium	Selenium	Hydrogen Selenide
OSHA PEL	0.1 mg/m^3 (fume) 1 mg/m^3 (dust or mist)	0.1 mg/m^3	0.2 mg/m^3	0.05 ppm (0.16 mg/m3)
ACGIH TLV	0.2 mg/m^3 (fume) 1 mg/m^3 (dust or mist)	0.1 mg/m^3	0.2 mg/m^3	0.05 ppm (0.16 mg/m^3)
ODOR THRESHOLD	NA[1]	NA	NA	0.3 ppm (0.99 mg/m^3)

[1] Not Available

Table 5-5. Summary of Sampling and Analytical Methods for Copper, Indium, and Selenium

	Copper	Indium	Selenium
Method	OSHA ID-121 OSHA ID-125G & ID-206	OSHA in house files	NIOSH 7300 OSHA ID-105
Sampler	0.8 µm MCE[1] filter	0.8 µm MCE[1] filter	0.8 µm MCE[1] filter
Flow-rate (L/min)	2	2	2
Detection Limit (ug/m^3)	5 - 2000	NA	5 - 2000
Analysis	AAS[2] or ICP[3]	ICP[3]	AAS[2]

[1] Mixed Cellulose Ester Filter
[2] Atomic Absorption Spectroscopy
[3] Inductively Coupled Argon Plasma

Table 5-6. Respiratory Protection for Copper Fume	
Condition / Particulate Concentration	**Minimum Respiratory Protection Required Above 0.1 mg/m^3**
1 mg/m^3 or less	Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
200 mg/m^3 or less	A type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet or hood operated in continuous-flow mode.
Greater than 200 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Only NIOSH approved or MSHA approved equipment should be used.	

Table 5-7. Respiratory Protection for Copper Dusts and Mists

Condition / Particulate Concentration	**Minimum Respiratory Protection Required Above 1 mg/m^3**
50 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
2000 mg/m^3 or less	A type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet or hood operated in continuous-flow mode.
Greater than 2000 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Only NIOSH approved or MSHA approved equipment should be used.	

Table 5-8. Respiratory Protection for Selenium and its Inorganic Compounds (as Selenium)

Condition / Particulate Concentration	Minimum Respiratory Protection Required Above 0.2 mg/m^3
10 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
100 mg/m^3 or less	A type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet or hood operated in continuous-flow mode.
Greater than 100 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a face facepiece. Any escape self-contained breathing apparatus with a full facepiece.

Only NIOSH approved or MSHA approved equipment should be used.

Table 5-9 . Respiratory Protection for Hydrogen Selenide	
Condition./Gas Concentration	**Minimum Respiratory Protection Required Above 0.05 mg/m^3**
0.5 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
2 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 2 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against hydrogen selenide. Any escape self-contained breathing apparatus.
Only NIOSH approved or MSHA approved equipment should be used.	

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6. CADMIUM TELLURIDE

N. M. Bernholc, P. Moskowitz, R. Chapin and M. Harris

ABSTRACT

Cadmium telluride (CdTe) is one of the new materials being used by the photovoltaic industry. This paper summarizes the toxicology data for cadmium telluride and its precursor compounds, reviews established control processes, and describes components that comprise an effective industrial hygiene program to control exposures for CdTe in the photovoltaic processes. The limited information on toxicity showed that at low dose levels, no adverse reproductive effects were observed in animal studies. The toxicity of the precursor compounds (i.e., cadmium and tellurium) was not demonstrated. The results of industrial monitoring indicate that in photovoltaic research and development operations, exposures are well controlled using traditional engineering controls, personal protective equipment, work practices, and monitoring. Because of the toxicity of the parent compounds an ongoing effective industrial hygiene program is needed to ensure that workers' health is not compromised.

INTRODUCTION

The photovoltaic industry is developing new materials that will improve the efficiency of thin-film solar cells and reduce production costs. For many of these new chemical compounds, such as cadmium telluride (CdTe), there is limited information on their toxicity. In light of new findings, this paper presents recent animal data, then analyzes and interprets those data in combination with information on related compounds to provide a more coherent overview for managers of CdTe research, development and production facilities. Specifically, this paper 1) summarizes the existing literature on the toxicity of CdTe and related compounds, 2) compares CdTe toxicity with other chemicals commonly used in photovoltaic production, and 3) reviews work practices and procedures for safely handling CdTe.

CHEMICAL AND PHYSICAL PROPERTIES OF CdTe

Cadmium telluride, CAS number 1306-25-8, is a brownish-black crystal, with a melting point of 1041°C, which is insoluble in water and most acids, except for nitric acid. It is oxidized in moist air, after a prolonged time. CdTe is used in semiconductor research and in the production of phosphorescent materials (ACGIH 1993). Table 1 summarizes its chemical and physical properties for CdTe; there were no reports on odor threshold.

TOXICOLOGICAL PROPERTIES OF CdTe

The only toxicological data for CdTe comes from Harris et al. (1994), who evaluated the systemic and reproductive toxicity of CdTe. Their studies were designed to provide a rapid, relatively inexpensive, short-term evaluation of the toxicity of CdTe in a common laboratory animal. Their short, 28-day study design made the selection of dose levels critical because dosages that ordinarily would kill an animal in a typical 13-week study often can be tolerated for 4 weeks. Therefore, inhibition of weight gain as well as other clinical parameters, were used as indicators of toxicity.

Range Finding Study

Harris et al.(1994) conducted a non-mating 28-day range finding study of CdTe with adult male and female Sprague-Dawley rats. Groups of eight animals of each sex received CdTe suspended in 0.5% methyl cellulose (aqueous) by gavage at 0 (control), 100, 250, 500, or 1000 mg/kg/day. The rats had *ad libitum* access to chow throughout the study. After 28 days, the rats were killed and clinical signs, in-life body weights, terminal body and organ weights, histology, clinical chemistry, and hematology were evaluated.

None of the rats given 1000 mg/kg/day CdTe survived to the end of the study. All female rats survived doses of 100, 250, and 500 mg/kg/day. Seven of eight (88%) male rats survived administration of 250 mg/kg/day, and five out of eight (63%) male rats survived 500 mg/kg/day. All males survived the 100 mg/kg/day dose. Hematological, clinical chemistry and body/organ weight effects were seen in all animals.

CdTe caused a statistically significant decrease in weight gain in all rats (100, 250, and 500 mg/kg/day). At doses of 100 mg/kg both males and females gained less weight than their controls (60% and 83%, respectively); this effect increased with dosage. At 500 mg/kg/day, males and females actually lost weight (-60.0 g and -38.8 g, respectively) over the duration of the study.

Relative kidney weights increased in all treated animals and this was significant at all levels of exposure. In all exposed females and in males at 500 mg/kg/day, significant increases in relative spleen weight also were seen. Platelets levels decreased in both sexes, but corpuscular changes were seen in males. Alterations in body clinical chemistry were seen in females, possibly indicating mild to moderate liver damage.

Developmental and Reproductive Toxicity

To identify whether CdTe had any effects on reproduction and development, Harris et al. (1994) administered aqueous suspensions of CdTe in 0.5% methyl cellulose by gavage for 28 days to groups of sexually mature male and female Sprague-Dawley rats. Based upon data from their range-finding study, dosages were set at 10, 30, and 100 mg of CdTe/kg/day.

All exposed males gained less weight by the end of the study than controls, with rats in the highest dose group being 7% (23 g) lower. Other endpoints remained unaffected. Food consumption variably decreased (≤18% at 30 and 100 mg/kg). The relative kidney weight was increased; liver and spleen weights and all reproductive indices (fertility, sperm number, and motility) were unchanged. Significant increases in serum albumin, ALT, and SDH (enzymes reflecting liver function) among the highest dose animals were seen, but no effects were demonstrated on hematology, histopathology, sperm measures or testicular structure. Urinary cadmium and protein levels, indicative of caded on hematology, histopathology, sperm measures or testicular structueded on hematology, histopathology, sperm measures or tested on hematology, histopathology, sperm measures or testicular structure. Urinary cadmium and protein levels, indicative of caded on hematology, histopathology, sperm measures or testicular structure. Urinary cadmium and protein levels, indicative of caded on hematology, histopathology, sperm measures or testicular structure. Urinary cadmium and protein levels, indicative of caded, nor in postnatal deaths or pup weights at or after birth.

Similarly, no reproductive effects were seen in any continuously exposed females, (dosed from day 1-28), despite their lower gain in weight than in controls (21.4 - 43.1 g less than controls). However, these females also consumed less food than their respective controls. No effect was observed in the number of corpora lutea, or live implants. The authors concluded that CdTe had no observable effects on ovulation, fertilization, implantation, or early embryo development.

Discussion

Based on the develop and reproductive evaluation of Harris et al. (1994), CdTe does not consistently cause adverse effects at the dosage levels evaluated. The chemical does not appear to produce the toxic effects of its parent compounds (i.e., cadmium or tellurium) See section 4.0. Since most occupational exposures occur through inhalation or dermal absorption, not ingestion, good work practices and procedures should minimize these routes of exposure. However, since this study was conducted in laboratory rats under oral administration, caution must be exercised in extrapolating toxicity data to occupational exposures. These studies also indicated that at the levels tested, CdTe does not produce reproductive or developmental toxicity. The authors speculated that since no vascular, renal or teratologic damage was seen (indicative of cadmium poisoning), circulating blood levels of cadmium were low. The normal urinary Cd and protein values seen in the study support this conclusion. Cadmium is poorly absorbed by oral administration, and is virtually insoluble in aqueous systems. Therefore, the CdTe may not be biologically available by this exposure route.

COMPARATIVE TOXICITY OF CdTe PRECURSORS

No clinical information is available on the potential human health effects from exposure to CdTe. As a surrogate, instead we review the known effects of cadmium and tellurium with other compounds that are used to produce CdTe photovoltaic modules. This information is summarized in Tables 6-2 and 6-3.

Cadmium

Cadmium is soft, blue-white, malleable metal with a molecular weight of 112.4 and a melting point of 321°C. Like other metals, its finely divided powder is flammable. It is soluble in acids and ammonium nitrate but not in water. Its oxide may be a white powder or red/brown crystal (ACGIH 1993). Cadmium is used in metal coatings, bearings, low-melting point alloys, brazing and welding rods, nickel-cadmium batteries, and nuclear reactor control rods. Its compounds are also used in diverse products, including pigments and dyes, dry film lubricants, lasers, semiconductors, pyrotechnics, rectifiers, solar cells, and scintillation counters (ACGIH 1993).

The literature on cadmium toxicity is quite extensive, and has been extensively reviewed elsewhere (29 CFR 1910.1027 Preamble to the Cadmium Standard). A summary review is provided here. The primary route of exposure is inhalation. In both humans and animals, the primary chronic adverse health effects are lung cancer, and kidney damage and chronic lung disease indicative of emphysema. Chronic exposure, also has caused gastrointestinal symptoms, anemia, eosinophilia, anosmia, rhinitis, discoloration of teeth, and microfractures. In the blood cadmium is bound to metallothionein and transported to the kidney. Blood cadmium levels in unexposed adults are usually less than 1 µg/dl (Amdur et al. 1991).

The acute health effects from inhalation of cadmium include pneumonitis, pulmonary edema, and death. Death was caused by 1 hr exposure to concentrations of 40-50 mg/m^3, and a 5 hr. exposure to 9 mg/m^3 (ACGIH 1993). Inhalation of only 0.2-0.5 mg/m^3 may produce non-fatal pneumonia, and levels as low as 0.01 -0.15 for 9-hrs produce symptoms resembling metal-fume fever (ACGIH 1993).

