Wuppertal Institute
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Appraisal of Laboratory Analyses Conducted on CdTe Photovoltaic Modules

Working Paper

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Over the last years, different photovoltaic (PV) technologies became commercially available, while several others are under development. PV technologies require diverse materials to generate electricity from sun light, including in some cases toxic materials. The use of cadmium-telluride (CdTe) in one of the existing thin-film photovoltaic technologies constitutes a case in point. Cadmium is classified as highly toxic while the compound CdTe is not as hazardous as cadmium alone, but as a cadmium compound it is still considered a hazardous substance. PV systems can also contain lead used in solders, another toxic metal.

Against this background, the Wuppertal Institute for Climate, Environment and Energy has conducted an independent, scientific and open-ended as regards its outcome appraisal of recent laboratory analyses performed on CdTe PV modules.* This short study covers two sets of laboratory test results. Additional CdTe PV laboratory analyses that may exist are not considered here. This paper briefly presents the testing methods, their purpose, in which context they are usually used, as well as the results of the tests. Implications in terms of resource management are drawn.

1. *Analyses conducted by the Norwegian Geotechnical Institute (NGI 2010a, NGI 2010b)*

1.1. Purpose and description of the testing

Financed by REC, SolarWorld, Wacker, and Photovoltech, the Norwegian Geotechnical Institute (NGI 2010b), in cooperation with an accredited laboratory (ALS), has conducted four types of analyses on samples of PV CdTe PV modules. These analyses are referred to as *total metal content*, *batch test*, *column test*, and *availability test*.

Those tests follow Norwegian standardized procedures that can be found in the Norwegian implementation of the relevant EU directives. The total metal content test aims at measuring the total mass of a list of elements per kilogram of sample. The batch and column tests† are standard methods for waste characterization as required before waste disposal by the Norwegian Waste regulation. The availability test‡ aims at measuring the maximum leaching potential release under extreme conditions (achieved through high dilution, controlled pH

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* Support by the Non-Toxic Solar Alliance is appreciated.

† Methods NS-EN 12457 and CEN/TS 14405, respectively.

‡ Method NT ENVIR 003

etc.).

All those analyses start with the crushing of the module material. The crushed material is then separated in representative samples for the first three tests. For the availability test, the samples are further grounded. The total metal content test consists of a chemical analysis of the crushed solid PV modules. The three other tests are leaching studies. For that, the crushed or finely grounded material is either shaken 24h with deionized water (batch test), or installed in a column through which deionized water is pumped for about three weeks (column test), or mixed during 24h with deionized water (ten times more than for the batch test) to which nitric acid is added in order to reach given pH values (availability test).

1.2. Results and implications of the testing

The ALS laboratory analysed the concentrations of a number of elements[§] but only the results for cadmium are summarized here since it is by far (with telluride) the most abundant of the tested elements in the samples. Compared to telluride, cadmium is of particular interest because of its extreme toxicity.

The *total metal content* analysis shows that the samples contain in total 383 mg of cadmium per kg of sample. This value is therefore the upper limit for all the subsequent analyses (obviously, more cadmium than is initially present in a sample cannot leach).

The results of the *availability tests* are shown in Table 1. The pH is at 7.7 when the samples are agitated in distilled water. It is the intrinsic pH of the PV module itself. In this case 7% of the total cadmium content in the sample is leached (26.4 mg make up 7% of 383 mg). If the pH is lowered through the addition of nitric acid, even more cadmium is dissolved and ends up in the solution: 29% and 40% of total cadmium at pH = 6.8 and pH = 3.2, respectively. When the pH is basic, cadmium is easily adsorbed by the recipient walls and also precipitates into cadmium salts. Precipitates are not soluble, therefore cadmium in that form is not measured as leached.

