Assessment of leaching tests for evaluating potential environmental impacts of PV module field breakage

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***Abstract* — Test methods from standard waste characterization leaching tests used in the U.S., Germany, and Japan were evaluated to determine if they can be used to help evaluate potential environmental impacts from PV field breakage. To assess the representativeness of leaching test methods, PV module breakage types were evaluated from warranty return data. Field breakages mainly consist of various types of stress and impact fractures in which modules remain largely intact with a number of glass fractures or cracks. By breaking modules into cm-scale pieces and tumbling them in solvent, waste characterization leaching tests can be more aggressive than PV field breakage conditions with regards to parameters such as fragment sample size, solvent, and treatment method. An alternative test method was previously used in Japan in which modules with a predetermined number of cracks were subjected to simulated rainwater. This approach is more representative of field conditions as modules are more likely to experience cracks under field conditions than to break into pieces.**

***Index Terms* —photovoltaic systems, environmental management, risk analysis**

I. Introduction

With global installed capacity reaching approximately 180 GW through 2014 [1], solar photovoltaics (PV) are making a significant contribution to new electricity supply in key markets around the world. By directly converting sunlight to electricity without emissions, solar PV can provide a sustainable alternative to conventional electricity generation. Development of utility-scale solar PV projects can require evaluation of a wide variety of potential environmental impacts, including impacts on biodiversity, land use, water resources, and human health [2][3]. Some stakeholders have raised concerns about the potential environmental impacts of PV modules due to the presence of environmentally sensitive materials, such as compounds of Pb, Cd, In, and Se. Under normal operation, PV modules do not pose a risk to human health or the environment, as the semiconductor layer is encapsulated between a layer of glass and a backsheet or a second layer of glass.

However, questions may arise with regards to non-routine events, namely broken modules subject to leaching by precipitation. Broken modules refer to modules with cracked glass or broken pieces which may result from extreme weather or human factors. In the case of thin film cadmium telluride (CdTe) PV modules, module breakage is rare, occurring in approximately 1% of modules over the 25-year warranty operating life (0.04%/yr) [4]. Of these breakages, over one-third occur during shipping and installation and are removed prior to plant operation. There is an observed decline in breakage rate after the installation and initial operating period (Fig. 1) [5]. In addition, a proportion of broken modules have only chipped glass that does not affect the semiconductor layer.

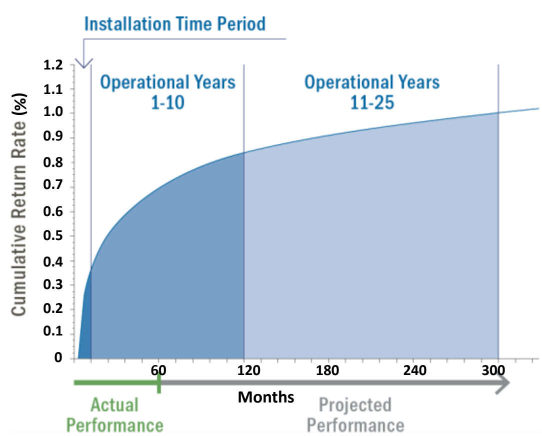

Fig. 1. Cumulative breakage rate as a function of months in service.

While rare, breakage followed by precipitation may potentially result in leaching of metals from modules and subsequent exposure in soil, air, or groundwater. Standard leaching tests could be used to try to evaluate the potential environmental impacts of broken PV modules. However, leaching tests have typically been designed for one of two objectives: identification of contents or waste characterization for landfill disposal.

Contents testing determines the total concentration of each target analyte in a sample. In the case of identifying metal constituents in PV modules, contents testing typically consists of acid digestion followed by spectrometry [6]. Samples are prepared by crushing module pieces to a powder (mm scale or smaller) and digesting with repeated additions of strong acid and oxidizing agent. The extracted metals are subsequently measured with methods such as inductively coupled plasma-atomic emission spectrometry. Waste characterization testing evaluates the soluble portion of analytes in a sample using conditions representative of a landfill. Test methods evaluate small (cm scale) fragments to account for potential crushing of waste by landfill equipment.

