Methods for recycling photovoltaic modules and their impact on environment and raw material extraction

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This work deals with methods of recycling of photovoltaic modules and evaluates contribution of recycling to the environment and reduction of raw materials extraction. The article describes the materials needed to manufacture photovoltaic modules and energy intensity of production processes. Three methods of recycling were used - thermal, chemical and mechanical. The experiments have shown that the recycling of PV modules by thermal method is more advantageous than using a chemical method. The length of the process is significantly shorter and there are lower financial costs. The disadvantage of thermal treatment is the formation of emission gases during decomposition of the EVA copolymer and also a risk of wafer damage. In mechanical recycling process it is very important to know which technologies and devices are suitable to creation of crushed material. If the PV modules are bigger than 1 x 1 m, it was necessary to divide them into two parts because the chain crusher must be able to crush the pieces as effectively as possible. From the entire mechanical recycling process it can be seen that the silver-containing crushed material up to 0.07 % is not economically advantageous to process chemically. The silver content does not cover the cost of basic operations during recycling process. The obtained data were used to calculate the amount of saved material due to PV module recycling until year 2025. Recycling could save up to 351 500 tons of glass, 51 500 tons of aluminium, 13 567 silicon and 425 tons of silver in Czech Republic.

Key words: *Photovoltaic module recycling, environmental impacts of photovoltaics, thermal recycling of PV modules, chemical recycling of PV modules, mechanical recycling of PV modules.*

Introduction

The price of photovoltaic systems has dropped each year by 10 % since 1980, while annual production is constantly growing (Tao & Yu, 2016). Several factors influence the fall in prices: the cell efficiency increase, falling prices of silicon, the use of thinner wafers and the growth in production volume. Energy return - the time the system produces the same amount of energy as was consumed for its production, was reduced to 1/10 at the same time (Bechnik et al., 2016). This also has a significant effect on the price. Another positive consequence is the reduction of the environmental impact (Tauš, 2009).

The end of the photovoltaic modules lifetime is defined by a 20 % power drop from the original. Almost all manufacturers of commonly available crystalline and thin-film modules guarantee the maximum efficiency drop by 10 % for 10 or 12 years and 20 % for 25 years. In the oldest installations, the real drop in efficiency after 20 years is even smaller, around 6 to 8 % (Hylský et al., 2015). The main reason for removing a module from PV power plants is its mechanical damage during transportation, installation, or degradation influences during its operation. However, it should be noted that the mechanical resistance of the panels is relatively high.

Photovoltaic systems (PV systems) do not produce any waste or emissions during the production of electricity. On the other hand, PV systems must be manufactured, installed and re-dismantled at the end of their useful life, which impacts the environment. Photovoltaic modules recycling has not yet been so important for research institution and industrial companies. PV system life is longer than for common goods and the number of modules to be recycled is still low - only a few hundreds of tons a year across the EU. According to Weibull's simulation, the amount of PV waste can be estimated about 100,000-545,000 tons in the Czech Republic till 2025 (Kumar et al., 2013). There are two approaches to recycling – PV modules recycling regardless of the production technology, and design modifications to make recycling easier. A challenging task is to develop optimal recycling technology and to finance its high investment costs.

The Lisa Krueger study on recycling programs shows that up to 97 % of the materials used during the thin film PV modules manufacturing processes can be extracted and reused by thermal recycling (Krueger, 2016). Recycling of silicon PV modules is more complicated because it is necessary to disassemble the modules mechanically or manually. Such a procedure involves removing the individual components and their subsequent reuse or crushing. This process is less efficient than thermal recycling, but the recycling efficiency still can achieve up to 95 %. It is estimated that from a 20 kg panel it is possible to recycle up to 19 kg of useful material

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(Granata et al., 2014). This amount would increase if a more efficient silicon recycling method were developed because of silicon non-separability from glass – this material often ends as a waste.

In the case of successful PV modules recycling, there can be reduced requirements for mining and processing of the elements necessary for their production. The following text will, therefore, deal with the materials needed to manufacture the PV modules and their recycling capabilities. Several recycling methods will be compared and evaluated, and their impact will be assessed from the environmental point of view.