Results from the *batch* and *column tests*, which can be seen in Table 2, clearly show that, solely based on these analyses, CdTe PV modules would not be characterised as hazardous waste. In the batch test, the leached quantity of cadmium is almost seven times lower than the regulatory threshold (0.73 mg/kg against 5 mg/kg). In the column test, the leached quantity of cadmium is far below the regulatory thresholds. The conditions of operations of both the batch and column tests are however quite basic (pH>8 during the whole test) which explains that only a fraction of the total cadmium content is to be found in the prepared solutions.

[§] As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, Zn, and Te

Table 1: Results of cadmium leaching from availability tests on samples of CdTe PV modules

Contaminant	Availability (mg/kg)		
	at pH = 7.7	at pH = 6.8	at pH = 3.2
Cadmium	26.4	109.7	154.3

Table 2: Results of cadmium leaching from batch and column tests on samples of CdTe PV modules

Contaminant	Batch test, at pH = 9.6 (mg/kg)		Column test, at pH = 10.3 (mg/L)	
	Results from the analysis	Regulatory level for hazardous waste	Results from the analysis	Regulatory level for hazardous waste
Cadmium	0.73	5	<0.002	1.7

More than the comparisons with regulatory levels, the influence of the pH on cadmium leaching is the crucial result of this series of analyses. The lower the pH (i.e. the more acidic the conditions), the higher the cadmium leaching release. If in the batch and column tests the solution had been more acidic, the leached concentration would have been measured closer to the values obtained from the availability test (Table 1). In laboratory conditions, material from crushed CdTe PV modules put in aqueous solution remains at its intrinsic pH (around 7.7 which is basic). However, this material has a low buffer capacity, which means that the pH of the solution would rapidly decrease if acidic compounds were added. This is precisely what might happen outside of the laboratory, in a waste deposit for example, where a crushed CdTe PV module could enter in contact with rainwater, which is naturally acidic (so-called "acid rain" is even more acidic). The pH of the solution [crushed module + rainwater] would decrease and hence foster cadmium leaching.

1.3. Further issues

The front glass layer of thin-film CdTe PV modules may shatter due to natural hazards, a hailstorm for example. The glass layer of faulty modules may crack because of the dilatation resulting from large and rapid variations of temperature. Such events, however, have a very low probability to occur: PV modules are designed and tested so as to reduce these risks. For instance, modules undergo "hail tests" to ensure that they can withstand hits from ice balls up to a certain size, travelling at up to a certain speed.

Nevertheless, if the front glass layer of a CdTe module were to be damaged, thus exposing the

CdTe film to natural precipitations, substantial cadmium leaching into the environment could occur. The low pH of natural precipitations (typically pH<6) would foster cadmium leaching. The duration of the contact between the CdTe film and the atmosphere would also play an important role. In that regard, it is unlikely that a module with only a broken front glass layer would stop producing electricity altogether. It could even exhibit for some time a production capacity close to that of an intact module. This would mean low incentives for the PV owner to promptly replace the damaged module, thus potentially increasing the time of exposition of the CdTe film to natural precipitations.

2. Analyses conducted by Sierra Analytical Labs, Inc. (Sierra Analytical Labs 2010)

2.1. Purpose and description of the testing

According to the Californian Code of Regulations (CCR)[**], solar farm operators who need to remove end-of-life solar panels from their farms have to first ask themselves whether the removed material is a waste, as it has been defined in statutes and regulations. In this example, the removed solar panels have served their intended purpose and, for whatever reason, can or will no longer be used. They will either be relinquished[††] or recycled[‡‡]. The material is considered to be discarded: it constitutes a "waste" and the solar farm operators are the "waste generators".

Under the Californian Code of Regulations it is the responsibility of the waste generators to determine whether their waste is hazardous, following the testing and analysis specifications established by the U.S. Environmental Protection Agency (US EPA 1986). If the generated waste turns out to be hazardous, the generator is required to comply with a series of standards regarding identification, labelling, storage, transport etc. of the waste.