TABLE I

SUMMARY OF WASTE CHARACTERIZATION LEACHING TEST METHODS AND RESULTS FOR PV MODULES IN THE U.S., GERMANY, AND JAPAN

Geography		**United States [7]**	**Germany [8]**	**Japan [9]**
Leaching Test		U.S. EPA Method 1311 (TCLP)	DIN EN 12457-4:01-03	Ministry of Environment Notice 13/JIS K 0102:2013 method (JLT-13)
Sample size (cm)		1	1	0.5
Solvent		Sodium acetate/ acetic acid (pH 2.88 for alkaline waste; pH 4.93 for neutral to acidic waste)	Distilled water	Distilled water
Liquid:Solid Ratio		20:1	10:1	10:1
Treatment Method		End-over-end agitation (30±2 rotations per minute)	End-over-end agitation (5 rotations per minute)	End-over-end agitation (200 rotations per minute)
Test Temperature		23±2˚C	20˚C	20˚C
Test Duration		18±2 hr	24 hr	6 hr
Leachate Cd Concentration (mg/L)	CdTe PV	0.22	0.0016 - 0.0040	0.10-0.13
	c-Si PV	Non-detect (<0.1)	-	Non-detect (<0.01)
	Limit	1	0.1	0.3
Leachate Pb Concentration (mg/L)	CdTe PV	Non-detect (<0.1)	-	Non-detect (<0.01)
	c-Si PV	3-11	-	Non-detect (<0.01) - 0.90
	Limit	5	-	0.3

The purpose of this study is to evaluate whether standard leaching tests can be used to help evaluate potential environmental impacts from PV field breakage. The focus is on waste characterization leaching tests, because contents testing provides data on the total quantity of metals but not their availability under field conditions. In this study, field breakage conditions are compared with waste characterization leaching test methods to determine the representativeness of the methods.

II. METHODS

Test methods from standard waste characterization leaching tests used in the U.S., Germany, and Japan were evaluated with regards to key parameters such as fragment sample size, solvent, and treatment method. To assess the representativeness of these parameters, product return data were obtained over nine years of field deployment of thin film CdTe PV modules. Module breakage types were analyzed, corresponding to standard categories recorded during warranty returns, including various types of stress and impact fractures. Data from the U.S. National Atmospheric Deposition Program were analyzed to assess the range of acidity typically present in rainfall, for comparison with solvents used in leaching tests.

III. RESULTS

Key test method parameters from leaching tests in the U.S., Germany, and Japan are presented in Table 1. These parameters are evaluated with regard to their relevance to PV field breakage conditions.

Sample size

The leaching test sample size in Table 1 ranges from 0.5-1 cm. In contrast, when PV modules break in the field, they tend to fracture (Fig. 2), rather than break into distinct pieces, due to the industrial laminate that encapsulates the module. Based on warranty return data over 9 years of service, field breakages largely consist of various types of stress and impact fractures (Fig. 3), not cm-scale fragments. Impact fractures are caused by external projectiles such as hail. Stress fractures are caused by dynamic/static loads such as wind, snow, and ice, or by thermal or physical propagation of undetected microscopic defects resulting from installation and handling damage. Module breakages can also occur at the attachment point due to improper clamping. Additional review of failure modes for

PV modules is available from the International Energy Agency [10].

Fig. 2. PV module with fractured glass (impact, edge breakage).

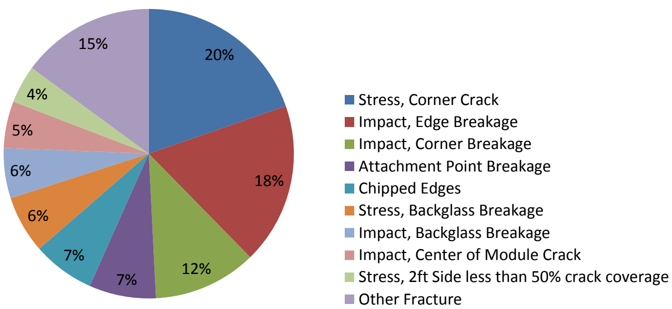

Fig. 3. PV module breakage types from warranty return data for modules put into operation (1-113 months in service).

Solvent

Solvents used in leaching tests range from organic acids to distilled water (Table 1). Organic acids are used to represent mixed waste disposal conditions in which organic acids are produced through fermentation of organic waste. Mixed waste conditions do not exist in PV field breakage. Based on data from the U.S. National Atmospheric Deposition Program [11], the average annual pH of rainwater in the U.S. ranges from approximately 4.7-6.7 (Fig. 4), which is less acidic than the range of 2.88-4.93 used in the TCLP test.

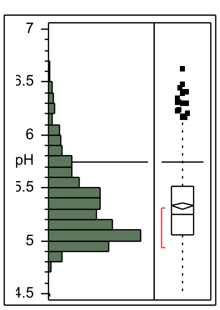

Fig. 4. Average annual rainfall pH in the U.S. (2011-2013) [11].