Materials and methods

The main objectives of the recycling of the PV modules are to reduce the amount of remaining waste and to maximize material recovered for further production. The most common PV module construction is schematically shown in Fig. 1 (Wealthdaily, 2017). The manufacturing process is as follows: On the front of the PV module tempered glass is placed. The glass is highly shock-resistant and can withstand relatively large hail. A plastic EVA (ethylene vinyl acetate) film is applied to the glass and the interconnected PV cells are placed on it. The EVA film is again deposited on the PV cells and the rear part is usually laminated by polyvinyl fluoride (Tedlar). The air is exhausted from the space between the glass and the Tedlar and the module is heated above the melting point of the EVA film. EVA melts in the space between the front glass and the rear laminate as a sealing compound. The modules are framed and sealed with silicone sealant into aluminium profiles and provided with a junction box with output contacts. The lifetime of high-quality PV modules based on crystalline semiconductors ranges from 20 to 30 years (Choi et al., 2014). Main recycled materials from them are glass, aluminium, plastic, photovoltaic cells and heavy metals.

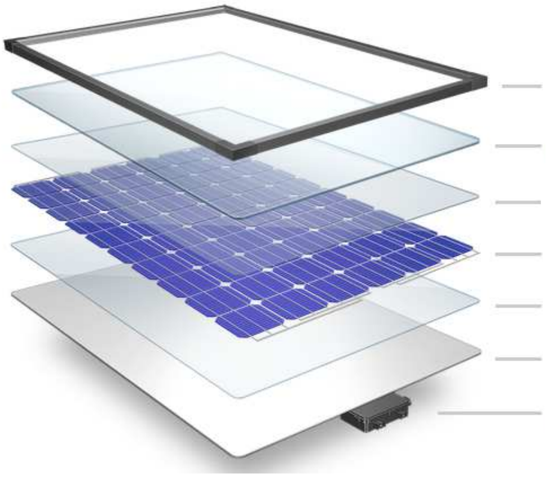

Fig. 1. Structure of the photovoltaic module (Wealthdaily, 2017).

Raw materials obtained by PV modules recycling

The largest proportion by weight of the crystalline modules is glass (60 – 70 %) and aluminium frame (around 20 %). For thin-layer modules, the proportion of glass and aluminium is over 95 % (Bechník et al., 2015), . Both of these materials are commonly recycled. Other metal materials are expensive commodities that are worth acquiring from the waste (Kudelas, 2014). Plastics can be recycled only partially or not at all. The following section provides a brief description of each component of the PV Module:

Aluminium - primary production has a high demand for energy of around 200 MJ/kg of electricity and constitutes about 8 % of energy consumption for PV modules production (Balomenos et al., 2011). Aluminium can be easily recycled with a very low energy consumption - 8 MJ/kg (especially thermal energy). The yield of aluminium approaches close to 100 %. Aluminium is the third most abundant element in the Earth's crust. According to the latest available data, 7.5-8.3 % of the Earth's crust (Rocchetti & Beolchini, 2015). Its concentration in seawater is very low, only 0.01 mg Al/l (Dias, 2016). The most common aluminium-based rock is bauxite. Bauxite is mined in large surface mines, which often cause massive occupation of the area, the requirement of local resettlement and displace agriculture and natural vegetation. Bauxite sources are often found in equatorial areas. Therefore its mining is mostly associated with the destruction of large areas of tropical rainforests. The world's bauxite reserves are estimated at 28 billion tons. Aluminium oxide is obtained from the extracted bauxite, from which the aluminium itself is produced electrochemically in refineries at about 950 °C. About one ton of pure aluminium can be obtained from four tons of extracted bauxite. One of the waste product in large quantities in the production of aluminium is toxic waste, known as red sludge (Meija et al., 2015).

Glass - or other transparent material - is a basic component that cannot be replaced or avoided. Glass recycling can reduce energy consumption for its production by about 40 % (Bechník et al., 2015). However, the reduction of mining and landfill capacity requirements is more important. In most cases, recycled glass can be used to manufacture the same product.

Soda-lime glass is the most common in photovoltaic modules. Typical sodium-lime glass consists of 71-75 % silicon dioxide (SiO_2, mostly from sand), 12-16 % sodium oxide (Na_2O, from calcined soda, Na_2CO_3), 10-15 % calcium oxide (CaO from calcium carbonate, $CaCO_3$) (McGraths et al., 2013). Silicon does not occur naturally in pure form, but only in its compounds. After oxygen, silicon is the second most represented element in the Earth's crust. Silicon is in 26 to 28 % of the Earth's crust, according to the latest available data. In seawater its concentration is relatively low, only 3 mg Si/l (Meija et al., 2015).

