USE OF CENTRIFUGAL GRAVITY CONCENTRATION FOR SEPARATION OF CADMIUM TELLURIDE FROM PHOTOVOLTAIC CELLS

KRATOCHVÍL Michal[1], JEZERSKÁ Lucie[2], DROZDOVÁ Jarmila[1,2], ZEGZULKA Jiří[2], LANDECKÁ Aneta[1], BROŽOVÁ Silvie[3], DRÁPALA Jaromír[3]

[1]VSB - Technical University of Ostrava, Faculty of Mining and Geology, Institute of Mining Engineering and Safety, Ostrava, Czech Republic, EU, michal.kratochvil@vsb.cz
[2]VSB - Technical University of Ostrava, ENET Centre, Bulk Solids Center, Ostrava, Czech Republic, EU
[3]VSB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Non-ferrous Metals, Ostrava, Czech Republic, EU

Abstract

In connection with the end of life of the first commercially produced thin-film photovoltaic panels, the issue of recycling them is very topical. One of the methods for the production of the first photovoltaic cells was thin film technology, based on the CdTe content. The work is therefore devoted to one of the possible methods for separation of CdTe and glass particles in the powder material obtained during the liquidation of worn photovoltaic panels aiming at their secondary use. For the above-mentioned separation, the method of centrifugal gravity concentration of particles was used. The influence of the separation method to a change in the mechanical and physical properties of the powder mixture, including the angle of internal and external friction or compressibility, was studied as well. A criterion for comparing the results for the separation products were the contents of SiO_2 and CdTe. A partial task was also time optimization of the separation process. The original material contained 46.05 wt. % of SiO_2 and 16.06 wt. % of CdTe and unit shares other oxides (CaO, MgO, K_2O) and metals. The samples were taken at 5-minute intervals. Using gravity concentration, it was possible to obtain the final concentrate with 29.28 wt. % of SiO_2 and 45.69 wt. % of CdTe during optimized process time of 20 minutes. Initial experiments demonstrated the basic possibilities of the above-mentioned material separation and differences in mechanical and physical parameters of individual products.

Keywords: Cadmium telluride, photovoltaic panels, gravity concentration, angle of internal friction, compressibility

1. INTRODUCTION

Recycling of photovoltaic panels is a currently addressed topic. At present, the old used panels are gradually being replaced with new ones due to their decreasing efficiency, but also due to the production of new equipments with innovative technology. Recycling of panels containing a number of rare elements and toxic substances is essential. This obligation is also mandatory by law. The type and processing of the panels used depends mainly on their type. There are two main recycling methods. Both have the same initial phase when it is necessary to remove the aluminum frame and the supply cables of the photovoltaic panel. The next stages already involve different approaches. The first one is mechanical-chemical recycling. The second method is so-called thermal-chemical processing. The thermochemical method is particularly advantageous for commercially available silicon panels. It was designed and used by the German company *Deutsche Solar* [1, 2]. The advantage of this method is the simplicity (removing the polymeric packaging from the photovoltaic panel by thermal methods) and the possibility of obtaining whole, undamaged cells that can be used after the post-processing in the production of new cells. The disadvantage is the high energy intensity and high proportion of manual work during manual separation of the individual loose parts. After using the thermal method and manual separation of the material, the solar cells must be chemically cleaned [3, 4].

For the disposal of thin-film cells containing CdTe, mechanical-chemical methods are usually used [5]. The mechanical-chemical method is suitable for thin-layer and crystalline panels with a low layer thickness. At present, the trend is to use the least possible amount of material to produce the panel. However, with the decreasing thickness of the article, its brittleness and sensitivity to manipulation increases. In the first step of the method, the panels are crushed into small pieces. Shredder or hammer crushers are used for crushing technology. Crushing takes place in several stages to ensure a particle size of about 4-5 mm. The crushed material is directed to a rotating drum where, by adding sulphuric acid and hydrogen peroxide, the photovoltaic film is removed from the glass. Then sorting takes place into different particle size classes and separating the glass from the liquid. Any fine glass particles that pass through the sorting sieve settle in the liquid and are discharged through the dispensing screw from the container. Vibrating screens are most often used for sorting, which primarily results in the separation of glass from other materials. For the separation of small particles it is also possible to use fluid and wet tables, which can ensure separation into size classes based on the specific weight of the sorted material. Another separation technology used for panel recycling technology is electrodynamic separation. Using an electrodynamic separator, non-ferrous metals can be separated from other materials. Subsequently, heavy, rare and toxic elements are obtained from the sorting and separation products by means of electrolysis, chemically or pyrometallurgically. Approximately 90% of glass and up to 95% of semiconductor material can be obtained by the described method [1, 4, 6].

