

Emissions and Encapsulation of Cadmium in CdTe PV Modules During Fires^{†‡}

V. M. Fthenakis^{1*†}, M. Fuhrmann¹, J. Heiser¹, A. Lanzirotti², J. Fitts¹ and W. Wang¹

¹Environmental Sciences Department, Brookhaven National Laboratory, Upton, NY 11973, USA

²Consortium for Advanced Radiation Resources, Univ. of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, USA

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 such emissions from fires in adequately designed and maintained utility systems is essentially zero. Published in 2005 by John Wiley & Sons, Ltd.

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

* Correspondence to: Vasilis Fthenakis, Brookhaven National Laboratory, Building 830, Upton, NY 11973, USA.

†E-mail: fthenakis@bnl.gov

‡ This article is a U.S. Government work and is in the public domain in the U.S.A.

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

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 lightning 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.^{1,2} 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.² 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	0.075*
Total Cu	0.011*
Other	1.180

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

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

<i>A</i>	<i>B</i>	<i>T</i> (K)	Reference
-9500	6.427	731-922	7
-11 493	7.99	1085-1324	8
-9764	6.572	773-1010	9
-10 000	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



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

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

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}

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

where the constants *A*, *B* and *D* 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 CdCl₂ in the temperature range of our experiments. The CdTe pressure due to sublimation at 800°C is about 2.4 torr.

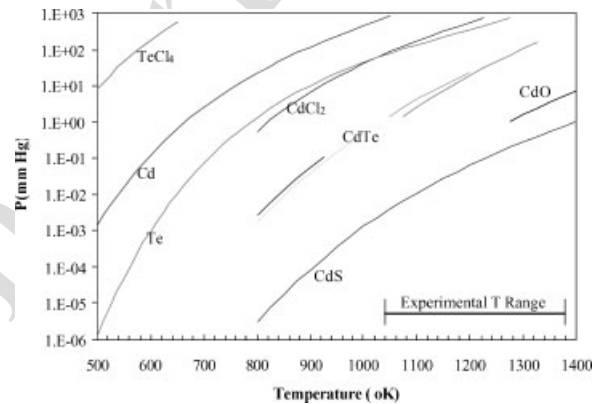


Figure 1. Vapor pressure of cadmium compounds

Table III. Vapor pressure coefficients for equation (3)

Component	A	B	C	D	E	T(K)
CdS(s)	16.06	-11 460	-2.5	—	—	298–1203
CdCl ₂ (s)	17.46	-9270	-2.11	—	—	298–840
CdCl ₂ (l)	25.907	-9183	-5.04	—	—	840–1233
CdO(s)	42.8498	-1 5 443	-10.651	2.0645×10^{-3}	-1.704×10^{-7}	1273–1832
TeO ₂ (s)	23.51	-13 940	-3.52	—	—	298–10 006
TeCl ₄	225.5681	-13 194	-80.8999	4.5316×10^{-2}	-1.044×10^{-5}	506–665

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.⁴ 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.

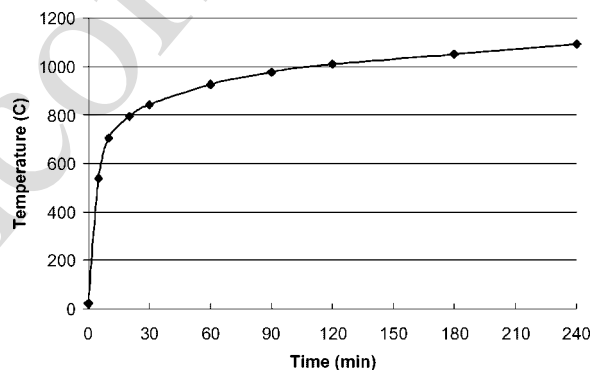


Figure 2. Temperature and heating duration for each experiment (as per ASTM E119-98 Standard)

Table IV. Measured loss of mass

Test	T ($^{\circ}\text{C}$)	Weight loss (% sample)	Cd emissions		Te emissions	
			(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 $^{\circ}\text{C}$, 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 FLUORESCENCE ANALYSES

