

## TOXIC SUBSTANCES IN PHOTOVOLTAIC MODULES

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### ABSTRACT

Most photovoltaic modules contain - without fundamental need - toxic substances. In case of crystalline Si, the copper strings within the module contain the heavy metal Pb in the solder. Most modules from Cu(In,Ga)Se<sub>2</sub> use a CdS buffer layer. In case of CdTe, the semiconductor itself is toxic; only a-Si modules are free of heavy metals. Within the last 30 years, the PV world market distributed about 1000 t of Pb and almost 600 t of CdTe over large areas. Nevertheless, the European "Restriction of Hazardous Substances" (RoHS) does not consider photovoltaic modules. Our leaching studies on CdTe modules show substantial leaching of Cd under close to rain water conditions.

### 1. INTRODUCTION

Despite the success of photovoltaics in science, technology and market, there exists a taboo, which is usually not outspoken: *toxic materials*. Only few companies produce really "green" modules.

Here, we estimate the total amount of toxic substances in PV modules. We report also results from leaching experiments at CdTe-modules. Substantial leaching of Cd occurs under acidic conditions.

### 2. MODULE MARKET

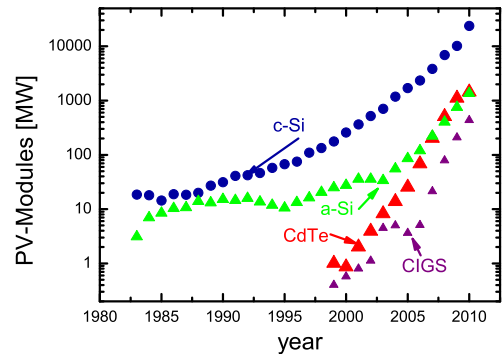
#### 2.1 Historic Development

Figure 1 presents the annual production of photovoltaic modules [1] which grew by a factor of 10<sup>3</sup>, from 20 MW in 1983 to 27 GW in 2010. If one sums up the numbers, one obtains a total number of 53 GW for crystalline Si (c-Si), 3.3 GW for amorphous Si (a-Si), 0.77 GW for CIGS, and 3.4 GW for CdTe-modules produced between 1983 and 2010.

#### 2.2 Toxic substances

*Modules from a-Si:* They do not contain any toxic substances, such as the heavy metals Pb or Cd.

*Modules from c-Si:* The solder of the cell strings contains 36 % of Pb [2]. In addition, there are traces of Pb (and sometimes even Cd) in the paste, which is used for screen printing the front and back contacts.



**Fig.1:** Within the last 30 years, the annual photovoltaic market grew by a factor of 10<sup>3</sup>, with crystalline Si (c-Si) still being the dominating technology.

Compared to the Pb in the strings (19.8 mg/W in a cell with two bus bars), the amount of Pb in the screen printing paste (0.2 mg/W) is small.

*Modules from Cu(In,Ga)Se<sub>2</sub>:* Apart from one producer (Solar Frontier), most so-called "CIGS" modules contain the toxic CdS as an about 50 nm thick "buffer" layer under the ZnO front contact [3]. The semiconducting Cu(In,Ga)Se<sub>2</sub> itself does not contain heavy metals.

*Modules from CdTe:* Here, the semiconductor itself of about 4 μm thickness is toxic.

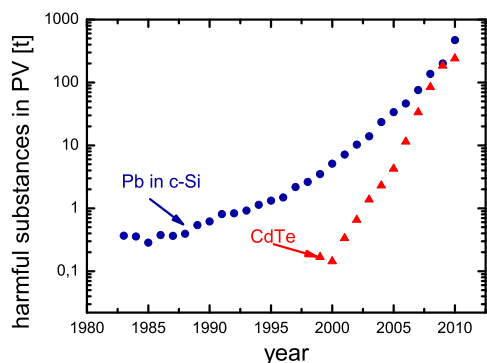
**Table I:** Toxic substances in PV modules. Our own measurements (numbers in *italic*) on CdTe deviate from the numbers in Ref. [4].