More recent studies revealed that 8 hr exposure to 5 mg/m^3 should not be regarded as the lowest concentration that can give rise to a fatal poisoning. In the preamble to its recently issued cadmium standard, OSHA indicated that is reasonable to believe a cadmium concentration of approximately 1 mg/m^3 over an 8 hr period is immediately dangerous to life and health (29 CFR 1910. 1027 Preamble to Cadmium Standard).

Experimental animals exposed to airborne cadmium compounds experienced acute pulmonary effects (29 CFR 1910. 1027 Preamble to Cadmium Standard). Cadmium exposures ranging from 5 to 10 mg/m^3 over 15 to 120 minutes, induced significant increases in lung weights indicative of pulmonary edema. In rats exposure to aerosols of 60 mg/m^3 for 30 minutes caused death from pulmonary edema within 3 days. Symptoms experienced by factory workers exposed to cadmium were duplicated in rabbits exposed to dust from that factory; they exhibited chronic inflammatory changes in the nasal mucosa and signs of emphysema in the lung (29 CFR 1910. 1027). Multiple experimental studies confirm these findings of acute pulmonary effects. In addition, animals (e.g., rats, rabbits, monkeys, guinea pigs, golden hamsters and calves) exposed to cadmium compounds showed acute effects in the testes, ovaries, liver, and blood.(29 CFR 1910. 1027 Preamble to Cadmium Standard). Chronic dosing adversely affected on spermatogenesis in rats given 0.005 or 0.0005 mg Cd/kg orally for six months. (HSDB 1994).

It has been shown that cadmium-induced renal disease may appear in workers months or years after exposure has ceased (29 CFR 1910.1027). Cadmium-induced kidney dysfunction is exhibited with increased urinary excretion of small proteins such as beta-2-microglobulin (ß-2) and retinol binding protein. Several studies have examined the prevalence of kidney dysfunction as it related to cumulative exposure to airborne cadmium. Cumulative exposures above 500 µg/m^3 show a dramatic increase in prevalence of kidney dysfunction (Thun et al. 1991). Levels as low as 1 µg/m^3 over a period of a year may result in a 10% likelihood of renal disease in exposed populations (Ellis 1988). Deposition studies show that about 50 to 75 percent of the body burden of cadmium is in liver and kidneys. Regardless of the route of administration or the type of cadmium compound, approximately one-half to one-third of the body burden of cadmium is found in the kidneys after chronic low-level exposure, with the highest concentrations found in the renal cortex. A greater proportion of body burden shifts to the liver as exposure increases. Kidney damage is irreversible (Amdur 1991). Cadmium-induced renal dysfunction is attributed to daily intakes in food of 140-260 µg cadmium/day for more than 50 years, or workroom air exposure of 50 µg/m^3, for 10 years or more (Amdur et al. 1991). In severe chronic cadmium exposure, workers also manifest bone injuries which include osteomalacia, osteoporosis, and spontaneous fractures; this may be attributed to changes in calcium metabolism following renal tubular dysfunction. The disease is similar to osteopathy observed in Japanese women who consumed a diet high in cadmium-contaminated beans and rice during World War II (Thun et al. 1991).

Cadmium compounds, (cadmium chloride, cadmium oxide, cadmium sulfide, and cadmium sulfate) all produce lung tumors in rats (IARC 1987; Takenata et al., 1983; Takenata etal. 1990; Oldiges et al., 1989), but the potency varies with the route of exposure and the compound (Moskowitz et al., 1992). These differences may be related to differences in bioavailability. Similarly, the fact that cadmium dust is more tumorigenic than cadmium fumes may reflect differences in the deposition in lungs. An extensive amount of evidence was submitted to OSHA during the cadmium rulemaking process indicative of variability in the potency of cadmium compounds. For cadmium sulfide specifically, some of the toxicity demonstrated may be due to cadmium sulfate, a photodecomposition product, rather than cadmium sulfide itself. Several epidemiologic studies have indicated a relationship between occupational exposure to cadmium and lung cancer (Thun et al. 1991; 29 CFR 1910.1027). Statistically significant increase in mortality from lung cancer was reported in five epidemilogy studies of cancer workers conducted in England, Swede and the U.S.. Dose response evidence of cacinogenicity was demonstrated in two of the five studies. Mortality from prostate cancer is *slightly* increased in several industrial cohorts, but there is no clear dose-response relationship with exposure.

Cadmium was shown to cause lung cancer in nickel-cadmium battery workers, and arsenic smelting operations. Workers at an alkaline accumulator factory exposed to cadmium dust at estimated concentrations of 3 to 15 mg/m^3 for 9 to 34 years experienced impaired olfactory sensation, shortness of breath, and impaired lung function with associated poor physical working capacity (29 CFR 1910. 1027 Preamble to the Cadmium Standard). NIOSH determined that there is a statistically significant increase in lung cancer deaths in workers exposed to a 20-year time-weighted average of 21-40 μg/m^3.

Tellurium

As discussed above, tellurium and its compounds vary greatly in form. Tellurium can exist as an isomorphous crystalline powder with a silvery-white, metallic luster, or as an amorphous, fine black powder (Friberg et al., 1986). Its chemistry resembles selenium and sulfur. When acidified, it forms hydrogen telluride, a toxic colorless gas with an arsenic-like odor. Potassium tellurite and sodium tellurate are both white odorless solids. Metallic tellurium is insoluble in water (Budavari 1989), but the dioxide can form tellurous acid in water (Reprorisk^R 1994). Tellurium is used as a metallurgical additive, catalyst, in daylight lamps, semiconductors, vulcanization of rubber, pottery glazes, metal finishing, explosives, antioxidants, and thermo-electric and electronic devices (ACGIH 1993).

Tellurium toxicity may be related to its solubility, and also to its particle-size distribution (Geary et al., 1974). Rats survived endotracheal injections of tellurium and some grades of tellurium dioxide, but developed lung hemorrhages and died from the same dose of another grade of tellurium oxide. There is some speculation that the tellurides and tellurites are more toxic than the metal. For example, the oral LD$_{50}$ for tellurium is greater than 5000 mg/kg in both rats and mice regardless of sex (STDA, 1992). This relatively low toxicity for tellurium metal contrasts sharply with the high toxicity for two inorganic tellurium salts, sodium tellurite (LD$_{50}$ of 20 mg/kg orally to white mice) and sodium tellurate (LD_{50} of 165 mg/kg). Therefore, the toxicity of tellurium compounds may be related to differences in solubility. Tellurium-induced hydrocephalus was found in 83% of the offspring from pregnant rats fed 3000 ppm of elemental tellurium. Tellurium dioxide injected intramuscularly into guinea pigs, caused disruption of the kidney tubules and hemorrhaging in the lung parenchyma (HSDB^R 1994). Oral doses of 0.5-1g telluride oxides resulted in digestive disturbances, vomiting, anorexia and somnolence in dogs. Acute exposure to tellurium and its compounds in animals has caused bleeding and damage in the liver, kidneys, nervous system, lungs and gastrointestinal tract (Friberg et al., 1986) as well as peripheral neuropathy, (caused by segmental demyelination), with paralysis of the hind limbs, anemia, and damage to the heart.

Tellurium is metabolized to dimethyl telluride, which is responsible for the characteristic garlic odor of the breath in chronically exposed persons; it may persist for up to 3 months after exposure is over. It is excreted in urine, sweat and expired air. Tellurium accumulates in the liver, kidney, and spleen (ACGIH 1993).

The vapor, which contains tellurium dioxide, has caused cough, shivering, pallor, general weakness, fever, and elevated white blood cell counts, all similar to the symptoms of metal fume fever (Friberg et al., 1986). Amnesia and black-green discoloration of the tongue and nasopharynx have also resulted from exposure to vapors (Friberg et al., 1986).

Tellurium salts have shown potent mutagenic activity in the Ames *Salmonella* assay, and in *E. coli,* and have caused chromosome aberrations in human lymphocytes (Reprorisk^{R}1994).

Prenatal exposure to tellurium in laboratory animals has produced reproductive effects such as hydrocephaly in rats (Reprorisk^R 1994) and central nervous system behavioral effects in rabbits (Reprorisk^R 1994).

There are no reports of serious occupational illness from exposure to tellurium or its compounds at this time (ACGIH 1993). The only serious non-occupational exposure occured when two of three individuals died from accidental injection of 2 grams sodium tellurite by ureteral catheter during retrograde pyelography (ACGIH 1993). Autopys found fatty degeneration and edema of the liver. Short-term exposure to tellurium can cause garlic odors of the breath and sweat, which occurs at air concentrations ten times lower than the American Conference of Governmental Industrial Hygienists (ACGIH) 8-hr. exposure limit of 0.1 mg/m^3 (Robin 1984). In workers, concentrations of 0.01-0.1 mg/m^3 tellurium oxide for 22 month caused garlic odor of the breath and sweat, dryness of the mouth, metallic taste, somnolence, loss of appetite and nausea (ACGIH 1993). In a copper refinery operations, where tellurium is a process contaminant, urinary levels of tellurium are usually about 50 µg/L (Robin 1984). Uriunary tellurium of 0.01-006 mg/l were reported in foundry workers exposed to airborne concentrations off 0.01-0.74 mg/m^3 (International Labor Office 1993).

STANDARDS

Both the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH), have set exposure limits for cadmium and tellurium (Table 6-4). Both the OSHA permissible exposure limit (PEL) and the ACGIH threshold limit value (TLV) are 8-hr, time-weighted average exposure concentrations to which nearly all workers can be exposed for a normal 8-hour work-day and a 40-hour work week, without adverse effect. In 1992, OSHA lowered its cadmium PEL to 5 $\mu g/m^3$. This revision was based on the determination that at the previous exposure limit of 200 $\mu g/m^3$, workers still faced a significant risk of developing lung cancer and serious kidney damage. Included in the standard was a small number of industries where it is not feasible to achieve the PEL by engineering and work practice controls. In these cases, sepatate engineering (and work practice) control air limits (SECALs) of 15 $\mu g/m^3$ and/or 50 $\mu g/m^3$ are established as the lowest levels feasible above the PEL (29 CFR 1910.1027). The ACGIH designated cadmium as a suspect human carcinogen, and set a TLV of 0.01 mg/m^3 for total cadmium dust and 2 $\mu g/m^3$ for respirable cadmium dust (ACGIH 1993). The total dust level was set to prevent preclinical kidney dysfunction while the respirable fraction recommendation was designed to prevent the development of lung cancer.

Conversation with OSHA indicates that OSHA considers all cadmium compounds to be toxic, and that cadmium telluride was specifically included in the standard (personal communication C. Freeman 1994). OSHA considerd data inadequate to develop public policy decisions that would allow some workers to be exposed to higher amounts of cadmium than other workers based on the type of cadmium compound alone since they believe the differential toxicities have not been adequately established and there is a lack of understanding of the underlying phamacokinetics and possible decomposition. This lack of information would make the evaluation of the toxicity of mixtures of cadmium compounds difficult and therefore chose to regulate err on the side of worker-health by considering all cadmium compounds equally toxic and regulated under 29 CFR 1910.1027.

OSHA and ACGIH have set a workplace standard for tellurium at 0.1 mg/m^3 to avoid systemic poisoning. Nevertheless, garlic breath still may occur at this level.