A waste is identified as hazardous if it exhibits at least one of the following characteristics: ignitability, corrosivity, reactivity, toxicity[§§]. Sierra Analytical Labs, based in California, has conducted toxicity tests on samples of CdTe PV modules provided by the Non Toxic Solar Alliance (NTSA). The NTSA applied the procedure that a waste generator is required to follow. The samples were received intact by the laboratory, and accompanied by all required documentation. Two separate standardized forms of analysis were then performed: the Total Threshold Limit Concentration (TTLC) and Soluble Threshold Limit Concentration (STLC). TTLC and STLC are used when determining the hazardous waste characterization under California State regulations. The latter overrules the Toxicity Characteristic Leaching Procedure (TCLP) which is the characterization method based on Federal guidelines.

[**] Title 22, Division 4.5, available from: http://www.dtsc.ca.gov/LawsRegsPolicies/Title22/index.cfm

[††] i.e. disposed of; burned or incinerated; accumulated, stored or treated [but not recycled] before, or instead of, being disposed of, burned or incinerated.

[‡‡] i.e. accumulated, stored or treated before recycling by being used in a manner constituting disposal [placed on land], burned for energy recovery, reclaimed, or accumulated for speculative purposes.

[§§] defined in CCR, Title 22, Division 4.5, Chapter 11, Article 3.

More precisely, the Total Threshold Limit Concentration (TTLC) analysis determines the total concentration of each target analyte in a sample. That is, the result of the TTLC (expressed in milligrams per kilogram) shows the total amount of a given toxic compound initially present in the tested sample. The procedure involves crushing the samples, sieving the resulting particles, mixing them for homogenization, preparing separate aliquots for each test (in triplicate), and finally getting the analyte of interest (here cadmium) in solution thanks to a rigorous acid digestion[***]. The solution (digestate) is analysed using an Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) technique[†††] as specified in the standards.

The Soluble Threshold Limit Concentration (STLC) analysis determines the amount of each analyte that is soluble in the "Waste Extraction Test" (W.E.T.) leachate. The intent of the W.E.T. procedure is to simulate the conditions that may be present in a landfill where water may pass through the landfilled waste and travel on into the groundwater carrying the soluble materials with it. Results are expressed in milligrams of chemical per liter of extractant. The STLC method uses the same homogenized samples as those prepared for the TTLC analysis but, instead of an acid digestion, the samples are agitated during 48h in a sodium citrate buffer solution. After that, the obtained solution is filtered and the filtrate is the WET extract, which is then put through an acid digestion[‡‡‡]. The resulting digestates are then analysed using an ICP-AES technique to determine the soluble concentrations, like in the case of the TTLC analysis.

Both TTLC and STLC methods come with a list of chemicals with concentration thresholds (regulatory thresholds). When any target analyte exceeds the limits, the waste is classified as hazardous and its waste code is determined by the compound(s) that failed the testing.

The TTLC and STLC methods are routinely applied to determine whether a waste is toxic and should therefore be characterized as hazardous. The California Department of Toxic Substances Control, for instance, put a number of electronic consumer goods (microwave ovens, VCRs, printers, CPUs, cell phones, telephones, and radios) through these tests in a study a few years ago (HML 2004). The results clearly showed that all products tested were hazardous waste, according to at least one criterion. Lead was the element that exceeded its limits most often.

To put this study into a European perspective, the *European Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment* (RoHS directive)[§§§] was designed *inter alia* to avoid that toxic metals such as cadmium and lead end up in waste streams. The RoHS directive forbids from 1 July 2006 the use of a number of toxic compounds in new electrical and electronic equipment put on the European market. So far, the USA did not put in place a comparable regulation, which may imply that in the future

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[***] E.P.A. Method 3050b

[†††] E.P.A. Method 6010b

[‡‡‡] E.P.A. Method 3010a (the digestion procedure in the STLC case is different than in the TTLC case because a solution and not a solid has to be digested)

[§§§] 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.