Treatment method

The sample treatment method of immersion in solvent and rapid end-over-end agitation (Table 1) is designed to accelerate the aging of the sample in order to allow a 6-24 hr test to represent long-term leaching potential in landfill conditions. However, there is an incentive to detect and remove non-performing modules, rather than leave them indefinitely in the field, which reduces the potential for long-term leaching. Broken modules can be detected though routine inspections of modules or power output monitoring. The latter may include diagnostic comparison of actual to expected performance or comparison of co-located arrays to identify low performance areas and modules that are nonfunctioning potentially due to breakage [4].

IV. DISCUSSION

The evaluation of test methods indicates that waste characterization leaching tests can be more aggressive than PV field breakage conditions with regards to parameters such as fragment sample size, solvent, and treatment method. In order to provide further bounds on worst-case leaching potential from field breakage, data from two additional cases are also discussed. Data are presented from previous leaching tests of the raw semiconductor material CdTe, and from intentional crushing of PV modules by a heavy-duty landfill compactor.

CdTe has a very low solubility product in water (K_{sp} = 9.5×10^{-35}) derived using Outotec HSC Chemistry software (V. 7.0) and experimental water solubility testing following OECD Test Guideline 105 [12]. The CdTe K_{sp} corresponds to an equilibrium Cd concentration in water of 9.7×10^{-18} mol/L based on (1)-(3), or 1.1×10^{-12} mg/L given the molecular weight of Cd (112.414 g/mol). The stoichiometric balance in (2) is based on the high purity (99.999%) of semiconductor grade CdTe.

$$K_{sp} = \left[Cd^{2+}\right]\left[Te^{2-}\right] \quad (1)$$

$$\left[Cd^{2+}\right] = \left[Te^{2-}\right] \quad (2)$$

$$\left[Cd^{2+}\right] = \sqrt{K_{sp}} \quad (3)$$

TABLE II

SUMMARY OF LEACHING TEST METHODS AND RESULTS ON THE RAW SEMICONDUCTOR MATERIAL CDTE*

	TCLP[a] [13]		WET[b] [13]		Dissolution [13]	Dissolution [14][15]	Bio-elution [14][16]
Sample size (μm)	63-125		63-125		63-125	92-262	74-<100
Solvent	Acetic acid, sodium hydroxide (pH 4.93)		Citric acid, sodium hydroxide (pH 5)		Hydrochloric acid, sodium hydroxide (pH 3.5)	CO_2-buffered water (pH 6)	Hydrochloric acid (pH 1.5)
Headspace	N_2	Ambient air	N_2	Ambient air	Ambient air	0.5% CO_2-in-air	Ambient air
Temperature (°C)	Room		Room		30	20-23	36-38
Treatment method	Agitation at 21 rpm for 18 hr		Agitation at 21 rpm for 48 hr		Agitation at 120 rpm for 72-600 hr	Agitation at 100 rpm for 168-672 hr	Agitation at 150 rpm for 1 hr, then resting for 1 hr
% Cd release (w/w)	0.58%	6.4%	0.56%	5.3%	≤3.6%	3.2 - 4.1%	2.3%

*See Discussion for interpretation for CdTe-containing devices

a – U.S. EPA Method 1311 Toxicity Characteristic Leaching Procedure

b - Waste Extraction Test

Given acidic conditions ranging from pH 1.5 to 6, leaching tests on the raw semiconductor material CdTe indicate a range of approximately 0.56% to 6.4% (w/w) solubility of Cd content in CdTe (Table 2). This range is nearly an order of magnitude lower than assumed in a previous worst-case environmental impact assessment [17], where the latter is based on modified availability testing that is more aggressive than standard waste characterization leaching tests and field breakage conditions.

Note that both the material tested and some of the test methods in Table 1 differ from those in Table 2. Table 1 provides leaching test methods and results for PV modules, whereas Table 2 provides leaching test methods and results for the raw semiconductor material (CdTe). Table 1 provides leaching test methods for waste characterization for landfill disposal. Table 2 provides leaching test methods for both waste characterization (TCLP and WET tests) and for evaluating solubility under a wider range of conditions (bioelution and long-term dissolution tests). The TCLP test is the federal U.S. waste characterization test whereas the WET test is the waste characterization test used in the State of California. For each of the TCLP and WET test methods in Table 2, two solubility results are provided corresponding to aerobic conditions (ambient air headspace) and anoxic conditions (N_2 headspace), with lower solubility observed under anoxic conditions.

Additional data is required to use the evaluation of the raw semiconductor material CdTe in Table 2 to try to understand potential leaching behavior of CdTe-containing devices. For example, CdTe PV modules contain approximately 6 g Cd content per 12 kg device [4] or 0.05% Cd content by mass, and the leaching potential is further limited by the monolithic glass-adhesive laminate-glass structure of the device that encapsulates the semiconductor material.