EXPOSURE MONITORING FOR PHOTOVOLTAIC MANUFACTURING

There is little published information on the monitoring results of employee exposures in the manufacturing of photovoltaic cells except through personal communication (Donley 1994; Meyers 1994). No detectable levels of cadmium were reported from personal monitoring of maintenance operations (CdTe physical vapor deposition system and CdTe oven overhaul), daily operations in physical vapor deposition, or sandlbasting cadmium target operations (Donley, 1994). However, area samples taken in line with exhaust flow during the during maintenance of the physical vapor deposition system were 0.03 mg/m^3. Initial wipe samples taken in the deposition and sample preparatory laboratories ranged from below detection to 0.59 mg, but dropped below detectable after good housekeeping procedures were established. Wipe samples in the physical vapor deposition laboratory ranged from 1.7 - 92 µg.

Personal samples were collected from the sandblasting/buffing operation, laser scribing room, and chemical treatment room of a thin film CdTe module facility. There were no exposures to cadmium above the current OSHA action level of 2.5 µg/m^3 (Meyers, 1994). Area samples found non-detectable levels of cadmium within and outside the cell production area (e.g., secretary's desk, lunch room, module chemical treatment room center of work area, analytical laboratory, and laser room). Wipe samples ranges from a low of 0.0038 mg (secretary's desk) to a high of 2.4 mg within the work area. Unadjusted urine cadmium levels ranged from 0.2-1.0 µg/L urine.

The literature contains limited information on other semiconductor production processes. Ungers et al. (1985) determined that arsenic can be released from freshly ion-implanted silicon wafers, manufactured under high vacuum conditions (10^{-6} torr). Although information is available about the behavior of dopant atoms on the crystal lattice of the substrate, there is little data on dopant atoms in the crystal lattice of the substrate, and nothing about the fate of atoms associated with this superficial deposition. The theory that these atoms diffuse out of the wafer and are released to the environment gained support from workers' complaints of odors in wafer-handling operations near the ion-implanter station. The implication is that there is potential for serious accumulation in any facility where the rooms are poorly ventilated. Odor problems also were reported in CdTe and other thin-film production (Luke 1993; Mosier 1994; Gay 1994). One solution has been to evacuate the deposition chamber several times before it is opened (Gay 1994). In epitaxial operations, arsine and phosphine have been found in the head space of the mechanical pump and as a contaminant in the vacuum pump's oil (Mosovsky, et al., 1992). Selenium contamination was similarly reported during thin-film production, (Mosier, Martin Marietta, personal communication). Contamination of the headspace of pumps used for chamber purging has been detected. Thus, while chamber purging may effectively control airborne releases of toxicants, the materials may be transferred elsewhere and later pose a maintenance problem.

METHODS OF CONTROL

Occupational exposure to CdTe and its precursors may occur during module production, installation, maintenance, and waste disposal. Although preliminary data suggest that CdTe poses little acute or sub-chronic toxicity, prudence dictates caution in working with this material, requiring continuous evaluation of the manufacturing process, and identification of key steps that may result in exposure to employees.

Inontinuous evaluation of the manufacturing process, and identification of key steps that may result in exposure to employees. Inontinuous evaluation of the manufacturing process, and identification of key steps that may result in exposure to employees. Inontinuous evaluation of the manufacturing process, and identification of key steps that may result in exonontinuous evaluatononoontinuous evaluation of the manufacturing process, and identification of key steps that may result in exposure to employees. Inal monitoring is required by OSHA for regulated chemicals. Other OSHA requirements, such as training in hazard communication and medical surveillance, also are triggered by monitoring results. Samples must be taken within the employee's breathing zone (i.e., personal samples) and must reflect the employee's exposure over 8 hrs, without regard to the use of respirators, to airborne concentrations of a specific chemical or chemicals. Representative sampling is permitted when there are several of employees performing essentially the same job, with similar duration and level of exposure, under essentially the same conditions. Initial monitoring of workplace exposures is required for regulated chemicals and is a good work practice for other toxic chemicals. Additional monitoring is required whenever processes change that may expose employees to a chemical at or above the action level. Such changes may occur in the production process, raw materials, equipment, personnel, work practices, or finished products. Therefore, monitoring can reflect the effectiveness of control processes. It also may indicate changes in work practices, or failure of equipment. Recently, OSHA determined that monitoring can be discontinued in instances where sampling results indicate exposures below the action level. OSHA acknowledges that monitoring can be a time-consuming and expensive endeavor (29 CFR 1910.1027, "Preamble to the Cadmium Standard).

As discussed in Section 5, exposure limits have been set for cadmium and telrium. OSHA recently revised its exposure standard for cadmium, which is considered to be a carcinogen and a potential lung and kidney toxin, and set an 8-hr PEL of 5 $\mu g/m^3$. The OSHA PEL for tellurium is 0.1 mg/m3. Therefore, in many processes where simultaneous exposures to cadmium and tellurium may occur, cadmium may be used as a surrogate compound because its PEL is lower than that for tellurium. Sampling and analytical methodology should follow either NIOSH- or OSHA-approved procedures. Table 6-5 lists monitoring methodologies for Cadmium and tellurium. These methals can be collected on 0.8 micron mixed cellulose ester filters using a pump with a maximum flow rate of 2 liters/min. For cadmium and tellurium, OSHA has validated analytical methods using atomic absorption spectroscopy.

Quality Control

Air samples should be analyzed in laboratories with demonstrated proficiency for measuring the analyte under study; this is both required by OSHA, as well as a good work practice. It is not unreasonable to require a precision and accuracy of monitoring within the designated action level limits set by OSHA. For example, the OSHA Method ID-189 for cadmium provides analytical precision and accurancy capabilities that are five times lower than the PEL for this compound. Proficiencies for specific types of analyses can be demonstrated by participating in the proficiency accreditation testing programs of NIOSH or AIHA. Where these are unavailable, laboratories should demonstrate proficiency to meet either EPA or state requirements for the specific chemical under examination, because the failure to use a certified laboratory can challenge the credibility of a control program by invalidating the results of sampling.

Biological Monitoring

OSHA does not require biological exposure monitoring for CdTe or its precursor compound tellurium. However, biological monitoring techniques are available for cadmium. Additionally, it is a requirement of the cadmium standard to perform biological monitoring as an adjunct to routine air sampling. Techniques also are available for evaluating tellurium levels in the blood and uring (Nackowski 1989).

Under OSHA's cadmium rule (29 CFR 1910.1027), monitoring of biological specimens and periodic medical examinations are required. Medical monitoring includes analysis of cadmium in blood (CDB), cadmium in urine (CDU), beta-2-microglobulin in urine (B2-MU), and creatinine in urine (CRTU). Despite these requ9rements, a standard method for reporting CDU has not been developed. The importance of consistent reporting of results is critical for the credibility of the program and to allow meaningful analysis of long-term employee biological exposures. Non occupationally exposed adults excrete less than 2 μg of Cdg creatinine. Provisions have been established for the removal of workers where CDU levels exceed 15 μg/g creatinine, or if the level of CDB exceeds 15 μg/L whole blood, or B2-MU exceeds of 1,500 μg/g creatinine. (29 CFR 1910.1027). In addition to biological monitoring, the medical surveillance requirements also includes screening by chest x-rays for changes in the lung. and screening for kidney dysfunction independent of blood and urine values.

Analytical methods for tellurium are available for hair, blood and urine using atomic absorption spectroscopy (Nackowski 1989) (detection limit <1.0 μg/1 (Travis 1994)). If the average urinary tellurium concentration for a whole shift of workers exceeds 0.05 mg/1, the workers should be transferred to other work and the workign conditions should be investigated (International Labor Office 1983). While hair samples give a long-term history of exposure, these numbers are hard to interpret. Urine determination is most commonly conducted and will reflect recent exposures.

Engineering Controls

Three main categories of engineering controls are generally accepted as good industrial hygiene practices: substitution, containment and isolation, and exhaust ventilation (general and local).

Direct chemical substitution is not always possible, especially in industries such as photovoltaic manufacturing that heavily rely upon specific compounds. While substitution often means replacing a more hazardous material with a less hazardous one, another kind of substitution is the exchange of one process for another. For example, changing from a powder to a pellet usually will reduceexposure. Similarly, automation of a process can also significantly reduce the potential hazard to employees. Occupational exposures also can be reduced by either containing the operation or isolating the workers from the operation by placing them in a clean room, a properly ventilated cab, or some distance from the source of exposure.

When other methods of control prove ineffective or infeasible, ventilation is an important engineering control available to the industrial hygienist. Local entilation is the most effective method of control because it captures contaminants at or near their source and exhausts them outside the workplace. Also, it requires a smaller volume of air and uses a smaller fan and dust collector than general ventilation. General ventilation (or ventilation by dilution) dilutes the concentration of a contaminant by circulating large quantities of air into and out of the workroom. Sheehy and Jones (1993) evaluated three factories producing gallium arsenide for arsenic exposures and control systems. The areas that were evaluated included crystal gorwing operations (Liquid Encapsulated Czochralski (LEC) and Horizontal Bridgeman (HB)); liquid encapsulated cleaning operations, and ingot grinding/wafer sawing. Only one plant had poor exposure control. All processes at that plant, except epitaxy, averaged arsenic exposures at or above the OSHA action level of 5 $\mu g/m^3$. The problems were attributed to poor ventilation and poor work practices. HEPA filtering of work areas, maintaining work areas under negative pressure, and isolating hazardous operations were effective control techniques. By analogy, similar control processes should be instituted in CdTe production areas, such as deposition, scribing, finishing, grinding, and any recovery and equipment cleaning procedures. These operations should be controlled by using ocal ventilation, and effective work practices and procedures. An additional operation that may require engineering controls is the mechanization of the oil change process by using quick-disconnect lines attached directly to waste lil drums. While fugitive emissions are still possible, these procedures will minimize the potential for airborne exposure. Exhaust gases and other effluents from photovoltaic cell production may require treatment before release from the facility. Scrubbers, filters, and other air pollution control equipment should be integrated into the engineering control system. For carcinogens, HEPA filter exhausted collection devices are recommended.

Personal Protective Equipment

Personal protective equipment includes, but is not limited to, coveralls, shoe covers, head coverings, and goggles. Protective suits and gloves as well as respirators are to be used when engineering controls do not reduce exposures to acceptable levels. During maintenance operations, such as machine-oil change, oven and deposition chamber maintenance and cleanup, the use of disposable protective outer garments (e.g., Tyvek^{TM} jumpsuits) are generally recommended to prevent personal contamination.

Respirators may be used when engineering and workpractice controls are not technically feasible, when such controls are being installed, when they fail and need to be supplemented, or for emergency situations. They also may be used for operations which require entry into tanks or confined spaces. Selection of respirators should follow the NIOSHts OSHA respirator selection guidelines, and only OSHA/NIOSH approved respirators and cartridges should be used. These selection guidelines are summarized in Tables 6-7. If airborne levels can be effectively controlled, as indicated by airborne and biological monitoring, then no additional respirator protection is required. A review of the limited results of monitoring (see Section 6.0) suggest that in these experimental areas, current routine operations do not require workers to use respirators. Areas where additional protective equipment may be required are during cleaning and maintenance operations, in emergencies, or equipment failure. Respiratory protection is not required for levels at or below the PEL. However, employees may elect to wear respiratory protection, even though sampling show that there is no need for such protection. If respirators are provided by the employer, the requirements for a respiratory protection program must be implemented, outlined in 29 CFR 1910.134 (Respiratory Protection); this standard includes the requirements for a minimal acceptable program.

Impermeable gloves must be used with all compounds. For cadmium and tellurium dust, glove selection is relatively simple since virtually all glove elastomers will adequately protect against solid particles which do not permeate through gloves. If the compounds are in other forms (e.g., acids), then acid-resistant gloves, such as butyl rubber should be used.

