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INFLUENCE OF THE FRAGMENT SIZE ON THE RECYCLING PROCESS OF THIN FILM MODULES BASED ON CdTe

Anna Kuczyńska-Łażewska*, Ewa Klugmann-Radziemska

Gdansk University of Technology, Faculty of Chemistry, ul. Narutowicza 11/12, PL-80-233 Gdansk, Poland

Abstract

For several years, the production of second generation cells (the so-called thin film), produced from amorphous silicon, cadmium telluride (CdTe) or copper indium (gallium) diselenide (CI(G)S), has been increasing. The total number of end-of-life panels by 2050 is expected to reach 9.57 million tonnes. They contain heavy metals that can be leached into the environment at the land field. The EU directive on waste electrical and electronic equipment WEEE2, introduced in 2012 obligated producers of photovoltaic panels to be responsible for the waste generated, and also for their disposal. Metal recovery would not only reduce the cost of cell production, but also reduce the consumption of raw materials. Therefore, the development of recycling technology for used and damaged modules of newer generations is important for environmental reasons.

The aim of the research is to develop a recycling technology for second generation photovoltaic modules. The work is focused mainly on cells made of CdTe. The developed method can be applied after prior thermal delamination. The efficiency rate of cadmium leaching form the different sized samples depending on different leaching solutions was tested. The next stage will be to develop a technology for the recovery of individual metals from the leaching solution.

Keywords: *Photovoltaics, Thin-film modules, Cadmium telluride, Recycling*

1. INTRODUCTION

Thin film photovoltaic cells include cells made of:

- amorphous silicon with 4-8% efficiency – a-Si,
- tandem, combination of amorphous and microcrystalline silicon with a yield of 9.8% – a-Si and μc-Si,
- cadmium telluride with 11% efficiency – CdTe,
- copper indium gallium disulfide/diselenide with a 12% efficiency – CI(G)S. (Paiano, 2015)

Basing technologies related to renewable energy sources on rare metals may be associated with negative impact on the environment, despite the apparent benefits due to the increase in demand for these raw materials. Therefore, it is important to analyze the life cycle of these products, monitor production and recycling processes to optimize the consumption of valuable raw materials. Based on the models, it is possible to assess the consumption of rare metals in the perspective of the development of photovoltaic technologies. It is estimated that by 2030 the demand for indium may reach the level of even 15,000 ton (Stamp, Wäger and Hellweg, 2014).

The estimated energy recovery time for modules from cadmium telluride (CdTe) is about 1 year while for modules made of copper-gallium-indium selenide (CIGS) is 2.8 years (Berger *et al.*, 2010). However, this time depends on the amount of available raw materials. In the Figure 1 percentage composition of CdTe modules is presented.

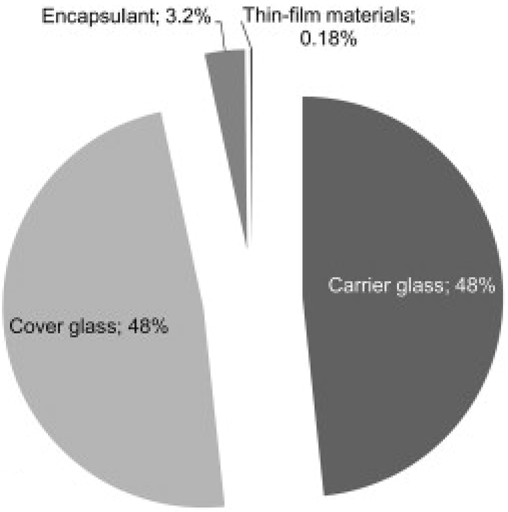


Fig. 1. The percentage composition of thin-film module CdTe

Source: (Marwede *et al.*, 2013)

With the development of the production technology of photovoltaic modules, the techniques for the recovery of materials from these processes have also evolved. Therefore, with the appearance of new cells on the market, techniques have been developed to recycle the materials used in the manufacturing process in order to return them to the production cycle.

