Water Solubility of Cadmium Telluride in a Glass-to-Glass Sealed PV Module

Jonathan Allen and Zoltan Kiss,
Amelio Solar, Lawrenceville, NJ 08648
and
Sezhian Annamalai, Ian L. Pegg, and Biprodas Dutta,
Vitreous State Laboratory, The Catholic University of America, Washington, DC 20064

Abstract

Cadmium Telluride (CdTe) is gaining a substantially increased role in the world's energy mix. The environmental safety concern of cadmium leaching out of CdTe solar panels has become a very important issue. Our recent study shows that naturally occurring groundwater and rainwater dissolve CdTe at a very fast rate, allowing cadmium to enter the groundwater at concentrations at least four orders of magnitude greater than the EPA allowed limits for drinking water. The study also demonstrates that water travels by capillary action between the various layers in a typical PV module structure, thus leading to delamination and hence contamination by cadmium at an even faster rate than otherwise anticipated. The behavior of the cadmium leaching out of CdTe solar panels makes it imperative not to discard rejected CdTe modules/panels in dumps or landfills.

Introduction

CdTe-based photovoltaic modules have gained a market penetration of approximately ten percent of the existing PV market. In 2010, this proliferation represents an annual manufacturing capacity of about two gigawatts and an installed capacity by the end of 2010 of approximately five gigawatts. Unless further manufacture of CdTe is curtailed, a cumulative installed capacity of about 50 gigawatts is possible by 2020. This increase means that 100,000 hectares or 1,000 square kilometers would be covered with this cadmium containing photovoltaic material. About 5,000 tons of water-soluble carcinogenic CdTe would thereby be spread over the 1,000 square kilometers of land area. Cadmium has been established by several international agencies as one of the most carcinogenic materials. The "Restrictions of Hazardous Substances" Directive (RoHS) was signed by many nations including the European Community, China, Japan, and India [ref. 1]. In the European Community, however, the promoters of CdTe have managed to get an exemption from the Directive for CdTe PV. Some other countries, such as Japan, China, and India, continue to ban cadmium telluride. In Europe and the US, cadmium telluride based PV modules are heavily marketed. In 2010, for example, the industry sold approximately 2 gigawatts of CdTe based modules. The initial exemption in Europe depended heavily on white papers published in the US by NREL personnel [ref. 2] and some other related institutions, such as Brookhaven National Laboratory [ref. 3]. Those papers claimed that CdTe is not water-soluble. Also, the manufacturers of the modules declared that the installed modules would be dismantled at the end of their useful live (20-30 years) and all cadmium would be subsequently reclaimed. To pay for this cost, the manufacturer sets aside approximately $0.015 per watt [ref. 4]. Keeping in mind the magnitude of the problem and the danger to humans and other living things, we have reexamined these two fundamental assumptions: the water solubility of cadmium from modules, and the cost and responsibility for recycling.

The makers of CdTe photovoltaic modules acknowledge the toxic and carcinogenic properties of cadmium and have therefore promised that when the modules reach the end of their useful life they will de-mount them, pack them, ship them "home" and salvage the cadmium [ref. 4]. Some companies have set up funds which are supposed to cover the cost of doing so even though that cost would nearly equal that of delivering and installing the modules in the first place. History has shown us, though, that such promises, however vociferously advertised, are not always fulfilled, especially when they involve projections of 25 to 30 years into the future. We have therefore examined the possibility that modules will end up in a landfill, broken and exposed to groundwater. We have attempted to answer the question: Under such circumstances, will dangerous amounts of Cd ions leach out of the panels, especially broken ones, to pollute the water table or groundwater?

Some past studies have indicated that such leaching would be minimal, but they used only pure water as the leaching solution [ref. 3]. In the real world, one is likely to encounter acidic leaching agents such as groundwater or acid rain. The leaching protocol adopted during experimentation addressed the basic problem of how to take into account the conditions of the broken panels that would be anticipated in a landfill. The idea was to "break" the panels as realistically as possible to prepare the samples. Breaking them by impact would closely simulate the "real world" but the breakage patterns would be inherently random and therefore not precisely reproducible from piece to piece nor in successive experiments. On the other hand, slots cut through the front glass with a diamond saw are reproducible, but not entirely realistic.

