

Peer Review of Major Published Studies on the Environmental Profile of Cadmium Telluride (CdTe) Photovoltaic (PV) Systems

Organized by European Commission, DG Joint Research Centre (JRC)

Moderated by German Ministry of the Environment (BMU)











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JRC 32882

EUR 24515 EN ISBN 978-92-79-16587-0 ISSN 1018-5593

doi: 10.2788/86177

Luxembourg: Publications Office of the European Communities

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Results of Peer Review of Studies on Environmental Aspects of CdTe Photovoltaic Systems

Organized by European Commission, DG Joint Research Centre (JRC)

Moderated by German Ministry of the Environment (BMU)



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TABLE OF CONTENTS

Executive	e Summary	7		
1. Introduction				
2. Peer Rev	2. Peer Review Purpose, Objective and Methodology			
3. Minutes	of the Review Meeting	10		
4. Review Results				
5. Conclusion	on	23		
Annex I	Presentations of the Peer Review Meeting, Berlin, 4 August 2005	25		
Annex II	Reviewed Studies	85		
Annex III	Review Forms	135		

EXECUTIVE SUMMARY

Following discussions with the German Ministry of the Environment (BMU), First Solar, a company manufacturing CdTe solar modules, requested an independent peer review of studies pertaining to the environmental aspects of CdTe photovoltaic systems. This review was organized by the European Commission, DG Joint Research Centre (JRC) and moderated by the BMU. Four reviewers were selected from the BMU and the JRC and asked to review the most recent studies on CdTe PV environmental, health and safety (EH&S) issues. A meeting took place in the Energieforum Berlin, were researchers from Brookhaven National Laboratory and First Solar made presentations and round-table discussions took place. Subsequently, the reviewers rated three journal articles summarizing the studies, for clarity, quality and relevance. Three of the reviewers were very supportive of the published studies, whereas one reviewer was very critical of the same.

The average rating of the studies was 3 on as scale of 1 to 4 (4 being the best rating) and the overall conclusions were that:

- The environmental risks of CdTe Photovoltaics are minimal, if materials are recycled and/or end-of-life systems and policies are in place.
- The emissions produced during the life-cycle of the modules are extremely low.
- Large scale use of CdTe Photovoltaic modules does not present any risks to health and the environment, and recycling of the modules at the end of their useful life would resolve any remaining environmental concern.

However, further research on leaching and recycling of metals from the modules is needed. Also, the toxicology of CdTe needs to be investigated and the global ecological acceptance of the CdTe technology has to be checked.

All industrial processes have some environmental impacts that have to be taken into account. To create a levelled playing field of energy technologies "Life Cycle Analysis" (LCA) should be used in order to evaluate the potentials and risks in a balanced way. Recent European studies (e.g., PVAccept) showed that CdTe PV has the lowest energy payback and the lowest emissions of CO₂, SO₂, NOX and particulates, among all commercial PV technologies (i.e., mono and polycrystalline silicon, copper indium selenide and cadmium telluride).

The presentations, discussions, comments and review ratings are included in this report.

1. INTRODUCTION

The use of solar photovoltaic systems to generate electricity is growing fast in Germany, due to the Energy Feed-in Law which went into effect in 2004. Several types of photovoltaic modules are used in the German market, one of which is CdTe-based. In the past concerns about the Environmental, Health and Safety (EH&S) aspects of CdTe solar cells were emerged whereas recent studies portrayed them as safe.

Following discussions with the German Ministry of the Environment (BMU), First Solar, a company manufacturing CdTe solar modules, asked for an independent peer review of studies pertaining to the environmental benefits and liabilities of CdTe photovoltaic systems. This review was moderated by the BMU and organized by the European Commissions Joint Research Centre (JRC). The following four reviewers were selected from the BMU and the JRC:

Prof. Hansjörg Gabler, ZSW, Stuttgart

Prof. Martha Ch. Lux-Steiner, Hahn-Meitner Institut, Berlin

Prof. Jürgen Werner, IPE, U. Stuttgart

Prof. Thomas B. Johansson, International Institute for Industrial Environmental Economics, Lund University, Sweden

Other participants and their affiliations:

Mr. Ullrich Bruchmann, German Ministry of the Environment (BMU)

Prof. Vasilis Fthenakis, Brookhaven National Laboratory (BNL) and Columbia University, NY

Dr. Chistoph Hünnekes, Projektträger Jülich (PTJ), Julich

Dr. Arnulf Jäger-Waldau, European Commission, DG JRC, Ispra

Mrs. Amy Meader, First Solar, Perrysburg, Ohio

Mr. Christof Stein, German Ministry of the Environment (BMU)

Mr. Jürgen Will, Unternehmensvereinigung Solarwirtschaft (UVS), Berlin

Mr. David Wortmann, First Solar, Berlin

The reviewers had received a set of published peer-reviewed studies by Brookhaven National Laboratory and Fraunhofer Institute of Solid State Technology. In addition, the authors of these studies gave presentations and answered questions, during a meeting that took place at the offices of the Energieforum, Berlin, Germany on August 4, 2005. The presentations are included in Annex I, and the reviewed studies are included in Annex II.

This meeting was moderated by the BMU and organized by the European Commission, DG Joint Research Centre (JRC). The reviewers were asked to rate the studies with the help of evaluation sheets (Annex III).

2. PEER REVIEW PURPOSE, OBJECTIVE AND METHODOLOGY

This peer review is defined as:

A rigorous and documented evaluation process using objective criteria and qualified and independent reviewers to make a judgment of the technical/scientific merit of studies on the environmental profile of CdTe, and the effectiveness of ongoing projects to safeguard the environment, occupational health and public health during the life cycle of CdTe PV.

The purpose of the review was to provide an independent and comprehensive assessment of the quality of CdTe PV environmental impact studies and the potential impact of a production expansion in Germany. The results of the peer reviews will be used for the planning, permitting and budgeting decisions of First Solar on a production expansion in Germany.

The aim of the review meeting was to discuss major studies on CdTe EH&S aspects, by Brookhaven National Laboratory (BNL), and Fraunhofer Institute of Solid State Technology, and identify possible flaws or inaccuracies in these studies. It was not intended to discuss availability of materials, market prospects or market successes, as this is considered a topic industry has to take care of. The crucial question was: Are CdTe solar electric systems safe with respect to EH&S aspects?

General Approach

The panel consisted of four reviewers who are thought to be qualified to evaluate the specific studies assigned. The panel displayed some technical diversity, ranging from silicon based solar cells, chalcogenide semiconductors to polymer solar cell concepts. None of the four reviewers has specific expertise on CdTe PV.

The reviewers were asked to base their evaluation of each project on:

- a) written material (published studies and supporting documentation);
- b) presentation of such studies, and
- c) a question and answer period.

The peer review used a consistent set of criteria for evaluating all assigned studies. The evaluation criteria are listed below.

- Clarity and Appropriateness of the Scientific/Technical Approach Evaluation of the approach to the experimental and analytical methods used in the research.
- Scientific/Technical Quality of the Research Evaluation of how well the project is designed and the documentation of the results.
- Relevance/Impact of the Research The contribution of the reviewed studies on establishing the CdTe PV environmental profile. The degree it answers definitively relevant questions (e.g., can cadmium leach out? Are cadmium emissions expected? Do emissions present a serious risk?)

Reviewers were asked to evaluate the CdTe PV environmental profile with an overall energy-environmental-economic optimization goal in mind, and use the following rating: 4 –Outstanding, 3 -Good; 2 -Fair; 1 -Poor

3. SUMMARY OF THE REVIEW MEETING

Participants:

Prof. Vasilis Fthenakis, Brookhaven National Laboratory (BNL) and Columbia University, NY

Prof. Hansjörg Gabler, ZSW, Stuttgart

Dr. Chistoph Hünnekes, Projektträger Jülich (PTJ), Julich

Dr. Arnulf Jäger-Waldau, European Commission, DG JRC, Ispra

Prof. Martha Ch. Lux-Steiner, Hahn-Meitner Institut, Berlin

Mrs. Amy Meader, First Solar, Perrysburg, Ohio

Mr. Christof Stein, German Ministry of the Environment (BMU)

Prof. Jürgen Werner, IPE, U. Stuttgart

Mr. Jürgen Will, Unternehmensvereinigung Solarwirtschaft (UVS), Berlin

Mr. David Wortmann, First Solar, Berlin

Mr. Stein from the BMU opened the meeting with the following statement:

"The initiative for the meeting today comes from First Solar. Some weeks ago we had a meeting here in the BMU about the recycling of solar modules. There we spoke about relevant problems of CdTe based solar cells at the end of the life cycle. However, First Solar – a US company – is very bold if it wants to invest considerable sums of money in constructing a production site for CdTe based solar modules in Europe – perhaps Germany -, given the present situation.

At present, there are some imponderables for such an investment:

- The current political situation and the uncertainty concerning the future of the Renewable Energy Sources Act
- The competition with the dominant silicon-based technology
- Consumer acceptance of a technology which is being developed on a CdTe basis

A meeting like the one today is to be welcomed since it provides more transparency concerning the effects of this technology and brings the stakeholders up to date.

The Federal Environment Ministry is open to all technologies. As Ministry for the Environment, however, we especially look at the influences on nature and the environment.

Even though CdTe as a semiconductor compound may not be toxic, it might not be possible to prevent consumers refusing to buy the product because of its cadmium content. It is difficult to sell a product which faces big prejudices. Cadmium certainly is a provocative subject.

But this will be decided by the market. We should concentrate on keeping to objective facts and I think that today's meeting is very appropriate for this purpose."

Then, Prof. Fthenakis presented an overview on "PV EH&S Issues and CdTe", based on several peer-reviewed articles¹. The salient points of his presentation are summarized as follows:

Cd is produced as a by-product of Zn production and can either be put to beneficial uses or be sequestered and stored in a way that won't allow for any releases into the environment. CdTe PV is the safest current use of Cd; it is in a stable form that doesn't leak into the environment during normal use or foreseeable accidents.

Air emissions of Cd from the life-cycle of CdTe PV (including mining, smelting and purification) are 100-360 times lower than Cd emitted into air routinely from coal and oil power plants that PV displaces. This comparison is based on the data-bases of the US Electric Power Research Institute (EPRI) data for the US power plants with well-maintained pollution electrostatic precipitators and bag-houses. Thus, the environmental issues related to CdTe PV are by far outweighed by the environmental benefits that PV displacement of fossil would generate.

Photovoltaics have distinct environmental advantages for generating electricity over conventional power technologies. Every PV technology has some EHS issues, but the industry is proactive in controlling them, and these issues should not restrict the commercial viability of any of the current PV technologies. For example, First Solar voluntarily initiated a recycling program funded by insurance warrantees, which fully resolves environmental concerns. Recycling research at BNL has proven that a 99.99% separation of cadmium and recovery of tellurium is feasible.

PV technologies should be evaluated on their potential for low-cost electricity production, and life-cycle externalities (e.g., energy payback times, life cycle CO2 emissions). Recent European studies showed that CdTe PV modules have shorter energy pay back times and lower life cycle CO2 emissions than crystalline silicon and CIGS PV systems. In addition, the cost of First Solar's modules is lower than that of the current c-Si PV production.

A low production cost technology like CdTe PV could accelerate PV inroads in the energy market. A significant market penetration of any technology will help the whole PV industry by improving the installation infrastructure and reducing the installation cost.

In addition, First Solar and Deutsche Solar who are investing in recycling, help the whole industry by setting-up an infrastructure that the whole industry will eventually

11

⁻ Steinberger H. Health, Safety and Environmental Risks from the Operation of CdTe and CIS Thin Film Modules, Progress in Photovoltaics: Research and Applications, 6, 99-103 (2003)

⁻ Fthenakis VM. Life cycle impact analysis of cadmium in CdTe PV production, Renewable and Sustainable Energy Reviews 2004; 8: 303–334.

⁻ Fthenakis VM., Bulawka AO., Environmental Impact of Photovoltaics, Encyclopedia of Energy, Volume 5, 61-69 (2004)

⁻ Fthenakis VM., Fuhrmann M., Heiser J., Lanzirotti A., Fitts J. and Wang W., Emissions and Encapsulation in CdTe PV Modules During Fires, Progress in Photovoltaics: Research and Applications, 2005 (in press)

need. The need for recycling is not limited to CdTe and c-Si PV. Recycling would be needed for all types of PV modules, when GW of photovoltaics are installed.

A round table discussion followed Prof. Fthenakis' presentation. This discussion focused on two topics:

- 1) Possible emissions from CdTe modules during fires, and
- 2) Possible leaching of Cd or Te from the modules in the case of landfill deposition.

In the case of accidental fires and emissions, one of the reviewers – Prof. Werner – questioned the validity of the used test methods but not the results of the tests. He claimed that "in real fires" the behaviour would be different and stated:

"The study investigates parts of CdTe modules in a furnace. In this case there is a homogeneous temperature distribution over the whole module. In addition the modules lie horizontally in the furnace. This experiment does not simulate the situation for a CdTe module in fire. In case of fire, there will be an inhomogenous and abrupt temperature change across the surface of the modules. The modules will crack. In addition, due to softening of the EVA, the modules will delaminate. In this case, the CdS, ZnO and CdTe will directly face the fire. The material will evaporate and will be released to the air. To me, the experiment of the authors is appropriately designed to make statements on the behaviour of a CdTe module in fire."

However, as noted by other reviewers, the tests were performed according to the Underwriters Laboratory (UL) Standard 1256 for Fire Test of Roof Deck Constructions² and the American Society for Testing and Materials (ASTM) Standard E119-98 for Fire testing of Building Construction and Materials³. When Prof. Werner was asked how a test should be designed, so that he would accept the results he stated that it was not up to him to specify the test procedure.

Prof. Fthenakis emphasized that there is absolutely no evidence that glass modules exposed to flames will break; in the contrary, it was proven by repeated experiments and synchrotron x-ray fluorescence analyses that the two sheets of glass will melt and fuse together, encapsulating cadmium in their matrix. He also noted that the tests were conducted by a team of experts at BNL and the University of Chicago (UC), that they were undertaken extensive peer-reviews, and were published in two peer review journals. Prof. Werner showed some pictures of cracked modules but their identification and condition was doubted by other reviewers. Prof. Fthenakis also commented that in extreme conditions, some modules could fall and break but the probability of such extreme conditions is much lower than the probability used to quantify the small emissions reported in the BNL/UC studies. These emissions were estimated based on the total probability of wood-frame house fires in the U.S. (i.e., 1 over 10,000 houses per year).

ASTM E119-98, Fire Tests of Building Construction and Materials (UBC Standard No. 71), April 2001, American Society for Testing and Materials, West Conshohocken, PA.

UL1256 Standard: Fire test of Roof Deck Constructions, October 2002, Underwriters Laboratories Inc., Northbrook, IL.

Other reviewers pointed out that the fire risk represents a limited risk and should not be overestimated. Dr. Gabler said that the tests were appropriately designed and that best efforts were put into these. He graded Fthenakis et al. studies as "outstanding" in his written review comments.

Prof. Johansson, in his written reviews also rated the BNL/UC studies as "outstanding", "well designed and clearly reported" and commented that "This study describes all stages in the life cycle of CdTe PV and their material flows and emissions. The study is thorough and conclusions well supported and balanced".

Prof. Lux-Steiner observed that cadmium is not really a problem when it is encapsulated and that glass has a high concentration of lead in it but it doesn't present an environmental hazard since its is encapsulated. She noted the need for developing toxicological data on CdTe. Prof. Fthenakis concurred and mentioned that the US National Toxicology Program (NTP) has nominated CdTe for toxicological studies and such may start soon. He noted that the current assessments are based on the "worst-condition" assumption that CdTe is as toxic as Cd and CdCl₂. However, he noted, CdTe is insoluble and as such it is likely that it is less hazardous than these compounds.

Subsequently the round table discussion focused on the leaching tests described by. H. Steinberger¹ of the Fraunhofer Institute of Solid State Technology. These were designed to simulate leaching of metals from broken (in small pieces) modules disposed in landfills and exposed to rain. These test were conducted according to the U.S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP), the German DEV S4 (Deutsches Einheitsverfahren) and a test procedure which is similar to the TCLP, but performed under outdoor conditions.

Prof. Werner again questioned the validity of the used test methods but not the results of the tests. He claimed that the case of a module, where large parts of the cover glass is missing is not taken into account. The response by Prof. Fthenakis that the crushing of a module in < 1-cm² pieces represent "worst conditions" and a larger than expected exposure, was not accepted by Prof. Werner. When asked how a test should be designed so that he would accept the results, he stated again that it was not up to him to design the test procedure, but at least a module without cover glass should be exposed to natural conditions and the possible leakage measured. Prof. Fthenakis rejected this suggestion as non-representative of any real conditions, because all commercial CdTe modules have cover glass. He also noted that the industry (i.e., First Solar) is committed to recycling of spent modules, so only incidentally modules could end up in landfills.

The questions of the other reviewers focused more on actual test accuracies and detection limits. The results were considered to meet high scientific standards and accuracy.

Amy Meader, Director of Environmental Affairs, FS outlined FS's industrial hygiene and recycling efforts. Her presentation revealed that no increase of cadmium levels for any of its employees could be observed. The validity of the industrial hygiene program and it results were verified by the Medical College of Ohio. Manufacturing waste is treated

inside the plant and filtered out of the air and water before released to the air or municipal water treatment plant.

The potential EH&S hazards in First Solar/s manufacturing processes were considered as assessed correctly and the results and conclusions were not questioned.

Dr. Hünnekes from the Projektträger in Jülich gave an overview about the funding of research for PV and CdTe. He pointed out, that no discrimination according to technologies is done, and that about € 11.25 million have been spent for CdTe research since the 1980s.

Mr. Will from the Unternehmensvereinigung Solarwirtschaft reported that the member companies do not experience any prejudice from customers concerning the CdTe solar technologies, as long as the common quality criteria concerning performance, safety and price are met. He called the discussion about the possible danger potentials of the CdTe solar technology "somewhat academic" and "not reflecting the reality".

In the afternoon of the same day, the discussion focused on "Recycling of CdTe modules". This started with a presentation by Prof. Fthenakis, who gave an overview of the technical options and some cost estimates. Then Mrs. Meader, outlined First Solar's recycling activities. At the current stage, modules broken during the production process or off-spec modules are treated in-house and then sent to copper smelters which use the glass as flux and the metals as raw materials in their processes. In the future, it is planned to use both PV manufacturing scrap and end-of-life modules to directly recover Cd and Te for re-use as raw material in solar cells. The development of this process is ongoing and is estimated that it will be available in a few years.

In addition to R&D and actual recycling activities, First Solar has set up an insuranceplan to warrantee funds for collection and recycling of end-of-life modules.

The discussion about recycling focused on the issue what percentage of modules could be claimed back and what would happen to the few percent of modules, which might end in landfills or small smelters. This lead to the same questions as in the first discussion session, that is:

- 1) What are the possibilities for leaching of Cd or Te from the modules in the case of landfill deposition? If there is leaching, would the leached amounts endanger the environment or drinking water?
- 2) In the case that CdTe PV modules end in municipal waste incinerators (MSW), would potential emissions present risks in addition to those already posed by MSWs?

The current studies on leaching state that landfill deposition of CdTe modules do not represent a risk for EH&S.

In the case of MSWs, the question is related to the total amount of modules processed and the pollution controls in place.

The vision of First Solar for the future are drastic reductions on cost and price. The way to reach CdTe solar module prices of 1 \$/Wp by 2010 are threefold:

- Increase of module efficiency from currently 9% to 12%.
- Reduction of material use
- Economy of scale (expansion plans:
 25 MW in 2005, 50 MW in 2006 and 100 MW by 2007)

In conclusion, the reviewers did not identify any results of the presented studies as inaccurate or non-scientific. However, the following recommendations were made:

- Additional leaching tests should be considered.
- According to one reviewer, new fire tests with different (unspecified) protocols should be done. However, the other three reviewers did not concur with this recommendation.
- The toxicity of CdTe is still unknown. Therefore, risk estimates are always based on the toxicity of metallic Cd itself, which is actually not present in the case of CdTe (semiconductor).
- For the evaluation of PV technologies and the CdTe technology, the "Total Life Cycle Analysis" should be used in order to evaluate the potentials and risks in a balanced way.
- Everybody agreed that the "Cadmium" discussion is a very emotional one, not always based on facts. Therefore, the transparency of First Solar was welcomed and it was stressed how important the publication of the real facts is.
- In light of the current discussion, the BMU is considering to commission a study about the cost reduction potentials and related environmental effects of different PV technologies.

4. SUMMARY of written PEER-REVIEW RESULTS:

The results of the review reports reflect the discussion during the meeting on 4 August 2005.

Title of Study #1: ""Life cycle impact analysis of cadmium in CdTe PV production", *Sustainable and Renewable Energy Reviews*, 8, 303-334, 2004

Abstract:

This paper describes the material flows and emissions in all the life stages of CdTe PV modules, from extracting refining and purifying raw materials through the production, use, and disposal or recycling of the modules. The prime focus is on cadmium flows and cadmium emissions into the environment. This assessment also compares the cadmium environmental inventories in CdTe PV modules with those of Ni–Cd batteries and of coal fuel in power plants. Previous studies are reviewed and their findings assessed in light of new data.

Conclusions (excerpt)

"In summary, the environmental risks from CdTe PV are minimal. The estimated atmospheric emissions of 0.02 g of Cd per GWh of electricity produced during all the phases of the modules' life, are extremely low. Large-scale use of CdTe PV modules does not present any risks to health and the environment, and recycling the modules at the end of their useful life completely resolves any environmental concerns. During their operation, these modules do not produce any pollutants, and, furthermore, by displacing fossil fuels, they offer great environmental benefits. CdTe in PV appears to be more environmentally friendly than all other current uses of Cd, including Ni–Cd batteries."

Reviewers Comments:

Two of the reviewers evaluated this study as "outstanding", one as "good", and one as "fair" to "poor".

The comments from the reviewer who gave the "poor" and "fair" ratings are as follows:

"The risks of a Cd based PV is higher than for any other PV technology. CdTe poses an additional risk. Why should it be taken? From both studies, I cannot conclude that there is no release of Cd from the modules. In addition, the statements that CdTe technology could make any significant contribution to preventing Cd waste is not justified."

The comments from the other three reviewers who commended the study were:

"Outstanding", "Study contains comprehensive additional information on environmental aspects and emissions of cadmium before the CdTe/PV module production phase."

"Outstanding"

"The study is the first one to give an extensive overview of the life-cycle aspects of CdTe solar modules. The given conclusions are comprehensible. The study uses accepted procedures and summarizes the results of capacious work going into the depth of the topic."

"Good", "the global ecological acceptance of the CdTe technology has to be checked more precisely. Diversity of inhabitants from industrialized and non-industrialized countries as national regulations has to be considered"; "Reliable data on life time of modules under various operating conditions should be gained"

"Offering the obligation to take back modules is excellent"

"This study describes all stages in the life cycle of CdTe PV and their material flows and emissions. The study is thorough and conclusions well supported and balanced"

"The evaluation is always limited to data availability. Data on toxicity of CdTe would be of interest"

"All the individual studies on the environmental profile of CdTe PV are related to elemental Cd. Quantitative data on the toxicity of the compound CdTe are missing. This would be of special interest, as the inertness of this ionic compound seems to be high under standard conditions (phase diagram)."

The organizer's conclusive comments are:

The tests were performed according to the UL Standard 1256 for Fire Test of Roof Deck Constructions⁴ and the American Society for testing and Materials (ASTM) Standard E119-98 for Fire testing of Building Construction and Materials⁵. Standard E119-98 is also adopted by the Uniform Building Code as UBC Standard 7-1. No other test standards are published and available for use. The performed study is in agreement with common test procedures and qualifies as scientifically sound. Therefore, the criticism about inappropriate experimental design is unfounded.

The organizer finds the conclusions of this study supported by the reviewers.

Title of Study #2: "Health, Safety and Environmental Risks from the Operation of CdTe and CIS modules", *Progress in photovoltaics research and applications*, 6, 99-103, 1998.

Abstract

"This paper identifies the materials embedded in one type of CIS (copper indium diselenide) and four different types of CdTe (cadmium telluride) thin-film modules. It refers to the results of our outdoor leaching experiments on photovoltaic (PV) samples broken into small fragments. Estimations for module accidents on the roof or in the garden of a residential house, e.g. leaching of hazardous materials into water or soil, are given. The outcomes of our estimations show some module materials

UL1256 Standard: Fire test of Roof Deck Constructions, October 2002, Underwriters Laboratories Inc., Northbrook, IL.

⁵ ASTM E119-98, Fire Tests of Building Construction and Materials (UBC Standard No. 71), April 2001, American Society for Testing and Materials, West Conshohocken, PA.

released into water or soil during leaching accidents. In a worst-case scenario for CdTe modules the leached cadmium concentration in the collected water is estimated to be no higher than the German drinking water limit concentration. For the CIS module scenario the estimated leached element concentrations are about one to two orders of magnitude below the German drinking water limit concentration. For broken CIS and CdTe modules on the ground no critical increase of the natural element concentration is observed after leaching into the soil for 1 year."

Conclusions

"During normal operation a release of critical elements into the environment and, finally, to humans can only occur as a consequence of accidents. Yet all investigated release scenarios, e.g. leaching of broken modules into garden water or into soil of a residential house, did not point towards an acute danger to human beings or the environment. For a long-term bulk production, however, we have to expect a huge number of defect modules as a consequence of the end of the module lifetime. This corresponds to the amount of modules produced at the beginning of their lifetime. Thus module disposing in landfills is limited for two reasons: the loss of high-quality materials like metals or glass, the increasing leaching concentration of critical materials in the drain water of the landfill. This situation occurs when the volume concentration of dumped modules becomes higher than in the scenario of crushed modules on the ground. As a consequence, PV module recycling seems to be a major issue for future manufacturing and developing efforts."

Reviewers Comments:

Three of the reviewers rayed the study as "outstanding" or "good". The fourth reviewer gave it a "fair" rating.

The comments from the "fair" rating review:

"The studies do not discuss PV market barriers."

"Barriers for PV are not addressed in this study"

"This study cuts the modules into small pieces. However, the semiconductor material is still protected by Ethylene Vinyl Acetate Copolymers (EVA) and glass from both sides. It is unlikely that this situation simulates what happens in case of a broken module. It is much more likely, that the CdTe is not protected by two glass plates. The experiments are not convincing to me."

"This study does not answer the question how much Cd is released to the environment in case of water that penetrates into a module. In fact, this case seems to appear much more often than previously thought. The special measures of First Solar - the information sheets which they send to their customers - indicates that there might be a serious problem with water penetration into their modules."

The positive comments from the other three reviewers:

"Leaching of Cd is a possible concern and the study provides useful and interesting information."

"The study uses accepted standard procedures (e.g. DESV leaching test) and therefore the results are very useful, although it might be argued that in some cases the reality is not perfectly represented."

"More extensive work would be of interest, expanding to the systems aspects of very large installations on a life-cycle basis. The importance of end-of-life procedures is indicated"

'The issues studied are well documented and reported"

The general conclusion on this study is that it is scientifically sound but it can be improved.

Title of Study #3: "Emissions and Encapsulation of CdTe Modules during Fires". *Progress in photovoltaics research and applications,* in press

Abstract

"Fires in residential and commercial properties are not uncommon. If such fires involve the roof, photovoltaic arrays mounted on the roof will be exposed to the flames. The amount of cadmium that can be released in fires involving CdTe PV and the magnitude of associated health risks has been debated. The current study aims in delineating this issue. Previous thermogravimetric studies of CdTe, involved pure CdTe and single-glass PV modules. The current study is based on glass-glass CdTe PV modules which are the only ones in the market. Pieces of commercial CdTe photovoltaic (PV) modules, sizes 25×3 cm, were heated to temperatures up to 1100°C to simulate exposure to residential and commercial building fires. The temperature rate and duration in these experiments were defined according to standard protocols. Four different types of analysis were performed to investigate emissions and redistribution of elements in the matrix of heated CdTe PV modules: (1) measurements of sample weight loss as a function of temperature; (2) analyses of Cd and Te in the gaseous emissions; (3) Cd distribution in the heated glass using synchrotron X-ray fluorescence microprobe analysis; and (4) chemical analysis for Cd and Te in the acid-digested glass. These experiments showed that almost all (i.e., 99.5%) of the cadmium content of CdTe PV modules was encapsulated in the molten glass matrix; a small amount of Cd escaped from the perimeter of the samples before the two sheets of glass melted together. Adjusting for this loss in full-size modules, results in 99.96% retention of Cd. Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the US (e.g., 10⁻⁴), results in emissions

of 0.06 mg/GWh; the probability of sustained fires and subsequent emissions in adequately designed and maintained utility systems appears to be zero.