US electronic waste (e-waste) may still be contaminated by lead and cadmium, while European e-waste may be free of those.

2.2. Results and implications of the testing

A waste is considered hazardous if it exhibits any of the characteristics identified in the Californian Code of Regulations. Toxicity is one such characteristic and Sierra Anlytical Labs tested it on samples of CdTe PV modules. Table 3 shows the results of the TTLC and STLC analyses and compares them with the regulatory thresholds. For each method, three samples were analysed whose results are represented by the ranges given in Table 3 (between 720 and 735 mg/kg for TTLC, and between 2.81 and 2.95 for STLC).

The tested representative samples of the waste clearly exceed the regulatory limits set for TTLC (100 mg/kg) and STLS (1 mg/L). As a consequence the end-of-life CdTe PV modules would be handled as fully regulated hazardous waste in the State of California.

It means that the waste would need to receive the EPA Hazardous Waste Number that corresponds to the toxic contaminant causing it to be hazardous (D006 for cadmium, the only element tested here). Generators of hazardous waste also need to obtain an Identification Number before they can treat, store, dispose of, transport or offer for transportation their waste. Transporters, transfer, treatment, storage or disposal facilities must also be registered and have received an Identification Number. These requirements involve fees.

Table 3: Results of the toxicity analyses on samples of CdTe PV modules (TTLC and STLC methods)

EPA Hazardous Waste Number	Contaminant	TTLC (mg/kg)		STLC (mg/L)	
		Results from the analysis	Regulatory level	Results from the analysis	Regulatory level
D006	Cadmium	720 - 735	100	2.81 - 2.95	1.0

2.3. Further issues

In the Californian Code of Regulations, a number of waste types that are tested toxic are in practice exempted from some of the constraints for the waste generator. For example, discarded electronic devices that exhibit the characteristic of toxicity may be managed as "universal waste" instead of hazardous waste. It implies reduced management standards compared with hazardous waste that is not exempted.

According to current standards, end-of-life CdTe PV modules belong to fully regulated hazardous waste in the State of California. But proposals to reclassify this waste and thus reduce the generator and transporter requirement are under discussion. One condition for any of the proposals to apply is that the end-of-life PV are recycled, whether or not as part of a reclamation and recycling program administered by a solar panel vendor. No official decision has been taken as of the date of this paper.

A reclassification by the State of California of end-of-life CdTe PV modules from hazardous waste into another waste category such as, for example, universal waste would of course not alter the results of the analyses conducted by Sierra Analytical Labs. The discarded CdTe PV modules would still exhibit the characteristics of toxicity as defined by the standardized test methods STLC and TTLC. The risk of leakage during waste treatment would still exist.

Recycling also poses a number of problems. Low-tech hazardous waste recovery facilities have a heavy environmental footprint (SVTC 2009). Recycling cadmium, in the hope of producing new CdTe PV modules from it, is not a realistic option either. In 25 to 30 years, when PV modules installed today reach end-of-life, cadmium will be widely banned. The photovoltaic technologies that will prevail then are probably unknown today.

For all these reasons, it is recommended not to craft a regulatory exception for hazardous end-of-life solar panels. The actual regulation offers a higher level of collective protection measures than the proposed alternatives. To improve the current state from an occupational health and environmental protection viewpoint, the substitution of hazardous material should be the top priority.

3. Conclusions

The conclusion of this paper is that recent independent laboratory analyses conducted on CdTe PV modules confirm that these present a threat to the environment and health if disposed of in an improper and unprofessional way. These analyses also hint at possible, though less probable, cadmium leakages during the use phase in case of shattered protective glass exposing the CdTe film to natural precipitations.

The only way to rule out the risks associated with the use of cadmium in PV is to refrain from using cadmium in the first place. This requires non-toxic substitutes to be readily available, which they are (e.g. silicon-based photovoltaics). Cadmium should not spread in "green" solar technologies, but need to be disposed of safely.

4. References

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