Plastic components - because of their degradation due to climatic conditions, it is difficult to recycle them. However, it is possible to use thermal energy during their combustion.

Heavy metals - they represent negligible items in terms of weight, price and energy consumption for PV modules production. Lead represents only 0.12 % of the PV module weight, silver 0.14 %, tin 0.12 % and copper 0.37 % (Yi et al., 2014). The energy and material demands of recycling are comparable to their production from primary raw materials. Recycling of heavy metals is necessary for other reasons. Heavy metals are toxic and must, therefore, be separated from the environment. In addition, especially in the case of silver, the exploitation reserves can be expected shortly, which will lead to higher mining costs. Currently, the world's total silver reserves are estimated at 540,000 tons (Dias, 2016). This amount also includes silver, which is not nowadays available due to insufficient technology. The silver yield from ore currently ranges from 40 % to 65 %. In a projection of the current increasing rate of mining, all silver would be harvested in about 17 years. After this, there will be only one source of silver, and that is from recycling processes (Dias, 2016).

World copper reserves are estimated at 720 million tons. Copper yield from recycled wiring is ranging from 78 % to 100 %, and the processing technology is very advanced (Ayres et al., 2012).

Photovoltaic cells have a negligible share of the weight of the PV modules. Nevertheless, PV cells contribute 50 % to module price and 80 % to energy consumption for their production (Bechník et al., 2015). From the material point of view, solar cells are unchanged at the end of their life. With their recycling, there is already first practical experience. Manufacturing of silicon for photovoltaic cells is either from monocrystalline or polycrystalline ingots. The production of monocrystalline ingots is done by the Czochralski method. A small seed of a monocrystal is immersed in a silicon melt at about 1415 °C. Seed is very slowly pulled out from the melt while it is rotating around the longitudinal axis. The whole process is carried out under an inert atmosphere under reduced pressure. Production of the polycrystalline ingot is easier. The material is melted and poured into a mould where it is slowly cooled. Cooling must be gradual, and it is controlled by inductive heating to create as large a single-crystal grain as possible because of minimal dislocations, stresses, etc. (Shin et al., 2016).

Environmental impacts of photovoltaics and energy demand of PV modules production

Photovoltaic technology is seen as environmentally friendly. The appropriate attention should be therefore given to monitoring of environmental impacts. Environmental impacts can be divided due to their origin into the direct and indirect way. Direct impacts relate directly to a particular manufacturing process. This includes, for example, land use, emissions from primary raw material extraction, water consumption in production and emissions of chemicals. Indirect impacts are mainly related to emissions from electricity generation and transport (Alsema & de Wild-Scholten, 2015). In terms of sustainability, the rate of utilisation of raw material resources is also important for evaluating their availability in the future.

The life cycle of the product includes all phases from raw material extraction, semi-finished products and finished products until the recycling or PV module at its end-of-life. Inputs of raw materials, semi-finished products, fuels and energy, waste and emissions, can be monitored at all stages. The following phases of the life cycle can be considered in the case of crystalline silicon photovoltaic modules (Latunussa et al., 2016):

- extraction of raw materials,
- manufacturing of metallurgical grade silicon (mg-Si),
- production of solar grade silicon (sog-Si),
- production of ingots and boards,
- manufacturing of PV cells,
- assembly of PV modules,
- installation of a photovoltaic system,
- PV system operation - electricity production,
- dismantling the system,
- component recycling.

PV module transport can also be considered (Tauš, 2016). The similar lifecycle can be used for other photovoltaic components such as a converter, support structure and tracker.

The PV modules production in terms of energy consumption

Some stages of the PV module production are more demanding for energy consumption. Namely production of mg-Si, refining Si, production of ingots and wafers, manufacturing of PV cells, completion of PV modules and their recycling. Other items are less important (system assembly, power consumption in operation, dismantling the system, transport). The share of each item depends on the manufacturer. The manufacturing of monocrystalline cells is more energy-consuming compared to multi-crystalline cells, see Fig. 2 (Alsema & de Wild-Scholten, 2015).