Conclusions

Heating experiments to simulate residential fires showed that most (i.e., 99.5%) of the cadmium content of CdTe PV modules was encapsulated in the molten glass matrix. This was confirmed with emissions chemical analysis, synchrotron-based X-ray fluorescence microprobe analysis and chemical analysis of the molten glass. Only $0.5 \pm 0.1\%$ of the Cd content of each sample was emitted during our tests that cover the wide flame temperature zone of 760–1100°C. The pathway for this loss was likely though the perimeter of the sample before the two sheets of glass fused together. In actual size PV modules, the ratio of perimeter to area is 13.5 times smaller than our sample; thus the actual Cd loss during fires will be extremely small (<0.04% of the Cd content). Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the US (e.g., 10⁻⁴), results in emissions of 0.06 mg/GWh (assuming 7 g Cd/m², 10% electric conversion efficiency and $1800 \text{ kWh/m}^2/\text{yr}$). As discussed in the introduction, the probability of sustained fires in utility systems must be much smaller, due to lack of combustible materials, and, therefore, emissions of cadmium during fires in central PV systems are considered to be essentially zero. The total cadmium emissions during the whole life-cycle of CdTe PV modules (ore mining, metal melting, purification, PV manufacturing) has been estimated to be about 20 mg/GWh. These results apply to glass-to-glass CdTe PV modules which are the only ones in the market. Similarly to Cd, only a tiny percentage of Te was released in the typical residential fire temperature range 760–900°C, but a significant fraction was released at higher temperatures (1000–1100°C). "

Two of the reviewers rated all the elements of this study (e.g., clarity, quality, relevance) as "outstanding", a third reviewer rated the same as "good" and the same fourth reviewer gave a "poor" rating" again.

The comments from the reviewer who gave the "poor" ratings are as follows:

"The study investigates parts of CdTe modules in a furnace. In this case there is a homogeneous temperature distribution over the whole module. In addition the modules lie horizontally in the furnace. This experiment does not simulate the situation for a CdTe module in fire. In case of fire, there will be an inhomogeneous and abrupt temperature change across the surface of the modules. The modules will crack. In addition, due to softening of the EVA, the modules will delaminate. In this case, the CdS, ZnO and CdTe will directly face the fire. The material will evaporate and will be released to the air. To me, the experiment of the authors is appropriately [sic] designed to make statements on the behaviour of a CdTe module in fire."

"Yes, the risks with CdTe PV are much higher than with other PV technologies"

The three reviewers who gave high ratings to this study commented:

"the study is well designed and clearly reported"

"Study deals with emissions in case of fire and reports valuable experimental information."

"The authors apply standard protocols and therefore give a realistic picture of possible hazards. The investigation is exhaustive and the description is very detailled so that the procedures can be reproduced."

The organizer finds the conclusions of this study supported by the reviewers.

In summary, one reviewer was negative for all the studies, whereas the other three reviewers were positive of the same. The former did not identify any results of the presented studies as inaccurate or non-scientific, but he did not accept the overall premise of the studies. The average rating from all four reviewers was 3.03 (i.e., "good") which means that "the approach is generally well thought and effective", "most aspects of the study will contribute to significant progress in overcoming barriers", and "the research is effective, but could be improved"

The following recommendations and statements can be summarized:

- CdTe does not represent an environmental risk during normal operation and foreseeable accidents.
- During the manufacturing process, EH&S potentials have to be taken into account and the plant and manufacturing process designed accordingly. This is a normal industrial procedure where manufacturing waste is treated inside the plant and filtered out of the air and water before release to the air or municipal water treatment plant. If operated correctly the manufacturing process does not pose an environmental risk.
- Additional test procedures for leaching should be considered (the module manufacturing technology used for the reviewed tests is not longer used).
- The fire-simulating tests were conducted according to standard testing protocols and, therefore, are representative of likely conditions during a fire. Emissions during these tests were correctly multiplied by the probability of fire risks in residential wood-frame houses. In extreme conditions some modules could fall and break, whereas other modules can be unaffected by the fire. In overall, average conditions and standard tests realistically describe potential emissions during a fire.
- The toxicity of CdTe is still unknown. Therefore, risk estimates are always based on the toxicity of metallic Cd itself, which is actually not present in the case of CdTe (semiconductor). From the phase diagram it is clear that the inertness of the ionic compound CdTe has to be high, and therefore current risk estimates may be overestimated.
- For the evaluation of PV technologies including the CdTe technology, "Life Cycle Analysis" should be used in order to evaluate the potential environmental

[&]quot;Outstanding study"

impacts in a balanced way. All industrial processes have environmental impacts mainly due to the use of energy in product production. CdTe has the lowest energy pay back times and, therefore, lowest total emissions of all commercial PV technologies.

- CdTe solar modules only recently entered the market. There is no specific standard to test the lifetime of CdTe modules, but the IEC 61646 test represents the currently best available test standard and should guarantee 20 years lifetime of the modules. All modules on the market are IEC 61646 tested and some are also UL 1703 tested.
- First Solar employs satisfactory industrial hygiene and environmental programs. The transparency of First Solar and the announced offer to take back the modules and recycle them is excellent.

5. CONCLUSION

The conclusion of this review is that CdTe modules do not represent an environmental risk under normal operating conditions. The potential of environmental impacts in the case of fire and landfill deposition is extremely low according to standard test protocols and standards. Nevertheless, a recycling option should be favoured to uphold an environmental friendly image of the CdTe PV technology. The announced insurance secured pre-funded take back and recycling programme of First Solar, LLC is on line with the Integrated Product Policy approach of the European Commission laid out in the Communication from the Commission to the Council and the European Parliament [COM(2003)302 final].

The "Cadmium" discussion concerning Photovoltaics is a very emotional one, not always based on facts. Since the toxicity of CdTe is still unknown and risk estimates are based on the toxicity of metallic Cd and soluble Cd compounds. It is possible, therefore, that the risks of CdTe exposure are overestimated, and it would be valuable to launch an international study on the toxicity of CdTe itself.

All industrial processes have some environmental impacts that have to be taken into account. To create a levelled playing field of energy technologies "Life Cycle Analysis" (LCA) should be used in order to evaluate the potentials and risks in a balanced way. Recent European studies (e.g., PVAccept) showed that CdTe PV has the lowest energy payback and the lowest emissions of CO₂, SO₂, NOX and particulates, among all commercial PV technologies (i.e., mono and polycrystalline silicon, copper indium selenide and cadmium telluride).

Last but not least, it has to be mentioned, that the CdTe solar cell technology is only one of many solar technologies. The success of solar technologies in the market place will be determined by the capability of the manufacturer to offer a cost-effective product to the customer. As more solar systems are produced and installed the cost of such installations is reduced. Therefore, every solar technology that makes inroads in the energy market helps to increase market share for all photovoltaic players.

Annex I Presentations of the Peer Review Meeting Berlin, 4 August 2005

Agenda

CdTe Studies Review Meeting Energieforum Berlin Stralauer Platz 34; 10243 Berlin

4 August 2005

Starting 10:00 A 10:00 - 10:15: C 10:15 - 10:30: T	Opening Remarks (BMU, JRC)
10:30 – 11:15:	EHS Issues in PV technologies and how does CdTe fit in (EHS Issues in PV technologies
11:15 – 11:30:	coffee break
11:30 – 12:30:	Round Table discussion: Topic: "Emissions during manufacturing and operation" (chairman: V. Fthenakis)
12:45 – 14:00:	Lunch
14:00 - 14:20: 14:20 - 14:40: 14:40 - 15:00:	Overview on research activities (Projektträger Jülich) Overview of Industry Association (Jürgen Will, UVS) Overview of First Solar
15:00 – 15:15:	Coffee
15:15 – 16:15:	Round Table discussion Topic: "Recycling" (chairman: V. Fthenakis)
16:15 – 16:30:	The way forward by First Solar
16:30 – 17:00:	Résumé and future actions (JRC, BMU)



PV EHS Issues and CdTe PV

Vasilis Fthenakis

Senior Chemical Engineer
Head, National PV EHS Research Center
Brookhaven National Laboratory

www.pv.bnl.gov

Professor of Earth & Environmental Engineering
Columbia University

Presentation at the JRC-EU CdTe PV Review Meeting
Berlin, 4 August 2005
BROOKHAVEN



■ It must be assured that large-scale implementation of PV technologies does not endanger the public or occupational health and safety, and that costs of environmental control are not so excessive as to limit their potential commercial viability





Identify potential environmental, health and safety (EHS) hazards for new photovoltaic materials, processes and applications <u>before</u> their large-scale commercialization, and define hazard management options.

- Transfer research results to the industry and assist them in overcoming EHS barriers.
- Provide direct support to DOE Headquarters, NREL and SNL to ensure that their facilities and the facilities of their contractors are operated in a safe and environmentally responsible manner.



3

OVERVIEW OF HAZARDS BY PV MODULE TYPE

Module Type	Types of Potential Hazards
c-Si	Acid burns, GHGs in dry etching SiH ₄ fires/explosions, Pb solder / module disposal
a-Si	SiH ₄ fires/explosions
CdTe	Cd toxicity, carcinogenicity, module disposal
CIS, CGS	H ₂ Se and Se toxicity, module disposal
GaAs	AsH ₃ toxicity, As carcinogenicity, H ₂ flammability, module disposal

Fthenakis and Bulawka, Photovoltaics, Environmental Impact, Encyclopedia of Energy, 5, 61-69, 2004



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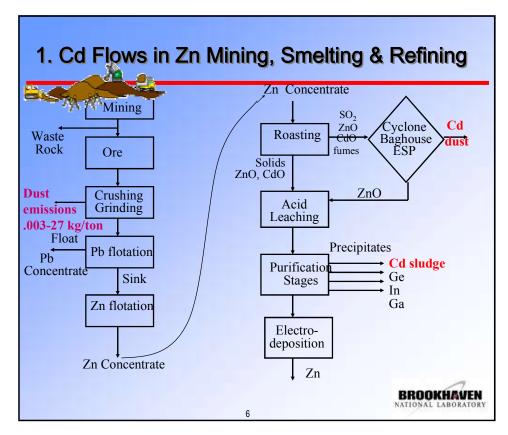
CdTe PV Life-Cycle Analysis (focus on Cd flows –air emissions)

- 1. Mining/Smelting/Refining
- Purification of Cd & Production of CdTe
- 3. Manufacture of CdTe PV modules
- Utilization of CdTe PV modules
- 5. End-of-life of CdTe PV modules

Fthenakis V. Life cycle impact analysis of Cd in CdTe PV, Renewable and Sustainable Energy Reviews, 8, 303-334, 2004



5



Cd Emissions from Mining/Smelting: Facts

- 1. Cd is a **byproduct of Zn**, Cu and Pb production. The main resource of Cd is CdS in sphalerite (ZnS) ores. The Zn/Cd ratio is 200/1 to 350/1.
- 2. Production of Cd uses <u>emissions and waste</u> of Zn production
- Cd output is dependent on Zn production, not on Cd demand
- 4. Before Cd production started in the US, ~85% of Cd from Zn concentrates was lost to the environment
- 5. Zinc mines in the US also produce:

100 % of Cd, Ge, In, Th

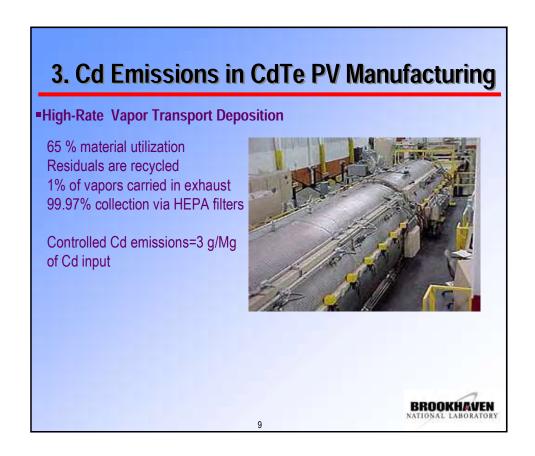
10 % of Ga

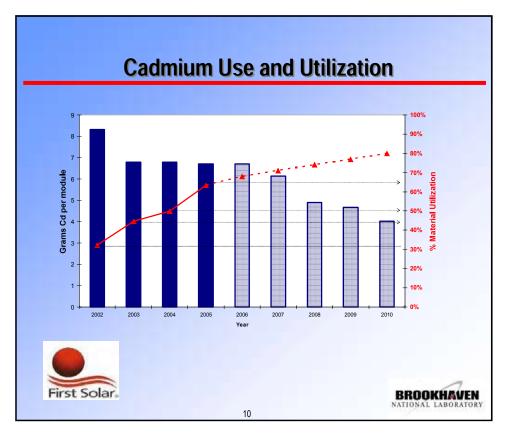
3 % of Au,

4 % of Ag

Liewellyn T. Cadmium , Bureau of Mines Information Circular 1994, US Department of the Interior BROOKHAVEN
Plachy J., U.S. Geological Survey Minerals Yearbook—2001, Cadmium—Chapter 17.

2. Cd Flows from Cd Concentrates to CdTe 1-2 % Cd loss Cd Dust & (sludge) Cd metallurgical **Sludge from** grade Zn & Pb Refining -Electrolytic Refinery (& Cd wastes from Iron Cd & Steel Industries) 99.9% Cd Production Melting & Milling Powder Atomization 99.999% 2 % Cd emissions Recycling (particulates) Recycling **HEPA Filters CdTe** Powder 0.03% gaseous emissions 6 g /Mg Cd Fthenakis V. Life cycle impact analysis of Cd in CdTe PV, BROOKHAVEN Renewable and Sustainable Energy Reviews, 8, 303-334, 2004





4. Utilization of CdTe PV Modules

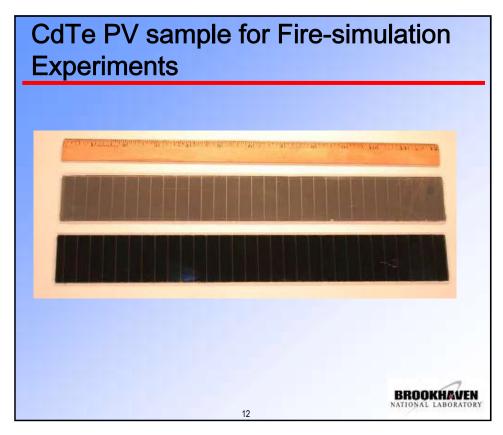
Zero emissions under normal conditions

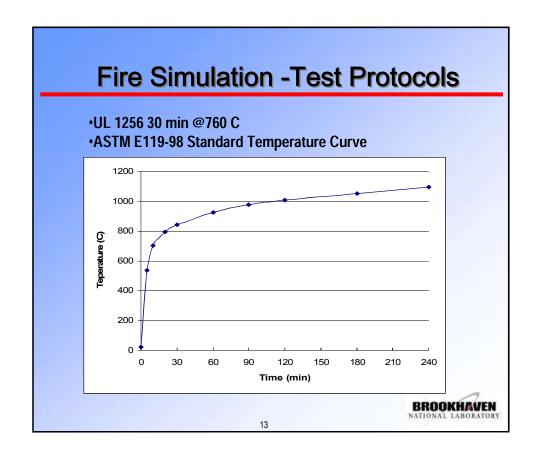
(testing in thermal cycles of -80 C to +80 C)

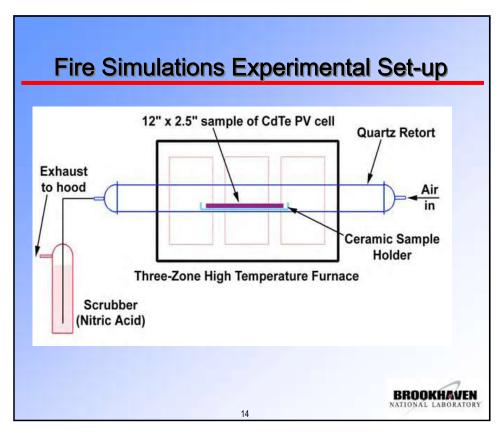
- No leaching during rain from broken or degraded modules (Steinberger, 1997)
- Negligible emissions during fires
 (Fthenakis, Fuhrman, Heiser, Lanzirotti, Fitts and Wang, 2005)



11







Fire-simulation Experiments

- Weight Loss Measurements
- ICP Analysis of Cd & Te Emissions
- X-ray Fluorescence Micro-Spectrometry of Cd in Heated Glass
- ICP Analysis of Cd & Te in Heated Glass



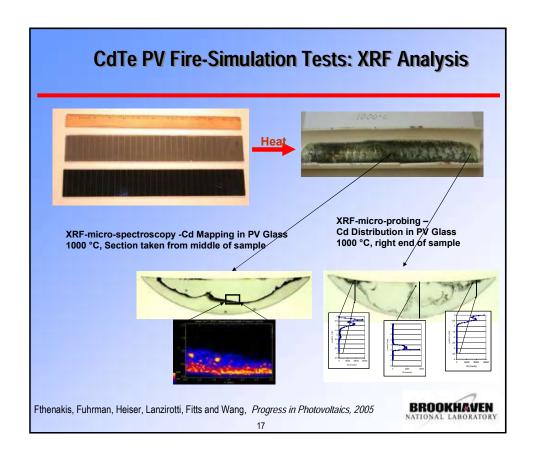
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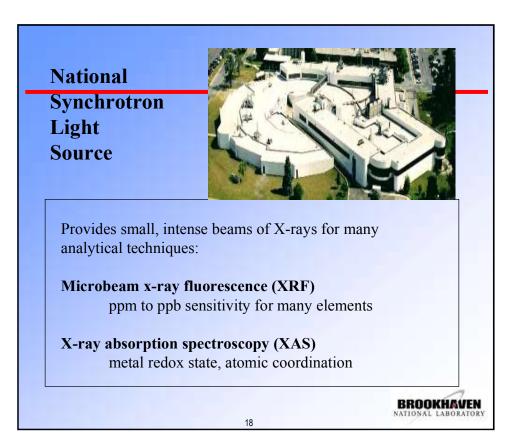
Thermogravimetric & Emissions Analysis

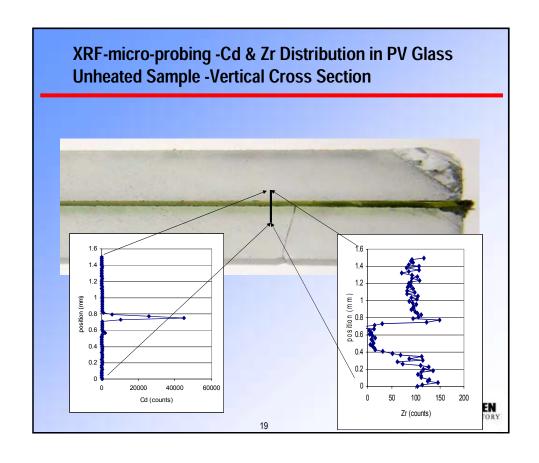
Temp (C)	Weight Loss (% sample)	Cd Loss (% Cd)	Te Loss (% Te)
760	1.9	0.6	0.4
900	2.1	0.4	1.2
1000	1.9	0.5	11.6
1100	2.2	0.4	22.5

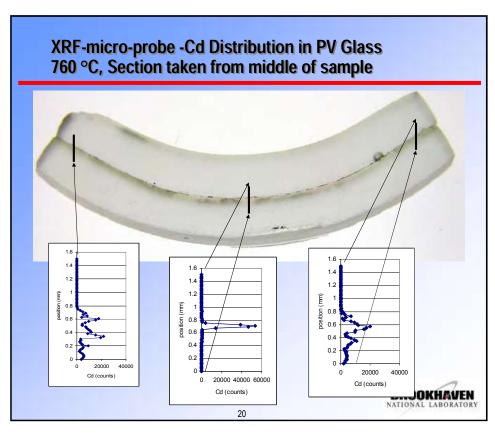


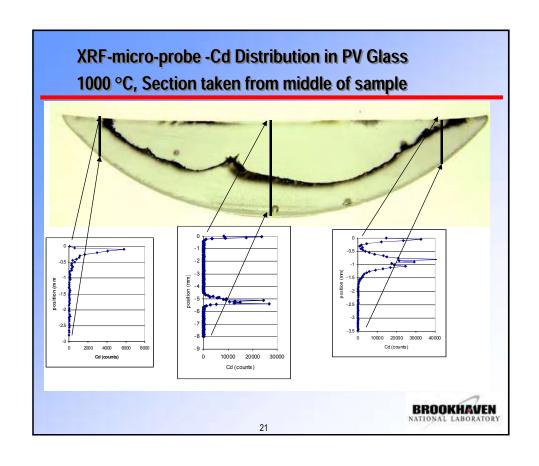
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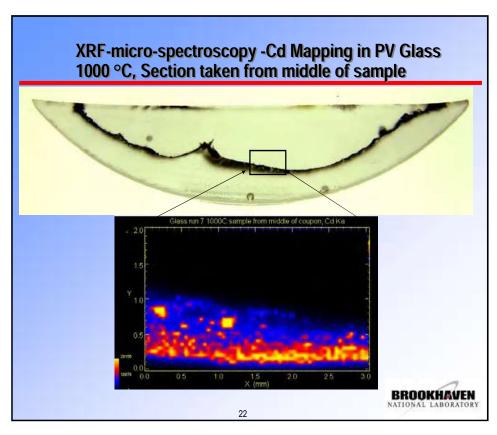


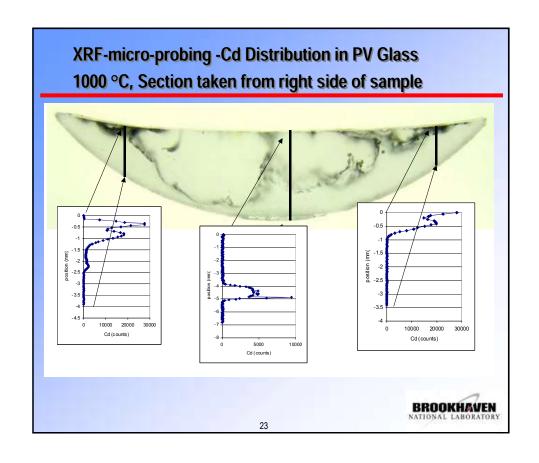


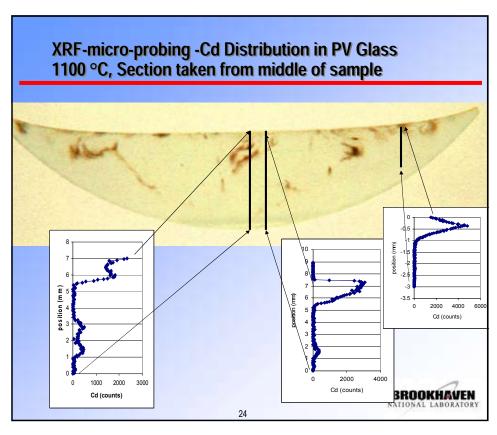












5. End-of-life of CdTe PV modules

- Concerns about leaching from PV modules disposed in municipal landfills
- This issue is not unique to CdTe PV
 - TCLP –US-EPA
 - DEV –S4 Germany
- Concerns about PV modules ending in MW incinerators
- Recycling will resolve these concerns
- Recycling is technically feasible and cost is not excessive



25

Atmospheric Cd emissions from the Life-Cycle of CdTe PV Modules –Reference Case

Process	(g Cd/ton Cd*)	(%)	(mg Cd/GWh)
Mining of Zn ores	2.7	0.58	0.02
2. Zn Smelting/Refining	40	0.58	0.30
3. Cd purification	6	100	7.79
4. CdTe Production	6	100	7.79
5. CdTe PV Manufacturing	3	100	3.90
6. CdTe PV Operation	0.05	100	0.06
7. CdTe PV Recycling	-	-	-
TOTAL EMISSIONS			19.86



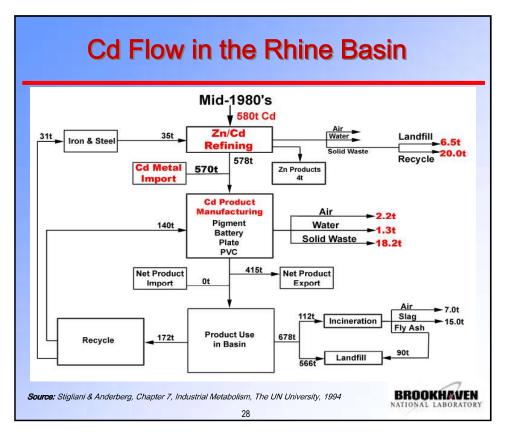
Cd Use in CdTe PV Production

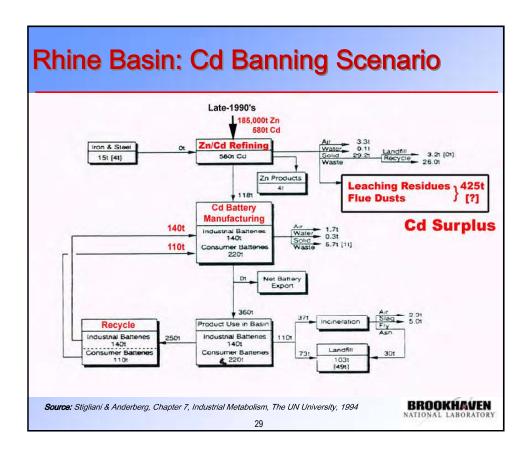
Cd is produced as a byproduct of Zn production and can either be put to beneficial uses or discharged into the environment

- Above statement is supported by:
 - US Bureau of Mines reports
 - Rhine Basin study (the largest application of Systems) Analysis on Industrial Metabolism)

- Liewellyn T. Cadmium, **Bureau of Mines** Information Circular 1994, US Department of the Interior. Plachy J., **U.S. Geological Survey Minerals Yearbook**—2001, Cadmium—Chapter 17. Stigliani W, Anderberg S. Chapter 7. In: Ayres R, Simonis U, editors. **Industrial metabolism**. Tokyo, Japan: The United Nations University Press; 1994.







Cd Use & Disposal in the Rhine Basin: The effect of banning Cd products

"So, the ultimate effect of banning Cd products and recycling 50% of disposed consumer batteries may be to shift the pollution load from the product disposal phase to the Zn/Cd production phase. This ... indicates that if such a ban were to be implemented, special provisions would have to be made for the safe handling of surplus Cd wastes generated at the Zn refineries!

One possible option would be to allow the production and use of Cd-containing products with inherently low availability for leaching. The other option, depositing the Cd-containing wastes in safely contained landfills, has other risks"

Source: Stigliani & Anderberg, Chapter 7, Industrial Metabolism, The United Nations University, 1994

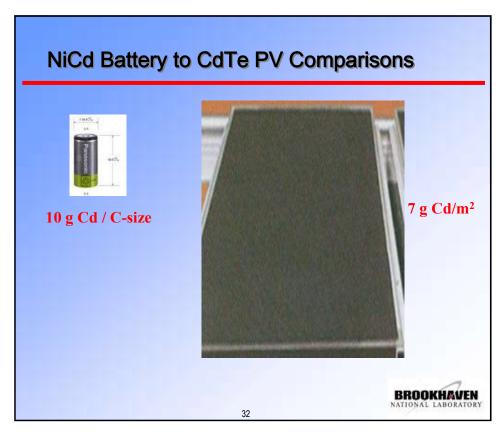


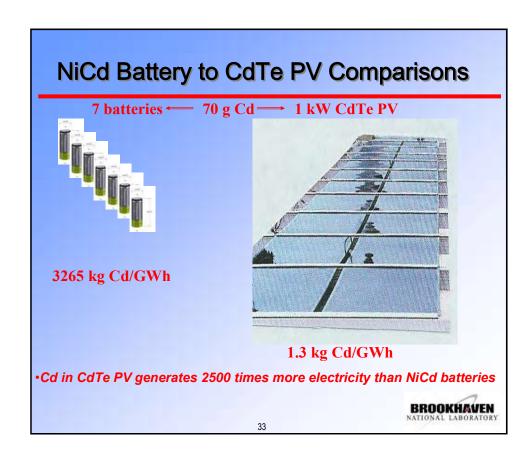
NiCd batteries vs. CdTe PV

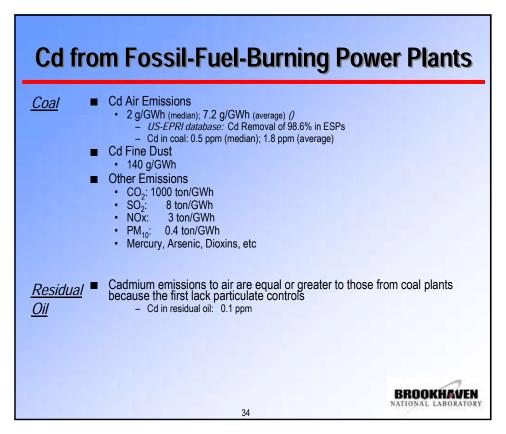
Compound	T _{melting} (°C)	T _{boiling} (°C)	Solubility (g/100 cc)	Toxic/ Carcinogen
Cd	321	765	insoluble	yes
Cd(OH) ₂	300	-	2.6e-04	yes
CdTe	1041	-	insoluble	?