Figure 3 shows an unheated (control) sample and Figure 4 shows the samples heated at 900, 1000 and 1100 $^{\circ}\text{C}$. 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 $^{\circ}\text{C}$ 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 μm 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 $\text{K}\alpha$ fluorescence. The spot size was focused to 30 \times 30 μm using Rh coated Kirkpatrick–Baez mirrors. Energy dispersive SXRF data were collected using a Canberra SL30165

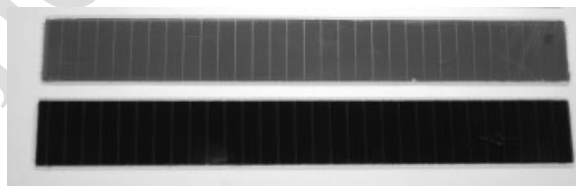
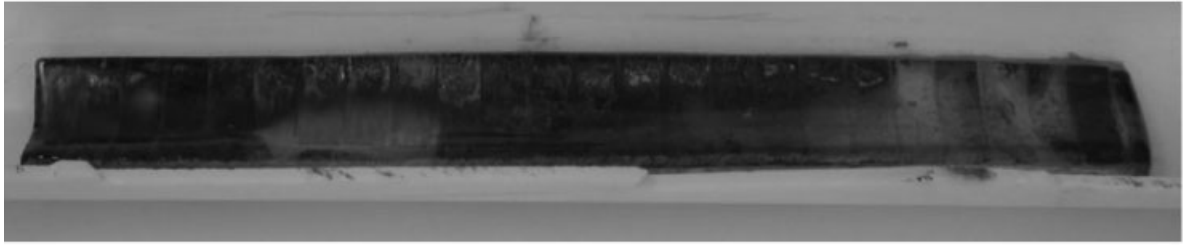
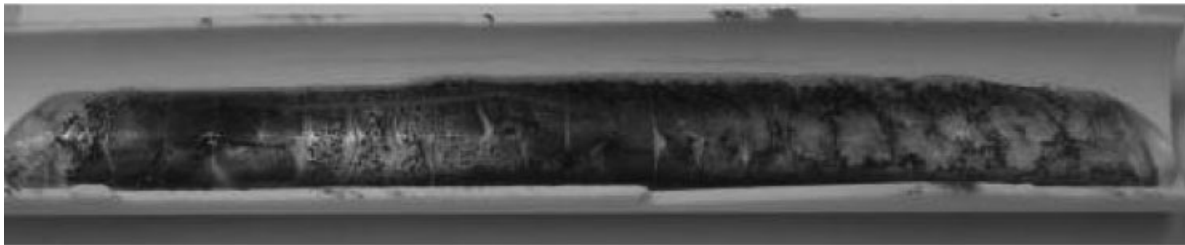


Figure 3. Top and bottom of an unheated sample

a)



b)



c)

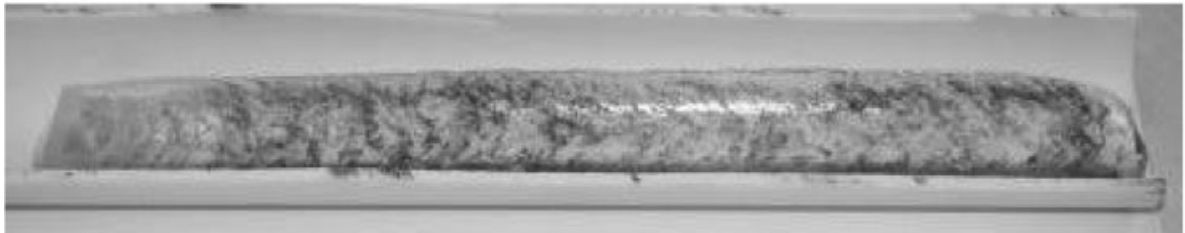


Figure 4. (a) Sample after being heated up to 900°C for 1 h; (b) after being heated up to 1000°C for 2 h; (c) after being heated up to 1100°C for 3 h

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 μm , 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.