When comparing conventional methods such as incineration or fine grinding with the material recovery process, the recycling process of CdTe-based modules is definitely less invasive to the environment, except for the space occupied by the installation (Tao and Yu, 2015).

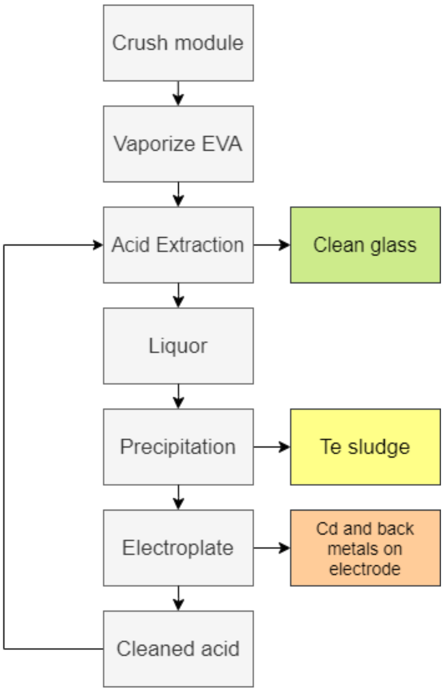
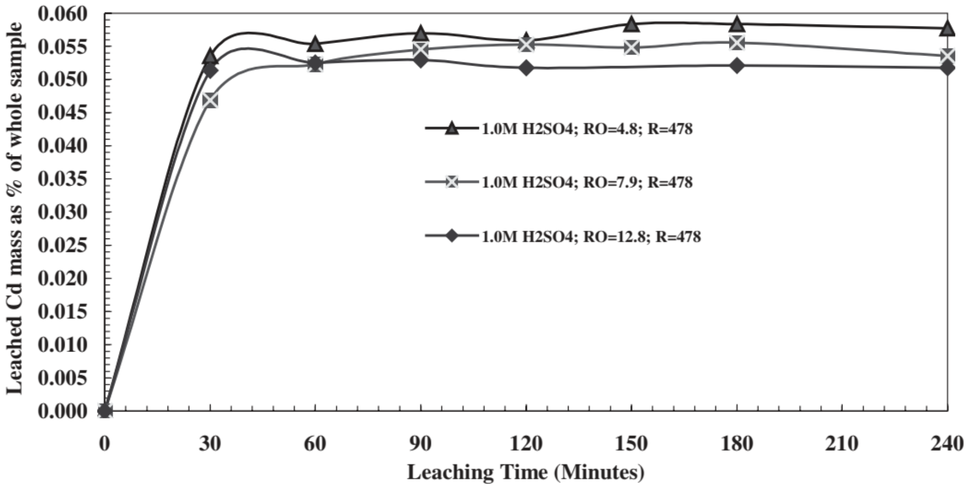


Fig. 2. The schematic of the recycling process for thin-film module CdTe

Source: (Sasala, Bohland and Smigielski, 1996)

We distinguish three main stages of the recycling process (Fig. 2). The first phase is delamination and polyethylene-vinyl acetate (EVA) removal. Finally, the semiconductor material is separated and the metals are recovered (Shibasaki *et al.*, 2006). CdTe modules are suitable for thermal (pyrolysis) and chemical treatment (Berger *et al.*, 2010).

Initially, the methods of recycling thin-film modules mainly consisted of leaching with nitric acid (V), which allowed for selective oxidation of metals, preventing the transfer of tin oxide into solution (Goozner *et al.*, 1997). With time, other leaching substances began to be used, such as a mixture of hydrogen peroxide and sulfuric acid (VI) (Berger *et al.*, 2010) . Example of such experiments are shown in the Figure 3 below.



(RO: ratio of H_2O_2 to glass in mL/kg; R: ratio of leaching solution to glass in mL/kg)

Fig. 3. Effects of acid strength on the efficiency of leaching Cd.