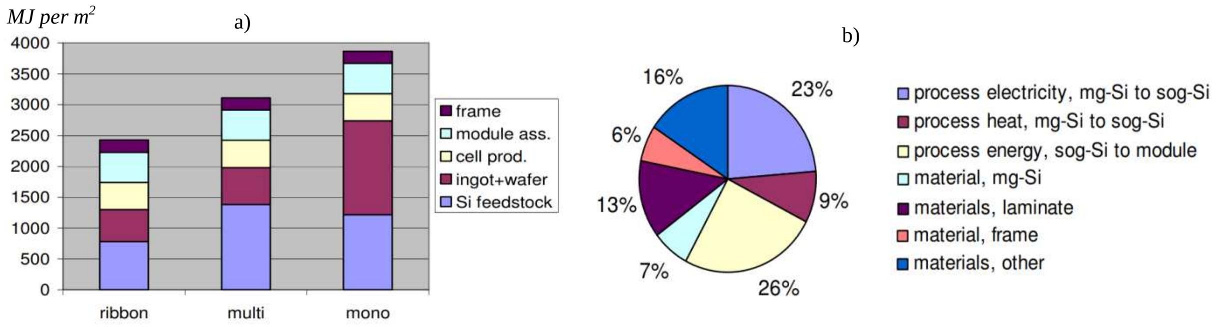

Fig. 2. a) Energy input for silicon modules, b) Primary energy input for mg-Si modules (Alsema & de Wild-Scholten, 2015).

First, for the manufacturing of photovoltaic cells waste silicon from the production of microelectronic components was used because the requirements for the quality of solar silicon are generally lower. This resource has become insufficient with the increase in production requirements. Therefore, new capacities have been built. The energy consumption of the photovoltaic cell production processes reaches 70-80 % of the total energy demands (Müller et al., 2011). The effort to reduce energy consumption in the manufacturing process is lower than the effort to increase the efficiency of the cells. As a result, energy consumption is slightly growing.

Energy consumption on PV modules assembly itself is relatively low. A higher proportion of the energy consumption is in the manufacturing of glass, frame, and lamination. The frame itself represents 8 % of the total energy consumption (Goe et al., 2014). However, with regard to easy and energy-saving recycling, this practice is not necessary. The consumption of silicon for cell production decreases both by reducing the silicon losses in production and by increasing the efficiency of PV cells or PV modules. Reducing the silicon consumption generally lead to a reduction of production costs. The current standard is 6 to 10 g/Wp (gram/watt peak) (McDonald et al., 2010). Value 2 g / Wp is considered as a technology limit. Waffers thickness has decreased to the current standard of 200 μm. PV cells can also be produced on wafers of 180 and 150 μm thickness. Wafers with thicknesses of 80 μm are planned for the future (Kang et al., 2012). Thin wafers, however, require automation. Hand manipulation is almost impossible because of the possible damage to wafers.

Methods of photovoltaic modules and cells recycling.

PV modules recycling is becoming increasingly important with the higher demands for silicon. PV recycling process consists of two main phases (Park et al., 2015):

- Separating of PV cells. Using chemical or thermal procedure, the cells are separated in the recycling process.
- Cleaning the cell surface. During this phase, separated cells from PV modules are cleaned chemically or by laser techniques. The cleaning process removes unwanted layers (anti-reflective coating, metallization and PN junction and a silicon substrate which is prepared for its further use.

PV modules delamination is also required for the recycling process. EVA, glass, Tedlar, aluminium frame, steel, copper and plastics are removed and separated from each other in this step.

In the following section, three experiments for PV modules and PV cells recycling are presented and compared (chemical, thermal and mechanical methods) together with the laser method to obtain silicon wafers.

Description of chemical recycling experiment

For the chemical recycling, monocrystalline solar cells from Solartec company were selected. The PV cells dimensions were 125 x 125 mm. After separating the cells from the photovoltaic modules, the individual layers were removed in a specific order: front metallization, rear metallization, antireflection layers and PN junction.

The main problem was the choice of the correct composition of the etching solution, its concentration and the optimum process temperature. Fig. 3. shows chosen chemicals and the procedure (Klugmann-Radziemska et al., 2010).