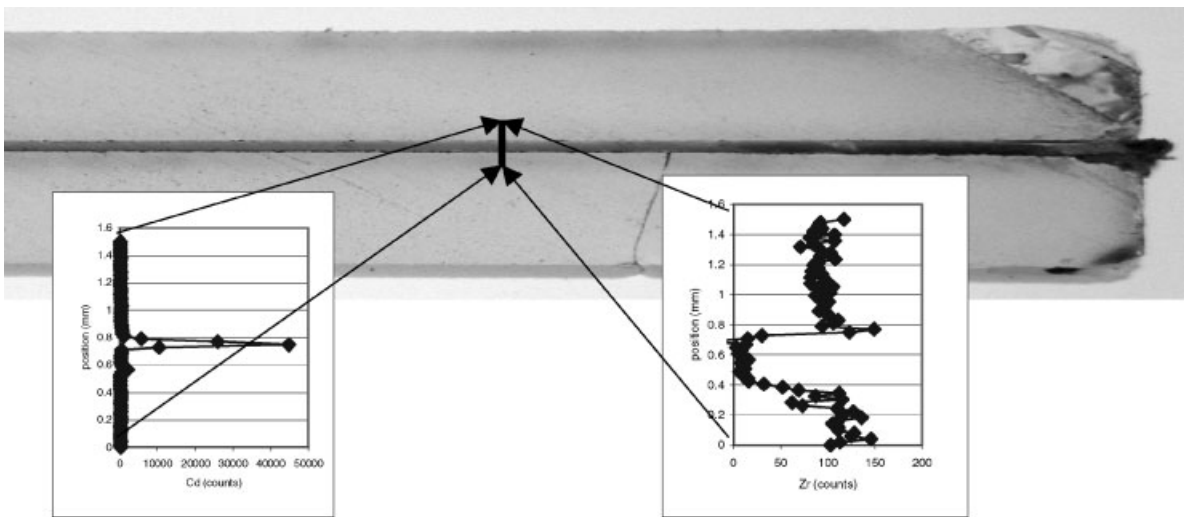


Figure 5. X-ray fluorescence microprobe analysis—vertical slice from unheated (control) sample; Cd and Zr counts

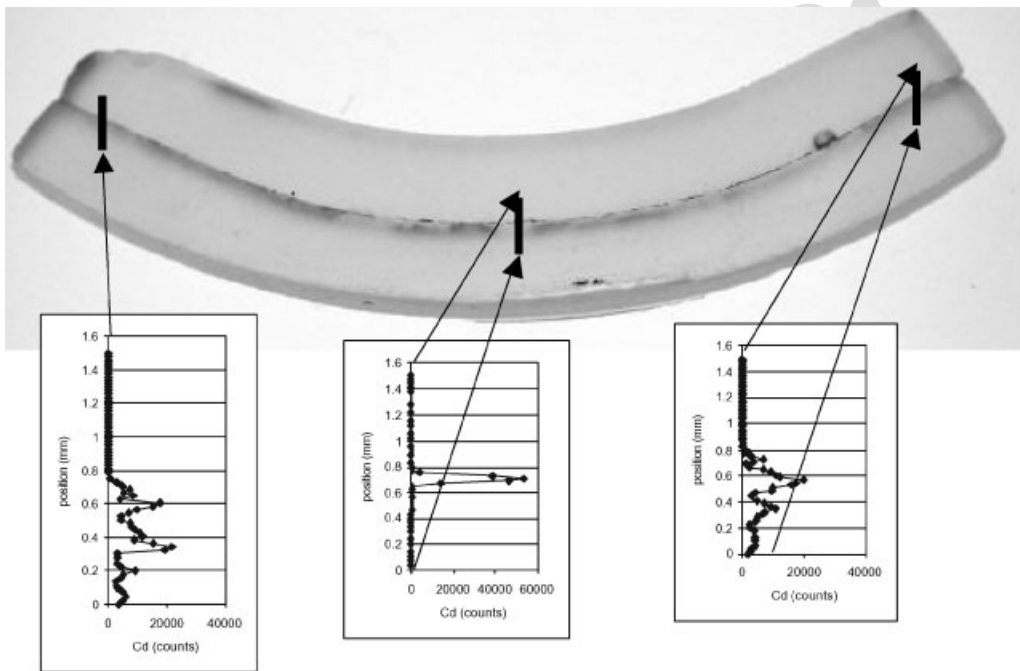


Figure 6. X-ray fluorescence microprobe analysis—vertical slice from middle of sample heated at 760°C; Cd counts in the center and the sides of the slice

Figure 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 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.