Work on the recycling of photovoltaic panels deals only with a narrow primary area. It has been experimentally investigated whether it is possible to obtain more concentrated cadmium telluride for secondary use, by applying a simple mechanical operation - gravity concentration using centrifugal forces. This is a pre-treatment of bulk material, obtained from old crushed photovoltaic cells. Additionally, the influence of the applied method on the change of two selected mechanical and physical parameters - angle of internal friction and compressibility, important for predicting the behaviour of the material, in connection with its further possible processing, was also studied. In the future, we would like to focus on further process adjustments, which will allow for the improvement of the input raw material before hydrometallurgical methods. This could lead to higher economic and process efficiency.

2. EXPERIMENTS AND METHODS

2.1. Particle size distribution

Granulometric analysis of the original sample was performed on the Cilas 1190 laser analyser. The wet path method was used. Determination of the particles proceeded on the basis of the passage of the measured material dispersed in water (carrier medium) through coherent light with a wavelength of 830 nm. The results were interpreted based on the Fraunhofer theory [7].

2.2. Gravitational Centrifugal Separation (WARMAN M16 Cyclosizer)

Warman Cyclosizer M16 is a device that employs centrifugal forces for sizing. The former treats dry samples in a spiral vortex of air created by a spinning disk. Particles are drawn inward against centrifugal force acting outward. The cyclosizer has a connected series of hydrocyclones with varying inlet and vortex diameters chosen to obtain size fractions in the 9 to 45 μm range. Each cyclone is inverted and has been fitted with closed apex chambers to permit repetitive sorting/washing. A sharp split is obtained as a result. **Figure 2** shows the major components of the cyclosizer. The principle of hydrocyclone is discussed in subsequent of this chapter [8].

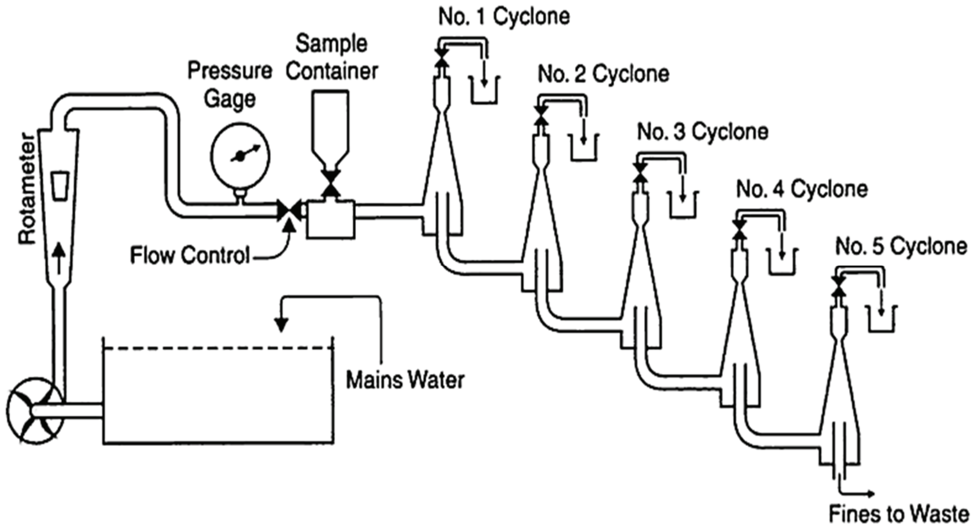

Figure 2 The major components of the cyclosizer [10]

2.3. Angle of internal friction and compressibility

The angle of internal friction and compressibility of the powders were measured on an FT4 Powder Rheometer. The FT4 Powder Rheometer rotary shear module for measuring friction parameters consists of a vessel containing the sample powder and a head with disk to cause normal and shear stress. The blades of the stainless steel head sink into the mass powder and start to apply normal stress to the surface of the powder. The stainless head moves downwards until sufficient and stable pressure is applied between the contact material and the powder bed. The shear plane is formed just below the end of the blades. Since the powder bed prevents rotation of the stainless steel head, shear stress in the measuring plane increases until a slippage occurs. Then, the maximum value of transferred shear stress is recorded and angle of internal friction is calculated [10].