- CdTe is much more stable than Cd and Cd(OH)₂ used in batteries
- In addition, CdTe in PV is encapsulated between glass sheets









Conclusions

- Cd is produced as a byproduct of Zn production and can either be put to beneficial uses or discharged into the environment
- CdTe PV is the safest current use of Cd; it is in a stable form that doesn't leak into the environment during normal use or foreseeable accidents
- CdTe PV uses Cd 2500 times more efficiently than NiCd batteries
- CdTe PV modules are easier to collect for recycling than NiCd batteries
- Air emissions of Cd from the Life Cycle of CdTe PV are 100-360 times lower than Cd emitted into air from coal and oil power plants that PV displaces

www.pv.bnl.gov



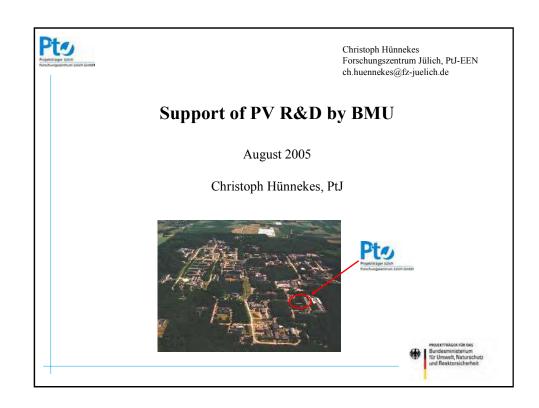
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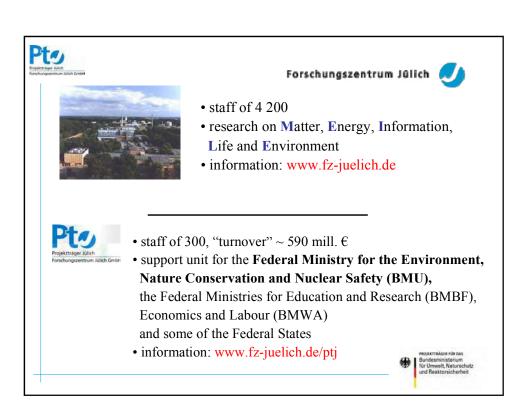
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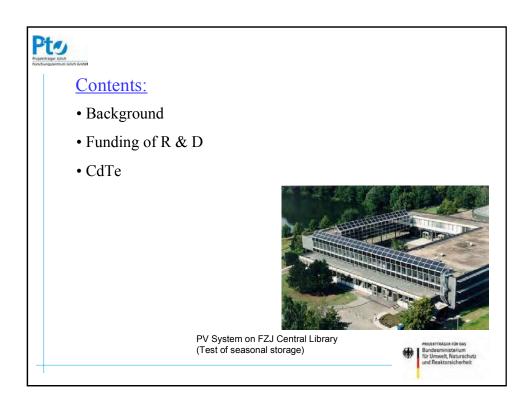
- Every PV technology has some EHS issues, but the industry is proactive in controlling them, and these issues should not restrict the commercial viability of PV.
- The environmental issues related to CdTe PV are by far outweighed by the environmental benefits that PV displacement of fossil would generate.
- The technology should be evaluated on its potential for low-cost electricity production, and total external costs (e.g., energy payback times, life cycle CO₂ emissions).

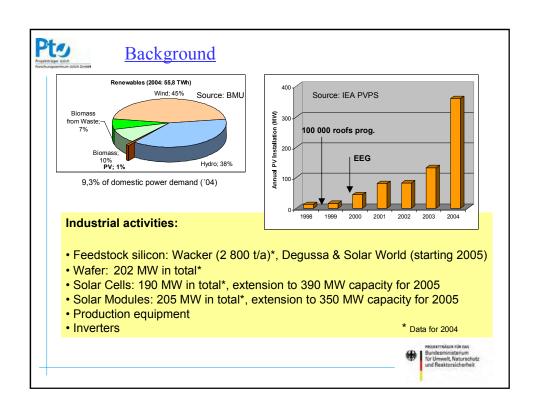
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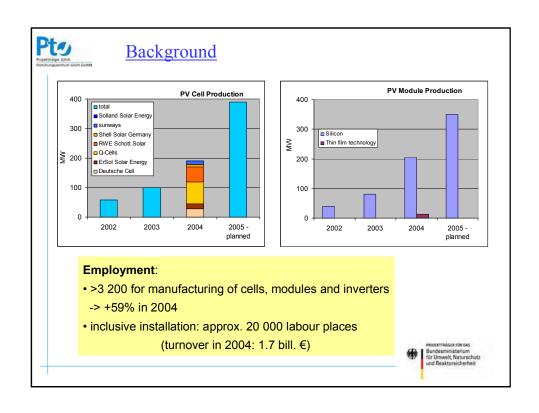


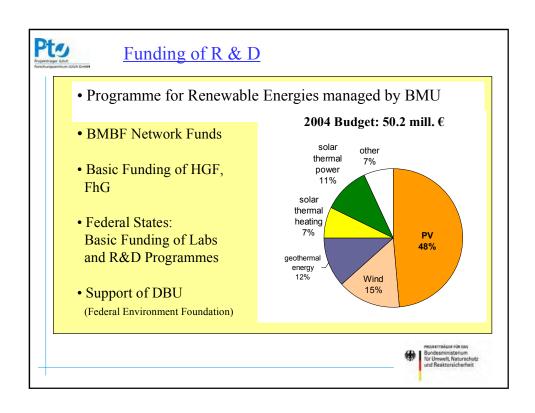


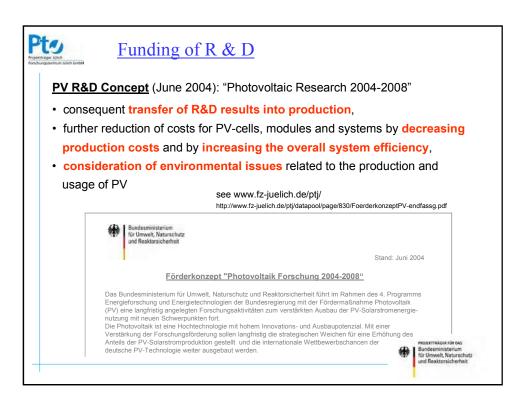


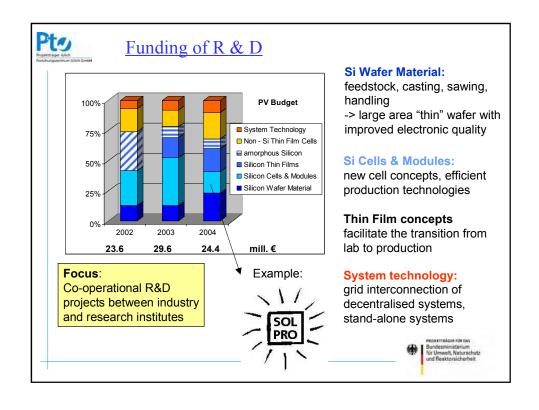


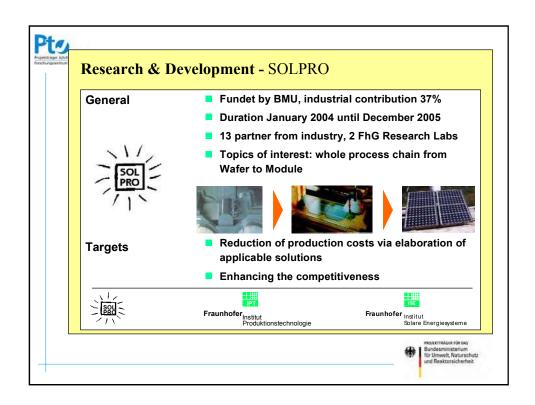


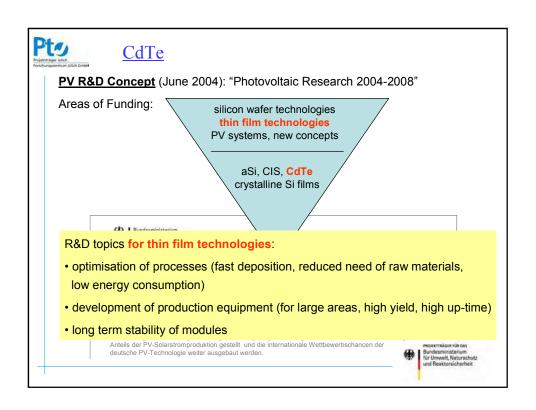














CdTe

Funding since 1998:

- ANTEC Solar (until 2000)
- ISFH (until 2002) Close-spaced Sublimation process (CSS)
- TU Darmstadt basic material research, interface engineering
- Uni Jena basic material research, achieving high η systems using CSS

(11,25 Mio. € since 1980th)



2001



Outlook

Markets:

- · Industry is planning significant extensions of production capacities
- Growth of Markets and Industry will and must be accompanied by R&D

Photo: FhG - ISE

CdTe
"other" non-



R&D:

Key topics of R&D funding for the coming years

- Si wafer technology
 - Efficient usage of Silicon for wafer based PV
 - \bullet new cell concepts (high η cells for thin wafer) and production technologies
- thin film technologies: Silicon based & others
 - production equipment
 - long-term stable modules





CdTe Studies Review Meeting Energieforum Berlin

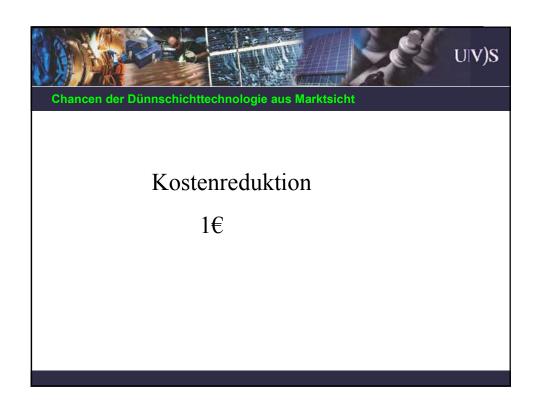
04.08.2005



Jürgen Will

Geschäftsführer Parabel GmbH seit 1995

Vorstand der UVS, Gründungsmitglied

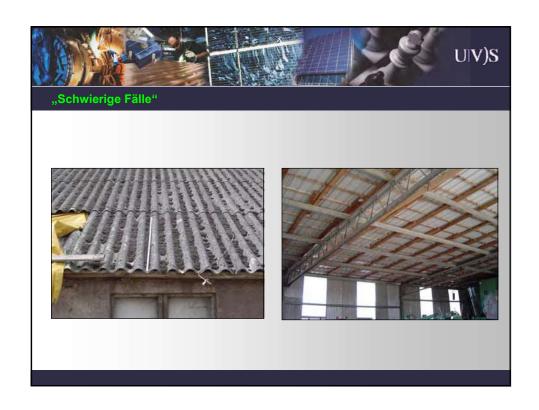














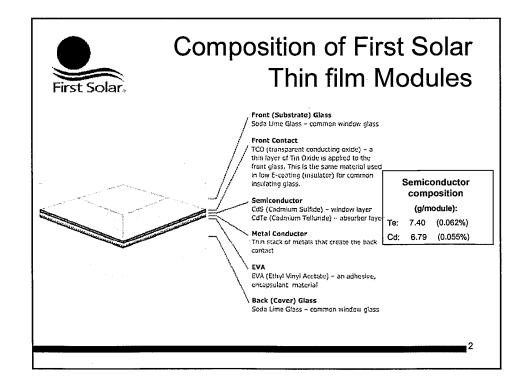
Forderungen an die Dünnschichttechnologie

- Klärung Gefahrenpotential für den Dachbesitzer
 - normaler Betrieb
 - Feuer
- Rücknahme / Recycling
- Stabile Wirkungsgrade
- kurzfristige Verfügbarkeit
- Mengen



First Solar Responsibility

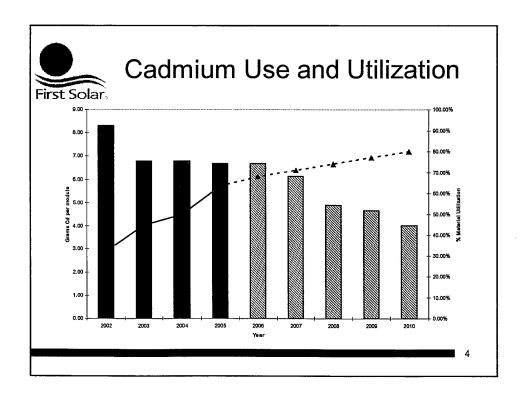
August 4, 2005





The Different Steps of Responsibility

- · Cadmium Use and Utilization
- Industrial Hygiene Program
 - Aspects of the program
 - Track Record
 - Independent verification of results
- · Manufacturing waste
 - Emissions during manufacturing
 - Hazardous Waste
 - Waste Water
- · Recycling
 - Recycling for water treatment solids
 - Current recycling process for manufacturing
 - Alternative recycling process
 - Research in recycling





Industrial Hygiene Program

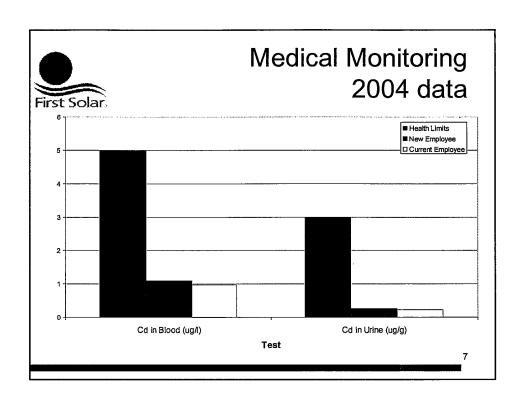
- Aspects of the program
- Track Record
- Independent verification of results

5



Aspects of the IH Program

- Written Cadmium Compliance Plan
- Pre-employment Medical Examinations and Evaluation
 - Blood (Short Term Exposure)
 - Urine (Long Term Exposure)
 - Beta-2-micro globulin (protein analysis for kidney function)
- Medical Testing repeated
 - Production operators and technicians annually
 - Engineers and supervisors 2 to 5 years
 - Office and management workers 3 to 5 years





Independent Verification of Results

"We have monitored First Solar employees for cadmium exposure in both the former and current facilities. This was done as an additional safeguard in addition to the aggressive industrial hygiene program. To date, we have not had any First Solar employees that have had elevated blood cadmium readings from work exposures."

"Based on review of the data, I believe that the non-occupational exposures are a more significant predictor of blood cadmium due to the very low occupational exposures."

Eric Schaub, M.D., Medical College of Ohio, May 2002



Success of IH Cadmium Program

Individual monitoring:

First Solar has never had an occupational increase of cadmium for any of its employees.

Average medical data also shows success:

	Employees who smoke	Employees – non-smokers
Blood (mcg/L)	1.7	0.6
Urine (mcg/g Creatine)	0.51	0.14



Aspects of the IH Program

- Air Sampling (Area & Personal)
 - Production areas sampled initially and every 6 months
 - All employees notified of results
- Proper Training
 - Prior to beginning employment
 - Annually
- **Engineering Controls**
 - HEPA Filtration
 - Downdraft Tables
 - Ventilated Enclosures
- · PPE for employees working in areas over permissible exposure limit
 - No respiratory protection is required for standard operations
 - Respirators are required for some maintenance or clean up procedures



Manufacturing Waste

- · Emissions during manufacturing
- Hazardous Waste
- Waste Water

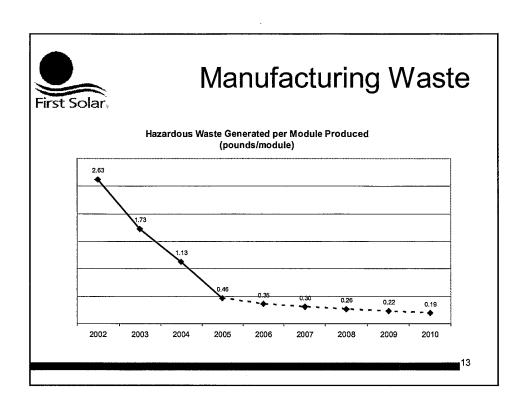
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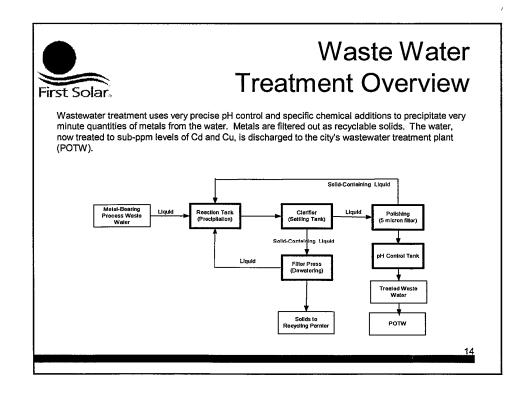


Emissions During Manufacturing

- Process equipment is designed with HEPA filters
 - High Efficiency Particulate Air Filters capture at least 99.97% of particles that are 0.3 microns or larger
- Although Cadmium is considered a Hazardous Air Pollutant by the US EPA, no air permitting is required by First Solar's manufacturing due to the minuscule amounts emitted.

12

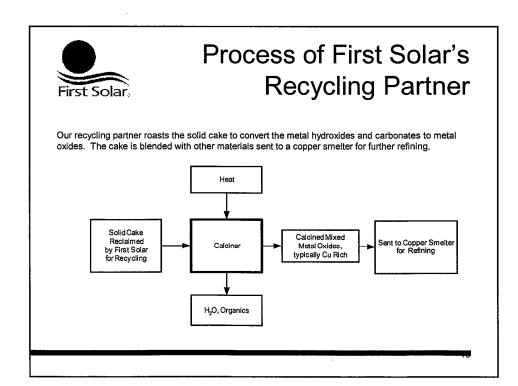


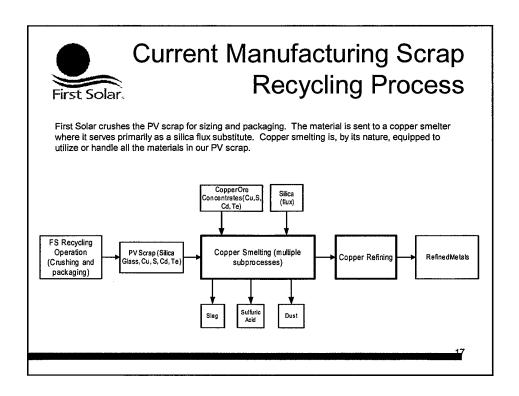




Recycling

- · Recycling for water treatment solids
- Current recycling process for manufacturing
- Alternative recycling process
- · Research in recycling

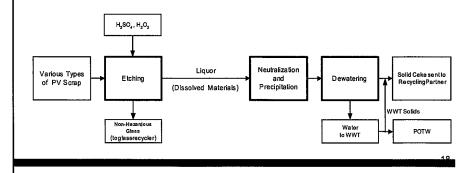






Alternative Manufacturing Scrap Recycling Process

The process starts by etching crushed PV scrap with a strong acid and peroxide solution. The glass, after rinsing, can be sent directly to a glass recycling operation. The etchant solution is pH-adjusted to precipitate the metals. The precipitates are filtered and pressed into a solid cake and sent to recycling partners. The water is further processed for metal removal by a wastewater treatment system so it can be discharged to the POTW (Publicly Owned Treatment Works). First Solar has operated this process as a pilot-scale system.





Research in Recycling

- BAM Resolved project
 - Wet, mechanical removal of films and separation
- CRADA with Brookhaven National Lab
 - Chemical etching of films followed by metal separation and recovery
- Partnership with CdTe supplier
 - Process to refine output of First Solar's alternative process and reuse Cd and Te
- Development projects with other independent metal recyclers



Advances on Recycling of CdTe and CIGS Photovoltaic Modules

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CdTe PV Review Meeting Berlin, 5 August 2005

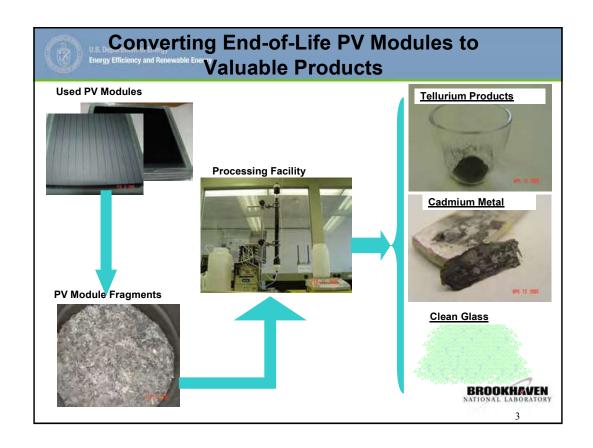


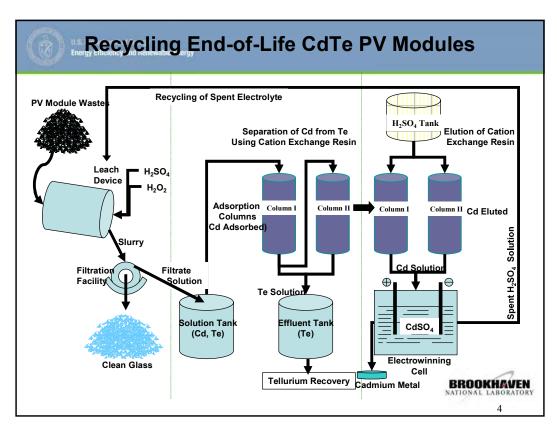
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Research Objectives

- Complete separation of Cd in CdTe and Se in CIGS glass modules to produce clean glass
- Recovery of Te and In in high purity so that can be re-used in PV manufacturing
- Achieve recycling at ¢/W









Part I. Leaching of CdTe PV Modules

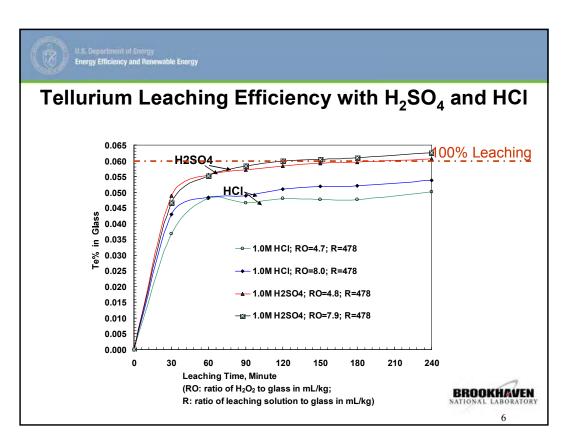
Experimental Parameters

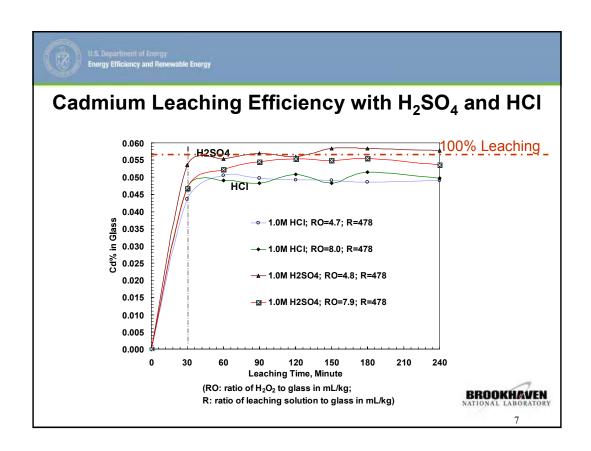
- 1. Selection of leaching agent (HCl, H₂SO₄, HNO₃, and FeCl₃ solution)
- 2. Concentration of leaching agent (1M ~7M)
- 3. Ratio of leaching solution to module glass fragments-R (mL-solution/kg-glass)
- 4. Amount of oxidizing agent-RO(hydrogen peroxide)(mL-solution/kg-glass)
- 5. Leaching time

Studied Range

- Acid-HCl and H₂SO₄
- Strength-1.0 M ~4.0 M
- R=220~478
- RO=4~13
- Time:15~240 minutes







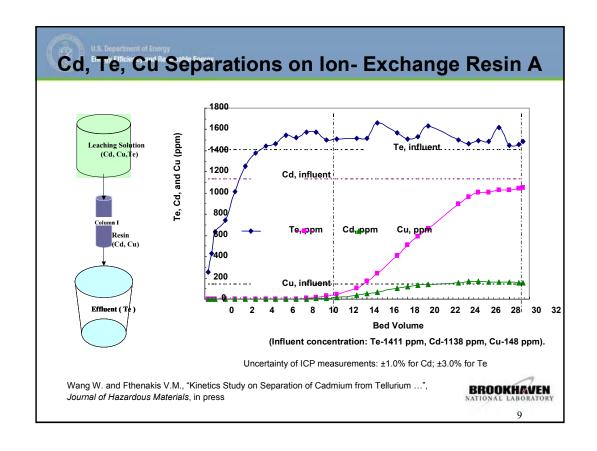


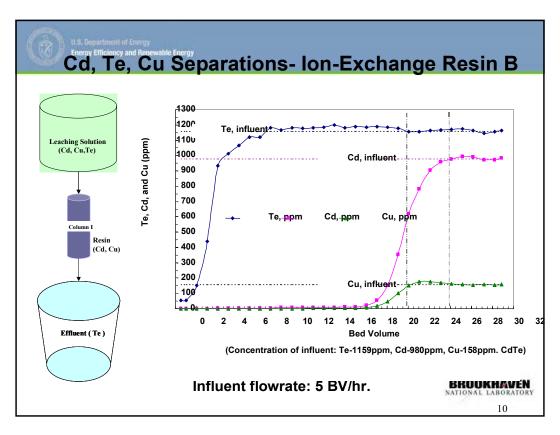
 $\rm H_2SO_4/H_2O_2$ leaching yielded a Cd & Te containing solution (~1000 ppm). How to Separate Cadmium from Tellurium and other Metals in the Leaching Solution?