Source: (Fthenakis and Wang W., 2005)

Most centers of research and development investments in the field of CdTe photovoltaic modules are mainly in Europe, China, Japan and Korea. The biggest company that produce and recycle 3rd generation modules is First solar. The environmental impact of the recycling process in mass scale can be decreased by the enclosed equipment, HEPA filtration and onsite water treatment (Fthenakis *et al.*, 2020).

2. MATERIALS AND METHODS

2.1 Materials

Samples of thin film module made of CdTe by Advanced Solar Power Hangzhou INC were prepared by cutting into squares 1x1 cm, 3x3 cm and 5x5 cm and milled in the Pulverisette 9 vibratory disc mill from Fritsch GmbH.

Thermal decomposition was performed in horizontal tube furnace PTF 12/105/500 equipped with PC 442 / MP20 controller. The following pure for analysis leaching solutions were used: 3M H_2SO_4, 30% H_2O_2 and a Piranha solution.

A 250 FEG scanning electron microscope from QuantaFEI with an Energy-Dispersive X-ray spectroscopy attachment was used. Other equipment used was the SensAA Dual atomic absorption spectroscopy from GBC Scientific Equipment with a hollow cathode tube lamp also from GBS.

2.2 Methods

First step was mechanical delamination in the vibratory disc mill. The batch material in the mill was 100 g of fragments of CdTe module in size below 30 mm. The samples were milled for 10 minutes at 1500 rpm.

Thermal delamination was performed on all samples in the rural furnace in the air atmosphere. Ground CdTe modules weight was about 3 g and fragments of modules were in sizes of 1x1 cm, 3x3 cm and 5x5 cm. According to the results published and obtained previously (Kuczyńska-Łażewska and Klugmann-Radziemska, 2019) temperatures of delamination were chosen. Samples were placed in the crucible and treated at 600ºC for powdered samples and 700ºC for fragments. The rate of temperature increase in the furnace was 10 °C/min. After calcination and cooling, the samples were weighed to determine the weight loss.

The etching process was carried out at a constant temperature in oil bath at 30 ° C. Three leaching solutions were used: 3M H_2SO_4, 30% H_2O_2 and a Piranha solution. Piranha's solution was made of 3M H_2SO_4 and hydrogen peroxidel in a ratio of 3:1. The volume of the leaching solution was optimized to the weight of the sample. There was 30 ml of solution for each 1 g of the sample. Process was performed during 15 min, 30min, 1h and 2h time. Leaching process parameters were chosen based on the literature research (Fthenakis and Wang W., 2005). After the etching process, the sample was filtered under vacuum and the precipitate was dried, weighed and the absolute weight loss was calculated.

Samples before and after the thermal treatment and etching process were examined using Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-ray (EDX) spectroscopy in order to find out their morphological structure and chemical composition before and after the etching process.

For marking the cadmium ion concentration Atomic Absorption Spectrometry (AAS) technique was used. At the beginning, a calibration curve was prepared, which allowed to determine the relationship between the absorbance and the concentration of silver ions (Cd ^{2}+) in the sample. The curve was prepared for five solutions of 1, 2, 3, 4 and 5 mg/L. The Limit of Detection (LOD) for the above method is 0.0595 mg/L, and the Limit of Quantification (LOQ) is 0.1785 mg/L. Prior to AAS analysis, the sample was additionally filtered to prevent damage to the measuring equipment. In the case of too high concentrations, the samples were diluted.

3. RESULTS

3.1 Sample preparation

After the thermal treatment for all samples we can assume the constant weight loss between 3-4% (Fig. 4). Results are compatible with the amount of the encapsulant in the thin film modules based on CdTe which is 3.2% (Marwede *et al.*, 2013) That mean that thermal delamination was complete for all sizes of the module fragments. For powdered samples temperature was lower to prevent cementation, for bigger samples it had to be higher to penetrate the whole surface.