The potential leaching behavior of CdTe PV modules in a standard 1 L TCLP extraction fluid can be estimated using (4).

$$C_{Cd} = \frac{M_{EF} \times SL \times CO_{Cd} \times L_{Cd}}{AF_{EN} \times V_{EF}} \quad (4)$$

where,

C_{Cd}: TCLP Cd leachate concentration (mg/L),

M_{EF}: mass of extraction fluid (10^6 mg),

SL: TCLP solid-liquid ratio (1/20),

CO_{Cd}: Module Cd content (0.05%),

L_{Cd}: leaching potential of Cd content (6.4%),

AF_{EN}: adjustment factor to account for raw semiconductor material encapsulation in glass-adhesive laminate-glass structure, and

V_{EF}: volume of extraction fluid (1 L).

By taking the measured value of C_{Cd} from TCLP testing in Table 1 (0.22 mg/L), the adjustment factor (AF_{EN}) is estimated as ~7. In other words, in addition to the low mass concentration and solubility of the raw CdTe semiconductor material, the glass-adhesive laminate-glass encapsulation is estimated to further reduce solubility under standard TCLP conditions by nearly an order of magnitude, with the TCLP conditions already aggressive compared with field breakage.

In addition to the raw semiconductor material evaluation, a hypothetical case that provides perspective on field breakage is the intentional crushing of PV modules in a landfill. This is a hypothetical case because tractor compaction cannot take place in an operating PV array; however, even under six passes over the PV modules by a heavy-duty landfill compactor (Fig. 5), PV modules remain largely intact (Fig. 6) with the vast majority of pieces larger than the sample size (0.5-1 cm) used in waste characterization leaching tests (Fig. 7) [18].

Fig. 5. Aljon model 91K compactor used to crush PV modules in a Municipal Solid Waste Landfill in the State of Arizona, USA.

Fig. 6. Compactor foot punch-out of a PV module crushed in a Municipal Solid Waste Landfill in the State of Arizona, USA.

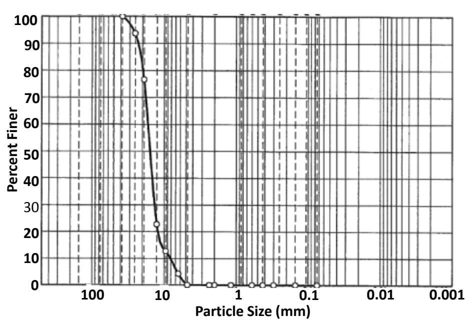

Fig. 7. Fragment size distribution of a PV module crushed in a Municipal Solid Waste Landfill in the State of Arizona, USA.

In testing of early generation PV modules, the New Energy and Industrial Technology Development Organization (NEDO) in Japan commissioned the study of leaching potential of thin film CdTe PV modules using methods more representative of field breakage conditions [19]. Instead of breaking modules into cm-scale pieces and tumbling in solvent, the testing subjected intact modules with 1 to 5 cracks to a quantity of simulated acid rain (pH 5) equivalent to 40 days of average rainfall. This approach is more representative of field conditions as modules are more likely to experience cracks under field conditions then to break into pieces.

Instead of developing leaching tests that more closely resemble field breakage conditions, some recent investigations have modified test parameters to be even more aggressive than standard waste characterization tests [20-22]. The use of finely ground samples and multiple extraction cycles in these investigations mimics the recycling process for PV modules [23] more closely than any environmental conditions, where the recycling process has the explicit objective to separate and then recover and reuse metals from end-of-life modules. As with contents testing, such worst case leaching tests provide data on the total quantity of metals but not their availability under realistic field conditions.

In addition, leaching tests are used to estimate potential chemical emissions; however, emissions are not equivalent to impacts. In order to conduct environmental impact analysis, fate and transport analysis is further needed to evaluate the chemical transformations and dispersion of chemicals in the environment in moving from the point of emissions to the point of exposure (or impact) [4]. Other factors such as breakage rate and exposure factors (frequency, type, and duration of exposure to impacted soil/water/air) also have to be accounted for to estimate potential impacts to human health and the environment.

V. Conclusion

Leaching tests used to evaluate the potential health and environmental impacts of rainwater leaching of broken PV modules need to reflect realistic PV field conditions. The evaluation of test methods indicates that waste characterization leaching tests can be more aggressive than PV field breakage conditions with regards to parameters such as sample size, solvent, and treatment method. Some recent worst case leaching tests are even more aggressive than waste characterization leaching tests and more closely resemble the PV recycling process or contents testing than realistic field conditions. An alternative test method was previously used in Japan in which modules with a predetermined number of cracks were subjected to simulated rainwater. This approach is more representative of field conditions as modules are more likely to experience cracks under field conditions then to break into pieces.

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