For cadmium and tellurium fumes, protective clothing and foot coverings are necessary to prevent employee's body, street clothing, and shoes from becoming contaminated. If provided and used properly, protective clothing helps to prevent chemical exposure spreading beyond the workplace.

Work Practices

Good work practices include: (1) Following the proper procedures to minimize exposures in production and control equipment; (2) not eating, drinking, smoking, chewing tobacco or gum, or applying cosmetics in regulated areas or carrying items associated with these activities into regulated areas; (3) good housekeeping, and (4) using separate washing and changing rooms.

Good housekeeping plays a key role in controlling of occupational health hazards. Accumulations of dust in the workplace on overhead ledges, equipment, and floors, should be removed before some disruption, like traffic or random air currents, re-entrains the dust and makes it airborne again. A regular cleanup schedule using HEPA-filtered vacuum cleaners is an effectively removes dust from the work area. Similarly, immediate cleanup of any toxic spills is a very important control measure.

Periodically inspecting and maintaining process and control equipment, such as ventilation systems, is another important work-practice control. This practice can help detect abnormal conditions so that timely maintenance can be performed. In plants where total containment is used as an engineering control, the failure of the ventilation system can result in hazardous exposures since equipment which is near failure or in disrepair will not perform normally or predictably.

In addition to these work practice controls, workers must know how to carry out their tasks to maximize the effective use of engineering controls. Failure to properly operate engineering controls also may contaminate the work area. Workers can be alerted to safe operating procedures through fact sheets, discussions at safety meetings, and other educational means.

Other effective work practices include administrative controls such as scheduling production and/or worker tasks in ways that minimize the employee's exposure (e.g., scheduling high exposure operations or clean-up when the fewest number of employees are present). However, rotation of workers is not an acceptable administrative control and should never be used as it increases the number of employees exposed, albeit, hopefully, at lower exposure levels.

CONCLUSIONS

Recent toxicity studies of CdTe reported no adverse reproductive effects on animals at dosages of 50, 100 and 250 mg/kg/day. Higher levels showed toxic effects. The study did not show any of the effects produced by the individual elements cadmium and tellurium. The only effect seen in the CdTe study was a mild regenerative anemia. Based on these results, it appears that short term oral administration of these levels of CdTe does not produce toxic effects. However, since we have no information on the pharmacokinetic and toxic effects of long-term inhalation, manufacturers and researchers should continue to control exposure to CdTe as if it were another cadmium compound. This includes monitoring, engineering controls, the use of personal protective equipment, and good work practices. Additionally, control measures most be implemented for the precursor compounds and other chemicals used in the production of CdTe photovoltaic modules.

Future research should identify the effects of long-term inhalation and elucidate the pharmacokinetic behavior of CdTe including its routes of deposition, distribution, metabolism, and elimination. If it can be demonstrated experimentally that long-term inhalation exposure to CdTe is less toxic that exposure to other compounds, then the implication may be that populations exposed to CdTe will be evaluated differently than those exposed to other cadmium compounds.

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HSDB^R. Hazardous Substance Database. Copyright Micromedex, 1994.

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Table 6-1. Properties of Cadmium Telluride (CdTe)	
Name	Cadmium telluride
Formula	CdTe
CAS No.	1306-25-8
Molecular Weight	240
Appearance	Black, crystalline powder
Odor	Not Available
Boiling Point	Not Available
Melting Point	1041°C
Vapor Pressure	< 1 mm Hg
Reaction with Water	Insoluble in water
Solubility	Nitric acid, insoluble in water, other acids
Decomposition Products	May evolve metal oxide fumes above melting point

Table 6-2. Availability of Toxicity Information and Exposure Limits

	Cadmium	Tellurium	CdTe
Carcinogenicity	x	--	--
Reproductive/ Developmental Effects	x	x	x
Pharmacokinetics/ Metabolism	x	x	--
Human/ Epidemiology studies	x	--	--
Exposure Limits	x	x	--
x information available **-- information not available**			

Table 6-3. Summary of Toxicity Information for Cadmium, Tellurium and Selected Compounds and Compounds

Name	Cadmium	Tellurium
CAS Number	7440-43-9	13494-80-9
Atomic weight	112.4	127.6
Specific gravity	8.7	6.-6.3
Melting Point	321°C	449 °C
Boiling Point	765°C	990 °C (amorphous) 1390°C (crystalline)
Solubility	Acids and ammonium nitrate solutions; insoluble in water.	Insoluble in water, benzene and carbon disulfide.
Vapor Pressure @ 20°C	< 1 mm Hg 0.095 @ 321°C	<1 mm Hg
Flammability	Finely divided metal dust presents a moderate fire hazard. Cadmium oxide is formed whenever cadmium is burned or heated, producing fumes which can cause a metal fume fever similar to that of zinc oxide.	Finely divided metal dust presents a moderate fire hazard.
Incompatibility	Slightly reactive with oxidizing agents, acids. Reacts with sulfur, selenium, tellurium and zinc. Violent reaction with potassium.	Oxidizers, chlorine. Reacts with nitric and concentrated or fuming sulfuric acids. Major compounds are tellurides, including H_2Te an unstable gas, halides, oxides, sulfides and tellurites and tellurates.
LD	LD_{Lo}: 50 mg/m3 and 40 mg/m^3 for 1hr; inhalation; human: LD_{50}: 225 mg/kg, oral; rat LC_{50}: 3 mg/m^3, inh, 4 hr; rat.	LD_{LO} 200 mg/kg; rat Intratracheal; toxic effects: lungs, thorax, or respiration - Other changes; liver, kidney, ureter, and bladder LD_{50} 83 mg/kg;oral; rat; 20 mg/kg; oral; mouse (sodium 167 mg/kg; oral; rabbit (sodium tellurite) 45 mg/kg; oral; guinea pig: LD 2 g, uretal catheter, as sodium tellurite. Acute fatty degeneration and liver edema.

Table 6-3. Summary of Toxicity Information for Cadmium, Tellurium and Selected Compounds and Compounds

Carcinogenicity	Rats: Cadmium chloride CdCl2): primary lung carcinomas at 12.5, 25, or 50 µg/m3 at 23 hours/day for 18 months. Cadmium chloride, Cadmium oxide, cadmium sulfate and cadmium sulfide: lung nodules Human: OSHA human carcinogen (lung).	No demonstrated carcinogenic effects in rats, mice or humans.
Reproductive/ Developmental Effects	Male Limited information: testes and fertility in men. Female In animals, Oral and inhalation exposures shown to cause embryotoxic, fetotoxic and teratogenic during pregnancy	Rat, Oral: During pregnancy produced developmental abnormalities (CNS, craniofacial and tongue) at levels hazardous to mother. (1693-6064 mg/kg) Intramuscular 13 mg/kg for female 10D - post-implantation mortality, central nervous system
Pharmacokinetics/ Metabolism/ Distribution	Cadmium, in the form of cadmium sulfate, caused ultrastructural deterioration in the thyroid gland of pregnant rats Humans and animals: 50-75% accumulates in the kidney damaging renal tubular function. Interferes with calcium metabolism resulting in skeletal changes (osteomalacia, osteoporosis).	It is metabolized to dimethyltellurium, which is responsible for the characteristic garlic odor of the breath in chronically-exposed persons

FROM RTECS, ACGIH, HSDB^{R}, IRIS^{R}, Clayton al., and Amdur et al.

Table 6-4. Regulations, Standard and Guidelines for Cadmium and Tellurium

	Cadmium		Tellurium
OSHA: PEL	5.0 µg/m^3 2.5 µg/m^3 (Action Level)		0.1 mg/m^3
ACGIH TLV	10 µg/m^3 (total dust) 2 µg/ m^3 (respirable fraction)		0.1 mg/m^3 as Te
NIOSH REL	No REL		0.1 mg/m^3
IARC	Group 2A, probable human carcinogen.		Not evaluated
NTP	Group 2, reasonably anticipated to be a carcinogen.		Not evaluated
NOAEL RfD	0.005 mg Cd/kg/day for Cd (water); 0.01 mg/kg-day(food) 0.0005 mg Cd/kg/day (water)	1E-3 mg/kg-day (food)	Not evaluated

PEL - 8-hr Permissible Exposure Level
TLV - 8-hr Permissible Exposure Level
REL - 8-hr Recommended Exposure Level
NOAEL -No-Observed-Effect Level
RfD Reference Dose for Chronic Oral Exposure

Table 6-5. Sampling and Analytical Methods for Cadmium and Tellurium Compounds

	Cadmium	Tellurium	Tellurium Hydrofluoride
Method	ID-189	OSHA in house files OSHA ID-121 NIOSH 7300	NIOSH S-187
Sampler	0.8 µm MCE[1] filter	0.8 µm MCE filter	0.8 µm MCE with a Charcoal Tube
Flow-rate (L/min)	2	2	1
Detection Limit (µg/m3)	0.27 - 0.7 AAS[2] 0.007-0.025 AAS-HGA	0.6	Not available
Analysis	AAS	AAS/ICP[3] AAS/GF[4]	AAS

1 Mixed Cellulose Ester Filter

2 Atomic Absorption Spectroscopy (either flame atomic absorption spectroscopy (AAS) or flameless atomic absorption spectroscopy using a heated graphite furnace atomizer(AAS-HGA).

3 Conndductively Coupled Argon Plasma

4 Graphite furnace

Table 6-6. Respiratory Protection for Cadmium

Condition/Particulate Concentration	Minimum Respiratory Protection Required Above 5 $\mu g/m^3$
50 $\mu g/m^3$ or less	Any half mask, air purifying respirator equipped with a high efficiency particulate filter.
125 $\mu g/m^3$ or less	A powered air-purifying respirator equipped with a loose fitting hood or helmet equipped with a HEPA filter. Any supplied-air respirator with a full facepiece, loose-fitting helmet or hood operated in the continuous flow mode.
250 $\mu g/m^3$ or less	A high efficiency particulate filter respirator with a full facepiece. A powered air-purifying respirator with a tight-fitting half-mask equipped with a high efficiency particulate filter. A supplied air respirator with a tight-fitting half-mask operated in the continuous flow mode.
1.25 mg/m^3 or less	A powered air-purifying respirator with a tight-fitting full facepiece equipped with a high efficiency particulate filter. A supplied-air respirator with a tight-fitting full facepiece operated in continuous flow mode.
5 mg/m^3 or less	A supplied-air respirator with half mask or full facepiece operated in the pressure demand or other positive pressure mode.
Greater than 5 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode and an auxiliary escape type self-contained breathing apparatus operated in the pressure-demand mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Only NIOSH approved or MSHA approved equipment should be used.	

Table 6-7. Respiratory Protection for Tellurium and Compounds	
Condition/ Particulate Concentration	**Minimum Respiratory Protection Required Above 0.1 mg/m^3**
0.5 mg/m^3 or less	Any dust and mist respirator, except single-use.
1 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
5 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet or hood. Any self-contained breathing apparatus with a full facepiece.
50 mg/m^3 or less	A powered air-purifying respirator with a high efficiency particulate filter. A type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 50 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any high efficiency particulate filter respirator. Any escape self-contained breathing apparatus.
Only NIOSH approved or MSHA approved equipment should be used.	

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7. STRATEGIES FOR ENSURING THE COMMERCIAL SUCCESS OF CdTe-BASED PHOTOVOLTAICS

Chris Eberspacher and Charlie Gay
UNISUN

SUMMARY

Photovoltaics technology is evolving toward a new generation of low-cost thin film technologies; one of the most promising materials in this new generation is cadmium telluride (CdTe). Given the impending market entry of CdTe PV technology in the U.S., it was an opportune time to quantitatively consider issues related to CdTe PV commercialization, especially the Environmental, Health and Safety (E,H&S) issues related to CdTe materials and products. Brookhaven National Laboratory hired UNISUN to study these issues and to propose strategies for gaining acceptance of CdTe-based photovoltaics.

