



Thermal treatment of waste photovoltaic module for recovery and recycling: Experimental assessment of the presence of metals in the gas emissions and in the ashes



Marco Tammaro^{*}, Juri Rimauro, Valeria Fiandra, Antonio Salluzzo

ENEA, Italian National Agency for New Technologies, Energy and the Environment, Centre of Research of Portici, Naples, Italy

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ABSTRACT

The rapid expansion of the photovoltaic (PV) module market in the last years will determine in the near future a remarkable growth of corresponding waste. Then, the hazardous materials contained in the modules, such as Cd, Pb and Cr, could be released in the environment if the waste panels will not be handled adequately. Recycling processes of silicon crystalline panels, finalized to separate PV cells from the glass, involve the removal of the EVA (Ethylene Vinyl Acetate) layer through different methods, as the thermal treatment. During this treatment, some hazardous components can be released due to thermal degradation process. In this paper the metals released in the gas emissions and in the ashes due to the thermal treatment of modules were evaluated. For this purpose, three samples of crystalline panels were heated in furnace up to 600 °C and the complete degradation of the EVA was obtained. A mass balance between the sample and its components, before and after treatment, was performed in order to assess the weight loss percentage. Finally, after thermal treatment a qualitative analysis on the separated PV cell surface was performed by SEM-EDS (Scanning Electron Microscope equipped with Energy Dispersive Spectrometer).

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1. Introduction

The photovoltaic modules are power generators connected with solar energy and so they are considered environmental friendly compared to the fossil energy. However, in last years the environmental hazard of photovoltaic panel life cycles has attracted the attention of several scientists [1–12]. The life of a PV panel can be divided into three phases: manufacture, production and end life. The manufacture phase is critical because it involves the use of toxic liquid, solid and gaseous substances [13,14]. The second phase can to present emissions due to accidental events such as fires and/or destruction [15,16]. The third phase is assuming a growing importance due to the prevision of increasing of PV wastes [17–19] and to the possibility to recycle the PV materials [17,20]. In fact, with the increasing of the cell efficiency and the decreasing of the production costs, the PV industry has extremely grown in the last

fifteen years. In 2000 the total world PV production was 278 MW with respect to the 6330 MW produced in 2008 and 56,000 MW around produced in 2012 [21,22]. The amount of PV waste in the future is correlated to the amount of modules produced, taking into account that to 1 MWp corresponds 70–80 tons around of waste [19]. The case of the photovoltaic panel is unique because it has a long time lag from the manufacturing of the product to the decommissioning of the waste, which usually lasts 25–30 years [23]. Based on the abovementioned data, the amount of waste will grow drastically after 2030 [19,24].

There are various types of photovoltaic cells which differ substantially for semiconductor materials and for production technologies employed. It is usual to make a distinction between crystalline and thin film technology. For the first, the semiconductor used is the crystalline silicon. There are two main types of crystalline silicon (c-Si) cells:

- > Monocrystalline: high homogeneity, high degree of purity of the material;
- > Polycrystalline: low degree of purity.

^{*} Corresponding author. ENEA Research Center, P.le E. Fermi, 1, 80055 Portici, Naples, Italy. Tel.: +39 0817723272; fax: +39 0817723296.

E-mail address: marco.tammaro@enea.it (M. Tammaro).

In the thin film cells, the semiconductor material is generally deposited on a glass substrate. The main types can be subdivided as following:

- > Amorphous silicon (Si-a): the atoms of silicon used as semiconductor are oriented randomly as in a liquid, while retaining the characteristics of the solids;
- > CIS/CIGS: the semiconductor material is a polycrystalline compound, composed by copper, indium diselenide for the CIS and by copper, indium, gallium diselenide for the CIGS;
- > CdTe: the semiconductor is a polycrystalline compound of cadmium telluride.

Some materials contained in the PV modules are classified as hazardous. The principal concern regards the presence of cadmium in thin film module [13,25,26], and of lead and chromium in crystalline modules [5,27]. Then, these dangerous substances could be released in the environment at end of life of the panels, if special requirements for their handling and disposal are not adopted.

In July 2012 the Directive 2012/19/EU of the European Parliament and of the Council on Waste Electrical and Electronic Equipment (WEEE) has included the photovoltaic panels and established percentages and deadlines for their recovery and recycling. This Directive established that recovery and recycling should be 75% and 65% in 2012, until to become 85% and 80% since 2018, respectively. According to recent studies, the recycling of crystalline photovoltaic modules has significant economic and environmental benefits, given that this technology occupies over 90% of the present PV module market [17,19,21–23,28–32].

For the recovery and recycling processes from the waste PV crystalline modules it is necessary to disassembly the panel in its components. Generally, the first step is the removal of the aluminum frame, followed by removal of the EVA layer, in order to separate the glass from the cell [17,19,33]. For the removal of the EVA, several methods such as dissolution by using nitric acid and thermal decomposition were employed [17,34]. Among these methods, the thermal treatment is more diffuse. The EVA begins to decompose around 350 °C, and completes its decomposition at around 520 °C, under an air atmosphere [25,35–37].