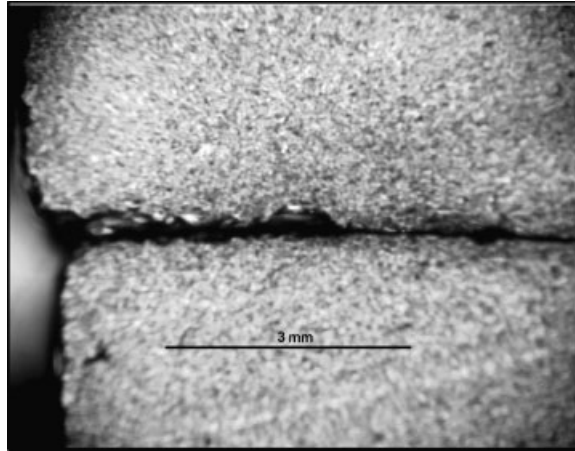


Figure 7. Microphotograph of the edge of a sample heated at 760°C for 30 min

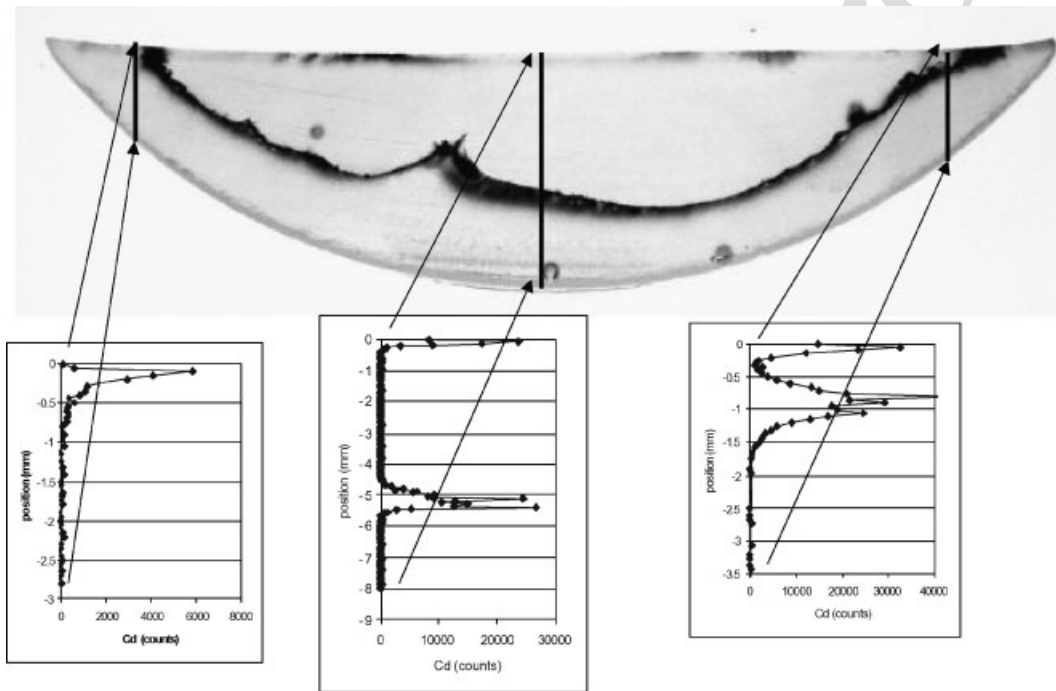


Figure 8. X-ray fluorescence microprobe analysis—vertical slice from middle of sample heated at 1000°C; Cd counts in the center and the sides of the slice