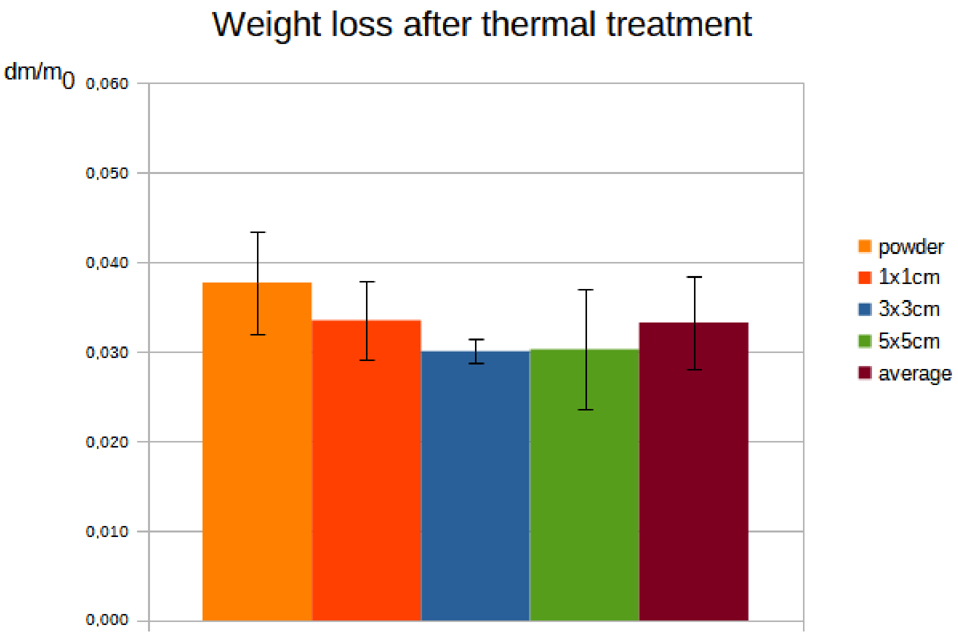


Fig. 4. Weight loss after thermal treatment sorted according to the type of module fragment size

After the thermal treatment the front layer of glass can be easily removed and the semiconductor film is exposed for the leaching solution. Experiments have to be performed carefully because the thin film after thermal treatment starts to peel from the back glass and is light enough to be blown of by sight breeze.

3.2 Material characteristic

Powders after leaching were examined using SEM combined with EDX spectroscopy. The SEM pictures (Fig. 5) taken show slight changes in the powder morphology before the process and after calcination at 600 ° C, as well as after 2 hours of leaching in each of the etching solutions (3M H_2SO_4, 30% H_2O_2).