This study focused on issues of public perception and customer preference and of economics and logistics related to the field use and end-of-life of CdTe PV products. The study sought to identify what customer concerns exist (if any), what might be pro-actively done to respond to customers' concerns, and how these pro-active strategies might be implemented. The study consisted of five tasks. Existing scientific data was assessed. Public acceptance strategies of industries facing comparable E,H&S issues were analyzed. A cross-section of the PV industry and of prospective PV customers were surveyed. The logistics and economics of CdTe PV module recycling were examined. The results were assembled into strategy recommendations for the CdTe PV industry.

The assessment of existing E,H&S scientific data on CdTe PV products revealed the need for additional scientific testing, the need for quantitative surveys of existing customer opinions, the value of appropriate positive comparisons, and the potential advantages of collection and recycling programs.

The analysis of public acceptance strategies of industries facing comparable E,H&S issues revealed that public relations, regulatory politics, and/or commercial necessity may justify collection and recycling programs for end-of-life CdTe modules, even if such programs are not economic. The economics of reclaiming CdTe PV modules will likely be negative in large part because there is likely not enough metals reclaim value in a CdTe PV module to offset collection and processing expenses. Quantitative estimates of four disposal and recycling scenarios were made. Costs of \$0.15 - 0.25/Wp were estimated. CdTe PV manufacturers need to work proactively to identify lower-cost alternatives to these at-present-most-likely scenarios.

A survey focusing on commercialization issues was drafted to collect quantitative data on the knowledge, perceptions, preferences and values of prospective purveyors and users of CdTe PV modules. The survey results indicated that prospective users were not overly concerned about E,H&S issues, that they identified Cd content as a key issue when explaining any concerns they did have, and that they are willing to purchase CdTe PV modules if the price and performance are competitive, if CdTe PV technology is endorsed by users like themselves, and if there exists a convenient method of handling end-of-life modules.

The results of this study were assembled into a set of strategy recommendations for the CdTe PV industry and its supporters. Three key strategy recommendations of this study are that additional scientific testing is needed to clearly establish E,H&S hazards for CdTe-based compounds, that programs are needed to educate customers and the public on the nature of these compounds, and that end-of-life module collection and recycling options need to be further explored.

This study focused on proposing workable domestic strategies for CdTe PV. Further work should focus on implementing the domestic strategies, on defining suitable international strategies, and on identifying comparable strategies for other emerging PV materials.

INTRODUCTION

Photovoltaic (PV) technology which converts sunlight directly to electricity is a versatile power source for many applications. Today PV power modules are cost-effective in a wide variety of remote and stand-alone applications, and, as PV module costs continue to decrease, PV power promises to become cost-effective for many more of the world's energy needs.

Photovoltaics technology is undergoing a rapid transition, evolving from the traditional products based on expensive crystalline silicon to a new generation of low-cost products based on thin films of photoactive materials deposited on inexpensive substrates like ordinary window glass. One of the most promising materials in this new generation of thin film PV technologies is cadmium telluride (CdTe).

CdTe is a well-known semiconductor often used in high-performance infrared sensors. CdTe absorbs visible light very strongly, and very thin films (e.g., ca. 1-2 μm) are sufficient to absorb most sunlight. Small-area thin film CdTe solar cells have been fabricated with sunlight-to-electricity conversion efficiencies near 16%, comparable to crystalline silicon solar cells in large-scale manufacturing today (USF93). Large-area monolithic integrated CdTe modules have been fabricated with efficiencies of ca. 10%, comparable to crystalline silicon modules commercially available today (BP94a). Given the low manufacturing costs possible with thin film processing techniques and the high efficiencies of CdTe photojunctions, it is widely anticipated that in full-scale production CdTe PV modules will be very competitive in both performance and price.

Companies in the United States, Japan and Europe are actively working to commercialize CdTe PV technology in the near future. CdTe PV modules are available in limited quantities and sizes from a Japanese manufacturer today, and two U.S. companies - Golden Photon in Colorado and Solar Cells Inc in Ohio - have announced their intention to market CdTe PV products in the near future.

Given the impending market entry of CdTe PV technology in the U.S., it is an opportune time to quantitatively consider issues related to CdTe PV commercialization, especially the E,H,&S issues related to CdTe materials and products. To this end Brookhaven National Laboratory under the aegis of the U.S. Department of Energy hired UNISUN to study the E,H&S issues related to the commercialization of CdTe and to propose strategies for gaining acceptance of CdTe-based photovoltaics. This report summarizes UNISUN's findings.

Study Tasks

The complete E,H&S field is quite broad and complex. For any given manufactured product, the E,H&S field spans a matrix of four general areas - raw materials, manufacturing, field use, and end-of-life - and four general issues -science, law, public perception and customer preference, and economics and logistics - for each area. This study was limited to a subset of this E,H&S matrix, namely the public perception & customer preference and economics & logistics issues related to the field use and end-of-life areas for CdTe PV products. Stated in a different way, this study focused on issues of customer acceptance of CdTe PV products, namely what customer concerns exist (if any), what might be pro-actively done to respond to the customers' concerns, and how might these pro-active strategies be implemented.

The study consisted of five tasks. First, existing scientific data was assessed. Second, public acceptance strategies of industries facing comparable E,H&S issues were analyzed. Third, a cross-section of the PV industry and of prospective PV customers were surveyed. Fourth, the logistics and economics of CdTe PV module recycling were examined. Fifth, the results were assembled into strategy recommendations for the CdTe PV industry.

Existing Data - A Brief Reality Check

Existing E,H&S scientific data on CdTe PV products were briefly assessed in order to identify the issues to be addressed in the subsequent industry comparisons and customer surveys, and to put the E,H&S issues related specifically to CdTe PV into some perspective.

One of the first observations possible from this study is that comparatively little E,H&S scientific data exists for CdTe materials in general and CdTe PV modules in particular. In fact the E,H&S data on CdTe and related compounds is sufficiently scant that most existing statutes regulate CdTe based on the better-known hazards of elemental cadmium (Cd) and tellurium (Te). Setting aside momentarily that the true hazards of CdTe might well be quite different from the additive hazards of Cd and Te (just as the nature of H_2O is quite different from the simple sum of the properties of H_2 and O), it is clear that elemental cadmium and tellurium and their respective oxides pose significant E,H&S risks if not handled properly, and that CdTe PV products may reasonably be expected to face challenges in the marketplace related to customers' concerns about CdTe based in a large part on the lack of differentiation between CdTe and Cd + Te. Two key strategy recommendations of this study are that additional scientific testing is needed to clearly establish accurate E,H,&S data for CdTe-based compounds, and that programs are needed educate customers and the public on the nature of these compounds.

Acknowledging that little data is available on CdTe compounds, one can seek some perspective on CdTe PV by quantitatively comparing total Cd and Te usage. The primary use of Cd today is for rechargeable NiCd batteries, with a lessor (and decreasing) amount used in coatings and pigments (US93a, CC93). The primary use of Te is as an alloying element in free-machining low-carbon steels (US93b). For quantitative perspective one can compare the consumption of Cd and Te in future CdTe PV manufacturing to the existing uses today. Today the total annual output of the PV industry worldwide is about 60 MWp/yr and growing at 10 - 20% per year. The cost-effective size of a thin film PV factory is 5-15 MWp/yr. Assuming then that CdTe PV is successful in gaining a significant market share of the total PV market, one could reasonable expect CdTe PV production to reach 100 MWp/yr in time. Assuming conservative module designs (i.e., relatively thick constituent CdTe and CdS films of 2 um and 0.15 μm, respectively), a 100 MWp/yr CdTe PV production would consume approximately 8 metric tons per year each of Cd and Te, compared to present world consumption of 20,000 and 300 metric tons per year, respectively (US91, US93c). Thus, CdTe PV module manufacturing will consume a small fraction of the present supplies of these metals, and in the case of the metal of greater concern (i.e., Cd) will likely not add significantly to total consumption or production.

Additional quantitative perspective is possible be considering the potential emissions of Cd from different energy sources. Estimates of the amount of airborne Cd released primarily as CdO from burning coal range from 0-1 kg Cd per GW-hr of electricity (US89, NREL92, FI93). If instead 1 GW-hr of electricity were generated using 8% efficient CdTe PV modules, the amount of Cd encapsulated in the CdTe PV modules as CdTe and CdS compounds equates to 1-3 kg Cd. Thus, comparable amounts of Cd are involved with coal-powered generation and CdTe PV generation, but in the case of CdTe PV the Cd is more safely "packaged" as relatively insoluble compounds in a durable module structure. The risks of CdTe modules would be further reduced by an effective collection and recycling program aimed at diverting end-of-life CdTe PV modules from uncontrolled landfills.

A third quantitative comparison can be made by comparing the Cd content in a residential roof-mounted PV system versus the Cd content in household rechargeable batteries. A 2 kWp CdTe PV module array contains the equivalent of ca. 150g Cd. A typical house might have, say, eight each of size C and size AA rechargeable NiCd batteries. At ca. 15 wt% Cd the household NiCd batteries contain 60-90g Cd, comparable to or more than the amount to the Cd content of the roof-top PV system when one considers the 3-7 year useful life of the batteries versus the 10-20 year useful life of the PV system (EY92). Again, the relative risks of CdTe PV modules could be further reduced by an effective recycling program, and funding for such a program should be easier for the ca. $10,000-20,000 PV array than for the $30-60 battery set.

Everyday comparisons of this sort are useful in educating the customer (and the customer's neighbors) on the relative risks and benefits of CdTe PV versus other energy sources and other well-accepted products. Additional positive comparisons of this sort would aid CdTe PV market acceptance.

A brief survey of the exposure pathways and the present scientific estimates of the hazards posed by the exposure pathways revealed an additional issue to be further addressed in the scientific testing, namely the issue of CdTe PV modules in a fire. Scant test data is available, but what does exist (BNL90, BP93, BP94a) suggests that the risks from CdTe modules in a fire are low, and common sense suggests that a burning structure might well pose much more significant primary hazards far exceeding the incremental risks of the CdTe PV; but the issue has sufficient import to some customers that additional scientific testing is warranted.

Beyond the scientific data existing, an informal survey of published and unpublished opinions by present PV industry players revealed a wide spectrum of pre-conceived notions related to CdTe PV E,H&S risks, ranging from a strong assertion that no E,H&S barriers exist to successful CdTe PV commercialization to equally strong assertions that CdTe PV faces debilitatingly high E,H&S barriers that preclude successful commercialization. Clearly, the existing dearth of well-documented and widely-known information on CdTe PV has polarized many PV industry participants on the perceived risks and benefits of CdTe PV. This underscores the importance of scientific testing, of sampling of potential customers' existing concerns, and of assembling of responsive educational materials.

Overall, the assessment of existing E,H&S scientific data on CdTe PV products identified several key issues related to CdTe PV commercialization, including the need for additional scientific testing, the need for quantitative surveys of existing customer opinions, the value of appropriate positive comparisons, and the potential advantages of collection and recycling programs. Pathways for addressing these issues were sought by analyzing the strategies of existing industries facing comparable challenges.