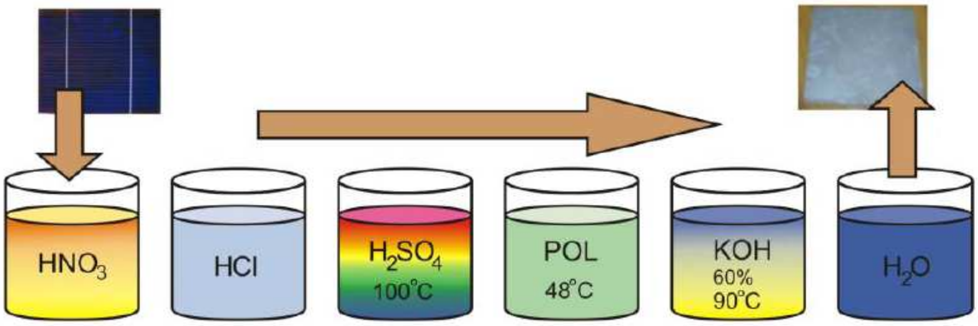

Fig. 3. Chemical treatment of the Solartec solar cell. First, the solar cell is immersed in nitric acid, then in hydrochloric acid, sulfuric acid, potassium hydroxide and in the end rinsed in water.

Due to chemical processes, it was possible to remove the materials of the damaged PV cell. The effectiveness of the chemical method was unfortunately insufficient. The reason was a relatively long time of the etchant's action and the high cost of the solvents. Chemical treatment of one solar cell requires almost twenty minutes. This method is not suitable for commercial use in a large scale (Klugmann-Radziemska et al., 2010).

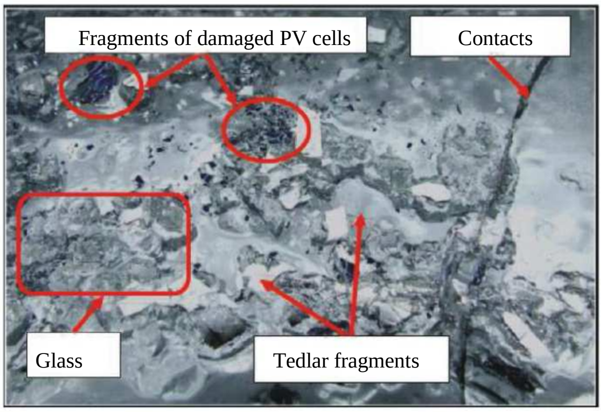

Fig. 4. The process of removing of encapsulated PV cells using potassium hydroxide.

Thermal recycling of PV modules

Several methods have been proposed for thermal recycling. Some were universal; others were suitable only for certain types of modules. In most cases, the result of thermal recycling process was raw material. This article lists only two of them.

A SOLARTEC SMP 6-180 minimodules were used in the experiment. See the specification in Table 1. The manufactured modules have a predetermined number of cells and were hermetically encapsulated by EVA copolymer and Tedlar. Solar cells were encapsulated for protection against climatic conditions and mechanical damage. The EVA copolymer material has covered both sides of the cells, while the Tedlar was used on the rear side. The front of the PV module was covered with glass.

Tab. 1. Parameters of the Solartec SMP 6-180 PV modules.

Length [mm]	162
Width [mm]	134
Thickness[mm]	8
Weight [kg]	0.32
Terminal [mm^2]	2×0.15
Front glass [mm]	3
Solar cells [mm]	16 pieces, Si (14,6×51,2)
Solar cells encapsulation	EVA (Ethylene) - Vinyl - Acetate)
Rear side	Tedlar
Frame	Aluminium

Thermographic analysis (TGA) was performed at the beginning of the experiments. Thermographic analysis, or briefly thermogravimetry (TG), is an analysis that quantitatively monitors the weight change (gain, loss) of the measured sample (Zhang et al., 2017). In a static arrangement, the instantaneous weight *w* is measured as a function of time *t* at constant temperature (isothermal technique):

$$w = f(t)\ T = constant. \tag{1}$$

The result was a thermographic curve that indicated the instantaneous weight of the sample depending on temperature and time. The decomposition temperatures of the separated plastic materials and polymers was determined as 445.44 °C, see Fig 5. a) and also heating rate and maximum temperature of 479.22 °C at which the PV module was heated in a special furnace, see Fig. 5. b).