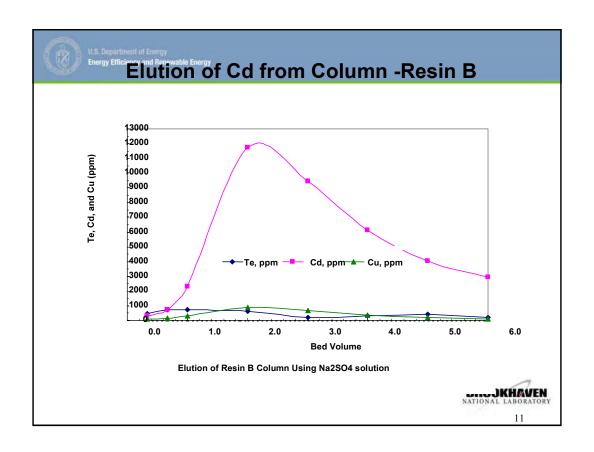
Strategy: Ion Exchange Separation

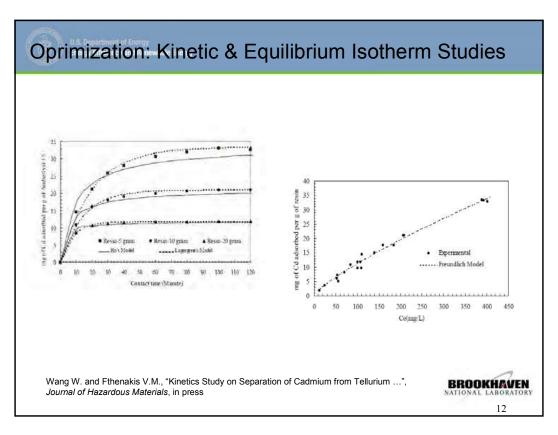
- Type of Resin: Cation Exchange Resin
- Criterion for resin selection: High Selectivity to Cadmium over Tellurium

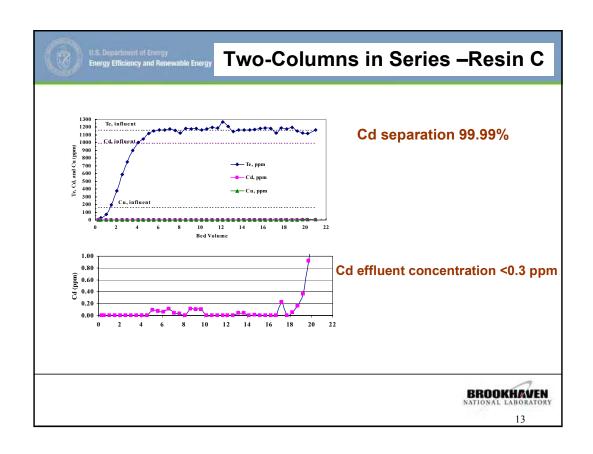


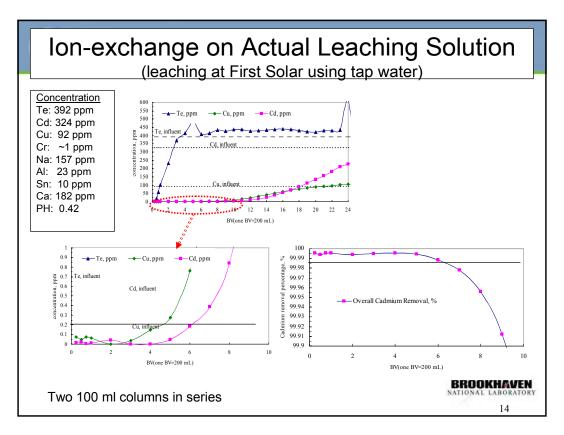


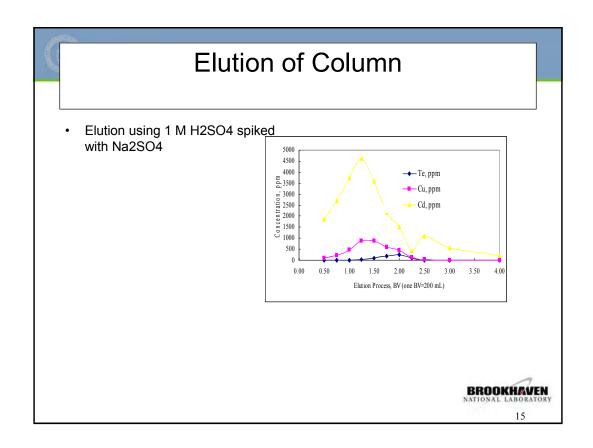


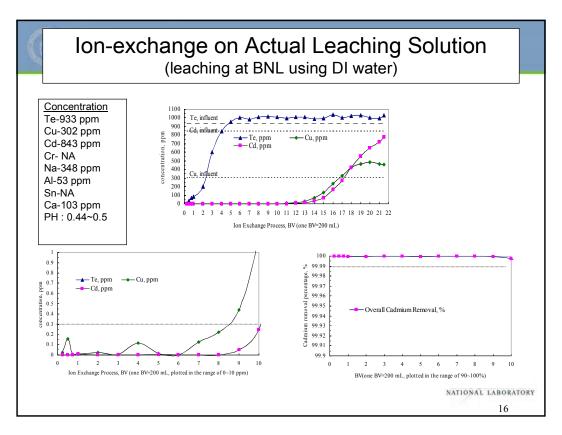


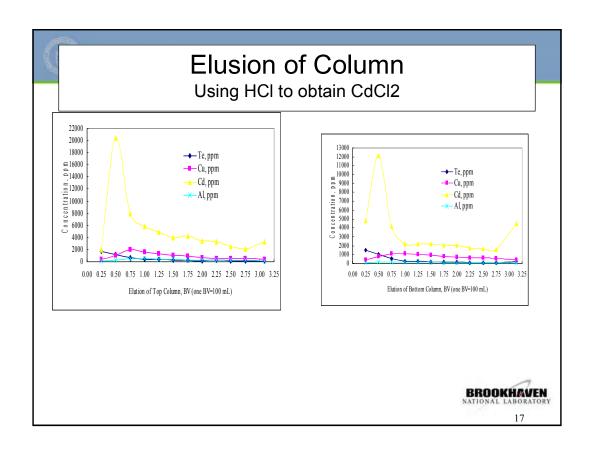












Cost Estimates						
MATERIALS	\$/tonne PV scrap	Cent/W	CAPITAL Hammer Mill	(2005 \$) 50,000	Source (FS est.)	
Leaching Reagents	49.7	1.0	Leaching Station			
			drum tumblers	75,000	(FS est.)	
Resin (500 cycles)	2.2	0.0	Resin Column	40,000	(PropSep Ltd)	
Reagents for Resin Elusion	43.2	0.9	Resin Column Install (est)	10,000		
TOTAL MATERIALS	94.0	1.9	Recovery Tanks			
DAILY VOLUMES	8.3	tonne of PV mo	dule/day 10 MW/y	r, 181,818 pane	els/yr	
Glass Recovery	8.2	tonne/day		727 panels/	day	
Te Recovery	5.3	kg/day				
Cd Recovery	4.5	kg/day		NA	BROOKHAVEN	
					18	

Cadmium Recovery

- Electrowinning from sulfate solution after Cu cementation with Cd produced 93-99% purity.
- Work in progress; 99.99% purity is expected

BROOKHAVEN

19

Te Recovery

(Two steps precipitation using Na2CO3 and Na2S)

Test #	Te Initial (ppm)	Te Final (ppm)	Te Removal (%)
7	979	0.23	99.98
8	979	14	98.57
9	979	0.33	99.97
12	1051	1.69	99.84
13	1051	1.39	99.87
14	1051	1.5	99.86
15	1212	0.39	99.97

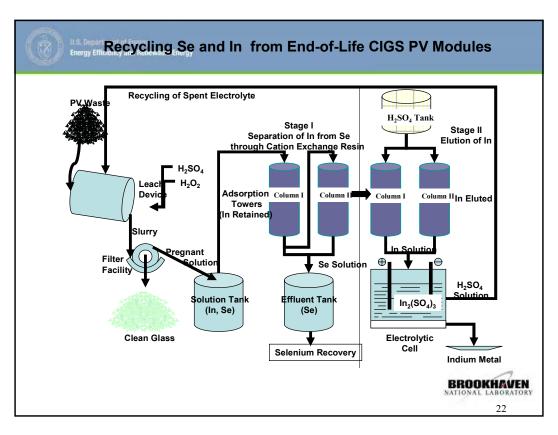
1 stage: ~60% recovery, 92.5% Te 2nd stage ~40% recovery, 37% Te

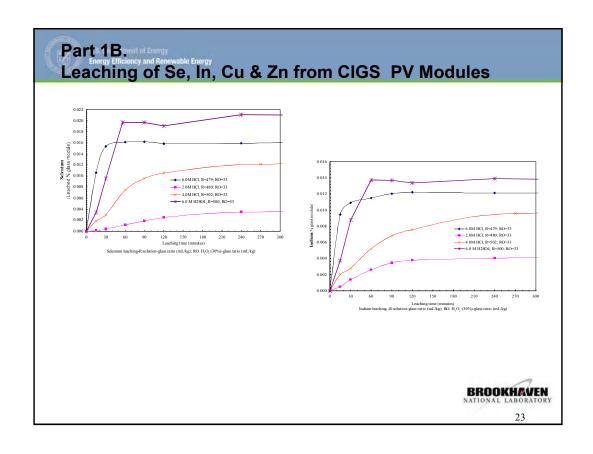
BROOKHAVEN NATIONAL LABORATORY



- Semi-metals can be effectively leached from fragments of CdTe and CIGS PV modules with different strength H₂SO₄/H₂O₂ solutions.
- 99.99% separation of Cd from Te was achieved
- On going work on CdTe on the purity of recovered products and their re-use in PV manufacturing.
- Future work on CIGS on optimizing Se removal, and recovering high-purity indium.









First Solar The Way Forward

August 4, 2005



First Solar Overview

Key Facts About the Company

- Founded in 1999 to commercialize technology developed since 1990.
- Currently 220 associates operating from 4 locations:
 - (1) Perrysburg, Ohio manufacturing and development,
 - (2) Mainz, Germany sales, marketing and customer service,
 - (3) Phoenix, Arizona corporate offices and project development,
 - (4) Berlin, Germany -International Business and Governmental Affairs.





Executive Summary

- ☐ First Solar has achieved high volume solar module production with a technology breakthrough that will make solar electricity competitive with conventional electricity by 2010.
- □ Based on a semiconductor material, CdTe, that is optimal for converting sunlight into electricity, the technology will yield continuous performance improvements and cost reductions for many years, supporting a mass market for solar energy.
- Continuous improvement across all areas is enabling First Solar to increase market share in current customer segments and expand into attractive new customer segments, eventually reaching mass markets.
- ☐ First Solar executes its business activities while practicing industry-leading product life cycle management practices, creating an exemplary sustainable 21st century business model.



3

Producing Solar Modules That Make Solar Electricity Cost Effective



First Solar manufactures solar modules with advanced high throughput, high yield automated processes:

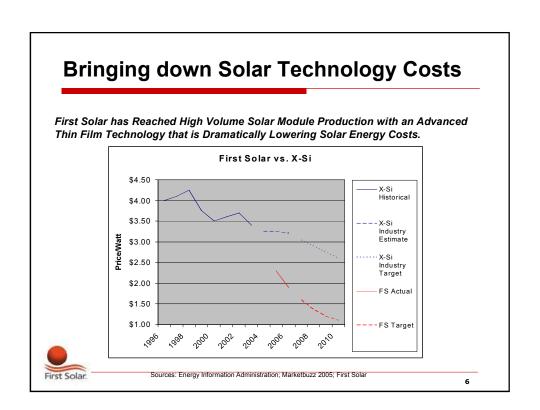
- Very thin CdTe and CdS semiconductor films are deposited on a 2' x 4' glass plate in seconds using a patented vapor transport deposition process.
- High-speed automated manufacturing steps rapidly process the semiconductor coated plate into finished solar modules
- As a result, First Solar modules require a fraction of the material, labor and processing time needed for conventional solar modules.
- Approx 50% of the manufacturing equipment is procured from German technology companies
- Intensive R&D activities with German industry partners and research institutes are possible



Improving Performance of Unique CdTe Technology **Attributes** Projected Module Performance $\hfill\Box$ Has an energy bandgap that is optimally matched to the solar 18.0% spectrum, resulting in higher efficiencies with less semiconductor material. 14.0% ☐ Has a low thermal coefficient and a higher spectral absorption, translating to high energy 12.0% production. 10.0% ☐ Is a robust material that yields high quality products while being 8.0% deposited with rapid, low cost methods. □ Does not suffer from the inherent instability of some other thin film materials.

5

First Solar



Bringing down Solar Technology Costs

First Solar's Thin Film Technology Will Continue to Reduce Solar Electricity Costs Over a Long Term Improvement Cycle Beyond 2010, Leading to Continuous Expansion of a Mass Market.

- ☐ The technology supports continuous long term cost reduction and efficiency improvement, analogous to "Moore's Law" that has characterized the improvement cycle of microprocessors.
- The U.S. Department of Energy characterizes First Solar's CdTe technology as having the potential for lowest costs among photovoltaic technologies, eventually achieving prices of \$0.03 \$0.04 per kWh, low enough to support utility scale generation.

U.S. Department of Energy (NREL) CdTe Thin Film Long Term Potential					
Thin Film Solar Module Costs	Intermediat e Goal	Longer Term Target			
Materials	\$25/M2	\$10/M2			
Capital	\$.10Wp	\$.04Wp			
Labor	\$5/M2	\$2/M2			
Operating Expenses	\$8/M2	\$6/M2			
Efficiency	14%	16%			
Cost/Wp	\$0.37Wp	\$0.15/Wp			
Solar Electricity Cost/kWh	\$.04 - \$.06/kWh	\$.03 - \$.05/kWh			

Cost/Wp estimated by researchers at the U.S. Department of Energy's National Renewable Energy Laboratory. Conversion to Cost/kWh by First Solar assuming 6% after tax levelized financing cost, equivalent BOS cost reductions and high irradiance levels.

7



Bringing down Solar Technology Costs

The Module Cost Breakthrough Puts First Solar on Track to Reduce Solar Module Prices to \$1.00/Watt by 2010, Enabling Consumers to Generate Their Own On-Site Solar Electricity at Prices Competitive with Conventional Electricity.

First Solar Targets

	Solar Electrcity Price per kWh			
Irrandiance Level				
Module Price* System Price		High	Medium	Low
\$1.00 \$2.00		\$0.062	\$0.085	\$0.124
\$1.00	\$2.00	\$0.095	\$0.127	\$0.191

* Price per kWh is calculated with a simplified model that assumes no tax or other financial incentives and (1) no financing costs in the first example and (2) annual after-tax levelized project financing costs of 6% in the second example.

Retail Prices of Conventional Electricity

Retail Electricity Prices	2005	Inflation Rate	2010 (est)
California*	\$0.126	0.00%	\$0.123
U.S. Average**	\$0.079	3.00%	\$0.091
Germany***	EUR 0.164	3.00%	EUR 0.190
EU Average***	EUR 0.135	3.00%	EUR 0.157

^{*} California Energy Commission forecast for all consumers

** Based on Energy Information Administration 2003 average for all consumers; inflation rate estimated

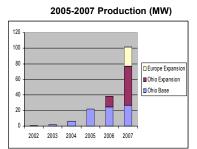
*** 2005 residential price from European Electrcity Price Review (Accenture May 2005); inflation rate estimated

First Solar

First Solar Plant Expansion

First Solar Has Become One of the Fastest Growing Renewable Energy Companies in the World.

- Annual production and sales have increased at an average compound annual growth rate of 230% over 2002-2005.
- High quality, high performance products have lead to strong product acceptance by leading European solar companies. Estimated production is sold out through 31 December 2006. By Q4 2005, estimated 2007 production will be sold except for small "strategic" reserve.
- In Q1 2005, First Solar launched a tripling of production capacity. Continued excess demand for First Solar modules is leading to an additional production capacity expansion in Europe in 2006.
- First Solar has quickly become the lowest cost solar module manufacturer and among the fastest growing solar module manufacturers in the world.



* European plant currently planned for initial production ramp stage in 2007. Production from European plant currently planned to reach approximately 100MW in 2008.



First Solar

9

Product Life Cycle Management

First Solar combines low cost technology with industry-leading life cycle management practices to create an exemplary sustainable 21st century business model.

- ➤ CdTe is stable compound made from cadmium and tellurium, both mining waste products.
- > The modules are manufactured in state of the art, emission-free, ISO 14000-certified facilities.
- Once compounded and encapsulated in First Solar modules, cadmium is removed from the environment and cannot escape under use or accidental conditions.
- > First Solar modules are reclaimed at end of life and recycled.
- > Estimated future reclamation and recycling costs are pre-funded through an insurance program with one of the largest insurers in the world.



First Solar Improving Environmental Profile

- Continue dialog with politics and science (e.g. BMU, JRC, BNL, Juelich etc.)
- Decreasing the amount of Cd and increasing its utility in manufacturing
- Improving Recycling Program for Manufacturing Waste and Modules
- Continuing FS Take-Back-System Program
- Support of Industry-Wide take back system



11

First Solar's Contribution to the Solar Age

By Reducing Solar Electricity Prices Substantially Toward Conventional Electricity Price Levels, First Solar is Contributing a Sustainable Solution to Two of the Most Pressing Problems Facing Mankind: Global Climate Change and the Scarcity of Natural Energy Resources.

- ➤ By generating on-grid or their own on-site solar electricity, consumers can replace a significant portion of their peak time demand for conventional electricity with emission-free solar electricity.
- ➤ A community-wide distributed solar electricity infrastructure will greatly reduce overall GHG emissions, peak time demand for conventional electricity generation and peak transmission and distribution.
- ➤ Distributed solar generation can also bring clean, life-changing power to many parts of the world not served by reliable grids and conventional electricity.

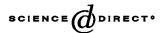


First Solar.

Annex II Reviewed Studies



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Renewable and Sustainable Energy Reviews 8 (2004) 303–334

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Life cycle impact analysis of cadmium in CdTe PV production

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Received 30 October 2003; accepted 1 December 2003

Abstract

This paper describes the material flows and emissions in all the life stages of CdTe PV modules, from extracting refining and purifying raw materials through the production, use, and disposal or recycling of the modules. The prime focus is on cadmium flows and cadmium emissions into the environment. This assessment also compares the cadmium environmental inventories in CdTe PV modules with those of Ni–Cd batteries and of coal fuel in power plants. Previous studies are reviewed and their findings assessed in light of new data. Published by Elsevier Ltd.

Keywords: Cadmium emissions; Photovoltaics; Solar cells; Cadmium telluride; Life cycle analysis; Emissions allocation

Contents

1.	Introd	luction .		304
2.	Produ	ection of	cadmium and telluride	305
	2.1.	Cadmi	um production	305
		2.1.1.	Mining of zinc and lead-ores	305
		2.1.2.	Zinc and lead smelting/refining	307
		2.1.3.	Production of cadmium in zinc-lead smelters/refiners	313
	2.2.	Telluri	um production	314
	2.3.	Purifica	ation of cadmium and tellurium	316
	2.4.	Produc	etion of CdTe from cadmium and tellurium	316

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3.	Allocation of emissions	317
4.	Manufacturing of CdTe photovoltaics	318 319 320
5.	Operation of CdTe PV modules	320 320 321
6.	End-of-life disposal or recycling	322
7.	Total atmospheric emissions	324
8.	Comparisons with other energy technologies 8.1. Ni–Cd batteries 8.2. Coal-burning power plants	325 326 327
9.	A fundamental question: what happens to cadmium if it is not used?	328
10.	Conclusion	330 330 331 331

331

V.M. Fthenakis / Renewable and Sustainable Energy Reviews 8 (2004) 303-334

1. Introduction

10.4.

304

Life Cycle Assessment (LCA) involves analyzing the inventory of material and energy flows in and out of a product, and assessing the impacts of such flows. Previous applications of LCA to photovoltaics focused on determining energy payback time (EPT) and reductions in carbon-dioxide emissions [1–4]. Kato et al. [4] emphasized the need for further studying the environmental aspects of CdTe photovoltaics, including decommissioning and recycling of end-of-life CdTe modules. The current study characterizes material flows and emissions in thin-film CdTe PV modules, from acquiring the raw material through their production, use, and disposal or recycling. It describes in detail the flows of the major photovoltaic compound (CdTe); other materials in the PV module (e.g. glass, EVA, metal contacts) are generic to all technologies and, therefore, are not discussed. In addition to reviewing the published literature, I examined the environmental reports of several primary producers of the metal. This assessment also discusses the allocation of Cd emissions in co-production of metals, and makes a comparative evaluation of CdTe with other uses of cadmium.

Below I describe the material flows and emissions in the following phases of the life of CdTe modules: (1) mining of ores, (2) smelting/refining of Cd and Te, (3) purification of Cd and Te, (4) production of CdTe, (5) manufacture of CdTe PV modules, and, (6) disposal of spent modules.

2. Production of cadmium and telluride

CdTe is manufactured from pure Cd and Te, both of which are byproducts of smelting prime metals (e.g. Cu, Zn, Pb, and Au). Cadmium is generated as a byproduct of smelting zinc ores (~80%), lead ores (~20%), and, to lesser degree, of copper ores. Tellurium is a byproduct of copper refining. Cadmium is used primarily in Ni–Cd batteries. Its previous uses in anticorrosive plating, pigments, and stabilizers were drastically curtailed. Cd also is used in the control rods of nuclear reactors. Tellurium is a rare metal used in ma ufacturing photosensitive materials and catalysts.

2.1. Cadmium production

Cadmium minerals are not found alone in commercial deposits. The major cadmium-bearing mineral is sphalerite (ZnS), present in both zinc and lead ores. Cadmium occurs in the crystal structure of zinc sulfides; only rarely does it form (in combination with sphalerite) its own isostructural sulfide—greenockite. The cadmium content in the various ores are as follows: sphalerite, 0.0001–0.2%; greenockite, 77.8%; chalcopyrite, 0.4–110 ppm; marcasite, 0.3–50 ppm; arsenopyrite, ~5 ppm; galena, 10–3000 ppm; and, pyrite, 0.06–42 ppm [5]. Table 1 shows the cadmium content in other mineral feedstocks.

2.1.1. Mining of zinc and lead-ores

Zinc is found in the earth's crust primarily as zinc sulfide (ZnS). Zinc ores contain 3% to 11% zinc, along with cadmium, copper, lead, silver and iron, and small amounts of gold, germanium, indium, and thallium. Lead-rich ores also contain zinc, copper, and silver in sulfide forms. In underground mines, the ore is excavated by drilling machines, processed through a primary crusher, and then conveyed to

Table 1 Cadmium content in mineral feedstocks

Material	Concentration range (ppm)	US median (ppm)
Zn ores	0.1–2000	220
Zn ore concentrates	3000–5000	5000
Copper ore concentrates	30–1200	NA
Iron ore	0.12-0.30	NA
Coal	0.4–10	0.5
Heavy oil	0.01-0.10	_
Phosphate ore	0.25–80	_

the surface. In open-pit mines, the ore is loosened and pulverized by explosives, scooped up by mechanical equipment, and transported to the concentrator.

The concentration of zinc in the recovered ore (called beneficiating) is done by crushing, grinding, and flotation processes (Fig. 1). Standard crushers, screens, and rod- and ball-mills reduce the ore to powder of 50–210 microns. The particles are separated from the gangue and concentrated in a liquid medium by gravitation and/or selective flotation, followed by cleaning, thickening, and filtering [6a]. At this stage, organic xanthate and a froth-promoter, usually pine oil, are added. The mixture is treated in banks of flotation machines—shallow tanks in which a rotating impeller disperses fine bubbles of air. When the pH and reagents have been adjusted, the air bubbles carry the sulfide minerals to the surface of the pulp for removal. The proper combination of reagents causes the selective flotation of zinc sulfides, lead sulfides, and copper sulfides, and rejects the iron sulfides and rock to tailings. The metal concentrates are dewatered, dried, and shipped to metallurgical plants, with each sulfide being sent to the appropriate smelter; the water is recycled to the mill. The waste, called tailings, is discharged in tailing ponds. Zinc concentrates contain about 85% zinc sulfide and 8-10% iron sulfide. The cadmium content of the zinc concentrate is around 0.3% to 0.5% [7]. Limited information exists on the cadmium content of tailings. Measurements of soil contamination in a mine site at Brooksville, Maine, which ceased operations in 1972, show cadmium in the soil, tailings, and waste rock ranging from undetected levels to 150 ppm [8]. Data from a lead-zinc mine in Maarmorilik, Greenland, showed 57 ppm of Cd in the tailings in 1978, but, by 1985, this had fallen to 14 ppm (Table 2); more recent

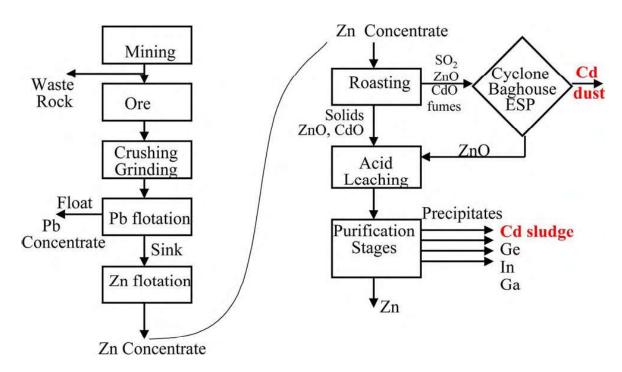


Fig. 1. Cd Flows in Zn mining and refining.

data were not found. Assuming that the initial Cd concentration in the ores was 220 ppm, this reflects a loss of 6% in the tailings. This value is the middle point of the range given in a 1994 report of the US Bureau of Mines [7]. According to Liewellyn [7], between 90% and 98% of the cadmium present in zinc ores is recovered in the mining and beneficiting stages, and the balance of cadmium remains in the mine tailings.

Similarly to zinc ores, lead-bearing ores are processed by crushing, screening and milling, to reduce the ore to powder. These activities, if not adequately controlled, could generate significant levels of dust (e.g. 3 kg/ton of mined ore), ranging from 0.003 kg to 27 kg per ton of ore [9]. However, ASARCO and Cominco, two major metal producers, report that implement controls which minimize dust emissions. All of the mining, crushing, and grinding takes place underground and wet scrubbers and dry cyclones are utilized to collect the dust. Cominco uses a wet grinding process resulting in a slurry from which, reportedly, there are essentially no dust emisions [6b]. Therefore, the low limit of the range (i.e. 0.003 kg/ton ore) was used in our analysis.

In both zinc and lead mining operations, in addition to intrinsic waste, mining generates an assortment of wastes, including liquids from maintaining equipment in mills, and from mobile equipment at mines. Major North American producers have waste-reduction and residuals-management programs. Large open-pit mines create large volumes of waste oil, which is recycled on-site. Waste oil from Canadian operations is collected and recycled off-site. In some other locations, waste oil is reused by cement plants as a source of energy.

2.1.2. Zinc and lead smelting/refining

The zinc and lead concentrates are transferred to smelters/refiners to produce the primary metals; sulfuric acid and other metals are frequent byproducts from most smelters (Fig. 2). In addition to Zn, the mines in the United States also produce 100% of the Cd, Ge, In, and Th, 10% of Ga, 6% of Pb, 4% of Ag and 3% of Au used in the country [10,11]. Also, integrated zinc-lead smelters/refiners recycle significant volumes of solid- and liquid-wastes (lead acid batteries, waste grease, drums, plastic pails, tires, conveyor belting, wood, office paper, cardboard, and many other end-of-life-consumer goods). For example, 22,000 tones of lead acid batteries and other battery materials were reprocessed at the Teck Cominco Trail smelter in 2002.

Table 2
Data from the Black Angel lead–zinc mine, Greenland*

Metal	Average content in ore (%)	Content in tailings		
		1978	1985	
Zn	12.3	1.1%	0.23%	
Pb	4	0.44%	0.15%	
Cd	?	57 ppm	14 ppm	

^{*}Source: http://www.geus.dk/minex/go02.pdf.

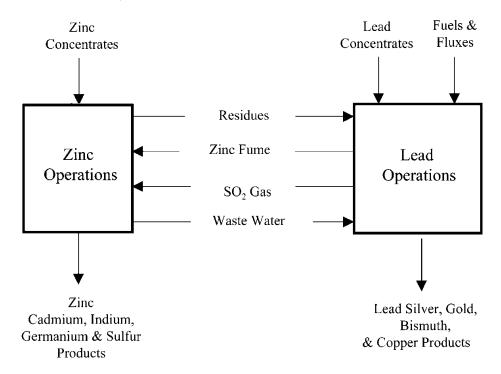


Fig. 2. General process schematic for zinc/lead smelting (*Source*: http://www.teck.com/environment/articles.htm).

- 2.1.2.1 Zinc production. Zinc can be refined by either pyrometallurgical or hydrometallurgical treatment of its concentrates (Fig. 3). There are four primary zinc-smelting operations in the United States. Three of them utilize electrolytic technology, and one uses an electrothermal process [6]. Older roast/retort smelters are no longer employed in North America and Northern Europe. The electrolytic zinc process consists of five main operations, roasting, leaching, purification, electrodeposition and melting/casting (Fig. 3). These are described below:
 - (i) Oxidizing roast at high temperature removes sulfur and converts the zinc, iron, cadmium, and other metals to oxides. The concentrates are fed to flui-dized-bed furnaces where they react with oxygen. The product, calcine, which mainly is zinc oxide with small amounts of iron, cadmium, and other metals, is pneumatically transported to storage bins before the next phase of treatment. The roaster gases, containing sulfur dioxide, are separated from the calcine and cooled in a waste-heat boiler, to recover heat and generate steam. They are usually treated to recover mercury, while the collected particulates are processed to recover cadmium. Sulfur dioxide is used to produce sulfuric acid.
- (ii) Calcine and spent electrolytes from the subsequent electrolytic process are leached in sulfuric acid. This process, in one or two steps, dissolves the zinc to make a solution of zinc sulfate and other acid-soluble metals. Iron is precipitated and filtered from the process as a residue. Depending on the ore, the residue may also contain lead, copper, silver, and gold. The leachate is sent to the purification section.