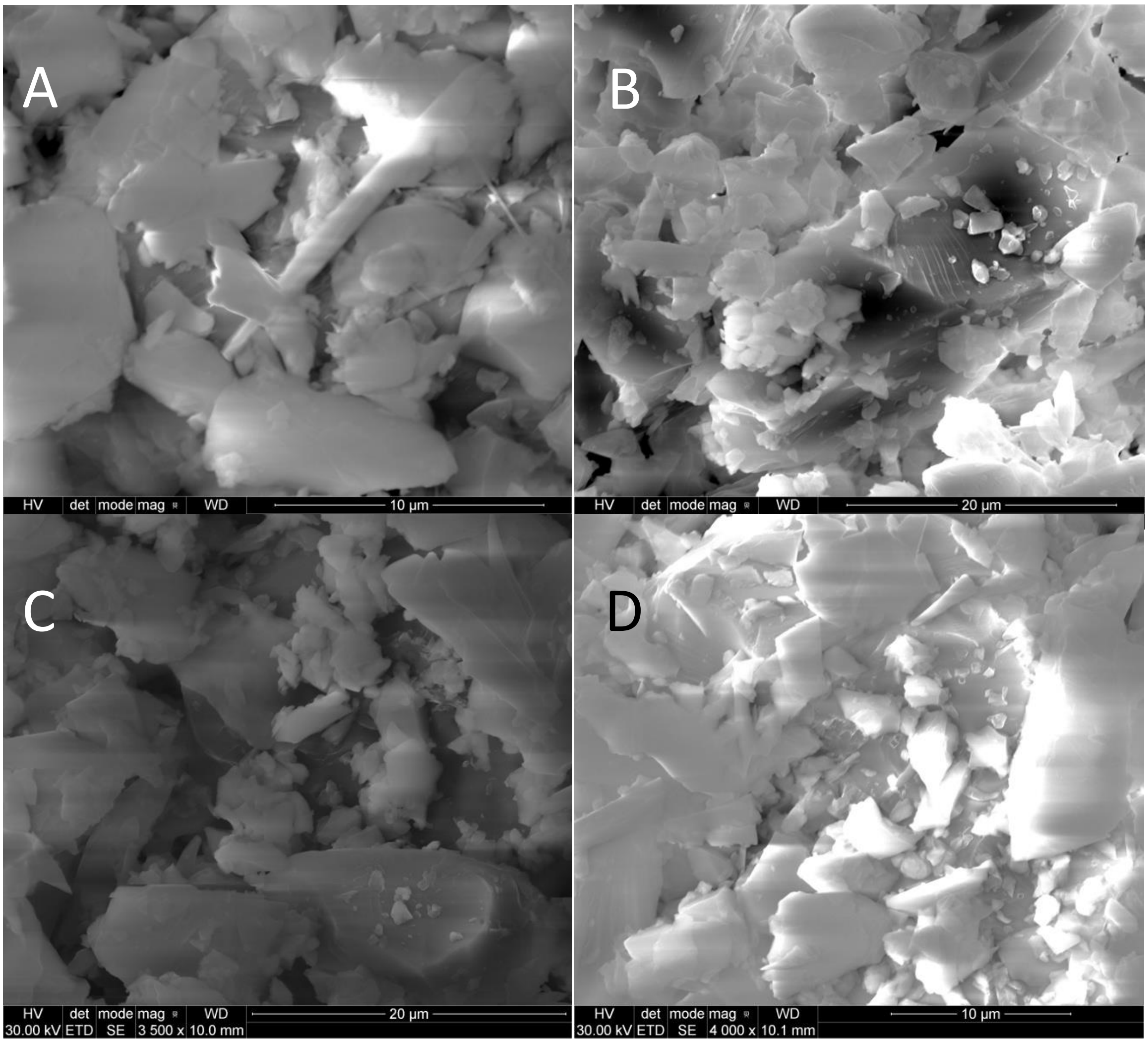


Fig. 5. SEM photos of thin-layer powders A- before treatment, B- after calcination at 600 °C for 3 hours , C- after 2 hours of the leaching process with 3M H_2SO_4 solution at 50 °C, and D- after 2 hours of leaching with 30% H_2O_2 solution at 50 °C.

When observing under a microscope, it was possible to notice the electrostatic charge of the samples after calcination, which increased after the leaching process. Charging of the sample surface under the influence of the electron beam indicates its reduced conductivity. On this basis, it can be concluded that the structure of the semiconductor was disturbed both during thermal treatment at temperatures above 500 °C and during the leaching process.