Compressibility is measured as the change in volume depending on a normal load. The data obtained are quantified by expressing the percentage compressibility for a normal load of 15 kPa applied by the module, which is a part of the FT4 Powder Rheometer. Changes in volume are evaluated by compression index (C). The compression index (%) is calculated as the ratio of compressive density (at 15 kPa) and the density.

2.4. Analytical method

Samples of the studied raw material obtained by gravity concentration were quarried before homogenization and sputtering in a FRITCH Pulverissette spherical micro-mill for grain size below 100 μm before chemical analysis. Determination of the quantitative composition of samples was performed using X-ray fluorescence analysis. The analysis was carried out by the DELTA PROFESSIONAL Innov X mobile X-fluorescence spectrometer.

3. RESULTS AND DISCUSSION

3.1. Granulometric analysis

The results of the granulometric analysis are shown in **Table 1**. The original sample contained fine particles with an average size of 61 μm.

Table 1 Distribution of the particle size of the original sample

Original sample	*d*10	*d*50	*d*90
Particle size (μm)	13.8 ± 0.4	61.2 ± 0.5	187.7 ±0 .4

3.2. Gravitational separation using centrifugal forces

As already mentioned (Chapter 2.2), the powder mixture was sorted while wet (in water) on the Warman Cyclosizer M16. Different times of separation have been applied so that it was possible to compare the time at which the sorting process ends. 20 g of sample per test were always used. In total, the experiment was performed 3 times at the same time of separation. The resulting products were mixed at the same time of separation. **Table 2** shows the analysis of the original sample using X-ray fluorescence analysis, which was obtained from the Laboratory of the Institute of Geotechnics of the Slovak Academy of Sciences. The sum of all analytes was 85.8%, the rest being laminates that cannot be determined by this method. **Figure 3** shows the individual yields of the separation products and their metal content determined by X-ray fluorescence analysis method as well.

Table 2 X-ray fluorescence analysis results

Sample	CdTe	SiO_2	CaO	K_2O	MgO	Na_2O	Al_2O_3	SO_3	CuO	SnO_2	Ag	Mo
Feed (%)	16.06	46.05	10.12	1.70	2.46	7.31	0.28	0.66	0.11	0.29	0.06	0.17