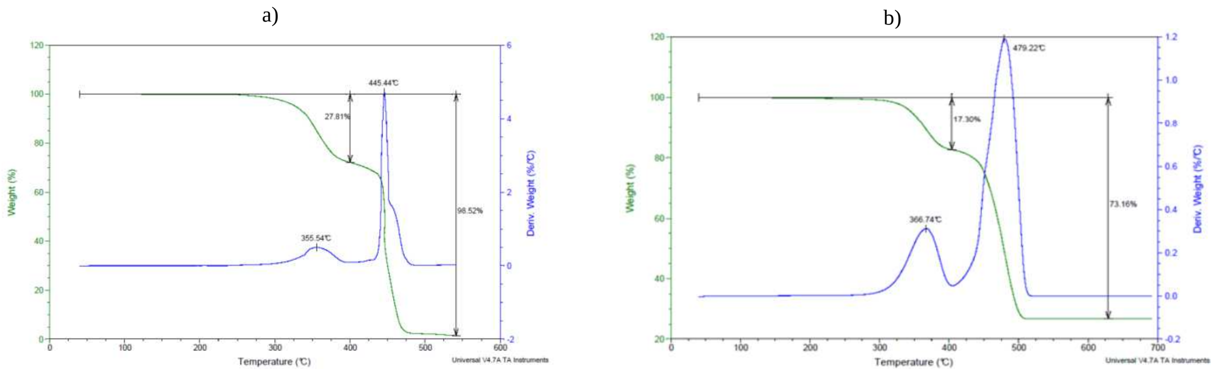

Fig. 5. a) thermographic measurement of EVA foil, b) thermographic measurement of PV cell.

The high-temperature furnace JAPA D 03-1F was used according to TGA analysis. Furnace parameters are:

- temperature range +30° to +1500°C
- temperature accuracy ± 7 °C
- temperature slope: 1–100°C/min.

The PV module was placed in a vessel and heated to a temperature above 420 ° C. The temperature increase was around 20 °C/min. The photovoltaic module was heated in the furnace for 25 min. The plastic materials evaporated, and the PV cells were separated from the glass, see Fig. 6. and Fig. 7.

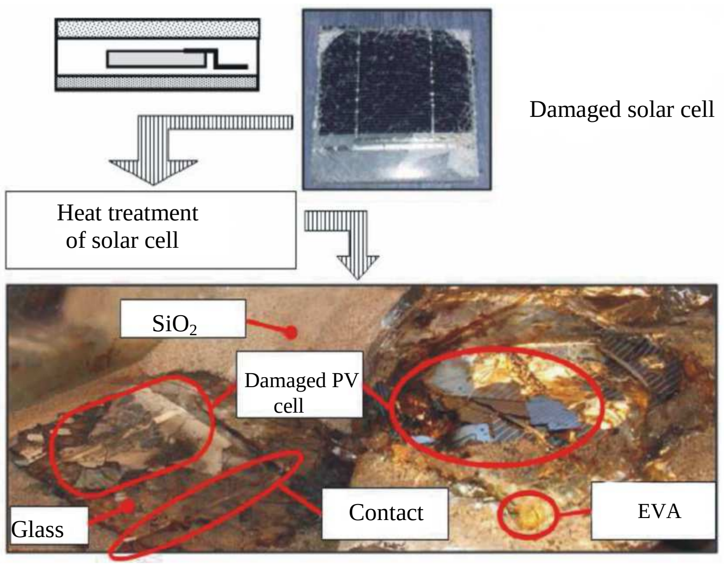

Fig. 6. Thermal recycling process of the encapsulated Solartec PV module.

Fig. 7. Heat treatment of PV modules.

The length of the process was significantly lower in comparison with the chemical treatment (25 minutes for the entire PV module). Also, there wasn´t problem with the solvents. The cost of the chemical compounds is high, given both by the quantities used and the actual cost of waste disposal.

The disadvantage of thermal recycling is the formation of emission gases during thermal evaporation of the EVA copolymer. The recycling process is energy-consuming, but up to 85 % of the recycled cells can be reused and reduce manufacturing energy consumption of the new PV modules up to 70 %. This method due to its simplicity and high efficiency can be used for commercial recycling of PV modules with better results than chemical method.

Surface cleaning of photovoltaic cells.

Another possibility of recycling photovoltaic cells after separation of them from the PV module is to use laser surface cleaning method. This method has been developed to obtain clean silicon substrates. Laser pretreatment of PV modules before the separation of its components is a very successful technique used especially in some PV module recycling companies in Germany (Wagner – Solar., 2017).