As consequence of the thermal treatment of PV panel, some hazardous components, as metals, can be released in the gaseous phase. Then, if the flue gas treatment section is not equipped adequately, for example with an electrostatic precipitator or fabric filter, this fraction can be not captured. Moreover, also the ashes must be handled adequately. Since the ashes can contain precious metals, as silver, together with dangerous metals, as the lead, different recycling processes or disposal may be foreseen relying on the amount of metals detected in the ashes.

There is a lack of experimental data about possible emissions from recovery and recycling processes of PV panels. In this paper the presence of metals in the gas during the thermal treatment for recycling of silicon crystalline panels, and in the solid residue, composed by ashes and small fragments, are determined. For this purpose, experimental tests are performed with three representative samples, obtained from three panels manufactured in the late 80s and early 90s. These samples are heated in furnace from room temperature up to 600 °C, and kept at this temperature for 30 min. A continuous air flow rate was passed through the furnace throughout the tests and the gas on exit line was sampled and analyzed. At end of each test, the solid residue was collected, separated and analyzed.

Finally, morphology and chemical composition of PV cell surface after thermal treatment were determined by Scanning Electron Microscopy (SEM) and by Energy Dispersive X-ray Spectrometer (EDS) respectively.

2. Materials and methods

2.1. Experimental apparatus

The experimental apparatus used for the test is reported in Fig. 1. It is composed by a furnace, where the sample was placed, inside a ceramic plate. The furnace, having a capacity of ≈ 12 L, is equipped with a one way inlet and one way outlet line for gaseous flow. In the outlet line a gas sampling setup was placed and a vacuum pump which draws the environmental air forcing it to flow through the entire circuit. In the inlet line a bed of silica gel was placed in order to remove humidity from environmental air. The gas sampling setup was composed by five Drechsel (D1–5) traps (volume 250 ml each). The first four Drechsel were filled with 50 ml of a 1% solution by weight of HNO₃ (superpure grade), which allows to capture the metals carried by the bubbling gas. The last trap was left empty to collect any drop due to entrainment by the gas stream. The sampling setup was placed into a thermostatic bath at 0 °C, in order to facilitate the mass transfer from the gaseous to the liquid phase. The flow rate was measured by a flow meter float. Two traps containing glasswool were placed before the pumps and the flow meter respectively, in order to safeguard them by potential oily residues due to a partial combustion of organic samples.

After sampling, the exhaust gas was sent to the hood.

2.2. Analysis

The analytical activity was aimed to detect the following metals, chosen among the ones potentially present in the PV module: Al, Cr, Mn, Cu, As, Cd, Pb, Fe, Se, Sn, Zn, Te, Sb, Ag, Ga, In, Mo and Ni. These metals were analyzed both in the gas phase and in the solid residue.

The metals in gas phase were detected through the analysis of trap solutions. Each acidic solution contained in the Drechsel bottles was placed in a 100 ml volumetric flask and brought to this finale volume by adding a 1% HNO₃ solution. Acid mineralization was then performed with a microwave system (Multiwave Anton Paar) on aliquot of each sample. The reaction mixture was composed by 15 ml of liquid sample, 4 ml of HNO₃ (65%) superpure grade (Romil Ltd.) and 1 ml di H₂O₂ superpure grade (Romil Ltd.).

The mineralization program was performed through three steps: (i) from 700 W to 1000 W in 6 min; (ii) 5 min at 1000 W; (iii) 10 min at 700 W and finally 15 min at 0 W for the cooling. For each mineralization cycle is carried out an analytical blank on 15 ml of pure water (MilliQ, 18 M Ω).

For the analysis in the solid residue, preliminarily 0.2 g of solid were mineralized in a mixture containing 3 ml of HNO₃ 67% and 1 ml of HF 47% superpure grade (Romil Ltd.), with the same illustrated digestion program. In order to eliminate the excess of HF, a second microwave mineralization programme was carried out using 4 ml of aqueous solution of H₃BO₃ 5% (extrapure by ACROS Organics) as reagent: 10 min at 1000 W and 10 min at 0 W for cooling.

The metal analysis was performed using ICP-MS (Perkin–Elmer Sciex Elan 6000 ICP-MS). The operating conditions were: ICP RF Power 1150 W, nebulizer gas flow 0.6 L/min; data acquisition took place by peak hopping with a dwell time of 50 ms. The mass calibration was performed with five multielemental standard solutions prepared using “ICP-MS Calibration Standard” (PE Pure, Perkin–Elmer) in HNO₃ 1%; the correlation coefficient R² was 0.9999 for each element.

Morphological and chemical composition of PV cell surface after thermal treatment were determined by Scanning Electron Microscopy (SEM) using LEO 1530 Gemini at field emission gun, coupled to an Energy Dispersive X-ray Spectrometer (EDS). The elemental analysis was performed in a “spot mode” in which the beam is

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