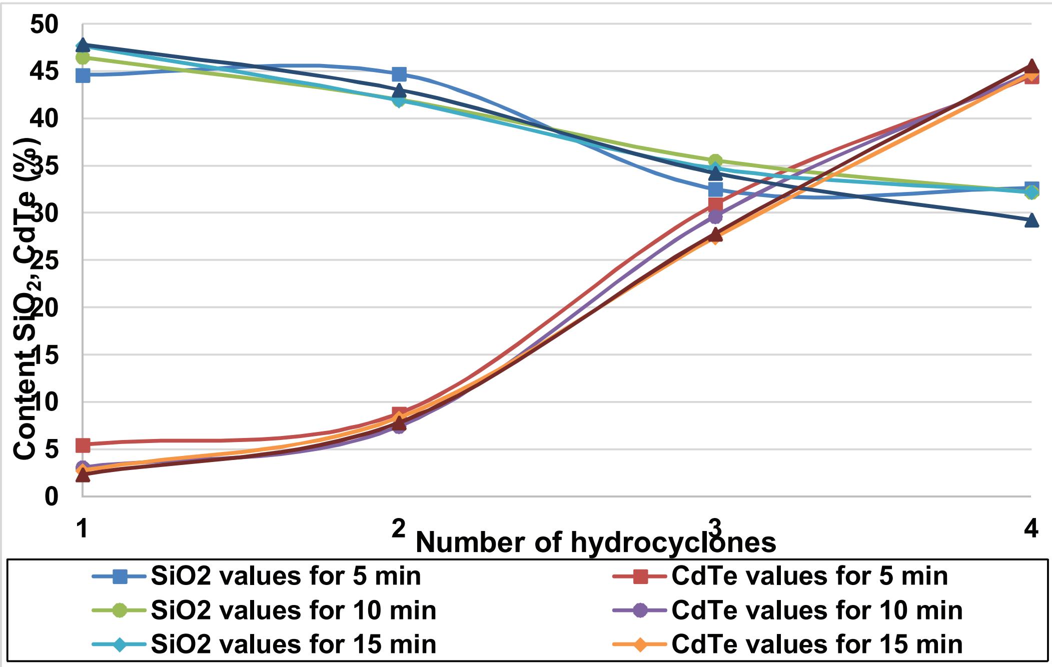

Figure 3 SiO_2 and CdTe contents in the individual products obtained from hydrocyclones

As can be seen from the results obtained (**Figure 3**), the gravitational separation of the monitored raw material is not very positive. Different results of metal content are recorded in the individual products, but the change is not very pronounced. The original raw material contained 46.05 wt. % of SiO_2 and 16.06 wt. % of CdTe. Better results were achieved within the CdTe separation, when hydrocyclone no. 1 contained only 2.36 wt. % of CdTe at 20 min wash time. In contrast, hydrocyclone no. 4 contained 45.64 wt. % of CdTe. If this value is compared with the CdTe content in the original sample, there was up to 2.5 times more CdTe concentration in the product that is considered the final one. Unfortunately, there is a significant amount of SiO_2 in the final product that degrades it. Overall, the results regarding SiO_2 separation at different times did not bring any positive data. The best separation was reached after 20 minutes, when hydrocyclone no. 1 contained 47.86 wt. % of SiO_2 and hydrocyclone no. 4 contained 29.29 wt. % of SiO_2. This is probably due to the fact that a portion of the CdTe coating was still applied to the surface of the glass (micron size) and therefore there was no good separation of the blends from each other.

3.3. Angle of internal friction and compressibility

The angles of internal friction and compressibility were determined for both the original unseparated sample and for the individual hydrocyclone fractions no. 1 - 4, separated for 20 minutes (**Figure 4**). According to the results of X-ray fluorescence analysis, the efficiency of the separation process was the highest after 20 minutes (the largest amount of CdTe and the smallest amount of SiO_2). The effect of gravity concentration on the change in mechanical and physical properties of the separated powdery material was monitored.

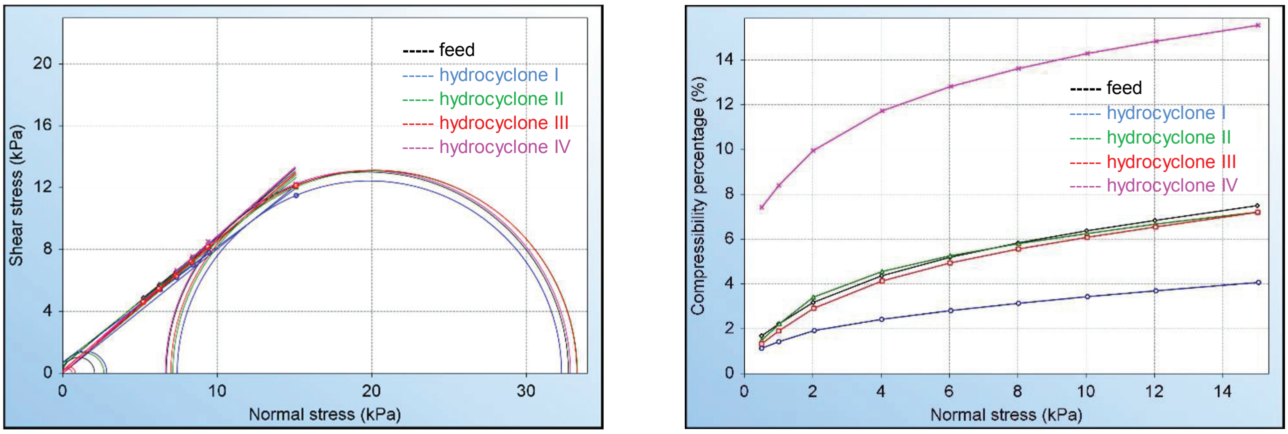

Figure 4 Left - angle of internal friction, right - compressibility tests for individual fractions and feed