Our investigation therefore included two independent studies, both using approximately 2-inch (50 mm) squares taken from a "First Solar" CdTe module. One set of samples was broken by impact while the other set was slotted with a saw. All samples were kept at normal room temperatures (20 to 25°C) throughout the leaching process. The first study examined five pieces broken by impact. We struck each square a single blow on the front surface with a 5-ounce cross-peen hammer to induce the kind of breakage that would likely occur when modules are thrown into a landfill. Each sample was then submerged in about 150 ml of leaching solution in a covered 8-ounce Mason jar. One jar contained pure (DI) water. The other four samples were submerged in citric acid-based buffer solutions with pH values of 3, 4, 5, and 6, respectively. These were intended to span the range of acidity one might encounter in actual groundwater as rain seeps into the pile of discarded modules. Initial ICP spectrometry analyses (blanks) of the leaching solutions showed no cadmium with a MDL of about 3 ppb. After 32, 120, and 206 days of submersion we analyzed each solution for cadmium by ICP emission spectrometry. We also tested the pH of each buffer solution at the end of 206 days and found it still within 0.1 pH unit of its nominal value. The pure water, lacking any buffer, had acquired a final pH value of 6.4. The sample in pure water appeared to suffer no additional destruction beyond that caused by the hammer blow, but those in the more acidic solutions underwent increasing degrees of delamination with decreasing pH values. In fact, the samples in pH 3, and 4 solutions were completely delaminated with all of the front glass fragments having settled to the bottom of the jar, and all the active layers were removed. Only the laminating polymer remained attached to the back glass. The samples in pH 5 and 6 solutions had at least 75% of their front glass area delaminated and the underlying active material gone. The analysis results are shown in the accompanying graph (Figure 1), which plots cadmium concentration of the solutions versus time for each pH value. Concentrations are in parts per million (mg/l). For reference, the maximum level of Cd permitted by the EPA in drinking water is 5 parts per billion (5 micrograms/liter). It is not clear why for pH 4 the final (206 days) reading is less than the previous one. One possibility is that the cadmium may not have distributed itself uniformly throughout the solution. Another possibility is that there may also have been some adsorption on the EVA plastic after the sample delaminated.

The leaching solutions, especially the more acidic ones, show cadmium levels 4 orders of magnitude greater than the EPA limit. Thus, even if this experiment does not mimic the conditions in a landfill perfectly, it is hard to argue that the cadmium in CdTe modules is safe against polluting the environment. The other set of tests also used squares from a "First Solar" module approximately 50 mm on a side, but these were carefully cut through the front glass with a diamond saw to make six slots each approximately 25 mm long. All the samples had the same pattern as shown in Figure 2. Two such samples were immersed in buffer solutions with pH values of 4 and 10, respectively. The pH 4 simulated acid rain, as in the broken-sample tests, while the alkaline solution simulated the properties of some groundwater that passes through calcium salts. The third sample was put into rainwater collected during a storm on 3 June 2010 in Washington, DC, which had a measured pH of 6.9 (essentially neutral). All three samples were kept in plastic containers with airtight lids and maintained at room temperature. After 7, 10, 14, 21, 30, 45, and 64 days, we withdrew approximately 10 ml specimens of the leaching solution for analysis by DCP-AES to determine the Cd concentrations. To maintain constant solution volume, each sample withdrawn was replaced with 10 ml of fresh solution.

The results of the analyses are summarized in Table 2, and graphed in Figures 3 through 5. Comparing results, at 64 days the broken sample in pH=4 solution had about 85 mg/l Cd, while the scribed one had 54 mg/l. The difference might be explained by noting that the broken sample had a much closer pattern of cracks so as to expose more of the active layer to the leaching solution. Both, however, had Cd concentrations four orders of magnitude above the EPA limit for drinking water. What is even more striking is that the sample in the alkaline solution with a pH of 10 reached a concentration of 110 mg/l Cd after 64 days. According to NREL's Cadmium Telluride Fact Sheet [ref 5], CdTe PV modules contain between 3 and 10 grams of Cd/m_2. The nominal value is 7. So a 5x5 cm (25 cm_2) sample would contain about 17.5 mg of Cd. If all of this dissolved in 0.15 liter of solution the concentration would be 117 mg/l. The final concentrations of cadmium given in Table 1 show that at least the majority of this element did leach into solution for the jars with pH values of 3, 4, and 5, and that a significant fraction leached out at pH 6. We were not able to measure the original amounts of cadmium in the samples, but based on the nominal value it should be clear that substantial amounts of the element leach out effectively in all but the pure water. One observation that supports the conclusion that most of the cadmium is being leached is that the concentration-versus-time curves tend to level off after 60 to 100 days. Therefore, it is very probable that in the real world virtually all the cadmium will be leached out within the first year after the modules are dumped.