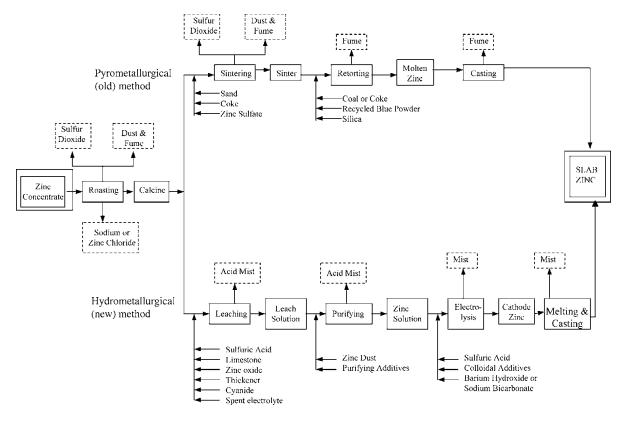


Fig. 3. Generalized process flow for primary zinc smelting [6a].

- (iii) In subsequent purification, iron and various other valuable metals (e.g. copper, cobalt, nickel, cadmium, germanium, indium, and gallium) are removed, usually in three stages. After the third stage, the solution, which contains zinc sulfate and residues of copper and cadmium, is pumped to the electrowinning stations. The cadmium extracted at this step is formed into briquettes that then are melted. This refining results in metallurgical grade (99.95% pure) cadmium, which is cast and cut into sticks.
- (iv) Recovery of metallic zinc from the sulfate solution is accomplished by electrowinning. Zinc is reduced from a solute into a metallic form by electrodeposition on aluminum sheet cathodes. Every 36 h or so, the Zn-covered cathodes are removed and the pure zinc layer covering them is stripped off and fed into induction furnaces. Also sulfuric acid is regenerated in this stage.
- (v) The final steps in zinc production are melting, casting, and alloying. The zinc stripped off from the cathodes is melted, and cast into ingots, slabs, or larger blocks of slab ready for delivery to customers [6,14a].

In addition to cadmium, zinc smelting also produces (as byproducts) other photovoltaic materials (i.e. Ge, In, and Ga). Because economic growth has steadily increased the demand for zinc for decades, impure cadmium is produced, regardless of its use. Before cadmium production started in the United States in 1907, about 85% of the Cd content of the zinc concentrates was lost in roasting the concentrate,

and in the fractional distillation of Zn metal [7]. The feed material for producing cadmium consists of residues from the electrolytic production of zinc, and of fume and dust, collected in baghouses from emissions during pyrometallurgical processing [6].

Primary zinc production produces air emissions, process wastes, and solid-phase wastes. The zinc roasting process primarily emits sulfur dioxide. These emissions often are recovered on-site in sulfuric-acid production plants. Zinc roasters also generate particulates containing cadmium, lead, and other metals. The particulate emission streams are controlled with cyclones and electrostatic precipitators (ESPs), and the particulates collected in the control equipment constitute hazardous waste. As discussed later, this waste comprises the feed to the cadmium-production plant.

Wastewater produced from leaching, purification and electrowinning usually is treated and re-used or discharged.

Solid wastes include slurries from the sulfuric-acid plant, sludge from the electrolytic cells and copper cakes, and the byproducts of zinc production from the purification cells which contain cadmium, germanium, indium, and other metals. Much of the waste is RCRA¹ hazardous waste. Copper cakes are captured and sold to copper processing plants. Purification byproducts and other solid wastes are recycled or stockpiled until they can be economically used. Table 3 shows the US EPA's estimates of particulate emissions for US plants; I estimated their cadmium content based on a typical concentration of Cd in Zn concentrate (e.g. 0.5%).

Berdowski et al. [13a] reported on the emissions from zinc-smelting operations in other countries; these are summarized in Table 4. Cd emissions vary widely depending on the ore used and the abatement measures applied. For electrolytic production, emission factors of 0.5 g Cd/ton Zn were reported in 1992 for the Netherlands, 2 g Cd/ton Zn in 1991 for Germany, and a range of 0.4–20 was reported for 1980–1992 for Poland. More recent data show 0.2 g Cd per ton of Zn product for North European countries [12a,12b,13a]. This corresponds to about 40 g per ton of Cd produced.

Slightly higher emissions are reported from one of the world's largest integrated zinc- and lead-smelting and refining complexes, the Teck Cominco complex in Trail, British Columbia, Canada [14b]. In addition to zinc and lead, 18 other products are formed including silver, gold, indium, germanium, bismuth, copper products; and sulfur compounds (e.g. ammonium sulfate fertilizer, sulfuric acid, liquid sulfur dioxide and elemental sulfur). The reported cadmium releases from all operations at Trail in 2002 were 95 kg in air and 208 kg in water; they correspond, per ton of metals produced, to 0.27 g of Cd air emissions, and 0.59 g of water discharges (Table 5). Only total emissions from all operations were reported; the contribution of the cadmium plant to these emissions is difficult to determine because feeds and residuals were transferred between plants in the same facility. Also, the

¹ The RCRA, the Resource Conservation and Recovery Act, characterizes what constitutes hazardous waste by either listing or leaching tests.

Table 3
Particulate emission factors in zinc smelting by thermal (old) and electrolytic (new) methods

Process	Uncontrolled emissions (kg/ton of zinc ore)	Post-control emissions (kg/ton of zinc concentrate)	Estimated ^a Cd emissions (kg/ton of zinc concentrate)
Roasting			
Multiple hearth	113	ND	ND
Suspension	1000	4	0.02
Fluidized bed	1083	ND	ND
Sinter plant			
Uncontrolled	62.5	NA	NA
With cyclone ^b	NA	24.1	0.14
With cyclone and ESP ^b	NA	8.25	0.05
Vertical retort	7.15	ND	ND
Electric retort (electro-	10.0	ND	ND
thermic process)			
Electrolytic process	3.3	ND	ND

ND, not detected.

Trail smelting facility processes metal scrap and other waste in addition to Zn and Pb ores. These data show a continuing improvement from 1989 to 2002. The actual emissions of Cd into the air declined by 84% between 1999 and 2002 (Table 5). Releases in the water within this period remained approximately the same.

The shift to electrolytic processing of zinc ore was a great technological advance that drastically reduced cadmium emissions because it eliminated the sintering step in zinc refining, and thus, much of the particulates burden. The Cd emissions in previous generation smelters amounted to 100 g of Cd per ton of Zn produced (Table 6), whereas those from current roast/leach/electrolytic European plants have fallen to 0.2 g of Cd per ton of Zn. In the past, high cadmium concentrations were found in the vicinity of lead and zinc smelters. Also, the early practice of roasting zinc sulfide and discharging the SO₂ into the atmosphere was replaced by

Table 4
Emission factors for primary zinc production (g/ton product) [13a]

Compound	Germany	1991	Poland 19	80–1992	Netherlands 1992	Europe 2	002
	Thermal	Electrolytic	Thermal	Electrolytic	Electrolytic	Thermal	Electrolytic
Cadmium	100	2	13	0.4–29	0.5	50 ^a	0.2
Lead	450	1	$31-1000^{b}$	2.3-467	_	1900	_
Mercury	5-50	_	_	_	_	8	_
Zinc	_	_	420-3800	47–1320	120	16,000	6

^a With vertical retort and limited abatement: 200 g/Mg product; with imperial smelting furnace: 50 g/Mg product.

^a Cadmium content in particulates is estimated assuming a zinc/cadmium ratio of 200 (0.5% Cd).

^b Data not necessarily compatible with uncontrolled emissions.

^b Limited abatement.

Table 5
Production and emissions at the Trail smelter and refineries, British Columbia, Canada [14]^a

	1998	1999	2000	2001	2002
Annual production			,		
Zinc (tonnes)	274,300	288,700	272,900	168,100	269,000
Lead (tonnes)	63,900	75,700	91,300	55,200	80,700
Cadmium (tonnes)		1400	1400	1400	1400
Specialty metals (tonnes)		28	28	28	28
Silver ('000 ounces)	12,215	11,382	12,212	9,182	17,690
(tonnes)	463	431	463	348	670
Gold ('000 ounces)	86	46	56	48	127
(tonnes)	3	2	2	2	5
Fertilizer (tonnes)	273,000	240,700	220,300	167,500	225,000
Cd releases to air from all oper	ations				
(kg/year)		600	250	100	95
(g of Cd/ton metal products)		1.64	0.69	0.45	0.27
Cd releases to water from all op	perations				
(kg/year)		208	290	170	208
(g of Cd/ton metal products)		0.57	0.79	0.76	0.59

^a *Source*: Teck Cominco; http://www.teck.com/operations/trail/index.htm (For specialty metals and cadmium only 2002 production levels were reported; we assumed that production in 1999–2001 was at the same levels as 2002.

converting the gas to sulfuric acid. The remaining particulate emissions are controlled with ESPs and bag-houses having efficiencies of 98–99.5%.

2.1.2.2 Lead production. Lead comes to smelters in the form of lead-sulfide concentrate and automotive battery scrap. They are processed by a combination of pyrometallurgical and hydrometallurgical operations. The feedstocks are heated in a furnace with oxygen, fluxing and fueling agents. Smelting creates impure lead bullion, slag, and gaseous emissions, primarily SO₂. Energy is recovered from the hot-emissions by passing the gasses through a heat exchanger, while an electrostatic precipitator removes the particles. The SO₂ emissions then are processed into sulfur products (e.g. sulfuric acid and liquid sulfur dioxide) [14a].

Table 6 Cadmium emissions from old and new zinc-production processes

Process	Cadmium emissions		
	g Cd/ton Zn	(% Cd loss)	
Roast/leach/electrowinning process	0.2	0.008	
Roast/blast furnace smelting (replaced in	50	2	
Canada and Europe)			
Roast/blast furnace smelting (not in use any	100	4	
more)			

The molten slag is transferred to a slag-fuming furnace to remove zinc, mainly in the form of a zinc-oxide fume. The fume is processed in the leaching plants in zinc operations to extract more zinc. The remaining "ferrous granules" (black sand-like slag) is sold to cement manufacturers.

The lead bullion is processed through a dosing plant to remove copper and other impurities. The remaining bullion is purified in the lead refinery by melting and electrolytic processing, and cast into the finished product. Byproducts of the refining process include silver, gold, arsenic, antimony, and bismuth. Emissions of cadmium from all sources range from 0.6 g/ton product for plants with cyclones and ESPs, to 22 g/ton product for plants with limited emissions abatement (Table 7).

The lead smelters also produce significant quantities of silver, gold, bismuth, and copper products (Table 5 and Fig. 2). These plants are designed to treat a wide range of feed materials including lead concentrates, various residues from the zinc plants, recycled lead battery scrap, and scrap copper [14a].

2.1.3. Production of cadmium in zinc-lead smelters/refiners

Cadmium recovery plants use as their raw materials cadmium residues from the leaching/electrolytic zinc production, particulates from roaster furnaces collected with electrostatic precipitators (ESPs), and recycled zinc metal which contains cadmium. In addition, they process particulates collected from lead smelting furnaces.

2.1.3.1 Cadmium production from zinc electrolyte purification residue. The cadmium sponge, a purification product from precipitating zinc sulfate solution with zinc dust at the zinc smelter, is 99.5% pure cadmium. This sponge is transferred to a cadmium recovery facility and is oxidized in steam for two days or so. Cadmium oxide, the product, is leached with spent cadmium electrolyte and sulfuric acid to produce a new recharged electrolyte. Impurities are precipitated with a strong oxidizing agent. The wastes are refined for other uses or stockpiled, usually until a use can be found for them. Non-corrosive anodes are used during electrowinning.

Table 7
Emission factors for primary lead production (g/ton product) [13b]

	Sweden 1	992	Poland 198			Germany 1999	Europe 1950– 1985
Abatement level	Limited	Improved	Limited	Improved	Unabated	Unknown	Unknown
Compound							
Arsenic	3	0.2	16-43	_	_	3	300
Cadmium	3	0.6	10–22	_	_	6	10
Copper	10	4	10	7	_	_	_
Lead	400	200	560-1200	_	_	400	3000
Mercury	_	_	_	_	_	_	3
Zinc	50	20	110	_	680	_	110

Additives (often animal glue) are used to enhance the smoothness of the resulting cadmium cathode. The cathodes are removed about every 24 h and are rinsed and stripped. The stripped cadmium is melted under flux or resin and cast into shapes.

In a slightly different route, purification residues from the oxide and the sulfide-leaching processes are further leached with sulfuric acid and filtered through three stages to remove zinc, copper, and thallium before recovering the dissolved cadmium. Cadmium can be further purified with vacuum distillation to 99.9999% purity [14].

2.1.3.2 Cadmium production from lead smelter emissions. The fumes and dusts of lead smelters are concentrated to 8–60% cadmium by weight and shipped to the cadmium recovery plant where they are reacted with sulfuric acid. The resulting calcined cadmium sulfate and impurities are roasted and then leached with water to dissolve the cadmium. The cadmium sulfate solution is first filtered to remove the lead sulfate, which is recycled to the lead smelter, and then further purified by electrolytic separation.

The resulting electrolyte is 99.995% pure. The cadmium is melted under flux or resin and cast into shapes. The spent electrolyte is recycled at the cadmium recovery plant. When excessive amounts of impurities accumulate in the spent electrolyte, the solution is recycled to another use or neutralized and discarded.

The total loss in emissions and residues at cadmium plants is about 5% [7]. Thus, about 95% of Cd from Cd concentrates is converted in metallurgical grade (99.99%) metal, which is used in all current applications, except for semiconductor CdTe and CdHgTe. High purity (i.e. 99.999%–99.9999%) Cd (and Te) powders are produced by electrolytic purification and subsequent melting and atomization or by vacuum-distillation followed by zone refining.

2.2. Tellurium production

Tellurium minerals are not found alone in commercial deposits. Tellurium is a rare metal that can be extracted as byproduct of processing copper, lead, gold, and bismuth ores. In 1982, about 90% of tellurium was recovered from the slimes formed during the electrolytic refining of copper [15]. Copper is mined from a variety of ores containing copper in the form of mineral compounds with sulfur, iron, arsenic, and tin. Copper concentrates of about 30% Cu are produced at the mine sites via crushing, grinding, and flotation. They are transferred to smelters where they are processed in furnaces to yield "mate" containing about 65% copper. The iron in this mate is oxidized to produce "blister" copper of 97% to 98.5% purity that can be further refined hydrometallurgically or by a combination of pyrometallurgical and hydrometallurgical separation. Impurities in blister copper include gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, tellurium, tin, and zinc. In pyrometallurgical separations, air is bubbled through the molten mixture to remove the impurities by oxidation. The fire-refined copper is cast into anodes for further purification by electrolytic refining. In electrolytic refining, the impurities are separated by electrolysis in a solution containing copper sulfate and sulfuric acid. The copper anode dissolves and metallic impurities precipitate forming a sludge. The copper collected on the cathode is about 99.95% pure [16].

The slimes contain copper, tellurium, selenium, and other metals. Copper typically is removed by oxidative pressure-leaching with dilute sulfuric acid at 80–160 °C. This completely extracts the Cu, and removes 50–80% of the Te according to one source [17] or more than 90% according to another [18]. The range of Te extraction is wide because its concentration in slimes varies significantly. Tellurium is recovered from solution by cementation with copper. Copper telluride is leached with caustic soda and air to produce a sodium telluride solution. The latter is used as the feed for producing commercial grade Te metal or TeO₂. As discussed in Section 4, both of these forms can be used in CdTe formation for PV.

Crushing and grinding of ores in copper mines generates dust emissions of the same levels as those in mining zinc- and lead-ores (discussed in Section 2.1.1).

Emissions generated from primary copper smelters include sulfur dioxide and particulates from the roasters, smelting furnace, and converters. Copper and iron oxides are the primary constituents of the particulate matter; other constituents include the oxides of arsenic, antimony, cadmium, lead, mercury, and zinc. There are eight copper smelters in the United States. Sulfur dioxide is recovered in the form of sulfuric acid in all but one of these smelters. Particulate emissions are treated in ESPs or combination spray/ESP systems with efficiencies of 95–99%. The emissions from copper smelting can vary widely depending on the ore used and the abatement measures applied. I found no explicit quantification of cadmium emissions in copper smelting in the literature. Indirect estimates can be made from comparing the Cd concentrations in copper and lead smelters; Table 8 shows those compiled by Ayres and Simonis [19]. According to these numbers, copper smelters would produce 3.2 to 5 times lower Cd emissions than lead smelters. These emissions are primarily related to pyrometallurgical operations. Emissions in hydrometallurgical/electrolytic plants are likely to be negligible unless the sulfuric-acid tanks are open to the atmosphere.

Table 8
Uncontrolled emissions from metallurgical operations [19]

Metal	Steel and foundries (ppm)	Smelt/refine copper (ppm)	Smelt/refine lead (ppm)
Arsenic	15.2	8000 (refinery 800–900)	
Cadmium	3.5-4.0	350–650	1750–2100
Chromium	6.5–7.0	_	_
Copper	17.5–22.5	2500–5000	_
Mercury	_	26 air 1 water	9 air 0.5 water
Lead	200–300	2000–5000 (refinery 25)	20,000–23,000
Zinc	27–370	9000-11,000	500–1000

2.3. Purification of cadmium and tellurium

Metallurgical grade (i.e. 99.99% pure) metal is used in all current applications except for semiconductor materials (e.g. CdTe and CdHgTe) that require higher purity. Teck Cominco reports that all the cadmium they produce is ultra-pure grade (i.e. 99.9999%, called six 9s). Purification residues from their leaching plants undergo additional leaching with sulfuric acid and are filtered though three stages to remove zinc, copper, and thallium. The final step is vacuum-distillation [11].

High purity Cd and Te powders from other manufacturers are produced by electrolytic purification and subsequent melting and atomization (Fig. 4), or by vacuum distillation. Both methods are proprietary and information about emissions is not published. According to industry sources, electrolytic purification does not produce any emissions and all waste is recycled. The melting and atomization steps needed to form the powder produce about 2% emissions that are captured by HEPA filters [20]. The efficiency of HEPA filters in collecting particulates of mean diameter of 0. 3 µm is 99.97%.

Zone-refining involves four steps during which the concentrations of impurities are reduced below levels detected by standard analytical techniques [21–25].

2.4. Production of CdTe from cadmium and tellurium

Currently, high purity Cd and Te are used in synthesizing high purity (five 9s to six 9s) CdTe for PV cells. CdTe is produced from Cd and Te powder via pro-

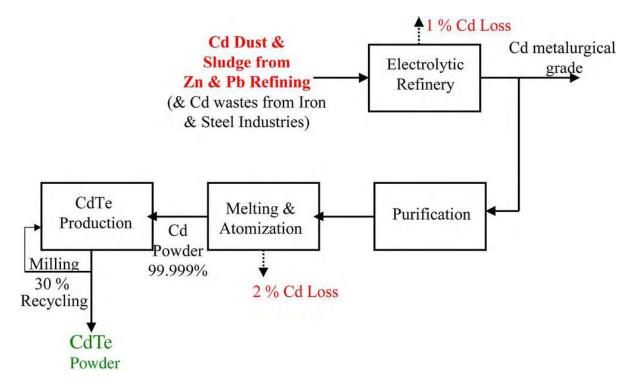


Fig. 4. Cd Flows from Cd Concentrates to CdTe.

prietary methods. CdTe is produced in small amounts for detectors and photovoltaics. Production is limited and the volumes produced are not published.

Reportedly, 100% of the feedstock is used and there are no quantifiable emissions during CdTe formation. The electrolytic purification does not produce any emissions and all waste is recycled. The melting and atomization steps necessary to form the powder emit about 2% of the feedstock which are captured by HEPA filters [20]. Milling produces some undesirably large particles, which are recycled into the process.

3. Allocation of emissions

Cadmium is a byproduct of zinc, lead, and copper production, and is collected from the emissions and waste streams of these major metals. Tellurium is a byproduct of copper production, and is also collected from waste streams. In obtaining cadmium from zinc ores, the emissions from the production of zinc are captured and used for this purpose. Should we allocate these cadmium emissions to the production of zinc, or to the production of cadmium and other byproducts? The recovery of low-value byproducts and waste for use as industrial raw materials is referred as "waste mining" [46]. Assuming a fixed level of demand for the prime metal (copper or zinc), the choice is between leaving the minor metal in gangue, slag, or dust, or recovering it for use. Recovery is encouraged for precious metals (e.g. gold and silver) that have value, and their applications are environmentally harmless. The value of recovering Cd is debatable. Cadmium used in pesticides and pigment stabilizers is dissipated and may not alter the environmental fate of cadmium waste from mining in any other way than by diluting it. On the other hand, semiconductors and batteries are products that are both collectable and recyclable (i.e. non-dissipative uses).

The problem of allocation in Life Cycle Assessment for joint production is a fundamental one [26]. The International Standard Organization (ISO) specifies a procedure (ISO 14041) for deciding such allocation [27]. It entails the following steps: (1) Allocation should be avoided, whenever possible, by dividing the process into subprocesses, and including the additional functions related to co-products. (2) Where allocation cannot be avoided, the system's inputs and outputs should be partitioned to reflect the underlying physical relationships between them (i.e. they must mirror the way the inputs and outputs are altered by quantitative changes in the products or functions). (3) Where physical relationships alone cannot be established or used as a basis for allocation, inputs should be allocated between the products in proportion to the products' economic values.

According to the first step of the ISO procedure, I considered separately zinc and cadmium production (Figs. 1 and 4 correspondingly). Thus, the zinc cycle starts with mining the Zn ores and ends with generating the Zn product, whereas the cadmium cycle starts with creating the Cd-bearing waste and emissions from zinc operations, and includes the steps related to the collection, concentration, and purification of waste/emissions. This approach avoids the allocation of co-products,

Table 9
Emissions allocation based on material output from Zn-ore

Metal	Typical grade in ore (ppm)	Emissions allocation (%)	
Zn	40,000	99.44	
Cd	200	0.50	
Ge	20	0.05	
In	4	0.01	

Table 10 Emissions allocation based on the economic value of products from Zn-ore

Metal	Typical grade in ore (ppm)	Prices 1998 ^a (\$/kg)	Primary production (10 ³ ton/year)	Production economic value (10 ⁶ \$/year)	Emissions' allocation (%)
Zn	40,000	1.1	7000	7700	97.82
Cd	200	0.6	20	46	0.58
Ge	20	1700	0.05	70	0.89
In	4	306	0.2	56	0.71
Total				7872	100

^a US Geological Survey, Commodity Statistics and Information; 1998 Prices for 99.99% Cu; 99.999% Cd; 99.9999% Ge; 99.97% In. http://minerals.usgs.gov/minerals/pubs/metal_prices/.

in agreement with well-accepted LCA practices [28]. Its justification is that zinc production alone determines the amount of cadmium produced; demand for it has zero effect on the quantity of cadmium generated.

However, for sensitivity analyses, I also estimated allocation of emissions according to the ISO's steps 2 and 3. Following step 2, the allocation is based on mass output, and, according to step 3, it is determined by the economic value of the produced metals. Tables 9 and 10 show these allocations. For determining the production economic value for each metal, we use the price (value) of the pure metal, although subprocess 1 produces waste streams, thereby slightly overestimating the allocation of emission to Cd and the other byproducts. The allocation in Table 10 is based on 1998 prices (the most recent year in which data for all metals were published by the USGS). Based on typical grade in Zn ore (40,000 ppm Zn, and 200 Cd), and current (June 27, 2003) prices of 0.78 \$/lb for zinc, and 1.0 \$/kg for cadmium, the economic value ratio of Zn-to-Cd is 168.

4. Manufacturing of CdTe photovoltaics

There are two leading methods of making CdTe/CdS thin films; electrodeposition of CdTe combined with chemical surface deposition of CdS, and high-rate vapor transport of the two compounds.

4.1. Electrodeposition and chemical surface deposition

In electrodeposition, a CdTe thin film is deposited on a substrate attached to the cathode of an electrolytic system using an aqueous solution of cadmium sulfate (CdSO₄) or cadmium chloride (CdCl₂), and tellurium dioxide (TeO₂). During deposition, the concentration of Cd ions is maintained by periodically adding solid precursor to the solution. The concentration of Te ions is kept constant by using a Te anode in addition to the graphite inert anode. The concentration of Cd is maintained between 0.1 and 1.2 M, and that of Te at 10⁻⁴ M, at a pH of 2–3. The electrolytic bath is replenished continuously and less than 1% of Cd and Te are wasted since deposition only occurs on surfaces held at the cathode.

Electrodeposition of CdTe usually is accompanied by chemical-bath deposition (CBD) of CdS, a process that, until recently, had a very low (e.g. <5%) material utilization. Precipitated Cd solids from CBD and residuals on the walls of the bath had to be recycled by converting them to Cd solids suitable for re-use in CdS deposition [29]. In a former commercial facility in Fairfield, CA, all aqueous waste containing Cd and Te compounds, from rinsing, plate stripping, and ion-exchange regeneration, were treated by a two-stage precipitation/ion exchange system that precipitated Cd compounds and, after filtration, removed the Cd solids, producing solutions with Cd levels as low as 10 ppm. In the second stage, the ion-exchange system removed Cd down to the 1–10 ppb range, leaving a liquid that could be disposed of or recycled, via the process deionizing water plant. Precipitated Cd solids were recycled by conversion to Cd salts [29]. In the laboratory, 99.999% cadmium has been recovered from CBD wastes by a combination of leaching and electrodeposition [30].

The volume of waste from CBD that needs to be recycled was reduced remarkably in a new development on CdS deposition. McCandless and Shafarman [31] obtained material utilization of more than 90% by applying the liquid precursors directly on a heated substrate (chemical surface deposition, CSD), instead of dipping it in a heated chemical bath. This already has become the baseline process at the Institute of Energy Conversion, University of Delaware, and will be the basis of our emissions' analysis. The liquid used is an aqueous solution of CdSO₄, CS(NH₂)₂, and NH₄(OH), with Cd⁺⁺ solution concentrations between 1.5 and 3 mM.

In summary, both electrodeposition of CdTe and chemical surface deposition of CdS are about 90% efficient, and, after recycling of the residuals, not more than 1% of the cadmium and tellurium used in the facility would be lost in the form of very dilute liquid and waste streams. Moskowitz et al. [32] estimated that for a 10 MW/year facility, using 1156 kg of CdSO₄ and 880 kg of TeO₂ to deposit a 3 µm CdTe layer, these losses correspond, respectively, to 11.6 kg (6.2 kg of Cd), and 8.8 kg (6.4 kg of Te).

4.2. Vapor transport deposition

In vapor transport deposition, CdS and CdTe are deposited from the compounds in powder form after vaporization in a close-spaced reactor. The current material utilization rates range from 35% to 70%, but higher utilization rates are expected in optimized scaled-up production. Most of the unused vapors condense on the reactor's walls or rollers from where they are removed periodically. The deposits are either disposed of or recycled; recycling is both feasible and economic, and will be practiced in large-scale production. Less than 1% of the vapors are carried in the exhaust stream. The vapor and dust emissions are collected at 99.97% efficiencies² using HEPA filters in the exhaust, and vacuum-HEPA tools during maintenance. The HEPA filters are disposed of as hazardous waste when they are saturated. In CdCl₂ systems, the material is deposited from liquid solutions at 80– 90% utilization efficiency. These systems are totally contained and all residuals are recycled. Under optimized conditions in a large facility, about 10% of the feedstock materials may eventually be disposed in the form of cadmium-contaminated solid wastes. For a 10 MW/year facility using 3720 kg of CdTe, 200 kg of CdS, and 480 kg of CdCl₂, this loss, respectively, amounts to 372, 20, and 48 kg of solid waste, containing a total of 850 kg of Cd. The above estimates are based on currently attainable 10% electrical conversion efficiency, 10% area loss, 83% production yield and 70% material utilization rates for depositing 3 µm CdTe and 0.15 µm CdS layers. Future generation CdTe solar cells may be thinner and production yields may be higher than those we assumed.

The two leading methods of making CdTe thin films—electrodeposition and vapor transport—use cadmium very efficiently. About 1% is wasted in the former process, and about 10–30% in the latter. In both processes, the cadmium is collected and is safely disposed of or recycled. The controlled (with HEPA filters) vapor emissions into the atmosphere amount to 3 g of Cd per ton of Cd used.

5. Operation of CdTe PV modules

5.1. Routine releases

Thin-film α-Si, CdTe, and CIGS solar cells are durable and do not produce any emissions during extreme conditions of accelerated aging in thermal cycles from +80 to -80 °C [33]. Every PV generation, regardless of technology, is a zero-emissions process. The thin CdTe/CdS layers are encapsulated between sheets of glass or plastic. Unless the module is ground to a fine dust, dust particles cannot be generated. The melting point of CdTe is 1041 °C, and evaporation starts at 1050 °C. Sublimation occurs at lower temperatures, but the vapor pressure of CdTe at 800 °C is only 2.5 torr (0.003 atm). The melting point of CdS is 1750 °C and its vapor pressure due to sublimation is only 0.1 torr at 800 °C. Therefore, it is

² For particles of 0.3 μm or larger.

impossible for any vapors or dust to be emitted when using PV modules under normal conditions.