Strategies of Comparable Industries

Numerous existing industries face E,H&S issues comparable to those facing CdTe PV, and the public acceptance strategies of those industries are useful guideposts for how the CdTe PV industry might proceed. In analyzing the strategies of comparable industries, we attempted to maintain the study's focus on issues of customer preferences and strategy economics and logistics, but repeatedly a clear understanding of the strategies of comparable industries required a careful consideration of the applicable legal and regulatory issues that to a large extent shape the reality of materials and products handling in the United States.

The list of applicable laws regulating the manufacture, transport, sale, use and disposal of products containing potentially hazardous materials is quite lengthy. The list includes the Clean Air Act, the Clean Water Act, the Toxic Substances Control Act, the Comprehensive Environmental Response, Compensation and Liability Act, and Occupational Safety and Health Administration rules, to name but a few. The most important law shaping the regulatory environment affecting CdTe PV product use and end-of-life handling is the Resource Conservation and Recovery Act (RCRA) and its various amendments.

RCRA regulates the disposal of hazardous wastes, including guidelines on what constitutes a hazardous waste and how such wastes must be handled. It includes a Hazardous Waste Management (HWM) program that sets strict guidelines for record keeping, labeling, packaging, transportation, siting, inspections, training, and emergency planning for the generation, transport, storage and disposal of hazardous wastes. The HWM requirements are sufficiently burdensome that RCRA regulations add considerably to the disposal of any hazardous waste.

A key differentiation in the complexity of handling a waste material is the determination of whether the waste is "hazardous" and must be handled according to the HWM guidelines, or whether a waste is non-hazardous and (at least in the eyes of the Federal Environmental Protection Agency) can be disposed of as non-hazardous trash. Hazardous wastes are determined either by definition (i.e., "listed" as such in the RCRA text) or by testing (i.e., judged by standardized tests against defined characteristics of hazardous wastes). CdTe is not "listed" as hazardous, so CdTe-containing products are tested using the Toxicity Characteristic Leaching Procedure (TCLP) test intended to predict risks of contamination of groundwater by contaminant leaching.

In preliminary tests on a very limited sample set, experimental CdTe modules failed the TCLP tests (NREL93). More recently, BP Solar reported that its prototype

CdTe modules passed the TCLP test (BP93, BP94b). Large-scale TCLP testing of U.S. prototype CdTe products has not been reported. At first glance these contradictory early data appear to pose two very different circumstances, but on further consideration some commercialization issues are common to failing and passing TCLP testing.

Consider the possibility that all CdTe modules "pass" the TCLP test. By U.S. Federal standards as defined by RCRA, end-of-life CdTe modules are then non-hazardous trash and require no special handling. This greatly simplifies disposal for both the manufacturer and the user, and, as will be quantified below, the economic impact of this simplification is sufficient that passing TCLP is a key to the profitability of any commercial product and should be a primary design goal for CdTe PV module. However, passing TCLP does not in itself end consideration of collection and/or recycling programs. For example, rechargeable NiCd batteries used in American households currently are exempted from being handled as hazardous wastes, albeit not because they pass the TCLP test, but because RCRA Part 261 exempts all household wastes from the HWM regulations. In spite of this exemption and at considerable expense, the NiCd battery industry in the U.S. has actively encouraged state and Federal laws facilitating used NiCd battery collection and recycling. The NiCd battery industry's motivations include corporate environmental responsibility and public relations, but frankly also include a realization that effective collection and recycling of NiCd batteries will reduce both the migration of Cd into municipal landfills via used NiCd's and the likelihood that more restrictive regulations will be promulgated to forcibly reduce Cd contamination by restricting NiCd use. So, whether for positive public relations or preemptive environmental politics, the CdTe PV industry may need to consider a collection and recycling program for end-of-life modules.

Conversely, consider the possibility that CdTe modules "fail" TCLP and as a result are defined under RCRA as a hazardous waste at end-of-life. This situation is not necessarily the CdTe PV module manufacturer's problem in that RCRA disposal regulations apply to the generator of the waste (i.e., who possesses the material when it is declared to be a waste) which in most cases will be the module user, not the manufacturer. However, if CdTe PV module users are faced with high module disposal costs, then CdTe module sales may suffer; so CdTe PV module manufacturers are probably faced with setting up and (co-)funding the proper disposal of end-of-life modules that fail TCLP. Unlike the previous case where CdTe PV modules are assumed to pass TCLP, in this case the end-of-life modules will need to be disposed of as hazardous waste. This complicates and makes much more costly the whole disposal chain, whether one chooses disposal in a controlled landfill or reclaim through various means. Present economics aside, reclaim has the advantage of eliminating most future legal liability, so again a collection and recycling program for end-of-life modules is a reasonable consideration.

Thus, either from public relations, regulatory politics, or commercial necessity, CdTe module manufacturers and resellers should consider a collection and recycling program for end-of-life CdTe modules. Several useful lessons in collection and recycling can be learned from comparable industries.

An obvious comparable industry is crystalline silicon PV modules. Aside from questions of solder composition, crystalline silicon PV modules have no obvious hazardous content and end-of-life silicon modules are not typically handled as hazardous wastes[1]. Nonetheless there are valuable components that might be recovered, including for example the silicon wafers. BP Solar has recently reported experiments to recover silicon wafers from end-of-life PV modules by dissolving the EVA pottant (BP94c). However, no commercial collection or recycling of PV modules is presently known.

Glass recycling is quite ubiquitous and in so much as the vast majority (> 99.5 wt%) of an unframed CdTe PV module is glass, it is reasonable to consider recycling CdTe PV modules through existing glass recycling pathways. Commercial glass is recycled today, but sheet glass manufacturers' cleanliness specifications are so high as to block most recycling of uncoated plate glass and would seem to completely block recycling of CdTe PV modules. Container glass is widely recycled and has lower cleanliness standards, and CdO is used in some processes to color glass; but the economics of glass recycling is generally negative and is driven in many locales as much by litter reduction and landfill space conservation as by the economic value of recovered glass. Issues of adding CdTe into the beverage container glass supply would need to be examined in more detail, but one could reasonably anticipate some complications.

Focusing on the metals content of CdTe PV modules, aluminum recycling was analyzed as a potential corollary. The recycling of aluminum beverage cans and scrap stock is an example of pure supply and demand economics at work. Average prices for virgin aluminum materials averages ca. 60¢/lb (US93d), manufacturers pay ca. 40¢/lb for collected cans, and recycle collection companies pay consumers 10-35¢/lb for cans and clean scrap. Some areas have deposit and refund programs that fund recycling programs to increase the fraction of aluminum cans recycled. In California for example, the Redemption Value program collects a per can deposit on retail purchases and returns the collected funds to the public by enhancing recycle payments, e.g., adding ca. 65 ¢/lb to what the collection company would otherwise pay the consumer. This example is illustrative of the incentives that might be necessary to encourage PV users to return end-of-life CdTe PV modules into a responsible collection program, either for proper disposal or recycling. Unfortunately, the positive economics of aluminum recycling are not shared by CdTe PV modules. Ironically, as will be discussed in more detail below, the economics of reclaiming CdTe PV modules is negative in large part because of the small absolute and relative amount of recoverable metals in the

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[1] End-of-life PV modules are already handled as hazardous waste in some foreign countries.

modules. Simply stated, there is not likely enough metals value in a CdTe PV module to offset collection and processing expenses.

Pb-acid and NiCd battery recycling were analyzed as examples of common products that are "hazardous" under RCRA but that are widely in use and widely recycled. Pb-acid batteries are in general use, mostly commonly in automotive applications, but also as energy storage in PV systems. The E,H&S hazards of Pb-acid batteries-most prominently electric shock, acidic electrolytes, and Pb exposure-are well-known to both the scientific community and to the general user community. End-of-life Pb-acid batteries are "hazardous" under RCRA classifications, ergo they would be subject to the full HWM handling regimen if not for specific exclusions in the RCRA regulations intended to encourage Pb-acid battery recycling by easing the costs and complexity of collecting and transporting used Pb-acid batteries.

Pb-acid battery recycling is driven primarily by positive economics. Pb-acid batteries are generally recycled by neutralizing or reclaiming the acidic electrolyte, burning or recycling the plastic casing and separators, and smelting the Pb for reuse in new batteries. The reclaim value of the Pb metal (and to a lessor extent the plastic casings) is sufficient to offset the used battery collection costs and electrolyte treatment costs. Recent low market prices for Pb have hurt the economics of Pb-acid battery recycling, but the basic economic gain of reclaiming Pb has funded Pb-acid battery recycling for the past 75 years. Today over 90% of Pb-acid automotive batteries sold in the U.S. are eventually recycled (BCI91). This high collection rate is the result in large part to state mandated programs requiring that battery retailers charge customers a deposit of $2-10 per battery on the sale of any new battery without a used battery trade-in. This deposit (plus years of customer education on the environmental hazards of Pb in landfills) is sufficient customer motivation. Retailers are in turn paid up to ca. 50¢/battery by intermediary collection entities and/or primary recyclers (e.g., secondary Pb smelters). Some states have additional payment requirements to better fund this "reverse distribution chain" collection of used batteries.

The well-established and highly-effective Pb-acid battery recycling system resulted in the EPA granting Pb-acid batteries special exclusions from some HWM rules in order to further encourage recycling and materials reuse. This underscores an opportunity for the PV industry to mitigate collection and recycling costs and complexity of PV modules by setting up an effective recycling program and seeking regulatory relief to improve the economics of such a program; the NiCd battery industry is pursuing a related strategy now. This also underscores the importance of cooperative collective action by, at a minimum, the U.S. CdTe PV module manufacturers to establish workable pro-active recycling and educational programs.

NiCd batteries are widely used in rechargeable applications, and sales of NiCd batteries are increasing as sales of portable electrical devices (e.g., phones, computers, tools, etc.) continue to increase. NiCd batteries "fail" the RCRA TCLP test and thus are considered "hazardous" and are subject to HWM rules. Currently manufacturers of large industrial NiCd's (e.g., those used as back-up and stand-alone power on airplanes) ease the HWM disposal burdens for their large commercial customers by providing a fully permitted collection and recycling program, often at little or no cost to the customer. As a result it is estimated that upwards of 80% of industrial NiCd's are currently recycled in some manner (PRBA94).

Two techniques are commonly used for NiCd battery recycling. The more common techniques are pyrometallurgical in which the battery casings are broken open, the battery pieces are heated to fume off the Cd (and condense it as CdO or Cd metal), and the Ni and the Fe support grids are smelted. Approximately 10,000 metric tons of NiCd batteries are recycled each year (CC93). The largest U.S. recycler of NiCd's is INMETCO in Pennsylvania. INMETCO is a large secondary metal smelter with a primary interest in smelting scrap for resale as feedstock to stainless steel mills. INMETCO's materials interest in NiCd batteries is the Ni and Fe content; Cd is a "tramp" metal that is processed at some economic penalty. Smelter slag is sold as roadbed material. The reclaim values of the Ni and Fe contents of NiCd's do not fully offset the processing costs, and INMETCO typically charges the battery user 30-40 ¢/lb to recycle NiCd's.

European and Asian NiCd recyclers share some similarities to INMETCO, but tend to focus more on completing the material life cycle by recycling the Cd in used NiCd's for reuse in new NiCd's. A large European NiCd recycler is SNAM in France. SNAM uses pyrometallurgical techniques to recover and purify Cd for reuse in NiCd batteries and Cd-containing pigments. As with INMETCO, the Ni and Fe contents are sold to steel mills. Also as with INMETCO, Cd metal reclaim value is less than NiCd processing costs, so SNAM typically charges battery users for the recycling of NiCd's.