Conclusions

If damaged, CdTe photovoltaic modules are exposed to essentially pure water, the leaching of cadmium is small but as the pH diverges from 7, leaching effects increase by a factor on the order of 100. Thus, when such modules are discarded and thrown into real world dumps or landfills, they will constitute a serious pollution hazard from leached cadmium. If CdTe were the only practical photovoltaic technology, we might have to accept the environmental risks, but such is hardly the case. Several other quite acceptable technologies exist without the presence of carcinogenic components.

References

1. Restrictions of Hazardous Substances (RoHS), Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment, http://www.rohs.gov.uk.
2. Zweibel, K., Moskowitz, P., Fthenakis, V. "Thin-Film Cadmium Telluride Photovoltaics: ES&H Issues, Solutions, and Perspectives," National Renewable Energy Laboratory, NREL/TP-520-24057, February 1998.
3. Fthenakis, V.M., "Life cycle impact analysis of cadmium in CdTe PV production," Renewable and Sustainable Energy Reviews 8 (2004) 303–334, Elsevier.
4. http://www.firstsolar.com/en/recycle_program.php.
5. Zweibel, K. and Fthenakis, V., "Cadmium Facts and Handy Comparisons," National Renewable Energy Laboratory, http://www.nrel.gov/pv/cdte/pdfs/cdte_factsheet.pdf.

Days	pH=3	pH=4	pH=5	pH=6	DI
0	0	0	0	0	0
32		35.4	27.8	11.1	1.11
41	55.8				
120	94.6	174	123	82.7	2.84
206	162	145	122	107	7.28

Table 1.

Cadmium concentration in ppm (mg/l) of broken leaching samples.

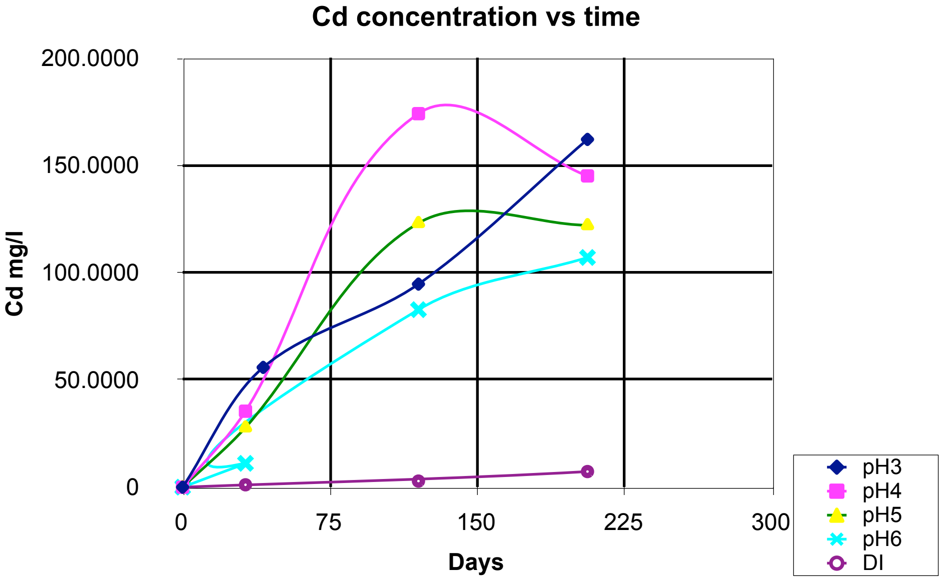

Figure 1. Cadmium concentration versus time.