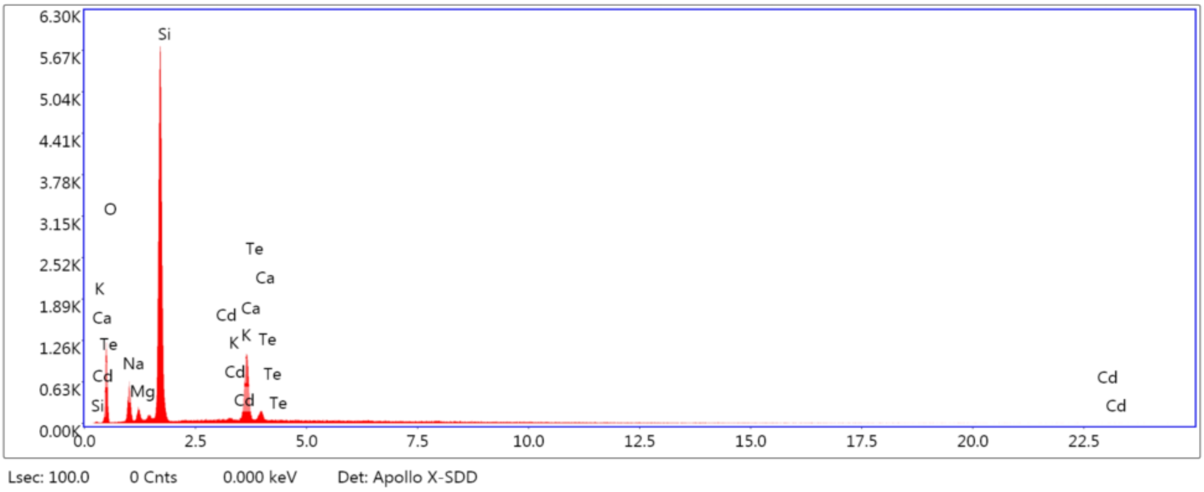


Fig. 6. EDX analysis of the sample composition before the treatment.

Element	Mass %	Error %
O K	41.32	10.12
Na K	10.46	10.09
Si K	36.52	5.32
Cd L	0.21	58.33
Te L	0.27	60.37

Table 1. Sample composition before the treatment

However, the EDX analysis (Fig. 6, Table 1) did not allow the identification of the semiconductor material, because cadmium and tellurium are present in the sample in amounts within the error limit. It means that a significant part of the sample is a matrix composed mainly of glass, which constitutes 96.7% of the mass composition of the module, where the semiconductor material is 0.11-0.13%.

Unfortunately, due to the negligible amount of cadmium and tellurium in the sample, it is not possible to quantify the efficiency of the process with this method at this stage of the research.

3.3 Leaching process

Mass loss of the samples after leaching process is in the error margin and is between 1-5% which is higher than the amount of the semiconductor material in the samples (3.2). Samples leached in the hydrogen peroxide or Piranha solution present slight higher mass loss (3-5%) than leached in the acidic solution.

For the hydrogen peroxide solution most of the results were below 1 mg/L or even below LOD limit of used AAS equipment. Highest result was obtained for the 5x5 pieces for 60 min in the amount of 2mg/L.

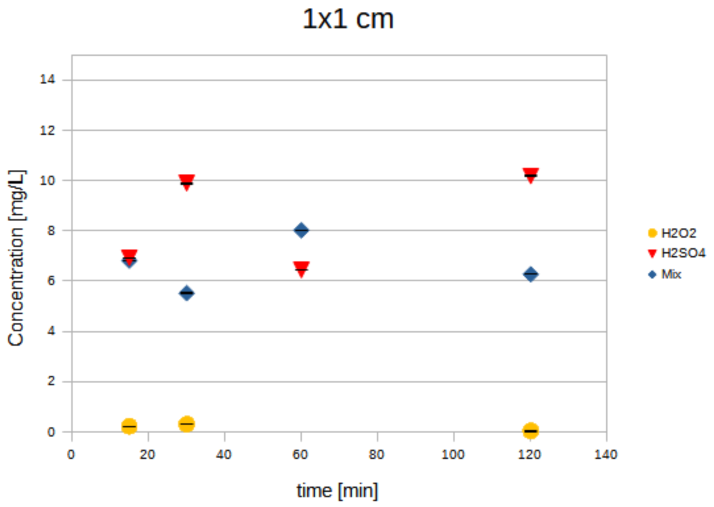


Fig. 7. Cadmium ion concentration [mg/L] in the solution after leaching process sorted according to the type of leaching solution for 1x1 cm pieces

For almost all leaching solutions and samples there is no visible time dependence of concentration. At Figure 7 we can observe that adding H_2SO_4 into hydrogen peroxide intensify the results. Difference between the pure 3M H_2SO_4 solution and the Piranha mixture is not significant and vary between 2% to 4%.