The mechanics and economics of industrial NiCd battery recycling reveals three important points for potential CdTe PV module recycling. First, at the prevailing prices of Cd it is not economic to recycle NiCd batteries for Cd reclaim. This suggests that the lower concentrations of Cd in CdTe PV modules (e.g., ca. 0.05 wt% in CdTe PV modules versus ca. 15 wt% in NiCd batteries) will obviate any economic recovery of Cd from CdTe PV modules. Second, in the absence of secondary components of high reclaim value (e.g., Ni and Fe in NiCd's), CdTe PV module recycling will be at some cost to the end-of-life module owner, be it the module user or the module manufacturer (e.g., through some used module return program). Third, in spite of the likelihood of some expense being incurred to recycle CdTe PV modules through existing NiCd battery recyclers, these existing recyclers provide a well-established, fully-licensed recycling option that should be more carefully examined for its role of, at least, a near-term recycling option while CdTe PV manufacturing is in its nascent stages.

The majority of NiCd batteries sold in the U.S. are smaller consumer batteries, and the majority of such batteries are not at present recycled. Consumer batteries are often disposed of in municipal solid waste landfills as regular trash, contributing to the contamination of community landfills with cadmium. RCRA allows such unregulated disposal by private citizens under its broad exemption for all "household" wastes, but businesses and institutional entities (e.g., cities) are faced with the full HWM regimen. Manufacturers of small NiCd batteries are seeking to reduce cadmium migration into uncontrolled municipal landfills and to assure long-term sales growth by working collectively to enact labeling and product design regulations that facilitate battery recycling and by working with the EPA to define new RCRA provisions simplifying the collection and recycling of NiCd batteries.

Labeling and product design regulations are intended to facilitate battery recycling by alerting the customer to the presence of a NiCd battery that must be recycled or disposed of properly and by simplifying the removal of the battery at the end of its useful life. The NiCd battery trade association named the Portable Rechargeable Battery Association (PRBA) has sought to enact laws mandating such labeling and product design rules, and many states have done so. The corollary for CdTe PV module manufacturers would be module labeling alerting the module user that the product contains cadmium and should be handled properly and perhaps listing a toll-free phone number enabling the user to contact the manufacturer or an industry association for information about recycling and/or proper disposal.

PRBA is among those working with the EPA in drafting new RCRA provisions simplifying the collection and recycling of NiCd batteries. Unlike Pb-acid batteries, NiCd's do not currently have exemptive provisions under RCRA to facilitate recycling. However, the EPA has recognized that as a consequence of its success in regulating large industrial generators of hazardous wastes that widely dispersed, large numerical volume, small individual quantity hazardous wastes like consumer NiCd batteries now account for a disproportionate fraction of the hazardous materials entering the uncontrolled solid waste stream. The EPA has termed these wastes as "universal wastes" and intends to amend RCRA with a Part 273 called the Universal Waste Rule (UWR). The UWR is directed at facilitating feasible and (cost) effective collection and recycling programs by easing key HWM requirements. Should the UWR be issued as expected in the summer of 1994, the PRBA will incorporate an independent entity to collect and recycle consumer NiCd batteries at no cost to the user. The NiCd battery manufacturers will voluntarily fund the activities of new entity through reinvesting profits from NiCd battery sales. Battery collection will be encouraged by setting up retailer collection programs that provide convenient store drop-off points for the user and compensation payments to the retailer from the recycling entity.

The importance of the consumer NiCd battery recycling program and the UWR to CdTe PV module collection and recycling is two-fold. First, public relations and regulatory issues can justify collection and recycling programs even if such programs are not economic on their own (e.g., via reclaim value). Second, the success or failure of such a recycling program hinges in large part on the improved economics possible under the proposed UWR provisions. It is still possible at the time of this writing to lobby the EPA to add PV modules to the broad UWR exemptions to be issued this summer. Though the UWR will likely contain provisions making it possible to petition for additional products (e.g., PV modules) to receive the UWR exemptions in the future, as with any much debated statute it is much easier to obtain such additions now while the rules are still in the draft stage.

PV Industry and Customer Survey

A survey focusing on commercialization issues was drafted to collect quantitative data on the knowledge, perceptions, preferences and values of prospective purveyors and users of CdTe PV modules. The survey was revised with input from Brookhaven, Golden Photon, Solar Cells Inc., and NREL, and was technology neutral in that it did not single out any one PV technology or focus on any specific E,H&S issue. The aim was to survey a cross-section of the PV industry and of prospective PV customers to quantify what commercialization challenges might be faced by any new PV module technology in general and thin film CdTe PV module technology in particular.

As of this writing, 18 surveys have been returned, including seven PV module and system sales organizations totaling ca. 6 MWp/yr annual sales, four electric utilities, three PV system design consultants, one battery manufacturer, one PV industry association, and two PV research centers. Seven responders were from outside the U.S.

The survey addressed seven general topics: battery recycling, module recycling, E,H&S concerns, public attitudes, applications, achievable prices, and sources of assurance.

With regards to battery recycling, many responders were not well-informed about the regulations or the mechanisms for properly disposing of or recycling used batteries. Most responders knew that Pb-acid automotive batteries could be recycled through battery suppliers (i.e., retail sources and/or battery manufacturers), and a minority knew that small consumer NiCd batteries are now generally disposed of in the U.S. with non-regulated non-hazardous trash. Non-U.S. responders were better informed on proper battery handling, probably due to the fact that local regulations for most non-U.S. responders require specific recycling and/or hazardous disposal of used batteries. In general the responses to the battery recycling questions suggest that PV sellers and users are familiar with battery recycling primarily through their private lives, not through their professional associations, which in turn suggests that PV module recycling would require pro-active education by the PV module manufacturers to assure positive cooperation.

With regards to PV module recycling, most responders indicated that they and their customers would voluntarily participate in a module recycling program, and the balance indicated that they and/or their customers would participate if they were compensated for handling costs and/or if their customers received some incentives. Half of the responders indicated that they and/or their customers would be more likely to purchase modules that could be conveniently recycled, but a quarter of the responders indicated that they would be less likely to purchase modules that by law must be recycled or handled as hazardous waste. As with battery recycling, the non-U.S. responders gave the strongest answers, predicting in one case that local laws would in the future require module manufacturers to take back end-of-life modules and in another case that modules requiring recycling or hazardous waste disposal could not be sold unless an incentive equal to 50% of the original purchase price was offered to adequately motivate users to return end-of-life modules. Overall, the module recycling questions indicated a general preference for recyclable modules, but an aversion to modules requiring recycling because of their hazardous materials content.

With regards to E,H&S concerns, half of the responders indicated that they had environmental or safety concerns about CuInSe2 and CdTe modules, and the most common reason cited for this concern was Cd content. Module and system sellers were the most concerned about materials content and the most likely to specifically identify Cd content as a primary concern. Utilities were the least likely to cite any concerns with any PV technology.

With regards to public attitudes, most responders now use products containing regulated materials (e.g., Pb in Pb-acid batteries) because those products are reliable and cost-effective, but would avoid purchasing such products if competitive non-hazardous products were available. Half of the responders indicated that their customers typically do not know or care about the (hazardous) materials content in products, and about a third of the responders indicated that they or their customers would buy such products if the products were conveniently recycled. Utilities were the least concerned about materials content. Overall, the E,H&S and public attitude questions suggest that many module users are concerned about materials content, especially about Cd content; but that products containing regulated materials (e.g., Cd in CdTe) would be purchased if the price and performance were competitive and if the modules were conveniently recycled. These questions also underscore the differences between customers and the importance of educational and marketing materials being carefully targeted to the different customer groups. The responses suggest that utilities are the least concerned about using PV modules that contain regulated materials, presumably because they already handle regulated materials in other aspects of their business; and this in turn suggests that utilities might be good target customers for the market entry of CdTe PV modules in so much as utilities would be technically sophisticated customers with no strong pre-conceived aversions to handling beneficial products containing regulated materials.

With regards to applications, few responders indicated that any PV technology was inappropriate for any particular market. Only one responder had a strong E,H&S concern, namely that it was completely inappropriate to sell modules that required hazardous waste disposal or recycling in rural areas of developing countries given the low probability that such modules would be suitably recycled and thus the high probability that local areas would be contaminated with hazardous materials.

With regards to achievable prices, the survey inquired as the effect of various module characteristics on market price relative to crystalline silicon assuming the example module was comparable to crystalline silicon in all other respects. A variety of module features were examined in order to separate E,H&S concerns from other issues affecting module price but unrelated to E,H&S issues. For example, any new module technology would likely command a price ca. 10% less than the well-established crystalline silicon technology assuming comparable modules in all other respects. One presumes that this 10% price differential would decrease with time as the new technology proved itself in years of field experience. The image of thin film modules appears to suffer from the legacy of the 1980's and would likely achieve (market entry) prices of 10 - 30% less. A module that must by law be recycled or disposed of as hazardous waste will achieve prices of 5 - 30% less, with required recycling being less disadvantageous (i.e., 5 - 15%) than hazardous waste disposal (i.e., 10 - 30%). Although all responders indicated a willingness to participate in module recycling and half indicated that module recycling was a positive influence on their choice of modules, few responders indicated that ease of module recycling would command a higher module selling price.

With regards to sources of assurance, the general result was that the most valuable endorsements come from entities most like the end module users. For example, utilities highly valued endorsements by utility-related groups like the Electric Power Research Institute and the Utility Photovoltaics Group. Endorsements by these utility-related groups were also highly valued by the module and system sellers. The second most common endorsement cited for its value was the scientific community as represented by NREL and ISPRA. International module sellers also cited environmental groups and funding agencies as important to endorsements. With regards to module safety and reliability, most responders were satisfied with standardized tests, such as UL testing of (electrical, structural, and fire) safety and JPL Block V testing of expected module durability.

Overall, the survey results reinforced what one might have expected from the existing lack of knowledge of CdTe, namely that prospective users were not overly concerned about E,H&S issues in general, that they identified Cd content as a key issue when explaining any concerns they did have, and that they are willing to purchase CdTe PV modules if the price and performance are competitive, if CdTe PV technology is endorsed by users like themselves, and if there is some convenient method of handling end-of-life modules (e.g., because they're non-hazardous trash, or because there is a reliable, low-cost recycling program).

Recycling Options

Real-world recycling is a dynamic trade-off between costs and benefits. Economics largely dictates whether a recyclable material is recycled or not. For CdTe PV modules the potential costs include collection permitting, collection incentive payments, transport and storage costs, recycling charges, and administrative overhead. The potential benefits of recycling include materials reclaim, positive public image, marketing advantages, future liability minimization, and regulatory incentives. The relative balance of costs and benefits is a strong function of the details of the recycling program and of the regulatory and market environment in which the program operates.

Assuming for the moment that end-of-life CdTe PV modules can be efficiently collected, a key issue is how one recycles a used CdTe module and what the economics of the process is. One possible route for PV module recycling is primary metals smelters. Cd and Te are ancillary products of Zn, Cu and Pb extraction. Unfortunately for recycling economics, a prototypical glass/glass module structure with 0.15 μm CdS and 2 μm CdTe layers has only 0.05 wt% each Cd and Te, well below the typical metals concentrations in the Zn, Cu and Pb processing byproducts from which Cd and Te are generally obtained. At the low concentrations present in a PV module, processing costs would almost assuredly exceed metals value, so that primary metals smelters would charge for recycling, not unlike NiCd battery recyclers today.