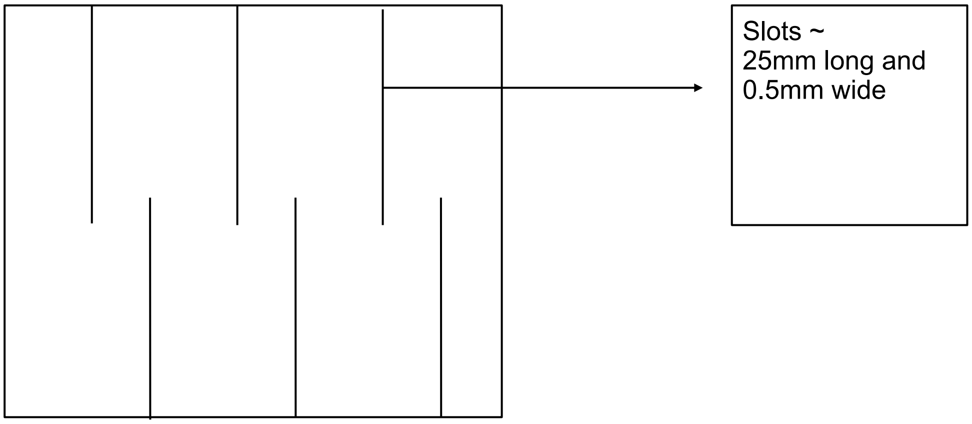

Figure 2. Diamond saw scribing pattern on leaching samples.

Days	RW (ppm)	B4 (ppm)	B10 (ppb)
7		7.10	30.00
10	1.30		
14		14.79	80.00
21		20.80	90.00
30	2.89	31.11	120.00
45		45.02	170.00
64		53.86	140.00

Table 2. Cadmium concentration in solutions for scribed samples in Rain Water, Buffer pH 4, and Buffer pH 10.

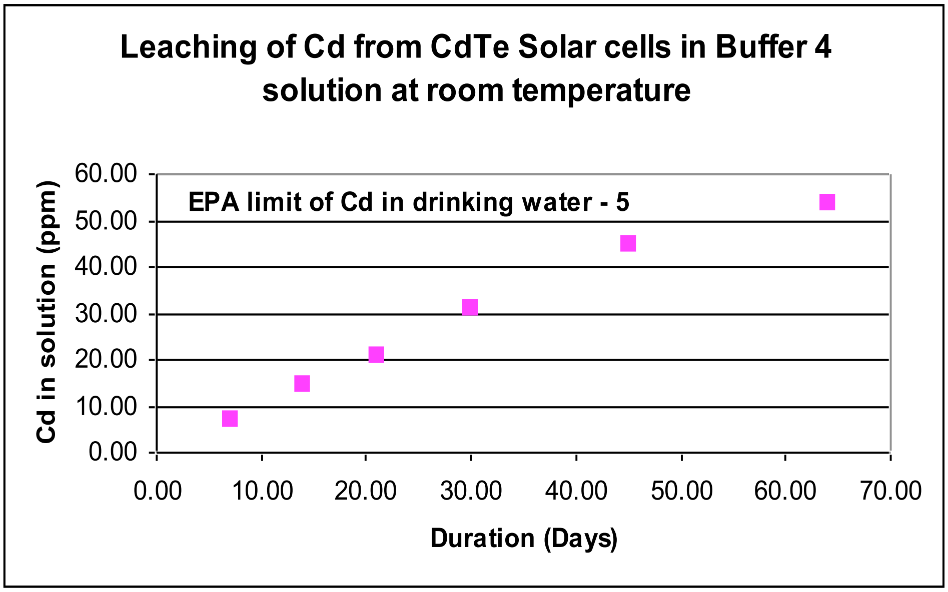

Figure 3. Cadmium concentration versus time in buffer solution, pH 4.