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

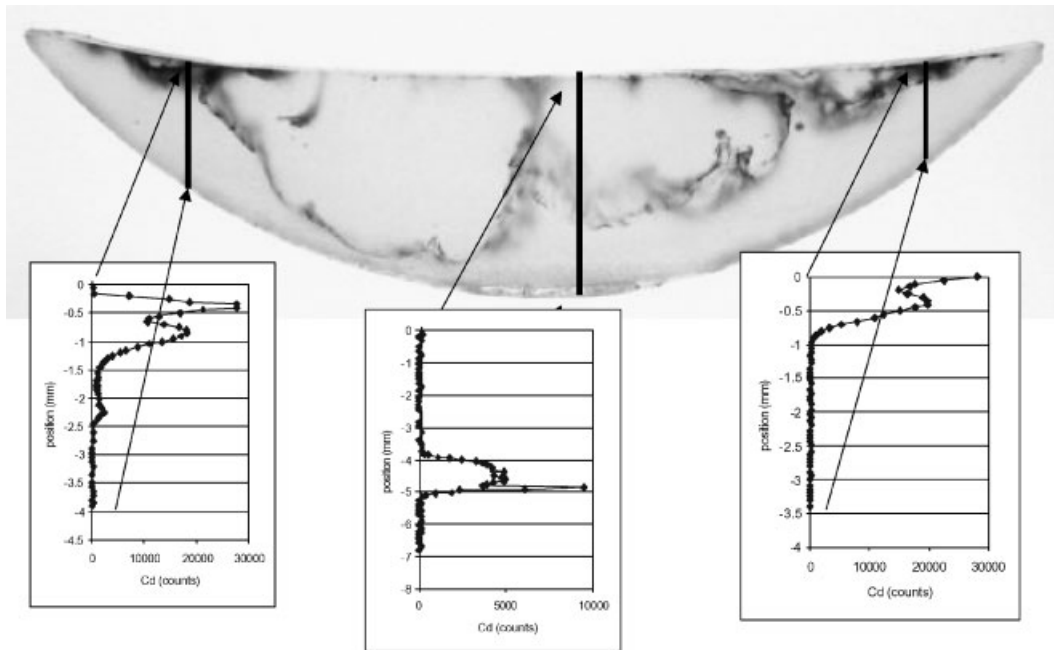


Figure 9. X-ray fluorescence microprobe analysis—vertical slice from side of sample heated at 1000°C; Cd counts in the center and the sides of the slice

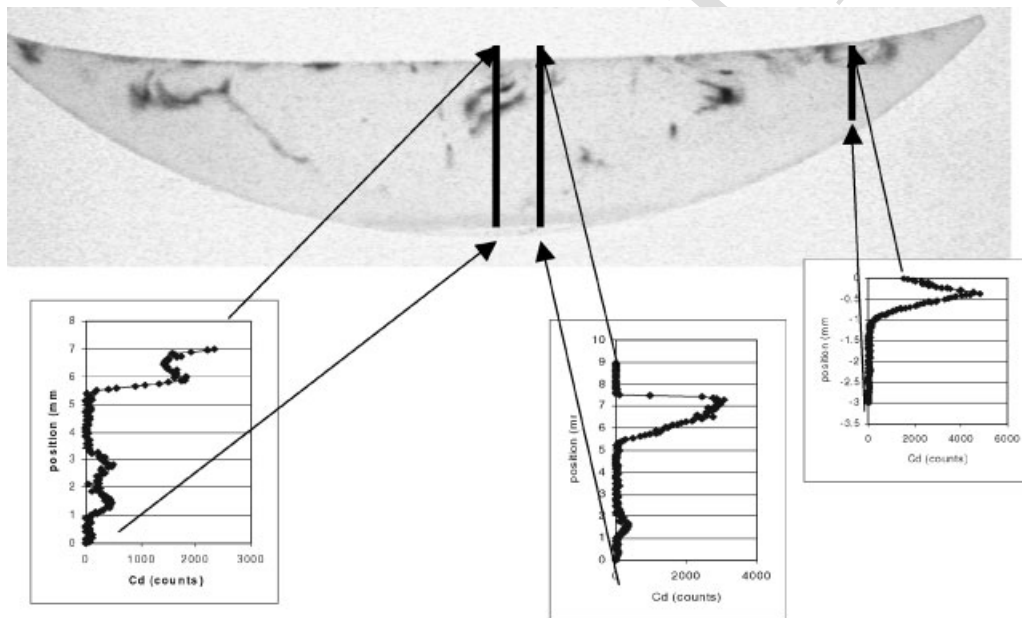


Figure 10. X-ray fluorescence microprobe analysis—vertical slice from middle of sample heated at 1100°C; Cd counts in the center and the sides of the slice

presented in Section 3-2 for two reasons: (1) with the exception of the unheated (control) sample, only a small 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.