5.2. Potential accidental releases

The only pathways by which people might be exposed to PV compounds from a finished module are by accidentally ingesting flakes or dust particles, or inhaling dust and fumes. Steinberger [34a] addressed the potential of Cd leaching out by rain from broken or degraded CdTe modules at the GSF Institute of Chemical Ecology in Germany. He concluded that CdTe releases are unlikely to occur during accidental breakage. The only scenario of potential exposure is if a fire consumes the PV module and releases cadmium from the material into the air.

In fully developed house fires, flame temperatures can reach 800–1000 °C. In industrial fires where other fuels are present, higher flame temperatures could occur. Steinberger [34b] conducted thermogravimetric analyses of *pure* CdTe and reported that the material, exposed to air, remains stable until about 1050 °C, whereas it started to evaporate at around 900 °C under non-oxidizing conditions

Table 11 Results of fire simulating tests on CdTe PV modules

$T(^{\circ}C)$	500	760	900	1000	1100	
Heating duration (min)	60	30	30	120	240	
Cd weight loss (%)	0.2	0.6	0.4	0.5	0.4	

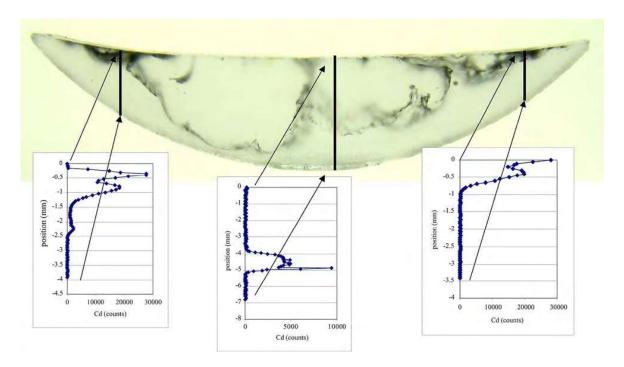


Fig. 5. Cd distribution in PV Glass Run #7, 1000 °C, sample taken from right side of coupon.

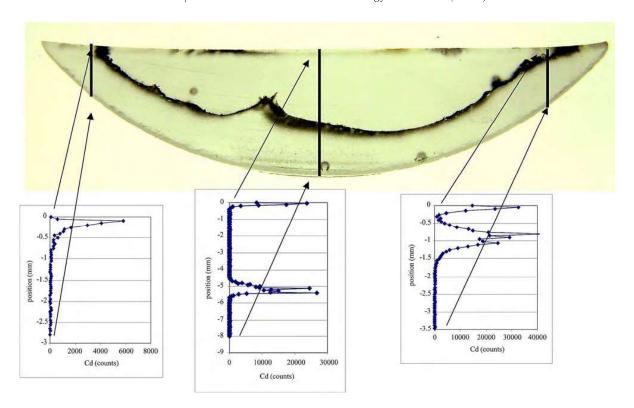


Fig. 6. Cd distribution in PV Glass Run #7, 1000 °C, sample taken from center of coupon.

(lack of air). I note that oxidizing conditions are the only realistic ones for high temperature tests, since lack of oxygen would extinguish the fire.

The fire effect on glass-to-glass encapsulated CdTe modules was recently investigated at BNL. In our studies, 1.5" by 12" pieces (coupons) cut from PV modules were exposed to temperatures of 760–1100 °C, for 30-min to 3 h, following standard protocols by the American Society for Testing and Materials (ASTM) and the Underwriters Laboratories (UL). In these experiments, CdTe was captured in the molten glass and was not released into the environment. Only 0.4% to 0.6% of the Cd content of the coupons was released during these tests (Table 11). This Cd release likely occurred from the open perimeter of the coupon before the two sheets of glass melted together, and is expected to be negligible in whole modules where the ratio of perimeter to surface area is 13.5 times smaller. The dissolution of Cd in the molten glass was confirmed with high-energy synchrotron x-ray microprobe analysis; two samples of these analyses are shown in Figs. 5 and 6. Details of this analysis can be found elsewhere [35].

6. End-of-life disposal or recycling

PV modules are expected to last 25–30 years. Should the modules at the end of their useful life end up in municipal landfills or incinerators, potentially heavy metals could be released into the environment. CdTe PV modules that pass leaching criteria for non-hazardous waste could be disposed of in landfills, according to

current laws. The leachability of metals in landfills currently is characterized by elution tests such as the US-EPA Toxicity Characterization Leachate Profile (TCLP), and the German DEV S4 (Deutsches Einheitsverfahren). Both assume a worst-case scenario. In these tests, small pieces (<1 cm²) of broken modules are suspended and rotated in an eluent for 24 h. The metals present in the eluent then are measured and compared with limits prescribed by each testing protocol. If the metals' concentration exceeds the limits, the modules are demonstrating the metals' leachability and may need to be recycled or disposed of in a hazardous-waste landfill; if the metals are not leaching above the limits, the modules can be disposed of in a commercial landfill. Some early CdTe modules failed the TCLP and the DEV tests [36]. Cunningham [37] reported that the Apollo modules produced by BP Solar pass the TCLP. Environmental regulations can increase the cost and complexity of dealing with end-of-life PV modules. If they were classified as "hazardous" according to Federal or State criteria, then special requirements for material handling, disposal, record keeping, and reporting would escalate the cost of decommissioning. Previous studies showed that PV recycling is technologically and economically feasible, but not without careful forethought [38,39]. A recycling program was outlined, based on current collection- and recycling-infrastructure, and on emerging recycling technologies. Metals from used solar-panels in large centralized applications can be reclaimed in metal-smelting facilities, which use glass as a fluxing agent and recover most of the metals by incorporating them into their product streams. In dispersed operations, small quantities and high transportation costs make this option expensive. For these operations, as well as small-scale recycling, hydrometallurgical separations are economical [40]. These processes start with physically separating module frames, junction boxes and wires; then, the modules are fragmented, and the metals are stripped in successive steps of chemical dissolution, mechanical separation, and precipitation or electrodeposition. Another option is to leave the glass substrate intact (and the SnO₂-conducting layer), potentially allowing their re-use for PV deposition. At the end, the mounts, glass, EVA, and a large fraction of metals are recovered (e.g. 80-96% of Te, Se, Pb). The remaining metals (e.g. Cd, Te, Sn, Ni, Al, Cu) are contained in a sludge, which must be disposed of, or further recycled. The estimated total cost, excluding transportation, is approximately 4–5 ϕ /W. The estimated total cost of recycling in smelters thin-film PV modules or scrap from large installations is about 5 ¢/W; from dispersed installations, it is about 12 ¢/W [39,41]. INMETCO recovers 100% of Cd from Ni-Cd batteries. Such extensive separation could be expected from CdTe PV modules.

A valid assumption is that CdTe PV modules will be either recycled or properly disposed off at the end of their useful life; therefore atmospheric emissions during/after decommissioning will be zero. Even if pieces of modules inadvertently make it to a municipal waste incinerator, cadmium will dissolve in the molten glass and would become part of the solid waste.

7. Total atmospheric emissions

Our estimates of atmospheric cadmium emissions during all the phases of the life of CdTe PV modules are shown in Tables 12–14. Table 12 shows the most likely case (Reference case). The results in Table 13 reflect the allocation of Cd emissions during mining, smelting and refining to Cd as well as Zn production. Allocations based on the mass output and on the economic value of the products were very similar and produced the same results. Table 14 shows estimated emissions assuming worst conditions, i.e. mining/smelting/refining by old methods (outside North America, West Europe and Japan), reduced effectiveness of HEPA filters, and reduced PV module life expectancy.

Our reference estimate of total air emissions is 0.02 g Cd/GWh of electricity produced, which is 25 times lower than the estimate (i.e. 0.5 g Cd/GWh) reported by Alsema [43]. The main contributor to Cd air emission in the later assessment was PV utilization, under the assumption of Cd loss during fires. As discussed earlier, extensive experimental tests proved that Cd is not emitted during fires. Also, our assessment uses more recent data for determining emissions during mining, smelting/refining, and decommissioning of end-of-life products. As discussed in Section 2.1.2 the Cd atmospheric emissions in North America and European smelters have been drastically reduced within the last 10 years.

Table 12
Reference case—atmospheric Cd emissions from the life-cycle of CdTe PV modules

Process	Air emissions	Allocation		Air emissions	
	(g Cd/ton Cd ^a)	(%)	(g Cd/ton Cd)	$(mg Cd/m^2)$	(mg Cd/ GWh)
1. Mining of Zn ores	2.7	0	0	0.00000	0.00
2. Zn smelting/refining	40	0	0	0	0.0
3. Cd purification	6	100	6	0.042	7.79
4. CdTe production	6	100	6	0.042	7.79
5. CdTe PV manufacturing	3	100	3	0.021	3.90
6. CdTe PV operation	0	100	0	0	0.00
7. CdTe PV disposal/	0	100	0	0	0.00
recycling					
Total emissions			15.00	0.11	19.48

Assumptions:

- 1. All emissions during mining/smelting/refining are assigned to Zn production.
- 2. The ratio of Zn to Cd content of Zn ores is 200.
- 3. The mean concentration of Cd in Zn ores is 220 ppm.
- 4. HEPA filters have a 99.97% effectiveness in collecting submicron size particulates in PV manufacturing exhaust streams.
- 5. Emissions per module area and energy output are based on:
 - $7 \text{ g Cd/m}^2 \text{ module}$
 - 10% Electric conversion PV efficiency
 - Average US insolation (1800 kWh/m²/year)
 - 30 years PV module life expectancy, thus
 - 1 kg Cd produces 0.77 GWh over its life-time in PV.
- ^a ton of Cd used in manufacturing.

Table 13
Sensitivity case 1—atmospheric Cd emissions from the life-cycle of CdTe PV modules (Allocation of emissions to co-production of Zn, Cd, Ge and In)

	Air emissions (g Cd/ton Cd ^a)	Allocation	Air emission		
		(%)	(g Cd/ton Cd)	(mg Cd/m ²)	(mg Cd/ GWh)
1. Mining of Zn ores	2.7	0.58	0.0157	0.0001	0.02
2. Zn smelting/refining	40	0.58	0.2320	0.0016	0.30
3. Cd purification	6	100	6	0.042	7.79
4. CdTe production	6	100	6	0.042	7.79
5. CdTe PV manufacturing	3	100	3	0.021	3.90
6. CdTe PV operation	0	100	0	0	0.00
7. CdTe PV disposal/recycling	, 0	100	0	0	0.00
Total emissions	7		15.25	0.11	19.80

Assumptions:

- 1. Mining of zinc ores produces 30 g of dust per ton of ore.
- 2. Smelting/refining of Zn produces 0.2 g of Cd per ton of Zn production
- 3. The ratio of Zn to Cd content of Zn ores is 200.
- 4. The mean concentration of Cd in Zn ores is 220 ppm.
- 5. HEPA filters have a 99.97% effectiveness in collecting submicron size particulates in PV manufacturing exhaust streams.
- 6. Emissions per module area and energy output are based on:
 - 7 g Cd/m² module
 - 10% electric conversion PV efficiency
 - Average US insolation (1800 kWh/m²/year)
 - 30 years PV module life expectancy, thus
 - 1 kg Cd produces 0.77 GWh over its life-time in PV

8. Comparisons with other energy technologies

The total Cd use in the United States in 1997 was 2600 tons; globally, it is approximately 20,000 tons per year. Cadmium is employed primarily (~65%) in nickel-cadmium rechargeable batteries, paint pigments (~17%), plastic stabilizers (~10%), for metal plating (~5%), and metal solders (~2%). Using only 1.5–3% of the nation's consumption of cadmium in manufacturing CdTe solar cells (i.e. 40–80 ton/year) would generate over 1 GW of new PV per year. I note that the total current PV capacity in the United States is only 0.3 GW and is projected to grow (under optimistic assumptions) to about 3.2 GW/year by 2020. Even envisioning an order-of-magnitude higher PV production (e.g. 32 GW/year) would require only about a sixth to a third of the current US Cd consumption. New solar energy at such very large scales would significantly change the mix of electricity sources in the US and abroad, preventing carbon dioxide and other emissions.

It is interesting to compare Cd flows in CdTe PV with those in Ni–Cd batteries and coal-burning power plants.

^a ton of Cd used in manufacturing.

Table 14
Sensitivity case 2—atmospheric Cd emissions from the life-cycle of CdTe PV modules (*Worst cases* in mining/smelting/refining, PV use and PV manufacturing)

			Air emissio	issions			
		(%)	(g Cd/ton Cd)	$(mg Cd/m^2)$	(mg Cd/ GWh)		
1. Mining of Zn ores	27	0.58	0.1566	0.0011	0.29		
2. Zn smelting/refining	1000	0.58	5.8000	0.0406	10.76		
3. Cd purification	12	100	12	0.084	22.26		
4. CdTe production	12	100	12	0.084	22.26		
5. CdTe PV manufacturing	6	100	6	0.042	8.57		
6. Fires during CdTe PV operation	0	100	0	0	0.00		
7. CdTe PV disposal/recycling Total emissions	0	100	0 35.96	0 0.25	0.00 66.71		

Assumptions:

- 1. Mining of zinc ores produces 30 g of dust per ton of ore.
- 2. Smelting/refining of Zn produces 50 g of Cd per ton of Zn production (old, thermal method).
- 3. The ratio of Zn to Cd content of Zn ores is 200.
- 4. The mean concentration of Cd in Zn ores is 220 ppm.
- 5. HEPA filters effectiveness in PV manufacturing reduced by a factor of 2 to 99.93%.
- 6. Emissions per module area and energy output are based on:
 - $7 \text{ g Cd/m}^2 \text{ module}$

10% electric conversion PV efficiency

Average US insolation (1800 kWh/m²/year)

20 years PV module life expectancy

thus, 1 kg Cd produces 0.51 GWh over its life-time in PV

8.1. Ni–Cd batteries

As discussed in Section 3, using Cd in Ni–Cd batteries is widely considered to be the least dissipative of its current major uses, and, therefore, the friendliest to the environment. This is because Ni–Cd batteries can be collected and their Cd content effectively recycled. For example, Ni–Cd batteries collected in the United States are recycled at the International Metals Reclamation Company (INMETCO) facility in Ellwood City, Pennsylvania. The plant relies on High Temperature Metal Recovery and produces cadmium at a 99.95% purity level that is used in new Ni–Cd rechargeable batteries.

However, the problem with small consumer type batteries is collecting them. In contrast, PV modules by virtue of their size would be more difficult to "escape" collection and end inadvertently in a landfill or municipal-waste incineration plant.

Cadmium in Ni–Cd batteries is in the form of Cd and Cd(OH)₂, materials which are less stable and more soluble than CdTe (Table 15). The latter is less soluble and possibly less toxic than its parent compound. CdTe modules are very well sealed and Cd cannot be released during normal operation, or even during fires in residential roofs.

^a ton of Cd used in manufacturing.

Table 15 Characteristics of Cd compounds used in Ni–Cd batteries and CdTe PV

Compound	$T_{\mathrm{melting}} (^{\circ}\mathrm{C})$	$T_{\text{boiling}} (^{\circ} C)$	Solubility (g/100 cc)	Carcinogen
Cd	321	765	Insoluble	Yes
$Cd(OH)_2$	300	_	2.6×10^{-4}	Yes
CdTe	1041	_	Insoluble	?
CdS	1750	-	1×10^{-4}	Likely
$CdCl_2$	568	960	140	Yes

The amount of Cd in a Ni–Cd batteries ranges from 3.2 to 21 g depending on the battery's size (Table 16). The amount of Cd in CdTe solar cells is very small, and could be reduced even further as the cells become thinner; a Ni–Cd C-size flashlight battery contains more Cd than a square meter of today's CdTe PV module. The Ni–Cd battery industry estimates that an AA or C size Ni–Cd battery can be re-charged 700–1200 times over its life [42]. Under this assumption, a battery would produce an average of 0.046 kWh per g of its weight, which corresponds to 0.306 kWh per g of Cd contained in the battery. This is a 2500 times lower efficiency in using Cd than in a CdTe PV module.

8.2. Coal-burning power plants

Other investigators have compared potential Cd emissions from operation of photovoltaics and from the operation of coal-burning power plants [43]. First, I note that such comparisons are erroneous since they compare potential *accidental* emissions from PV systems to *routine* (*unavoidable*) emissions from modern coal-fired plants. Second, assuming a 10% or higher release rate for Cd from CdTe PV, was recently found to be invalid. Our quantification of such releases for glass–glass encapsulated modules, under a wide range of fire conditions, showed that Cd diffuses in the molten glass and is not released in the environment.

Coal-fired power plants routinely generate Cd during operation in contrast to PV which can not generate emissions during normal use. According to data from the US Electric Power Research Institute (EPRI), under the best/optimized operational and maintenance conditions, burning coal for electricity releases into the air generates a *minimum* of 2 g of Cd/GWh (assuming well-maintained electrostatic precipitators or baghouses operating at 98.6% efficiency, and median concentration

Table 16 Cd Content in CdTe PV and NiCd batteries

	g/unit	mg/kWh (kg/Gwh)
PV CdTe	7 g/m^2	1.3
NiCd battery—AA size	3.2	3265
NiCd battery—C size	10.5	3265
NiCd battery—C size	21	3265

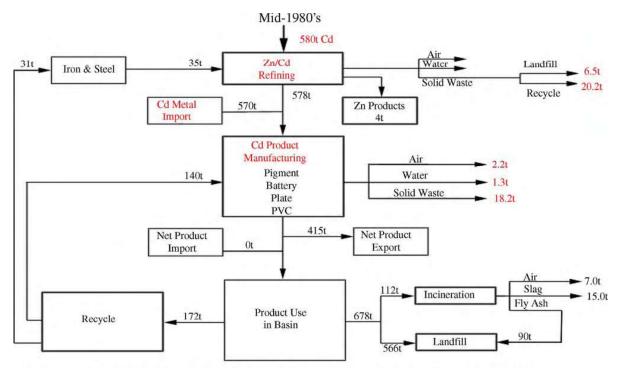
of Cd in US coal of 0.5 ppm)[44]. It is noted, that although very high effectiveness is expected for ESPs operating in North American, Western European and Japanese power plants, ESPs are much less effective, if they are installed at all, in developing, coal-burning countries. In addition, 140 g/GWh of Cd inevitably collects as fine dust in boilers, baghouses, and ESPs, thereby posing occupational health- and environmental-hazards. Furthermore, a typical US coal-power plant emits per GWh about 1000 tons of CO_2 , 8 tons of SO_2 , 3 tons of SO_2 , and 0.4 tons particulates.

9. A fundamental question: what happens to cadmium if it is not used?

As discussed in Section 2, cadmium is mainly a byproduct of zinc smelting, and its supply is proportional to the supply of zinc. When the market does not absorb all the Cd generated by metal smelters, the residues from which Cd is recovered are either stockpiled for future use, cemented and buried, or disposed of [45].

Therefore, there are two strategies for reducing the environmental releases of cadmium. The first is to cut back on producing and consuming zinc, and the second is to use cadmium in ways that prevent its flow to the environment. It is important to distinguish the uses of cadmium in terms of its dissipation (i.e. the degree of inevitable spreading into the environment), and cadmium-bearing waste streams in terms of their physical and chemical forms as they affect mobility and toxicity. Cadmium in fertilizers is inherently dissipative, whereas Cd in Ni/Cd batteries and photovoltaics is not, since the products can be collected at the end of their useful life. Although some dissipative uses of zinc (e.g. in pigments, chemicals) might be curtailed, it would be hard to find replacements for its major uses (e.g. steel corrosion protection, die casting, brass and bronze products). The most obvious way to cut down on the production of zinc, and subsequently cadmium, is to encourage recovery and recycling of secondary zinc, especially from galvanized metal sheet and zinc-based cells [46].

Regarding safe to the environment uses, major European studies have pointed out that using cadmium in Ni–Cd batteries is such a use, provided that they can be remanufactured or recycled effectively [19,46]. The Rhine Basin, one of the most industrialized regions of the world, experienced cadmium contamination in the 1980s from using phosphate fertilizers, and from the emissions of zinc smelters, steel production plants and coal-fired power plants. The largest contributor to cadmium contamination in the Rhine Basin was likely the production of cadmium, and the production, use, and disposal of cadmium products (Fig. 7) [19]. Cadmium metal, some of which is produced at the region's zinc refineries and some of which is imported, is the input to plants that manufacture the four major cadmium-containing products; pigments (mostly for plastics), nickel–cadmium (Ni–Cd) batteries, plates (for surface protection of steel and other metals), and stabilizers (in PVC plastic). Emissions of cadmium occurred for each of these manufacturing sectors. The Rhine Region study of industrial metabolism provided valuable insights into the various flows and environmental interactions of metals in the region. One



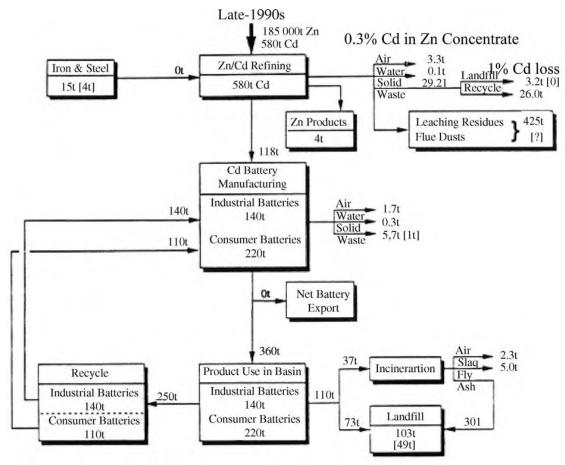
source: stigliani & Anderberg, Chapter 7, Industrial Metabolism, The UN University, 1994

Fig. 7. Cd flow in the Rhine Basin, 1980s [19].

of the scenarios explored is banning the dissipative uses of cadmium in the region and recycling 50% of the Ni–Cd batteries (Fig. 8). The following conclusion refers to this scenario [19]:

"So, the ultimate effect of banning Cd products and recycling 50% of disposed consumer batteries may be to shift the pollution load from the product disposal phase to the Zn/Cd production phase. This does not imply that banning Cd-containing products is not a wise strategy; rather, it indicates that if such a ban were to be implemented, special provisions would have to be made for the safe handling of surplus Cd wastes generated at the Zn refineries. One possible option would be to allow the production and use of Cd-containing products with inherently low availability for leaching. The other option, depositing the Cd-containing wastes in safely contained landfills, has other risks."

Some argued that using Cd to construct statues might be a good option [47]. However, it may not be a value-adding one. I concluded that using Cd in CdTe PV modules is more environmentally friendly than any other current approach. Such use is non-dissipative and the product is very stable. Compared to Ni–Cd batteries, CdTe photovoltaics use CdTe, a more stable compound than either Cd or Cd(OH)₂. CdTe modules are very well sealed and Cd cannot be released during normal operation, or even during accidental fires or breakage of PV modules. In addition, PV modules are much bulkier and, therefore, are much easier to collect



Source: Boehm and Schaefers (1990)

Fig. 8. Cd flow in the Rhine Basin, 1990s [19].

for recycling or safe disposal than consumer batteries. Using Cd in CdTe PV modules effectively isolates and sequesters this compound.

10. Conclusion

The flows and emissions of cadmium in CdTe PV modules were studied in detail for all the different phases of large-scale implementation of this technology. The following conclusions were derived for the different phases of the life of CdTe PV modules.

10.1. Cd production

Cadmium is produced primarily as a byproduct of zinc production. Because Zn is generated in very large quantities, there are substantial amounts of cadmium generated as byproduct. Then, no matter how much Cd is used in PV, the excess can either be put to *beneficial* uses or *discharged* into the environment. When the market does not absorb the Cd generated by metal smelters/refiners, it is cemented

and buried, stored for future use, or disposed of to landfills as hazardous waste. Arguably, encapsulating cadmium as CdTe in PV modules presents a safer option than its current uses and is much preferred to its disposal.

10.2. CdTe PV manufacturing

The two leading methods of making CdTe thin films—electrodeposition and vapor transport—use cadmium very efficiently. About 1% is wasted in the electrodeposition process, and about 10–30% is wasted in the vapor-transport process. In both processes, the cadmium can be collected and can be safely disposed of or recycled.

10.3. CdTe PV use

No emissions of any kind can be generated when using PV modules under normal conditions and during foreseeable accidents (e.g. fires, breakage). New studies proved that CdTe in glass-glass modules would not be released during fires because Cd dissolves into the molten glass and is retained there. Any comparisons made with cadmium emissions from modern coal-fired power plants are erroneous because they compare unlikely potential accidental emissions from PV systems to routine (unavoidable) emissions from conventional power plants. In reality, when PV replaces coal burning for electricity generation, it will prevent Cd emissions as well as large quantities of CO₂, NO_x, and particulate emissions. By comparison with Ni–Cd batteries, a CdTe PV module uses Cd about 2500 times more efficiently in producing electricity. A 1 KW CdTe PV system contains less cadmium than 10 size-C Ni–Cd batteries. Furthermore, CdTe is more stable and less soluble than the cadmium components used in batteries.

10.4. CdTe PV decommissioning

Releases to the aquatic environment could occur after decommissioning only if such modules end up in municipal landfills and the materials leach out. However, cadmium telluride is encapsulated between two sheets of glass and is unlikely to leach to the environment under normal conditions. No atmospheric emissions of Cd can occur under any foreseeable conditions. The PV industry is considering recycling of these modules at the end of their useful life; this would completely resolve any environmental concerns.

In summary, the environmental risks from CdTe PV are minimal. The estimated atmospheric emissions of 0.02 g of Cd per GWh of electricity produced during all the phases of the modules' life, are extremely low. Large-scale use of CdTe PV modules does not present any risks to health and the environment, and recycling the modules at the end of their useful life completely resolves any environmental concerns. During their operation, these modules do not produce any pollutants, and, furthermore, by displacing fossil fuels, they offer great environmental benefits. CdTe in PV appears to be more environmentally friendly than all other current uses of Cd, including Ni–Cd batteries.

Acknowledgements

The experimental investigation of emissions and redistribution of elements shown in Table 11 and Fig. 5 and 6 was conducted by John Heiser and Mark Fuhrman; their contributions are gratefully acknowledged. This work was supported by the Solar Technologies Program, Conservation and Renewable Energy, under Contract DE-AC02-76CH000016 with the US Department of Energy. Many thanks to Alec Bulawka, Jeff Maser, Richard King and Ray Sutula, DOE, and Ken Zweibel, NREL for their support and guidance.

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Prog. Photovolt. Res. Appl. 6, 99-103 (1998)

Utrecht Workshop

Health, Safety and Environmental Risks from the Operation of CdTe and CIS Thin-film Modules

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This paper identifies the materials embedded in one type of CIS (copper indium diselenide) and four different types of CdTe (cadmium telluride) thin-film modules. It refers to the results of our outdoor leaching experiments on photovoltaic (PV) samples broken into small fragments. Estimations for module accidents on the roof or in the garden of a residential house, e.g. leaching of hazardous materials into water or soil, are given. The outcomes of our estimations show some module materials released into water or soil during leaching accidents. In a worst-case scenario for CdTe modules the leached cadmium concentration in the collected water is estimated to be no higher than the German drinking water limit concentration. For the CIS module scenario the estimated leached element concentrations are about one to two orders of magnitude below the German drinking water limit concentration. For broken CIS and CdTe modules on the ground no critical increase of the natural element concentration is observed after leaching into the soil for 1 year. © 1998 John Wiley & Sons, Ltd.

INTRODUCTION

Large-scale and highly efficient CdTe and CIS modules consist of various active layers deposited on a substrate. The goal of a low-cost photovoltaic (PV) module operation demands optimized material selection to guarantee product quality and module stability on a long-term basis. In many PV applications the modules are exposed to extreme environmental conditions. Some modules are used under limited maintenance. Weather influences or human mishandling can cause technical defects of modules during operation. These problems are associated with material releases into the environment.

METHODOLOGY

The potential risks for the environment and health from thin-film modules may come from the release of hazardous substances, therefore we first identified the type and amount of chemical materials present in the investigated modules. By looking into the literature and interviewing the manufacturers, we derived the material selection and their mass contribution.