Technology	Pb [mg/W]	CdTe [mg/W]	Cd [mg/W]	Te [mg/W]
a-Si				
c-Si	20			
Cu(In,Ga)Se <sub>2</sub>			0.18	
CdTe		129	61	68
		<i>167</i>	<i>73</i>	<i>94</i>

#### 2.3 Toxic waste

Table I collects the toxic materials in PV-modules. From these numbers, and Fig. 1, we calculate the masses in Fig. 2. In order to estimate the module areas,

we use the following numbers for module efficiencies: 15 % for c-Si, and 10 % for CdTe.



**Fig. 2:** Heavy metals in photovoltaic modules. Summing up, yields 1060 t of Pb in a (crystalline Si-) module area of 350 km<sup>2</sup>, and 570 t of CdTe, distributed over 34 km<sup>2</sup> in CdTe-modules. Thus, the 3.4 GW module power of CdTe contain already more than 50 % of the toxic materials of the 53 GW of c-Si.

### 3. LEGISLATION

#### 3.1 RoHS

Cadmium and lead in electric and electronic equipment fall under the EU-directive "Restriction of Hazardous Substances" (RoHS) [5], which states in article 4: "Member States shall ensure that, from 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, ..." On May 27th, 2011, the Council of the European Union revised and clarified RoHS, maintaining an exception for photovoltaic modules.

Without that exception, which is under debate, Cd and Pb would not be allowed in PV-modules: The limiting concentration for Cd are 0.01 % and for Pb 0.1 % "by mass per homogeneous material". The limits hold for any single substance that could theoretically be mechanically separated - and not for the whole product! In case of crystalline Si modules, the soldering layer for the strings consists of about 36 % Pb; whereas the Pb-content in the screen printing paste is close to the RoHS-limit. Clearly, the compound CdTe with 50 % of Cd atoms cannot meet the RoHS. Also, CIGS-modules with CdS buffers, cannot meet the RoHS. However, CdS in CIGS-modules can be replaced by ZnS (as shown by the products of Solar Frontier), and Pb is not necessary in solder (as not only shown by the world wide electronic and car industry, but also by some Si modules manufacturers). Only the CdTe-technology, i.e. about 5 % of the annual module market, would severely suffer from the strict application of the RoHS. In return, PV modules would really be "green".

### 4. LEACHING EXPERIMENTS

At present, there is no specific regulation for the disposal of PV modules within the EU: Manufacturers of PV modules are not obliged to take them back; end-users are not obliged to discard them properly. Thus, PV modules might end up in trash cans, recycling containers for glass, and in building waste, which, for example, is used for the substructure of streets. Modules might also be shredded and simply dumped in normal landfills. Therefore, it is important to know how much toxic material is leached out by water of different pH-value.

In case of c-Si, leaching experiments have not been carried out. In case of CdTe-modules, previous leaching studies [6-8] yielded contradictory results. The company First Solar [6] claims that (unpublished) leaching experiments in Germany did not classify CdTe-modules as hazardous waste. This result contradicts leaching experiments of Sierra Labs, showing that under Californian law, CdTe-modules should be classified as hazardous waste [7]. A third, Norwegian study [8] yielded substantial leaching of Cd under *acidic* conditions. From standard batch and column tests performed at *basic* conditions (pH>8), the study concluded CdTe-modules would *not* be characterized as hazardous waste.

We have carried out worst case leaching experiments on CdTe modules, milled to pieces of 0.2 mm size [9]. Substantial leaching is observed: We find more than 50 % Cd to be leached out within 50 days for pH-values between pH=3.1 and 5. These results raise serious questions about the leaching in normal, "neutral" rain water, which (via the solution of CO<sub>2</sub> from the atmosphere) has pH=5.5. More studies are in progress.

### REFERENCES

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