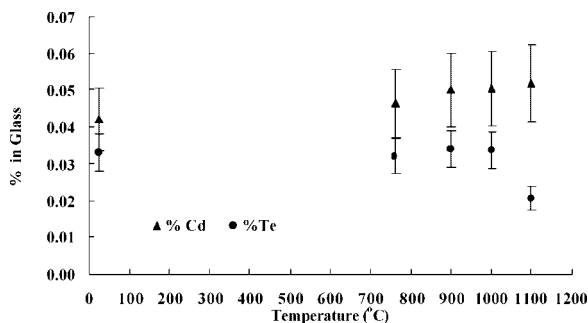


Figure 11. Cadmium and tellurium concentrations in unheated and in molten glass at different temperatures; average values and error bars showing % of error

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 and does not enter the vapor phase. 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°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 ability 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. 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/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°C, but a significant fraction was released at higher temperatures (1000–1100°C).

Acknowledgements

This work was supported by the Solar Technologies Program, Conservation and Renewable Energy, under Contract DE-AC02-76CH00016 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.

REFERENCES

1. Thumm W, Finke A, Neumeier B, Beck B, Ketrup A, Steinberg H, Moskowicz P. Environmental and health aspects of CIS-module production, use and disposal. *Proceedings the 1st World Conference on Photovoltaic Energy Conversion*, Waikoloa, Hawaii, 5–9 December 1994; [Q1](#)
2. Steinberger H. Health and environmental risks from the operation of CdTe and CIS thin film modules. *Proceedings of the 2nd World Conference on PV Solar Energy Conversion*, 6–10 July, 1998, Vienna, Austria. [Q1](#)
3. UL1256 Standard: Fire test of Roof Deck Constructions, October 2002, Underwriters Laboratories Inc., Northbrook, IL.
4. 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.
5. Frisson L, Lieten K, *et al.* Recent improvements in industrial PV module recycling. *Proceedings of the 16th European PV Solar Energy Conference*, Glasgow, UK, May 2000. [Q1](#)
6. Mills K. *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*. Butterworth, 1974. [Q2](#)
7. Korneeva I, Belyaev AV, Novoselova AV. *Zhur. Neorg. Khim.* 1960; **5**: 1. [Q3](#)
8. Lorenz MR. *Journal of Physical Chemistry of Solids* 1962; **23**: 1449. [Q3](#)
9. Goldfinger P, Jeunehomme N. *Transactions of the Faraday Society* 1963; **59**: 2851.
10. Brebrick RF, Strauss AJ. *Journal of Physical Chemistry of Solids* 1964; **25**: 1441.
11. Kubaschewski O, Alcock CB. *Metallurgical Thermochemistry*, 5th edn, Pergamon: Oxford, 1979.
12. Yaws CL. *Handbook of Vapor Pressure, Volume 4*, Gulf: Houston. [Q4](#)
13. Drysdale D. *Introduction to Fire Dynamics*, Wiley; 1985. [Q2](#)
14. Standard Test Methods for Chemical Analysis of Sod-Lime and Borosilicate Glass, C 169-89, May 26, 1989, ASTM Committee on Standards, Philadelphia, PA.
15. Fthenakis VM. Life cycle impact analysis of cadmium in CdTe PV production, *Renewable and Sustainable Energy Reviews* 2004; **8**: 303–334.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59

Author Query Form (PIP/624)

Special Instructions: Author please write responses to queries directly on Galley proofs and then fax back. Alternatively please list responses in an e-mail.

- Q1: Author: Please give page range.**
- Q2: Author: Please give place of publication.**
- Q3: Author: Please give full journal title.**
- Q4: Author: Please give year of publication.**

Uncorrected Proof