The laser method was compared with the chemical etching of the surface from the previous chapter through the experiment with neodymium laser. Two types of PV cells (mono and polycrystalline cells) were selected. Unnecessary layers such as aluminium metallization, antireflection and passivation layer were removed from the samples. The experiment was done using a neodymium laser pulse with λ = 1064 nm wavelength and frequency up to 120 Hz. Pulse duration was 10 ns. Beam energy reached 300 mJ per pulse. Irradiating a front surface and the back surface with such a laser energy has created heat in localised areas and removed unwanted layers, see Fig 8.

The layer removal process was performed at a Solartec company (Rožnov pod Radhoštěm, Czech Republic). The exact dispersion of the used parameters, unfortunately, were not specified by the company.

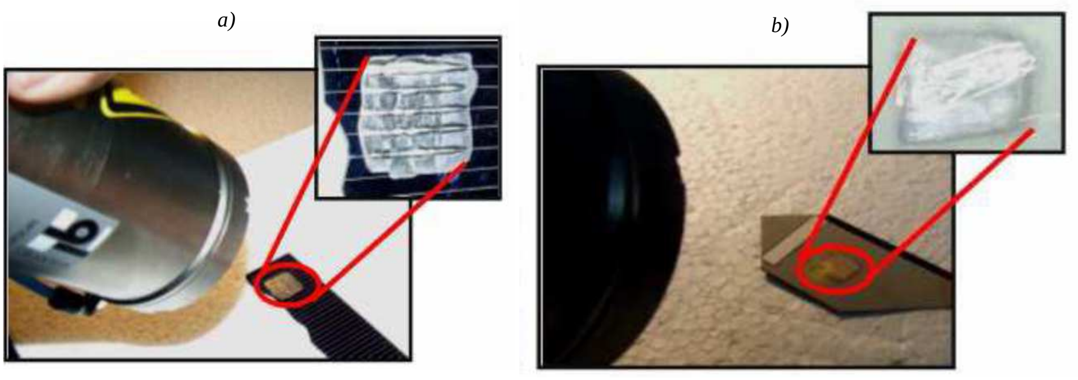

Fig. 8. PV cell surface cleaning with a neodym laser – a) front side, b) rear side of PV cell.

It has been found that the chemical treatment from the above procedure is far more advantageous than the laser method. The laser method is expensive, and the process is not very efficient. The time to remove the layers using the laser method is about 1 min/cm^2. It is possible to clean the whole surface of the cell by chemical treatment during this time.

Description of Mechanical recycling method

Mechanical recycling method is used for complete photovoltaic modules. Recycling process includes mainly mechanical and hydrometallurgical processing. PV modules are first crushed in the crusher and then shredded to the desired pieces of approximately 4 to 5 mm size. The PV module lamination is damaged in this way. The glass is separated from larger pieces of the laminate film due to the size of the milling cutter. Remaining parts of the laminate film are separated from the glass fragments in the vibrating network. The separated glass is then washed. In terms of output quality, better recycling results can be obtained from processes that are currently in the pilot phase. For example, combinations of mechanical and thermal processes allow recycling of crystalline and thin-film modules and make it possible to get more valuable materials with high yield and good quality. Pure glass shards are left to recycle in the glass industry. This creates additional environmental benefits in the following three main aspects:

1. Recycled shards are used to replace the original material in glass. Environmental burden is reduced and demands for primary energy are lower.
2. Reducing CO_2 emissions in the melting process. The basic composite for glass production consists of materials containing carbonates such as limestone, dolomite, soda/sodium carbonate. Resulting CO_2 emissions in relation to the carbon released from the primary materials is about 30 % of the total CO_2 emissions. It is therefore advantageous to reduce these emissions by using glass shards instead of primary materials.
3. Reduction of energy in the melting process. Lower glass melting temperature compared to the base material leads to lower energy consumption in the glass melting process. The potential for reducing the energy of glass is in the range of about 3 % to 10 % of glass shards. This is considered to be beneficial for reducing fuel consumption and associated emissions in the glass melting process.

Laminate wastes: They are exothermic during combustion. This energy can be further used and can partially replace the production of electricity and thermal energy from fossil fuels.

Recycling junction boxes and cables: There are no specific data on the treatment of the junction boxes or wires at the end of life. It is assumed that all plastic materials are burned in a waste incinerator and metal parts, mainly copper connectors and cables, are recycled by common methods for these metals.