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100 H. STEINBERGER

The release of critical materials occurs only in the case of crushed or broken modules, when the rainwater can reach the active layers and leach out substances of the module fragments. In our outdoor experiments with broken modules we determined the leaching rate of module materials under normal PV operational conditions in the city of Munich, Germany. The experimental set-up comprised three boxes: one box with a module crushed into about 10 mm pieces, one box with an unbroken module and one box without any module as a blank. Rainfall could be collected in each box an drained into separate bottles for sampling. The eluates of these bottles were analysed weekly. All three boxes were oriented south and had a 48° tilt angle.

In a theoretical model together with experimental leaching data we considered a residential house with PV modules on the roof. The model has been split into two scenarios for the estimations with respect to concentrations in water and soil: the broken module remains on the roof; and the module falls down to the ground. The estimated concentrations of critical elements were then compared to (legislative and guideline) limit concentrations, if available, in order to assess potential risks for the environment and human health.

MATERIALS

Material content of the modules

Table I provides a survey of the type and quantity of materials contained in the modules and identified within the framework of this work. The values represent the amount of material present at operation of the thin-film modules. The weight of the glass substrate used for the deposition of the thin films varies between 4·7 and 12·4 kg m⁻². For the encapsulation materials (front and back cover of glass and/or metal, EVA sheet, aluminium or metal frame, insulation or adhesive material, electrical contacts, etc) a weight of 10 kg was determined for all four CdTe modules as well as for the CIS module. However, the shares of the encapsulation materials involved varied considerably. Module CdTe 3 is commercially available and uses rather thick CdTe and CdS layers due to the screen-printing technique.

SCENARIOS

Fracture of the modules and entry of substances into garden or household water

In principle, only substances in solution are biologically available and thus have a potential effect on humans. In this context, we observe the hypothetical case of a module fracture on the PV roof of a residential house, which is also used for collecting water for garden irrigation or household water.

	CdTe 1	CdTe 2	CdTe 3	CdTe 4	CIS
CdS	0.96	28.9	48.2	1.4	0.24
CdTe	12.4	37-2	62.0	15.5	_
Cd total	6.55	39.8	66.4	8.3	0.19
Te	6.6	19.8	33.0	8.3	_
Cu	_	_	_	_	1.95
In	_	_	_	_	3.75
Se	_	_	_	_	4.95
Mo	_	_	_	_	8.16
Zn	7	-	_	_	6.78
Glass substrate	4960	7 400	4 660	12 400	4960
Encapsulation material	10 000	10 000	10 000	10 000	10 000

Table I. Material content (in g m⁻²) of thin-film modules¹

Element Concentration in the Concentration in the water Limit concentration of the collected from the roof outdoor test eluates German drinking water regulation CIS $10.5 \ \mu g \ l^{-1}$ $5 \text{ mg } 1^{-1} \text{ (guideline)}$ Zinc $2.1 \text{ mg } 1^{-1}$ 2.5 mg 1⁻¹ $12.5 \; \mu g \; 1^{-1}$ Molybdenum 0.4 mg 1-1 $2 \mu g 1^{-1}$ $10~\mu g~l^{-1}$ Selenium Cadmium $10 \mu g 1^{-1}$ 50 ng 1⁻¹ $5 \mu g 1^{-1}$ $30 \ \mu g \ 1^{-1}$ 150 ng 1⁻¹ Indium CdTe $1 \text{ mg } 1^{-1}$ $5 \mu g 1^{-1}$ $5 \mu g 1^{-1}$ Cadmium 0.3 mg 1-1 $1.5 \ \mu g \ l^{-1}$ Tellurium 0·1 mg 1⁻¹ $5~\mu g~l^{-1}$ Nickel $50 \mu g 1^{-1}$

Table II. Comparison of the element concentrations of the broken CIS and CdTe modules and the German regulations on drinking water

The following assumptions characterize the scenario:

- (i) The broken module has an area of 0.5 m^2 .
- (ii) The total PV roof area is 100 m².
 - \Rightarrow The area ratio is 1/200.

The German regulation on drinking water² provides limit concentrations for elements in drinking or household water. Their purpose is to avoid any negative effects for humans, even under constant exposure. In the worst-case scenario one can assume that people drink water collected from the roof on a regular basis. Thus, the limit concentrations of the German drinking water regulation are suitable for comparison to the element concentration in the water collected from the roof under the abovementioned assumptions.

Column 2 in Table II shows the concentration in the eluates from the outdoor test. Its element concentrations are taken from test conditions representing the most unfavourable case, i.e. a breaking of the module into relatively small fractions on purpose. The more common incident—a fracture due to stone impact or mechanical stress—will usually result in a much less extensive destruction of the module. Column 3 of Table II shows the element concentration in the roof-collected water. It corresponds to rain falling onto a roof of total area of 100 m² and washing out the contents of fragments of a 0·5 m² module. Column 4 represents the limit concentration of the German drinking water regulation.

For the CIS module type the zinc and cadmium concentration are approximately two and the selenium concentration one order of magnitude below the German drinking water limit concentration. The cadmium concentration of the CdTe module is in the regime of the German regulation. Generally, even in this worst-case scenario, only an insignificant danger for human health can be expected.

Fracture of the modules and entry of substances into soil

Due to a release of elements from the thin-film solar modules, critical substances may enter into soil as a consequence of washing out. As a comparison for the data gained in the outdoor tests with broken modules, here the Kloke list³ is used (Table III). This list is a comprehensive collection of basic data on the total amounts of individual elements that can be tolerated. It was used as a fundamental guideline for the regulations on sewage plants⁴ and a ruling of the State of Baden-Württemberg (Germany) on heavy-metal pollution on soil.⁵

This scenario is characterized by the following assumptions:

(i) The defect module remains on location in the garden for an entire year.

H. STEINBERGER

Table III. Broken CIS and CdTe modules: increase and natural concentration in soil-comparison to Kloke list³

Element	Increase of concentration in soil	Natural concentration in soil	Tolerable concentration (Kloke)
CIC			·
CIS Cadmium	83 $\mu g \ kg^{-1}$	0·1-1 mg kg ⁻¹	3 mg kg^{-1}
Gallium	16 μg kg ⁻¹	$5 \times 10^{-4}\%^{a}$	10 mg kg ⁻¹
Indium	20 μg kg ⁻¹	$10^{-45} \text{ mg kg}^{-1a}$	-
Copper	$10 \mu \text{g kg}^{-1}$	$1-20 \text{ mg kg}^{-1}$	100 mg kg^{-1}
Molybdenum	2.2 mg kg^{-1}	$0.5-5 \text{ mg kg}^{-1}$	5 mg kg^{-1}
Selenium	0.3 mg kg^{-1}	$0.1-4.3 \text{ mg kg}^{-1}$	10 mg kg^{-1}
Zinc	$2 \cdot 2 \text{ mg kg}^{-1}$	$3-50 \text{ mg kg}^{-1}$	300 mg kg^{-1}
CdTe			
Cadmium	$240~\mu g~k g^{-1}$	$0.1-1 \text{ mg kg}^{-1}$	3 mg kg^{-1}
Nickel	$30 \mu g kg^{-1}$	$2-50 \text{ mg kg}^{-1}$	50 mg kg^{-1}
Tellurium	$160 \ \mu g \ kg^{-1}$	$10 \ \mu g \ kg^{-1a}$	-

^aAbundance in the earth's crust.⁷

- (ii) Leached substances distribute in the soil down to a depth of 25 cm over the module area.
- (iii) The density of the soil amounts to $1.2 \text{ kg } 1^{-1}$ (according to Ref. 6, the soil densities range from $1.2 \text{ to } 1.8 \text{ kg } 1^{-1}$).

A comparison of the data demonstrates that in most cases the natural abundance of an element in the soil is increased only slightly due to eluates from broken solar modules. Moreover, for almost all elements the concentration in the soil remains below the tolerable concentration according to the Kloke list. Only for indium and tellurium is such a comparison not possible due to a lack of threshold values in the Kloke list.

CONCLUSIONS

During normal operation a release of critical elements into the environment and, finally, to humans can only occur as a consequence of accidents. Yet all investigated release scenarios, e.g. leaching of broken modules into garden water or into soil of a residential house, did not point towards an acute danger to human beings or the environment.

For a long-term bulk production, however, we have to expect a huge number of defect modules as a consequence of the end of the module lifetime. This corresponds to the amount of modules produced at the beginning of their lifetime. Thus module disposing in landfills is limited for two reasons: the loss of high-quality materials like metals or glass, the increasing leaching concentration of critical materials in the drain water of the landfill. This situation occurs when the volume concentration of dumped modules becomes higher than in the scenario of crushed modules on the ground. As a consequence, PV module recycling seems to be a major issue for future manufacturing and developing efforts.

Acknowledgements

This work was supported by the Bundesministerium für Bildung and Forschung BMBF (German Ministry for Education and Research). I acknowledge the important contributions to this work from Werner Thumm, Institut für Ökologische Chemie, GSF Forschungszentrum, Munich, Germany and from Paul Moskowitz, Department of Applied Science, Brookhaven National Laboratory, Upton, NY, USA.

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Prog. Photovolt: Res. Appl. (in press)

Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/pip.624

Broader Perspectives

Emissions and Encapsulation of Cadmium in CdTe PV Modules During Fires[‡]

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Fires in residential and commercial properties are not uncommon. If such fires involve the roof, photovoltaic arrays mounted on the roof will be exposed to the flames. The amount of cadmium that can be released in fires involving CdTe PV and the magnitude of associated health risks has been debated. The current study aims in delineating this issue. Previous thermogravimetric studies of CdTe, involved pure CdTe and single-glass PV modules. The current study is based on glass-glass CdTe PV modules which are the only ones in the market. Pieces of commercial CdTe photovoltaic (PV) modules, sizes 25×3 cm, were heated to temperatures up to 1100°C to simulate exposure to residential and commercial building fires. The temperature rate and duration in these experiments were defined according to standard protocols. Four different types of analysis were performed to investigate emissions and redistribution of elements in the matrix of heated CdTe PV modules: (1) measurements of sample weight loss as a function of temperature; (2) analyses of Cd and Te in the gaseous emissions; (3) Cd distribution in the heated glass using synchrotron X-ray fluorescence microprobe analysis; and (4) chemical analysis for Cd and Te in the acid-digested glass. These experiments showed that almost all (i.e., 99.5%) of the cadmium content of CdTe PV modules was encapsulated in the molten glass matrix; a small amount of Cd escaped from the perimeter of the samples before the two sheets of glass melted together. Adjusting for this loss in full-size modules, results in 99.96% retention of Cd. Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the US (e.g., 10^{-4}), results in emissions of 0.06 mg/GWh; the probability of sustained fires and subsequent emissions in adequately designed and maintained utility systems appears to be zero. Published in 2005 by John Wiley & Sons, Ltd.

KEY WORDS: CdTe; photovoltaics; LCA; life-cycle assessment; fire emissions; cadmium; leaching; ion-exchange

Contract/grant sponsor: US Department of Energy; contract/grant number: DE-AC02-76CH000016.

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 $^{^\}ddagger$ This article is a U.S. Government work and is in the public domain in the U.S.A.

1. INTRODUCTION

In the United States, about 1 in 10 000 wood-frame houses may catch fire during the year. If such fires involve the roof, photovoltaic arrays that are mounted there would be exposed to the flames. There are no studies in the literature regarding fire effects on a utility scale PV system, and we are not aware of a reported fire in any utility PV system. Tucson Electric in Arizona, US, has experienced two cases of incorrect wiring that each caused melting of a glass module, and also three cases of small fires in metal DC terminal boxes due to bad connections, but none of these incidents caused a fire to the rest of the field. In addition there were six documented lighting strikes on PV arrays, none of which resulted in a fire. Overall, due to the lack of combustible materials, the risk of a fire that could consume a utility array is extremely small. There is a risk of fire from external fuel sources (e.g., grass/bush fires), but this is controlled through design and operational practices (e.g., metal enclosures of potential ignition sources, firebreaks, controlling vegetation, limited access). Therefore, our study was designed to simulate the potential of toxic emissions only from roof-mounted photovoltaic arrays.

Previous thermogravimetric studies of CdTe at the GSF Institute of Chemical Ecology in Munich, Germany, involved pure CdTe and a small number of tests on single glass PV modules. The pure CdTe tests showed a small weight increase between 570 and 800°C, possibly due to oxidation. The oxidized product remained stable until about 1050°C, above which the compound began to vaporize. Other experiments at non-oxidizing conditions (Ar atmosphere), showed a high loss of CdTe in the 900–1050°C range. No experiments involving CdTe encapsulated between two sheets of glass are reported.

The current study is based on glass–CdTe–glass PV modules, which are the only ones in the market. (Single-glass panels are not considered by any manufacturer at this time). Pieces of commercial CdTe photovoltaic (PV) modules, approximately 25×3 cm, were heated to temperatures up to about 1100° C to simulate exposure to residential fires. The heating rate and duration in these experiments were defined according to standard Underwriters Laboratories (UL)³ and American Society for Testing and Materials (ASTM)⁴ test protocols. The total mass loss was calculated by weight measurements. The amounts of Cd and Te releases to the atmosphere were calculated by capturing these elements in solutions of nitric acid or hydrochloric acid and hydrogen peroxide. Also, the distribution of Cd in the burnt pieces was measured with synchrotron X-ray microprobe analysis.

2. CdTe PV MODULE THERMAL CHARACTERISTICS

The composition of the tested samples is shown in Table I. These samples were cut from standard commercial modules produced by First Solar Inc. of Toledo, Ohio. The frames, rails and wires were not included in the experiments. The concentration of the metals was determined by grinding a control piece and leaching in acid/oxidizer solution; these were also cross-referenced with mass balance calculations at the manufacturing plant scale. The concentrations of the glass and ethylene vinyl acetate (EVA) are based on weight measurements.

Table I. Composition of samples

Compound	wt (%)
Total glass	96.061
EVA	2.614
Total Cd	0.059*
Total Te	0.063*
Total Cu	0.011*
Other	1.192

^{*}The uncertainty of these measurements is 5% as determined by ICP analysis.

Table II. CdTe vapor pressure coefficients for equation (2)

A	В	T(K)	Reference
-9500	6.427	731–922	7
-11493	7.99	1085-1324	8
-9764	6.572	773-1010	9
-10000	6.823	1053–1212	10

The EVA is expected to either burn or decompose at approximately 450°C according to experiments involving EVA and back surface sheet on crystalline Si cells.⁵

The module's substrate and front cover are sheets of glass, which has a softening point of 715°C. The following compounds are present or can be formed during the heating (CdTe, CdS, CdO, TeO₂, TeO₄, CdCl₂ and CuCl₂); other oxides may also be formed. Some of these compounds produce vapors by sublimation at temperatures below their melting points.

The sublimation of pure CdTe is described by the reaction:⁶

$$CdTe(s) = Cd(g) + 0.5Te_2(g)$$
(1)

The vapor pressure due to sublimation of CdTe is estimated by the Antoine equation:

$$\log P(\text{atm}) = AT^{-1} + B \tag{2}$$

Values for the coefficients A and B are shown in Table II.

As shown by the CdTe curves in Figure 1, these four sets of coefficients give approximately the same vapor pressure estimates.

The vapor pressure of pure CdS and TeO₂ can be estimated by the following equation 11,12

$$\log P(\text{mm Hg}) = A + BT^{-1} + C\log T + DT + ET^{2}$$
(3)

where the constants A, B, C, D and E are listed in Table III.

As shown in Figure 1, CdS has the lowest vapor pressure of the considered pure cadmium compounds. The vapor pressure of CdTe is two orders of magnitude lower than that of $CdCl_2$ in the temperature range of our experiments. The CdTe pressure due to sublimation at $800^{\circ}C$ is about 2.4 torr.

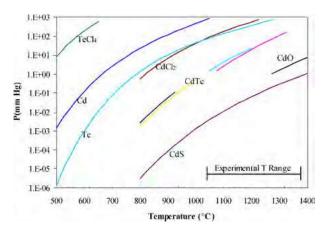


Figure 1. Vapor pressure of cadmium compounds

	Table III. Vapor pressure coefficients for equation (3)									
Component	A	В	C	D	E	T(K)				
CdS(s)	16.06	-11460	-2.5	_	_	298–1203				
$CdCl_2(s)$	17.46	-9270	-2.11	_	_	298-840				
$CdCl_2(1)$	25.907	-9183	-5.04	_	_	840-1233				
CdO(s)	42.8498	-15443	-10.651	2.0645×10^{-3}	-1.704×10^{-7}	1273-1832				
$TeO_2(s)$	23.51	-13940	-3.52	_	_	298-10006				
TeCl ₄	225.5681	-13194	-80.8999	4.5316×10^{-2}	-1.044×10^{-5}	506-665				

Table III. Vapor pressure coefficients for equation (3)

3. THERMOGRAVIMETRIC TESTS

Typical flame temperatures in residential fires are in the 800–900°C range for roof fires and 900–1000°C in fires involving the whole house as measured in basement rooms. ¹³ In this study we extended this range to the limit of our heating apparatus, which was 1100°C.

3.1. Protocol

There are several validated fire test methods used by the industry and the government in evaluating flammability and fire resistance of materials. Two test methods which are applicable to our task are the Underwriters Laboratories Inc., UL Standard 1256 for Fire Test of Roof Deck Constructions,³ and the American Society for Testing and Materials (ASTM) Standard E119-98 for Fire Tests of Building Construction and Materials. The later is also adopted by the Uniform Building Code as UBC Standard 7-1. The UL 1256 Standard involves direct fire heating at 760°C, for 30 min. The ASTM Standard involves gradual heating controlled to conform to the standard time-temperature curve shown in Figure 2. Our tests were done in a tube furnace where we adjusted the heating rate to exactly follow this standard temperature rate curve. Pieces of commercial CdTe photovoltaic (PV) modules, nominally 25×3 cm were used. The furnace was heated by electrical resistance and contained three zones, so uniformity of the central heated zone was accomplished. The pieces of PV module were placed on alumina plates and were positioned inside a quartz tube in the central uniform-temperature zone of the oven. The tube was fitted with an inlet and outlet for gas flow and was sealed from the outside atmosphere. Air was introduced into the furnace at a rate of 10 l/min, producing a linear velocity of 0.04 m/s above the sample. The airflow carried any released vapor/aerosols from the PV sample to the outlet. The effluent flow was passed through a glass-wool filter and two bubbler-scrubbers in series containing a 0.01 M nitric acid solution in order to capture the Cd and Te releases from the PV module. The quartz tube and glass-wool were leached for 24 h in nitric acid. Complete removal of the metals from the glass-wool filters was verified by additional leaching using hydrochloric acid and hydrogen peroxide solutions for 48 h in a tumbling machine.

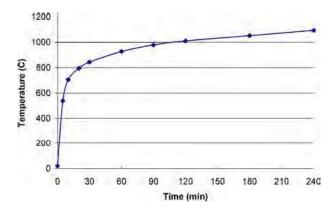


Figure 2. Temperature and heating duration for each experiment (as per ASTM E119-98 Standard)

			Cd	emissions	Te emissions		
Test	<i>T</i> (°C)	Weight loss (% sample)	(g/m ²)	(% of Cd content)	(g/m^2)	(% of Te content)	
1	760	1.9	0.056	0.6	0.046	0.4	
2	900	2.1	0.033	0.4	0.141	1.2	
3	1000	1.9	0.048	0.5	1.334	11.6	
4	1100	2.2	0.037	0.4	2.680	22.5	

3.2. Results

The PV samples were weighed before and after each experiment. Weight loss in the range of 1.9-2.2% of the total weight was recorded (Table IV). Observations of black residues in the reactor walls and filters indicate that most of this weight loss was caused by the decomposition and vaporization of EVA.

The acidic solutions from rinsing of the reactor walls, rinsing of the glass-wool filters in the reactor exhaust, and the scrubber liquids, were analyzed for Cd and Te by inductively coupled plasma (ICP) optical emission spectroscopy (Varian Liberty 100). A small loss of Cd amounting to 0·4–0·6% of the total Cd in the sample was recorded (Table IV). The loss of Te was also very small during heating at 760 and 900°C, but it increased significantly at higher temperatures.

Measurements of the total mass of Cd and Te in the untreated sample were obtained by breaking the sample and leaching the metal content in a tumbling machine with a solution of sulfuric acid and hydrogen peroxide. Complete leaching of the metals was verified by leaching with hydrochloric acid/ H_2O_2 solutions. The uncertainty of the ICP analysis was determined with frequent calibration to be $\leq 5\%$.

4. MICROBEAM X-RAY FLUORESENCE ANALYSES

Figure 3 shows an unheated (control) sample and Figure 4 shows the samples heated at 900, 1000 and 1100°C. In these tests it was visually evident that the glass sheets melted together. As will be shown in Figures 6 and 7, such 'soldering' did not occur at the 760°C experiment. Slices 1 mm thick were cut (vertically) from the center and the sides of the samples and were analyzed by microbeam X-ray fluorescence at beamline X26A at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory.

4.1. Method

The intensity of the X-ray beam produced at the NSLS is approximately 10 000 times greater than that produced by conventional laboratory X-ray sources. The X-ray beam also has a very small angular divergence due to the small cross-section of the electron source, and therefore, intense X-ray beams of the order of 5–10 μ m diameter can be produced using focusing optics. The X26A beamline at the NSLS was used for these experiments. The beam was tuned to 26·8 keV using a Si (111) monochrometer. This energy allowed excitation of Cd but not Te. Data were collected for Cd, Ca, Zr, and Sr K α fluorescence. The spot size was focused to 30 × 30 μ m using Rh coated Kirckpatrick–Baez mirrors. Energy dispersive SXRF data were collected using a Canberra SL30165

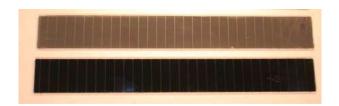


Figure 3. Top and bottom of an unheated sample

a)



b)



c)



Figure 4. (a) Sample after being heated up to 900° C for 1 h; (b) after being heated up to 1000° C for 2 h; (c) after being heated up to 1100° C for 3 h

Si(Li) detector. Incident beam flux was monitored using an ion chamber and changes in fluorescent count rate with time were corrected by normalizing to the ion chamber current values.

Samples were 1-mm-thick slices of the coupons. They were mounted on Kapton tape and placed in a slide holder, with the sample directly exposed to the beam for analysis. Data were collected in two ways. Line scans were collected at step sizes that ranged between 20 and 50 μ m, depending on line length. Count times ranged from 5 to 10 s/pixel. Data are shown as normalized Cd counts.

4.2. Results

Figure 5 shows Cd counts along a line scan collected across a slice cut from the control (unheated) sample. The Cd counts in the junction between the two sheets of glass reach a maximum of 50 000 while the Zr counts (indicative of the glass) in the same region are close to zero. Figure 6 shows the Cd line scans collected across the center and edges of a slice cut from the middle of the 760°C PV sample. The Cd count distribution in the center was approximately the same as the distribution in the unheated sample, whereas the distribution near the edges of the PV shows diffusion of Cd in a wider area. Microscopic analysis showed that a gap was created near the edges of the slice; thus, a likely path for Cd loss is from the perimeter of the sample before the two pieces of glass fuse together, as shown in Figure 7.

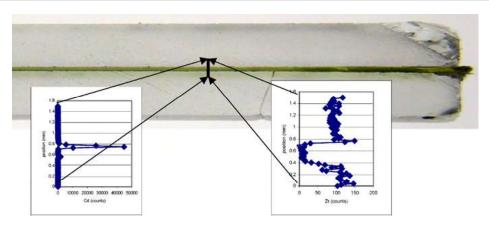


Figure 5. X-ray fluorescence microprobe analysis-vertical slice from unheated (control) sample; Cd and Zr counts

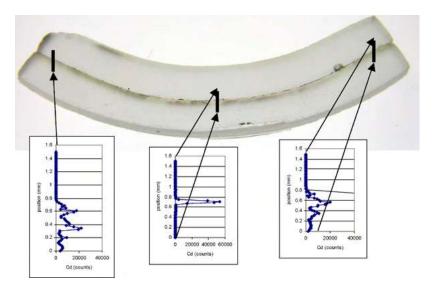


Figure 6. X-ray fluorescence microprobe analysis-vertical slice from middle of sample heated at 760°C; Cd counts in the center and the sides of the slice

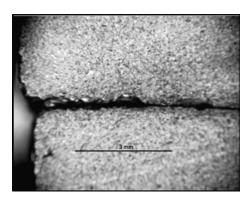


Figure 7. Microphotograph of the edge of a sample heated at 760°C for 30 min

Figure 8 show microprobe results, of a center section from the 1000° C sample and Figure 9 from a side section of the same sample. It is shown that Cd moved to considerable depths into the molten glass and 'froze' there after it cooled. The dispersion of Cd into the glass was more uniform in the side than in the middle of the sample. At the highest temperature we tried (1100°C) Cd diffused into greater depths around the junction

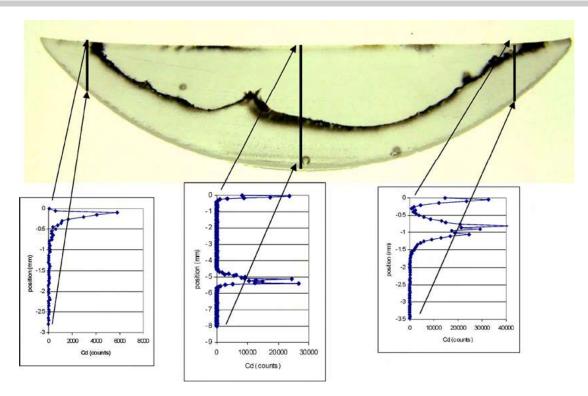


Figure 8. X-ray fluorescence microprobe analysis-vertical slice from middle of sample heated at 1000°C; Cd counts in the center and the sides of the slice

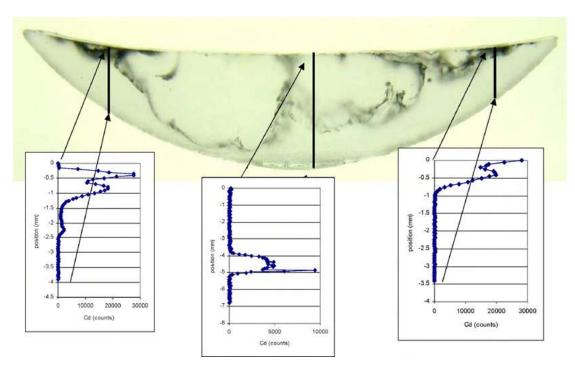


Figure 9. X-ray fluorescence microprobe analysis-vertical slice from side of sample heated at 1000°C; Cd counts in the center and the sides of the slice

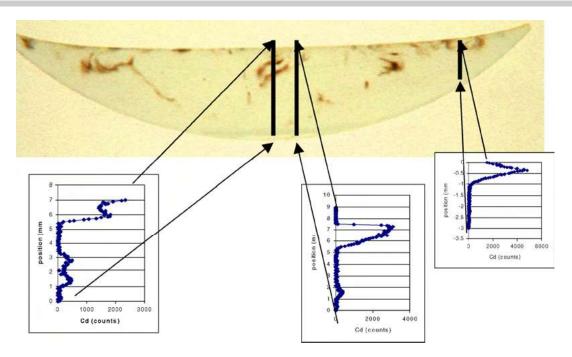


Figure 10. X-ray fluorescence microprobe analysis-vertical slice from middle of sample heated at 1100°C; Cd counts in the center and the sides of the slice

(Figure 10). Although higher temperatures produce greater Cd diffusion, the emissions analyses which show that the Cd loss was the same at all temperatures above 760°C indicate that Cd that has diffused into the glass does not enter the vapor phase in the temperature range of 760–1100°C.

5. ANALYSIS OF THE HEATED GLASS

We followed the standard ASTM C169-89 method¹⁴ for chemical analysis of glass, involving fusion with lithium tetraborate and dissolution in HNO₃. The samples were ground to a fine powder and fused at 1100°C with lithium tetraborate powder (as flux). The fused material was poured into a 20% HNO₃ solution, which was kept at elevated temperature until the fused sample was completely disintegrated and dissolved into the solution. ICP analysis was performed on the solution for cadmium and tellurium. The results of this analysis are shown in Figure 11. The uncertainty of these results is much greater than that the uncertainty of the results presented in Section 3·2 for two reasons: (1) with the exception of the unheated (control) sample, only a small

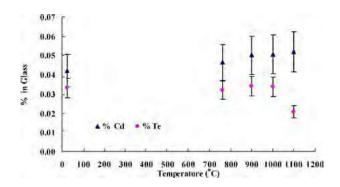


Figure 11. Cadmium and tellurium concentrations in unheated and in molten glass at different temperatures; average values and error bars showing % of error

part of the sample was ground and analyzed, and this may not represent the average concentration in the whole sample; and (2) the salts formed in solution increased the uncertainty of the ICP analysis to about 20% for Cd and 15% for Te.