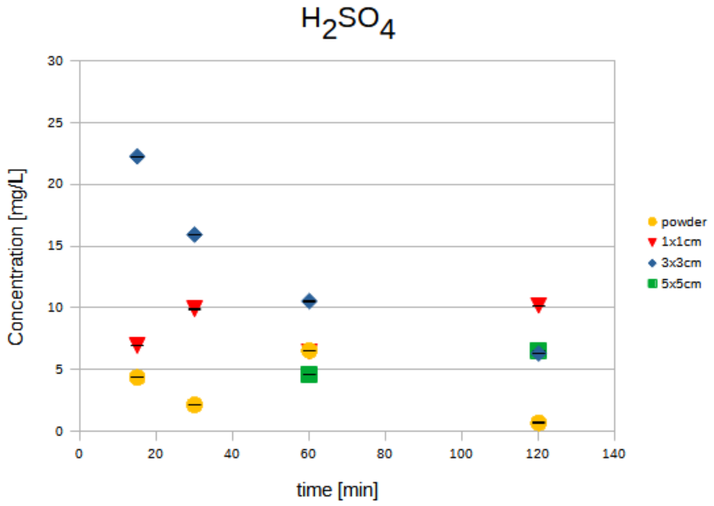


Fig. 8. Cadmium ion concentration [mg/L] in the solution after leaching process sorted according to the type of module fragment size for 3M H_2SO_4 solution

At Figure 8 we can see that in the 3M H_2SO_4 solution for the most size of samples the maximal amount of cadmium is between 30 min and 1 h leaching time. Only for 3x3 cm pieces we see continuous decrease of cadmium concentration from the beginning of the process.

Based at the literature data (Berger *et al.*, 2010) the maximum cadmium concentration in the samples was calculated. At the ratio 30ml of the leaching solution for 1g of the module the maximum amount would be 24.6 mg/L. Based on this calculation the highest efficiency above 90% was obtained for the 3x3 cm samples in 3M H_2SO_4 after 15 min of leaching process. Most of the results for the 3M H_2SO_4 and the Piranha solution were between 30-40 %.

4. DISCUSSION & CONCLUSIONS

The determinations carried out as a result of the EDX analysis confirm the composition of the module in accordance with the literature: glass 88.3 ± 8.8%, CdTe 0.48 ± 0.3% (Berger *et al.*, 2010).

Expected mass loss after leaching process would be lower than 1% according to small amount of the semiconductor material in the modules. Observed higher than assumed mass loss after leaching process can be connected with the possible wash out of the silicates from the glass. At high temperatures above 600°C, cadmium oxide and silicon oxide can react to form silicates and they can react with H_2SO_4.

Not stable results for the cadmium concentration in the solution samples may appear according to the potential high concentration of silicates in the solution after leaching process according to the information posted on the equipment manufacturer's website (*website, date: 2021-07-01*)

There is also possibility of re-adsorption of cadmium on fragments of the module and that can hence the decrease in concentration over time during the leaching process. According to this observations and theories elongation of the leaching time is not advised.

The AAS method will be not advised for the analysis of the cadmium amount in leaching solution because of the presence of the silicates. Experiments will be repeated with more samples and different ratios leaching solutions. Other analytic methods for the comparison will be used for example inductively coupled plasma mass spectrometry (ICP-MS). Presented research also is an introduction to the cadmium recovery from leaching solutions.

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