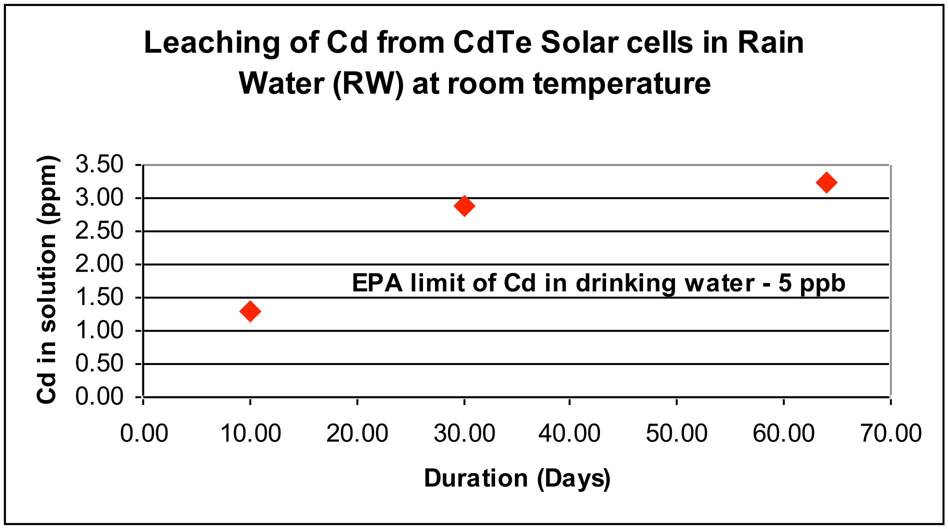

Figure 4. Cadmium concentration versus time in rainwater, pH 6.9.

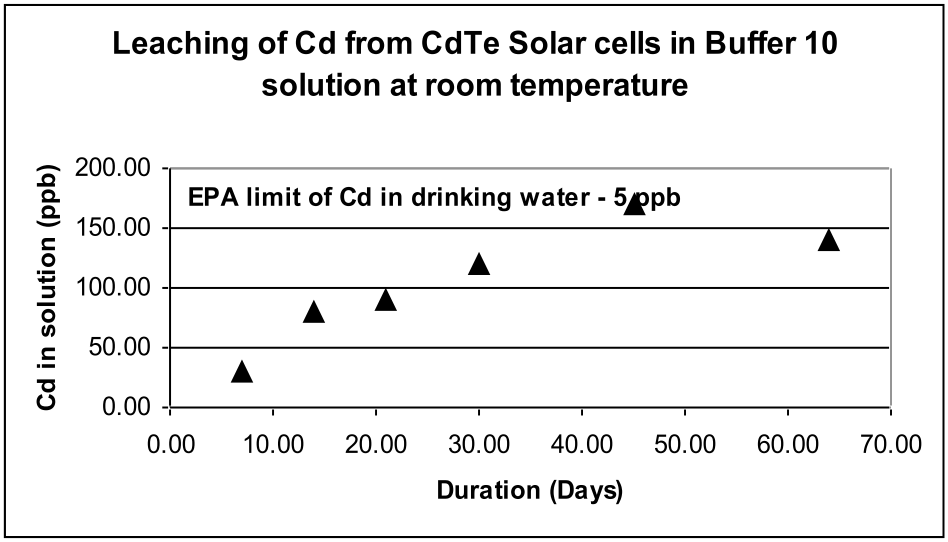

Figure 5. Cadmium concentration versus time in buffer solution, pH 10.

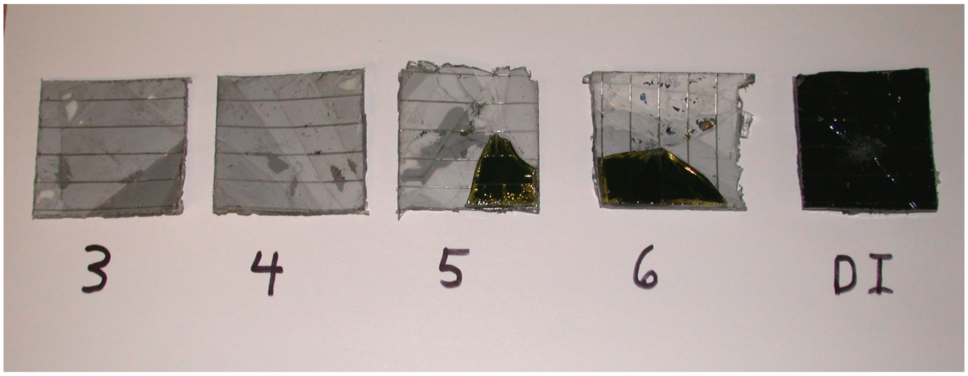

Figure 6. Broken samples after 206 days of soaking. Buffer pH values as written.