Alternatively, recognizing that non-ferrous smelters purchase silicas as fluxing agents for the smelting process, it is possible that PV modules have reclaim value for their glass content. Unfortunately the low-cost soda lime glass used in most PV modules has less free silica than the raw silica sources typically used, and U.S. smelters often use silicas containing trace amounts of precious metals to improve the economics of the overall smelting operation. Thus, it is likely that the economics of CdTe PV module recycling by U.S. primary metals smelters will be negative, which is to say that the smelters will charge the module user and/or manufacturer for recycling. These charges may however be less than the charges incurred by recycling by NiCd recyclers and less than disposal as hazardous waste.

Another set of options is secondary metals smelters and cement kilns. Various companies now market small specialty smelters for the purpose of destroying hazardous materials, and such units might be useable to process CdTe PV modules. Alternatively cement kilns now process a wide range of hazardous wastes at costs significantly below incineration costs, and it is possible end-of-life CdTe modules could be processed in a similar manner (CE94). The details and economics of these options were not investigated.

Quantitative estimates of four disposal and recycling scenarios were made as representative examples of the what the CdTe PV industry may face. The four scenarios considered were: hazardous waste landfill by the user, hazardous waste incineration by the user, hazardous waste collection and recycling, and non-hazardous waste collection and recycling.

Hazardous waste landfill disposal of end-of-life CdTe modules by the user is the most likely scenario in the event that CdTe modules fail TCLP tests. Module manufacturers are not at present required to accept end-of-life modules or take any economic or legal responsibility for such modules. Laws exist in some locales mandating, for example, battery manufacturers to accept returned end-of-life batteries (and be responsible for proper disposal and/or recycling), and while it is possible that such laws may spread geographically and in scope to include PV modules, no such regulations exist in the U.S. at this time. Assuming that the user is not a private citizen exempted from hazardous waste disposal rules under RCRA's household waste exemptions, the module user would be faced with three costs: landfill costs, taxes, and future liability. Landfill costs vary with waste type and location, but an average in Califo rnia is $400 per 55-gallon drum of dry solid hazardous waste. Assuming 10 MWp of 8% efficient, glass/glass CdTe modules ground up better use drum volume, this translates to 3400 drums at $1.4 million, or $0.14/Wp disposal costs. Taxes would be additional; for example in California a hazardous waste generator is charged ca. $200/ton (or $100/drum in this scenario) in state taxes for landfill disposal on top of actual landfill costs. Landfill disposal also incurs the future liability of, say, Superfund clean-up expenses and other liabilities as additional laws are implemented.

Hazardous waste incineration by the user largely eliminates future liability, but incineration incurs higher per drum costs and incurs various taxes. For example, in California solid hazardous wastes can be incinerated at a cost of ca. $600/drum, roughly 50% more than landfill. Various waste generator taxes would also be due. Incineration fees alone for 10 Mwp of CdTe modules would be ca. $2 million, or $0.20/Wp.

Hazardous waste collection and recycling, whether by the user, the manufacturer, or some separate recycling entity, incurs various costs. Focusing on the direct expenses, three costs are likely significant. First an incentive will likely be necessary to encourage users to return end-of-life modules to centralized collection locations, whether via reverse flow through the retail chain or directly to some specific module collection mechanism. In so much as auto batteries pay a $2-10 per battery incentive (on a ca. $60 battery), one could reasonably expect to pay a similar amount for a 30-40 Wp module selling at $1.50 - 2 /Wp. Assuming a $2/module incentive, ca. $0.7 million in incentive payments to users would be required. Shipping and handling costs for bulk, solid, non-radioactive, non-volatile hazardous wastes ranges from $800-1500 per ton for cross-country transport. Assuming a centrally located recycling site, one could reasonably expect $500/ton, or $0.8 million in shipping and handling costs. Actual module recycling would likely come at some cost to the party disposing of the module. NiCd battery recycling charges range from $0.20 - 0.70 per pound and costs would be higher without the Ni reclaim value. Assuming some simple process for module recycling might achieve the lowest present costs for battery recycling, module recycling charges could reasonably be $0.20/lb, or $0.7 million. Summing collection incentives, transport, and recycling costs, one estimates $2.2 million, or $0.22/Wp.

Non-hazardous waste collection and recycling would benefit from the simplified handling of non-hazardous wastes. One assumes in this case that public relations or strategic market considerations motivates collection and recycling of modules.

Ironically, it is likely that a higher incentive would be required to encourage module users to return end-of-life modules to collection points if the user was not otherwise faced with substantial disposal costs of a hazardous waste. A $5/module incentive, or $1.6 million is reasonable. Shipping and handling costs for non-hazardous wastes are much less than for comparable amounts of hazardous wastes, but ironically non-hazardous wastes would likely be faced with comparable overall transport costs because end-of-life modules would likely be shipped back in small shipments through transport means similar to those used to send out new modules. Assuming typical ground transport, one reasonably estimates $0.25/lb, or $0.9 million. Finally, assuming end-of-life CdTe modules are non-hazardous, it is possible that modules could be more readily reclaimed for their glass value. Assuming a reclaim value of $5/ton, equal to that for clean sheet glass, one reasonably estimates a gain of $80,000. Summing collection incentives, transport costs, and reclaim value, one estimates $2.5 million, or $0.25/Wp.

It is important to realize that these cost estimates are preliminary and approximate, and are based on conservative assumptions about the difficulty of collecting and recycling CdTe modules. It is very possible that the desire of modules users to purchase recyclable products and their willingness to voluntarily participate in recycling programs will provide much more positive economics than the four scenarios quantified above. If however, the four scenarios above are an accurate reflection of the disposal options for end-of-life CdTe modules, then CdTe PV technology faces significant challenges. The $0.15 - 0.25/Wp costs calculated above are a significant fraction of the gross profit margins of present-day PV modules selling at ca. $4/Wp, and are a large fraction of the projected total selling price of modules selling in the future at $1 - 2 /Wp. It is clear that CdTe PV manufacturers and researchers need to work pro-actively to identify low-cost alternatives to these at-present-most-likely scenarios.

Summary of Strategy Recommendations

The results of this study can be assembled into a set of strategy recommendations for the CdTe PV industry and its supporters. These recommendations can be grouped into seven categories.

First, with regards to scientific testing, additional data is needed on the E,H&S properties of Cd-containing compounds, specifically CdTe, CdS, and CdTeS alloys that often form at the CdTe/CdS interface. Additional scientific data is needed on the emissions and residues of CdTe modules in fires, and how specific module design features affect the results. Additional testing of CdTe modules is required to determine whether the present generation of CdTe modules pass the EPA's TCLP test and comparable international tests. Finally, it is apparent that testing and endorsement by the scientific community has commercial importance, as do standardized safety and durability certifications by, say, Underwriter's Laboratories.

Second, with regards to product design, important and perhaps decisive advantages accrue from end-of-life modules being classified as non-hazardous by, for example, EPA TCLP tests, and this should be the design goal for any CdTe module design. Glass/glass and glass/metal module package structures should be examined for their contribution to CdTe passing TCLP and any fire testing. Modules should be labeled in such a manner to facilitate module recycling and/or proper disposal. Recyclable modules and a reliable low-cost module recycling program can be positive selling points, though they may not translate directly into higher average prices.

Third, with regards to education, it is important to educate customers and the public about the nature of CdTe-based compounds. It is useful to identify, quantify and disseminate positive comparisons in an everyday context to help prospective users put the hazards and benefits of CdTe PV modules into proper perspective. Distinct educational and informational materials should be targeted to different customer and regulatory constituencies. Comprehensive education and information materials should be assembled now to best prepare customers, the public, and lawmakers for future commercialization of CdTe PV products.

Fourth, with regards to collective action, cooperative action by CdTe PV companies is essential to successful commercialization. A risk of intra-industry fratricide that erodes the general perception of PV as a clean beneficial energy source exists if intertechnology market competition focuses on poorly documented debates of E,H&S issues. The PV industry should organize a collective initiative for some form of environmental safety certification of PV products.

Fifth, with regards to customer selection, CdTe module manufacturers should focus their early efforts on sophisticated users with well-controlled sites; for example domestic electrical utilities.

Sixth, with regards to module recycling, it is clear that recycling is attractive to many potential customers, but that little module purchase price differential will likely accrue and that collection and recycling costs may exceed materials reclaim value or marketing advantages. Early efforts should focus on identifying simple, low-cost collection arrangements and on using existing NiCd recycling pathways. Existing glass recycling options should be further explored. To facilitate recycling, experiments with module disassembly and metals recovery and/or detoxification methods should be undertaken. The economics of CdTe module recycling via primary metal smelters, secondary smelters, cement kilns and other pathways should be quantified. The logistics and costs of a module recycling program should be further explored. Suitable user and distribution network incentives should be determined. The full economic and legal ramifications of manufacturer take-back and/or recycling programs should be examined. CdTe module manufacturers should consider creating a separate independent entity to manage end-of-life module collection and recycling.

Seventh, with regards to legislation and regulation, the experience of the U.S. battery industry underscores the value of a universal, well-run recycling program in simplifying many regulatory issues. Applicable regulations on in-house consolidation and concentration should be clarified. CdTe module manufacturers should seek to add PV modules to the RCRA Universal Waste Rule exemptions prior to its issuance. To this end the PV industry should meet with Federal regulators to advance pro-active collaboration on PV product life-cycle regulation. Current and pending regulations in major overseas markets should be investigated to better understand future testing requirements and marketing strategies for CdTe PV.

Recommendations For Further Work

This study focused on proposing workable strategies. Further work should focus on implementing the strategies. For example, suitable educational and informational materials should be drafted, and discussions should be held with the EPA to review adding PV modules to the Universal Waste Rule.

This study focused on Federal statutes and guidelines. Further work should include present and proposed state guidelines on materials and products testing, classifications, recycling, labeling, etc.

This study focused on domestic U.S. markets, regulations and economics. In so much as 65 - 75% of the PV products manufactured in the U.S. are subsequently exported, further work should be directed at international regulations and markets to better understand international testing requirements and optimal marketing strategies. For example, the impact of the Basel Convention on international exchange of hazardous wastes, EC Directive 91/157 on batteries containing hazardous substances, and EC Directive on Landfill Waste: COM 91/102 should be examined.

This study focused on field use and on end-of-life issues. Processes and permitting issues related to recovery and reclamation of processing residues and fall-out should be investigated, both because some potential customers surveyed expressed a concern about manufacturing environmental safety and because the quantitative estimates of end-of-life module recycling costs revealed the potential for significant cost burdens for manufacturing fall-out disposal.

This study focused on preliminary "paper" estimates for plausible recycling options. Further work should include actual field tests with existing recyclers and smelters to quantify recycling processes and costs.

This study focused on CdTe modules. Similar studies should be undertaken on crystalline silicon, amorphous silicon, and thin film CuInSe2.

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US91 = U.S. Dept. of Interior, Bureau of Mines, Mineral Industry Surveys, Annual Review, "Cadmium in 1990", May 1991.

US93a = U.S. Dept. of Interior, Bureau of Mines, Mineral Commodity Summaries 1993, January 1993, p. 40.

US93b = U.S. Dept. of Interior, Bureau of Mines, Mineral Commodity Summaries 1993, January 1993, p. 176.

US93c = U.S. Dept. of Interior, Bureau of Mines, Mineral Industry Surveys, Annual Review, "Selenium and Tellurium 1992", July 1993.

US93d = U.S. Dept. of Interior, Bureau of Mines, Mineral Commodity Summaries 1993, January 1993, p. 20.

USF93 = C. Ferekides et al. of the University of South Florida, "High Efficiency CdTe Solar Cells by Close Spaced Sublimation", 23rd IEEE Photovoltaic Specialists Conference, Louisville, 1993, p. 389.