These experiments showed that the Cd content in the unheated and the heated samples is the same (within the described level of analytical uncertainty), confirming the results of the emissions analysis that Cd was essentially retained in the glass during the heating experiments. The Te concentration in the heated glass, at 1100° C, was lower than the unheated sample, confirming the results of the air emissions analysis showing Te loss at high temperatures.

6. DISCUSSION

Pieces of CdTe PV modules of approximately 25 × 3 cm were heated to temperatures of 760–1100°C following standard UL and ASTM protocols. Four types of analyses were performed: (1) the thermogravimetric analysis showed weight loss of about 2%, which is equal to 77% of the weight of the EVA in the samples; (2) the Cd analyses (using inductively coupled plasma, ICP) showed that the total Cd emissions from each sample was about 3×10^{-4} g which corresponds to about 0.5% loss of the Cd content of the sample. The Te emissions were also very small at the typical residential flame temperatures of 700-900°C, but they were larger at higher temperatures (i.e., 1000–1100°C); (3) the synchrotron-based X-ray fluorescence microprobe analyses clearly show that Cd diffuses into the glass. Comparison of the Cd line scans in the center and the edges of each sample, together with microscopic analysis of the perimeter of the sample, show that the small Cd loss occurs from the edges of the PV module through the space of the two glass sheets before they fuse together. This loss is likely proportional to the ratio of the mass of cadmium (i.e., area of the sample) to its perimeter, and as such would be smaller in full modules. Our samples did not have 'edge delete', if the perimeter had a strip free of CdTe, Cd loss could have been even lower. On the other hand, the probability of a module being broken during a fire was not assessed; it is unlikely, however, that a large number of modules could be broken in pieces smaller than our samples; (4) pieces of heated samples were ground and fused with lithium tetraborate powder. The fused liquid was dissolved in HNO₃ and ICP analysis was performed for Cd and Te. The results of this analysis confirm that the Cd content remains constant, thus it is essentially retained into the glass matrix. The Te concentration in the burnt glass, at 1100°C, was lower than the unheated sample, confirming the results of the air emissions analysis showing Te loss at the high temperatures.

A possible explanation for the difference of the behavior of Cd and Te in the highest temperature experiments could be the difference in their oxidation states. Tellurium, when heated to high temperatures, likely oxidizes and subsequently vaporizes. On the other hand, cadmium oxide has a very low vapor pressure even at 1100°C (Figure 1). Additional studies are in progress to investigate the speciation of tellurium and cadmium in the glass matrix.

7. CONCLUSION

Heating experiments to simulate residential fires showed that most (i.e., 99.5%) of the cadmium content of CdTe PV modules was encapsulated in the molten glass matrix. This was confirmed with emissions chemical analysis, synchrotron-based X-ray fluorescence microprobe analysis and chemical analysis of the molten glass. Only $0.5 \pm 0.1\%$ of the Cd content of each sample was emitted during our tests that cover the wide flame temperature zone of $760-1100^{\circ}$ C. The pathway for this loss was likely though the perimeter of the sample before the two sheets of glass fused together. In actual size PV modules, the ratio of perimeter to area is 13.5 times smaller than our sample; thus the actual Cd loss during fires will be extremely small (<0.04% of the Cd content). Multiplying this with the probability of occurrence for residential fires in wood-frame houses in the US (e.g., 10^{-4}), results in emissions of 0.06 mg/GW h (assuming 7 g Cd/m², 10% electric conversion efficiency and 1800 kwh/m²/yr). As discussed in the introduction, the probability of sustained fires in utility systems must be much smaller, due to lack of combustible materials, and, therefore, emissions of cadmium during fires in central PV systems are considered to be essentially zero. The total cadmium emissions during the whole life-cycle of CdTe PV modules (ore mining,

metal melting, purification, PV manufacturing) has been estimated to be about $20 \, \text{mg/GW h.}^{15}$ These results apply to glass-to-glass CdTe PV modules which are the only ones in the market. Similarly to Cd, only a tiny percentage of Te was released in the typical residential fire temperature range $760–900^{\circ}\text{C}$, but a significant fraction was released at higher temperatures ($1000–1100^{\circ}\text{C}$).

Acknowledgements

This work was supported by the Solar Technologies Program, Conservation and Renewable Energy, under Contract DE-AC02-76CH000016 with the US Department of Energy. The X26A beamline at the NSLS of Brookhaven National Laboratory is operated by a team of scientists from The University of Chicago's Consortium for Advanced Radiation Sources (CARS), the University of Georgia's Savannah River Ecology Laboratory (SREL), and Brookhaven National Laboratory's Environmental Sciences Department. Thanks are due to David Albin and Ramesh Dhere, NREL, Alan Fahrenbruch, Stanford University, and Tom Hansen, Tucson Electric, for sharing their data and observations, Ken Zweibel, NREL for being a guiding force behind this project, and First Solar, Ltd. for kindly providing pieces of their PV modules. This paper is an extended version of a poster paper entitled 'Experimental Investigation of Emissions and Redistribution of Elements in CdTe PV Modules During Fires' presented at the 19th European PV Solar Energy Conference and Exhibition, Paris, France, June 2004.

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Annex III

Review Forms

Peer Review
Ratings
Outstanding 4
Good 3
Fair 2
Poor 1

	Study 1-Fthenakis			Study 2-Steinberg			Study 3-Fthenakis et al		
	Clarity	Quality	Relevance	Clarity	Quality	Relevance	Clarity	Quality	Relevance
Gabler	4	4	4	4	3	3	4	4	4
Johansson	4	3	3	4	3	3,5	4	4	4
Lux-Steiner	3	3	3	3	3	3	3	3	3
Werner Average	1	2	2		2	2	1	1	1
Rating Total	3	3	3	3,667	2,75	2,875	3	3	3
Average	3,032								

Prof. Martha Lux-Steiner, HMI Berlin

Study Reviewed: All three studies	
Instructions: Please provide a numerical rating in the far-right column for each reviewed study u criteria listed below. Also please include supporting comments for each rating.	sing the
1. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the degree which PV market barriers are addressed.	e to
4 – Outstanding. The study is sharply focused on one or more key technical barriers to the development of solar energy technologies.	
3 – Good . The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers.	X
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but the approach has significant weaknesses.	
1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers.	
Please provide supporting comments: The global ecological acceptance of the CdTe technology has to be checked more precisely: Dive inhabitants from industrialized and non-industralized countries as well as national regulations have considered. Reliable data on life time of modules under various operating conditions should be gained.	
Offering the obligation to take back modules is excellent.	
2. Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and are well documented	the results
4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly.	
3 – Good. The research is effective, but could be improved.	X
2 – Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses.	
1 - Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe PV.	
Please provide supporting comments: The comparison of the individual studies which describe the environmental profile of CdTe PV in the detailed evaluation and ranking of the corresponding reports should be distributed regularly to community.	
Unfortunately, all the individual studies on the environmental profile of CdTe PV are related to elect. Quantitative data on the toxicity of the compound CdTe are missing. This would be of special as the inertness of this ionic compound seems to be high under stardard conditions (phase diagrams).	interest,

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of $CdTe\ PV$.

Is cadmium expected to leach out during use of CdPV?Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks?Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologes? Other	
3 – Good. This study contributes significantly in answering the relevant question(s) below. (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdPV? Not under standard ambient conditions. Are cadmium emissions expected during use of CdTePV? Not under standard ambient conditions.	X
Do emissions present serious risks? During production, but not during use and not on a large scale.	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? <i>Not during use.</i>	
Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other <i>Not during use.</i>	
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below (Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other	
1 – Poor. This study does not contribute at all in answering the relevant question(s) below	
(Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdPV?	
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other	
ase provide supporting comments:	
production special safety requirements and regulations have to be taken into account.	

Dr. Hansjörg Gabler Dr. Johann Springer Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg Industriestraße 6, D-70565 Stuttgart

Date of Review: 15.08.2005 Study Reviewed: # 1 Life cycle impact analysis of cadmium in CdTe PV production	
Instructions: Please provide a numerical rating in the far-right column for each reviewed stude criteria listed below. Also please include supporting comments for each rating.	dy using the
1. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the dewhich PV market barriers are addressed.	egree to
4 – Outstanding. The study is sharply focused on one or more key technical barriers to the development of solar energy technologies.	ne X
3 – Good . The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers.	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers by the approach has significant weaknesses.	ut
1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers.	
Please provide supporting comments: The study is the first one to give an extensive overview of the life-cycle aspects of Cd modules. The given conclusions are comprehensible. The study uses accepted proce summarizes the results of capacious work going into the depth of the topic.	
2. Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid are well documented.	and the results
4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly.	X
3 – Good. The research is effective, but could be improved.	
2 – Fair. Some aspects of the study have value but the quality of the research demonstrate significant weaknesses.	:S
1 – Poor. The quality of the research is not responsive to the standards of the reviewers are is unlikely to contribute towards answering question on the environmental impact of CdTe PV.	
Please provide supporting comments:	

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of $CdTe\ PV$.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential	
environmental impact of CdTe PV production?	
Please mark the relevant question answered by the study:	
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
X	
Are the risks associated with CdTe PV greater than those posed by other PV technologes?	
Other	
3 – Good. This study contributes significantly in answering the relevant question(s) below.	
(Please mark the relevant question answered by the study):	
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below	
(Please mark the relevant question answered by the study)	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
1 – Poor. This study does not contribute at all in answering the relevant question(s) below	
(Please mark the relevant question answered by the study):	
Is cadmium expected to leach out during use of CdPV?	
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks?	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
<u> </u>	
Please provide supporting comments:	
tudy contains comprehensive additional information on environmental aspects and	
missions of Cadmium before the CdTe/PV-module production phase.	

Dr. Hansjörg Gabler; Dr. Johann Springer	
Date of Review: 15.08.2005 Study Reviewed: # 2 Health, Safety and Environmental Risks from the Operation of CdTe and CIS film Modules	<u>Γhin-</u>
Instructions: Please provide a numerical rating in the far-right column for each reviewed study using criteria listed below. Also please include supporting comments for each rating.	g the
. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the degree to which PV market barriers are addressed.)
4 – Outstanding. The study is sharply focused on one or more key technical barriers to the development of solar energy technologies.	X
3 – Good . The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers.	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but the approach has significant weaknesses.	
1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers.	
Please provide supporting comments:	
Please provide supporting comments:	
Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the	results
Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the re well documented. 4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly.	results
Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the are well documented. 4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly. 3 – Good. The research is effective, but could be improved.	results X
Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the re well documented. 4 - Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly. 3 - Good. The research is effective, but could be improved. 2 - Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses.	
2. Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the are well documented. 4 - Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly. 3 - Good. The research is effective, but could be improved. 2 - Fair. Some aspects of the study have value but the quality of the research demonstrates	
Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the are well documented. 4 - Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly. 3 - Good. The research is effective, but could be improved. 2 - Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses. 1 - Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe PV.	
Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the are well documented. 4 - Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly. 3 - Good. The research is effective, but could be improved. 2 - Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses. 1 - Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe PV. Please provide supporting comments: The modules which were investigated for the study may no longer be relevant for the	
the quality of the research to be improved significantly. 3 – Good. The research is effective, but could be improved. 2 – Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses. 1 – Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe	
Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the are well documented. 4 - Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly. 3 - Good. The research is effective, but could be improved. 2 - Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses. 1 - Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe PV. Please provide supporting comments: The modules which were investigated for the study may no longer be relevant for the	

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of $CdTe\ PV$.

Dr. Hansjörg Gabler; Dr. Johann Springer	
Date of Review: 15.08.2005 Study Reviewed: #3 Emissions and Encapsulation of Cadmium in CdTe PV Modules During Fire	<u>es</u>
Instructions: Please provide a numerical rating in the far-right column for each reviewed study us criteria listed below. Also please include supporting comments for each rating.	sing the
1. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the degree which PV market barriers are addressed.	e to
4 – Outstanding. The study is sharply focused on one or more key technical barriers to the development of solar energy technologies.	X
 3 - Good. The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers. 	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but the approach has significant weaknesses.	
1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers.	
Please provide supporting comments:	
2. Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and to are well documented.	he results
4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly.	X
 3 - Good. The research is effective, but could be improved. 2 - Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses. 1 - Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe PV. 	
Please provide supporting comments:	

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of CdTe PV.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential
environmental impact of CdTe PV production?
Please mark the relevant question answered by the study:
Is cadmium expected to leach out during use of CdPV?
Are cadmium emissions expected during use of CdTePV?X
Do emissions present serious risks?
Do emissions present serious risks? X Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?
Are the risks associated with CdTe PV greater than those posed by other PV technologes?
Other
3 – Good. This study contributes significantly in answering the relevant question(s) below.
(Please mark the relevant question answered by the study):
Is cadmium expected to leach out during use of CdPV?
Are cadmium emissions expected during use of CdTePV?
Do emissions present serious risks?
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?
Are the risks associated with CdTe PV greater than those posed by other PV technologies?
Other
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below
(Please mark the relevant question answered by the study)
Is cadmium expected to leach out during use of CdPV?
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?
Do emissions present serious risks?
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?
Are the risks associated with CdTe PV greater than those posed by other PV technologies?
Other
1 – Poor. This study does not contribute at all in answering the relevant question(s) below
(Please mark the relevant question answered by the study):
Is cadmium expected to leach out during use of CdPV?
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?
Do emissions present serious risks?
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?
Are the risks associated with CdTe PV greater than those posed by other PV technologies?
Other

Please provide supporting comments:

The authors apply standard protocols and therefore give a realistic picture of possible hazards. The investigation is exhaustive and the desription is very detailled so that the procedures can be reproduced.

Date of Review: ____5.8.2005 ____Jürgen H. Werner

Study Reviewed:_# 3 Emissions and Encapsulation of Cd in CdTe Modules During Fires

Instructions: Please provide a numerical rating in the far-right column for each reviewed study using the criteria listed below. Also please include supporting comments for each rating.

1. Clarity and Appropriateness of the Scientific/Technical Approach

Evaluate the approach to the experimental and analytical methods used in the research—the degree to which PV market barriers are addressed.

4 – Outstanding. The study is sharply focused on one or more key technical barriers to the	
development of solar energy technologies.	
3 – Good . The approach is generally well thought out and effective. Most aspects of the	
study will contribute to significant progress in overcoming barriers.	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but	
the approach has significant weaknesses.	
1 - Poor. The approach is unlikely to make significant contributions to overcoming the	X
barriers.	

Please provide supporting comments:

This study does not address market barriers of PV in general.

2. Scientific/Technical Quality of the Research

Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the results are well documented. .

4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for	
the quality of the research to be improved significantly.	
3 – Good. The research is effective, but could be improved.	
2 – Fair. Some aspects of the study have value but the quality of the research demonstrates	
significant weaknesses.	
1 - Poor. The quality of the research is not responsive to the standards of the reviewers and	X
is unlikely to contribute towards answering question on the environmental impact of CdTe	
PV.	

Please provide supporting comments:

The study investigates parts of CdTe modules in a furnace. In this case there is a homogeneous temperature distribution over the whole module. In addition the modules lie horizontally in the furnace. This experiment does not simulate the situation for a CdTe module in fire. In case of fire, there will be an inhomogenous and abrupt temperature change across the surface of the modules. The modules will crack. In addition, due to softening of the EVA, the modules will delaminate. In this case, the CdS, ZnO and CdTe will directly face the fire. The material will evaporate and will be released to the air. To me, the experiment of the authors is appropriately designed to make statements on the behavior of a CdTe module in fire.

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of CdTe PV.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential	
environmental impact of CdTe PV production?	
Please mark the relevant question answered by the study:	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks?Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologes? Other	
3 – Good. This study contributes significantly in answering the relevant question(s) below.	
(Please mark the relevant question answered by the study):	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below	
(Please mark the relevant question answered by the study)	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks?	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
1 – Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study):	xxxxxx
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other	

Please provide supporting comments: _____I would expect that Cd leaches out in a fire.

Yes, the risks with CdTe PV are much higher than with other PV technologies.

Date of Review: 5.8. 2005, Jürgen H. Werner

Study Reviewed: #2 Health, Safety and Environmental Risks from the Operation of CdTe and CIS modules (by H. Steinberger)

Instructions: Please provide a numerical rating in the far-right column for each reviewed study using the criteria listed below. Also please include supporting comments for each rating.

1. Clarity and Appropriateness of the Scientific/Technical Approach

Evaluate the approach to the experimental and analytical methods used in the research—the degree to which PV market barriers are addressed.

4 – Outstanding. The study is sharply focused on one or more key technical barriers to the	
development of solar energy technologies.	
3 – Good . The approach is generally well thought out and effective. Most aspects of the	
study will contribute to significant progress in overcoming barriers.	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but	
the approach has significant weaknesses.	
1 - Poor. The approach is unlikely to make significant contributions to overcoming the	
barriers.	

Please provide supporting comments:

Barriers for PV are not addressed in this study

2. Scientific/Technical Quality of the Research

Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the results are well documented. .

4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for	
the quality of the research to be improved significantly.	
3 – Good. The research is effective, but could be improved.	
2 – Fair. Some aspects of the study have value but the quality of the research demonstrates	X
significant weaknesses.	
1 - Poor. The quality of the research is not responsive to the standards of the reviewers and	
is unlikely to contribute towards answering question on the environmental impact of CdTe	
PV.	

Please provide supporting comments:

This study cuts the modules into small pieces. However, the semiconductor material is still protected by EVA and glass from both sides. It is inlikely that this situation simulates what happens in case of a broken module. It is much more likely, that the CdTe is not protected by two glass plates. The experiments are not convincing to me.

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of CdTe PV.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential	
environmental impact of CdTe PV production?	
Please mark the relevant question answered by the study:	
Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologes?	
Other	
3 – Good. This study contributes significantly in answering the relevant question(s) below.	
(Please mark the relevant question answered by the study):	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below	X
(Please mark the relevant question answered by the study)	х
(Please mark the relevant question answered by the study)	X
(Please mark the relevant question answered by the study)	Х
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(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies?	X
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Please provide supporting comments:

This study does not answer the question how much Cd is released to the environment in case of water that penetrates into a module. In fact, this case seems to appear much more often than previously thought. The special measures of First Solar, the information sheets which they send to their customers, indicates that there might be a serious problem with water penetration into their modules.

Date of Review:_	5.8.2005	Jürgen H. Werner_	
Study Reviewed:	#1_Life cycle in	mpact analysis	

Instructions: Please provide a numerical rating in the far-right column for each reviewed study using the criteria listed below. Also please include supporting comments for each rating.

1. Clarity and Appropriateness of the Scientific/Technical Approach

Evaluate the approach to the experimental and analytical methods used in the research—the degree to which PV market barriers are addressed.

4 – Outstanding. The study is sharply focused on one or more key technical barriers to the	
development of solar energy technologies.	
3 – Good . The approach is generally well thought out and effective. Most aspects of the	
study will contribute to significant progress in overcoming barriers.	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but	
the approach has significant weaknesses.	
1 – Poor. The approach is unlikely to make significant contributions to overcoming the	XXXX
barriers.	

Please provide supporting comments:

This study does not discuss PV market barriers.

2. Scientific/Technical Quality of the Research

Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and the results are well documented. .

4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for	
the quality of the research to be improved significantly.	
3 – Good. The research is effective, but could be improved.	
2 – Fair. Some aspects of the study have value but the quality of the research demonstrates	xxxxx
significant weaknesses.	
1 - Poor. The quality of the research is not responsive to the standards of the reviewers and	
is unlikely to contribute towards answering question on the environmental impact of CdTe	
PV.	

Please provide supporting comments:

In addition to giving data on the Cd-production, this manuscript repeats results from the two other studies. As a consequence, this paper (although nicely written) suffers from the principal flaws in the design of the experiments in the two other studies.

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of CdTe PV.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential	
environmental impact of CdTe PV production?	
Please mark the relevant question answered by the study:	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologes? Other	
3 – Good. This study contributes significantly in answering the relevant question(s) below. (Please mark the relevant question answered by the study):	
Is cadmium expected to leach out during use of CdPV?	
Are cadmium emissions expected during use of CdTePV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with Cd1e PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
A R.A. MILLS I	
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below (Please mark the relevant question answered by the study) Is codmium expected to leach out during use of CdPV?	XXXX
(Please mark the relevant question answered by the study)	XXXX
(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	XXXX
(Please mark the relevant question answered by the study)	xxxx
(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	XXXX
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(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study):	XXXX
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(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV?	XXXX
(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious ricks?	XXXX
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(Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdPV? Are cadmium emissions expected during use of CdTePV? Do emissions present serious risks?	XXXX

Please provide supporting comments: The risks of a Cd based PV is higher than for any other PV technology. CdTe poses an additional risk. Why should it be taken. From both studies, I cannot conclude that there is no release of Cd from the modules. In addition, the statements that CdTe technology could make any significant contribution to preventing Cd waste is not justified.

Reviewer: Prof. Thomas B. Johansson

Date of Review:_14-11-2005 Title of Study Reviewed:_#1- Life Cycle impact Analysis of Cadmium in CdTe PV Production	n
Instructions: Please provide a numerical rating in the far-right column for each reviewed study u criteria listed below. Also please include supporting comments for each rating.	sing the
1. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the degree which PV market barriers are addressed.	e to
4 – Outstanding. The study is sharply focused on one or more key technical barriers to the development of solar energy technologies.	X
3 – Good . The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers.	
2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but the approach has significant weaknesses.	
1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers.	
2. Scientific/Technical Quality of the Research Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and tare well documented.	he results
4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly.	
3 – Good. The research is effective, but could be improved.	X
2 – Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses.	
1 – Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe PV.	
Please provide supporting comments:The evaluation is always limited to data availability. Data on toxicity of CdTe would be of interest	

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of $CdTe\ PV$.

Please mark the relevant question answered by the study: Is cadmium expected to leach out during use of CdTe PV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? The the risks associated with CdTe PV greater than those posed by other PV technologies? Other 3 - Good. This study contributes significantly in answering the relevant question(s) below. (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdTe PV? Are cadmium emissions expected during use of CdTe PV? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 2 - Fair. This study may have only a minor contribution in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdTe PV? Are cadmium expected to leach out during use of CdTe PV? Are cadmium expected to leach out during use of CdTe PV? Are cadmium expected to leach out during use of CdTe PV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by the fossil technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdTe PV? Are cadmium emissions expected during use of CdTe PV? Are cadmium emissions expected during use of CdTe PV? Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Are the risks associated with CdTe PV greater than	 Outstanding. Does this study effectively and definitively answer questions related to the potential nvironmental impact of CdTe PV production?
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Other 3 - Good. This study contributes significantly in answering the relevant question(s) below. (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdTe PV? Are admium emissions expected during use of CdTe PV? No emissions present serious risks? X Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? X Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 2 - Fair. This study may have only a minor contribution in answering the relevant question(s) below (Please mark the relevant question answered by the study) Is cadmium expected to leach out during use of CdTe PV? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other 1 - Poor. This study does not contribute at all in answering the relevant question(s) below (Please mark the relevant question answered by the study): Is cadmium expected to leach out during use of CdTe PV? Are cadmium expected to leach out during use of CdTe PV? Are cadmium expected to leach out during use of CdTe PV? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other Are the risks associated with CdTe PV greater than those posed by other PV technologies? Are the risks associated with CdTe PV greater than those posed by other PV technologies?	Te the risks associated with Cure PV greater than those posed by the fossil technologies it will replace?
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Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace? X Are the risks associated with CdTe PV greater than those posed by other PV technologies? Other	(Please mark the relevant question answered by the study):
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Other	tre the risks associated with Cd1e PV greater than those posed by the fossil technologies it will replace?
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Other	are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?
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Reviewer: Prof. Thomas B. Johansson

Date of Review: 14-11-2005	CdTe and
Instructions: Please provide a numerical rating in the far-right column for each reviewed study criteria listed below. Also please include supporting comments for each rating.	using the
1. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the degree which PV market barriers are addressed.	ee to
	X
 3 - Good. The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers. 2 - Fair. Some aspects of the project may lead to progress in overcoming some barriers but 	
the approach has significant weaknesses.	
1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers.	
Please provide supporting comments:	
Leaching of Cd is a possible concern and the study provides useful and interesting information	
2. Scientific/Technical Quality of the Research	
Assess the degree to which the reviewed study is well-designed, if the assumptions are valid and are well documented.	the results
4 – Outstanding. The reviewed study is well-designed and documented. It is difficult for the quality of the research to be improved significantly.	
3 – Good. The research is effective, but could be improved.	X
2 – Fair. Some aspects of the study have value but the quality of the research demonstrates significant weaknesses.	
1 – Poor. The quality of the research is not responsive to the standards of the reviewers and is unlikely to contribute towards answering question on the environmental impact of CdTe	
PV.	
Please provide supporting comments: More extensive work would be of interest, expanding to the systems aspects of very large install a life-cycle basis. The importance of end-of-life procedures is indicated.	ations on

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of $CdTe\ PV$.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential	X
environmental impact of CdTe PV production?	
Please mark the relevant question answered by the study:	
Is cadmium expected to leach out during use of CdTe PV? Are cadmium emissions expected during use of CdTe PV?	
Do emissions present serious risks? Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace	. 0
Are the risks associated with Cd1e PV greater than those posed by the fossil technologies it will replace	e?
Are the risks associated with CdTe PV greater than those posed by other PV technologes? Other	
3 – Good. This study contributes significantly in answering the relevant question(s) below.	
(Please mark the relevant question answered by the study):	
Is cadmium expected to leach out during use of CdTe PV?	
Is cadmium expected to leach out during use of CdTe PV?X Are cadmium emissions expected during use of CdTe PV?X	
Do emissions present serious risks?	
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Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
2 – Fair. This study may have only a minor contribution in answering the relevant question(s) below	
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Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
Please provide supporting comments:	
_The issues studied are well documented and	
reported	

Reviewer: Prof. Thomas B. Johansson

Date of Review: 14-11-2005 Title of Study Reviewed:#3Emissions and Encapsulation of Cadmium in CdTe PV Module Fires	s During
Instructions: Please provide a numerical rating in the far-right column for each reviewed study u criteria listed below. Also please include supporting comments for each rating.	sing the
1. Clarity and Appropriateness of the Scientific/Technical Approach	
Evaluate the approach to the experimental and analytical methods used in the research—the degre which PV market barriers are addressed.	e to
4 – Outstanding. The study is sharply focused on one or more key technical barriers to the development of solar energy technologies. 3 – Good. The approach is generally well thought out and effective. Most aspects of the study will contribute to significant progress in overcoming barriers. 2 – Fair. Some aspects of the project may lead to progress in overcoming some barriers but the approach has significant weaknesses. 1 – Poor. The approach is unlikely to make significant contributions to overcoming the barriers. Please provide supporting comments:	X
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Please provide supporting comments:	-

Evaluate the impact of the research and the degree to which the technical accomplishments contribute in establishing the environmental profile of $CdTe\ PV$.

4 – Outstanding. Does this study effectively and definitively answer questions related to the potential environmental impact of CdTe PV production?	X
Please mark the relevant question answered by the study:	
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Do amissions present serious risks?	
Is cadmium expected to leach out during use of CdTe PV? Are cadmium emissions expected during use of CdTe PV? Do emissions present serious risks? X Are the risks associated with CdTe PV greater than those posed by the fossil technologies it will replace?	
Are the risks associated with Cure PV greater than those posed by the rossil technologies it will replace?	
Are the risks associated with CdTe PV greater than those posed by other PV technologes? Other	
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Are the risks associated with CdTe PV greater than those posed by other PV technologies?	
Other	
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ase provide supporting comments:	
he study deals with emissions in case of fire and reports valuable experimental information	
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European Commission

EUR 24515 EN – Joint Research Centre – Institute for Energy

Title: Results of Peer Review of Studies on Environmental Aspects of CdTe Photovoltaic Systems

Author(s): Arnulf Jäger-Waldau

Luxembourg: Publications Office of the European Communities

2005 - 155 pp. - 21 x 29.7 cm

EUR - Scientific and Technical Research series - ISSN 1018-5593

ISBN 978-92-79-16587-0 doi: 10.2778/86177

Abstract

Following discussions with the German Ministry of the Environment (BMU), First Solar, a company manufacturing CdTe solar modules, requested an independent peer review of studies pertaining to the environmental aspects of CdTe photovoltaic systems. This review was organized by the European Commission, DG Joint Research Centre (JRC) and moderated by the BMU. Four reviewers were selected from the BMU and the JRC and asked to review the most recent studies on CdTe PV environmental, health and safety (EH&S) issues.

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