Figure 4 shows the change in the angle of internal friction (left) and compressibility (right) for the individual fractions and the original sample. In the case of the internal friction angle, there is no significant change due to gravity concentration. The angle of internal friction is closely related to the mutual movement of particles (friction), which is the same for all fractions. The average value was 40.5° ± 0.8°. Flowability of all tested samples was classified as free-flowing based on Jenike's classification of powders [11].

The compressibility parameter appears more interesting for comparison. Significant changes in compressibility were observed between samples of fraction 1 (the highest SiO_2 content, C = 4.1) and fraction 4 (C = 15.5). The original sample showed medium compressibility (C = 7.5), which is typical for most powders. The most significant compression sensitivity was shown by the fraction 4. The compression index value of 15.5 indicates higher air content in the material for the appearance of fine particles that may be cohesive. Generally, powders of less than 30 µm in size have significant compressibility. It is likely that the separation process also caused particles size sorting that has a significant effect on the mechanical and physical properties of the material. For the sample from fraction 1, however, low compressibility was observed. The sample showed small changes in volume, even at high normal loads (15 kPa). It is evident from the data that it is a fraction containing rather larger particles of non-coherent character, with minimal air. The hydrocyclone fractions 2 and 3 are very similar in character to the compressibility of bulk materials. Their further process processing, for example, tabletting, extruding or pelletizing, will have a similar course.

3.4. Theoretical proposal of the technology of obtaining Cd and Te

Hydrometallurgical processing of enriched CdTe material with glass and laminate content using mechanical method would aim at obtaining individual metallic components of cadmium and tellurium, or refining could also be introduced to obtain semiconductor purity material. The first step of the proposed technology is to dissolve the material fraction from hydrocyclone no. 4 in a mixture of HCl + HNO_3 acids at a suitable ratio and concentration. The precipitation of tellurium and precious metals can be carried out in a solution of 3N HCl using sulphur dioxide. Cadmium can be separated from the solution in the column by ion exchange with the strongly basic anion AB-17 from 0.05 N HBr. In the case of Au, Ag occurrence, the precipitate can be dissolved in a 3:1 mixture of HNO_3 + HCl acids followed by extraction of precious metals with diethyl ether $(C_2H_5)_2O$ into the organic phase. Tellurium can be obtained from the solution electrolytically and then by vacuum distillation in semiconductor purity. An analogous procedure will be in the case of cadmium (from obtaining from the solution after ion exchange). Electrolytically eliminated cadmium can be converted into a form under a NaOH layer and then refined by distillation and zonal melting [12].

4. CONCLUSION

The method of separation described in the work can be used as treatment of a sample of recycled photovoltaic panels before hydrometallurgical processing. It has been shown that using the process of gravity concentration in centrifugal field it is possible to increase the CdTe content from 9.17 % to 21.40 % while reducing the SiO_2 content from 17.76 % to 13.69 %. This result was achieved after 20 minutes of the process in the fourth hydrocyclone. By doing so, it would be possible to reduce the cost of the chemicals used in the currently applied mechanical-chemical method and to reduce the negative impact on the environment. However, gravity concentration cannot be considered a major success in primary research, which is evident in terms of SiO_2 content in the final product. This is due to insufficient separation of CdTe from the glass before the separation process itself, so these two compounds are still sticking together.

The measurement of selected mechanical and physical parameters of the samples showed that the mechanical operation of gravity concentration did not have a significant effect on the angle of internal friction. Conversely, compressibility increased with decreasing SiO_2 content, or with a hydrocyclone fraction. In connection with the further processing of individual fractions, including storage, transport or densification, the samples of fraction 4 will therefore be more sensitive to process conditions.

The paper also presents a proposal for a possible technology for obtaining metal Cd and Te hydrometallurgically (from fraction 4), which can subsequently be refined to obtain a semiconductor purity. The hydrometallurgical method appears to be the most feasible for separating CdTe from glass and laminate. This method must be investigated and optimized in the next research phase.

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