Mechanical recycling method of damaged PV modules

Two damaged monocrystalline PV modules ASEC-230G6S were selected for recycling. The efficiency of the PV modules varied around 15 %; the dimensions were 1629 x 989 x 47.5 mm (height, width, depth) and the weight was 19 kg. PV modules consist of sixty solar cells with 156 x 156 mm dimensions and were protected by tempered anti-reflection glass and with EVA laminate. Visual inspection found defects, especially large cracks in the protective glass. Both modules were damaged due to natural influences. The aluminium frame was on both PV modules without damage, and the rear protective film showed no signs of mechanical damage. Junction boxes and connection cables were also fine. On both modules, electroluminescence measurements in the photovoltaic laboratory of the Brno University of Technology were done, see Fig. 9.

a) *b)*

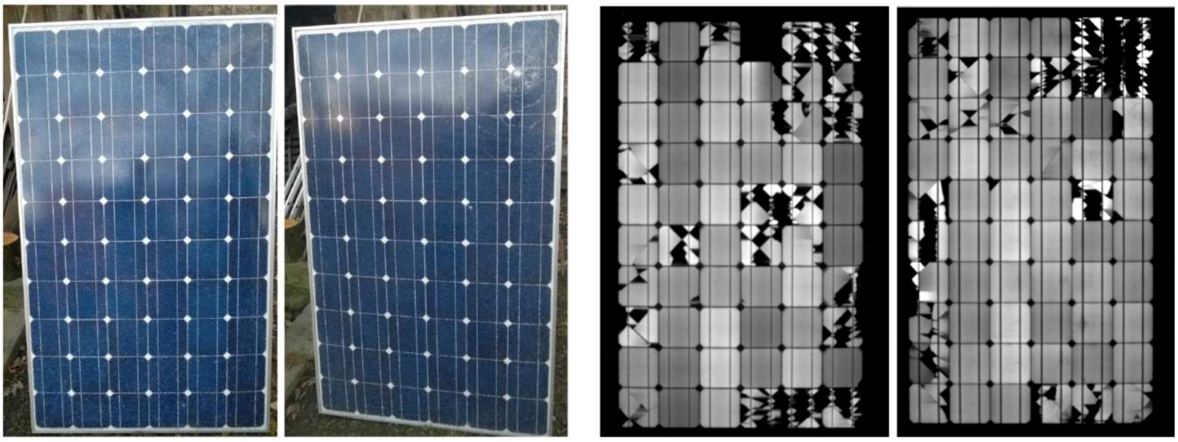

Fig. 9. a) Damaged PV module number 1(on the left) and number 2 (on the right); b) Electroluminescence measurement of module number 1 (on the left) and module number 2 (on the right).

In the first step, the modules were mechanically processed and prepared for recycling. The aluminium frames, which were silicone-secured and screwed together, were removed from the modules, see *Fig, 10 a)*. One aluminium frame weighed approximately 3.5 kg. Subsequently, the junction boxes were removed.

a) *b)*

Fig. 10. a) Removed aluminium frames and junction boxes, b) PV modules cutting into two halves.

In the second step, PV modules were rolled and cut into two halves on hydraulic shears for a better crushing process in a chain crusher, see *Fig. 10 b)*. The cut modules were placed on a conveyor that moved them to a chain crusher. The chain crusher crushed them again into different pieces and fractions, see *Fig. 11*. The sizes of the crushed pieces depend on the selected crushing programs.

a) *b)* *c)*

Fig. 11. a) Detail of the crusher, b) Shredded PV modules, c) Crushed material.

The resulting material was divided into individual fractions by size through a mechanical separator and sieves. Three sieves were placed above each other. The first sieve had a mesh diameter of 11.2 mm, a second sieve placed in the middle had a mesh 5.6 mm diameter, and the last one had mesh diameter of 1 mm. Individual fractions sizes were separated from each other and continued for further chemical processing to obtain metals. The largest masses (66.32 % of the weight) had the fractions of the middle and the smallest sizes, see *Table 2*. Most of the PV modules consist of protective glass, which pieces are, with the silicon parts, the smallest one. The rest of the crushed material like plastics remains in the form of larger pieces.

Tab. 2. Weight distribution of individual PV modules parts.

	Weight [kg]	**Percentage share** [%]
Total weight of the modules	38.00	100
Aluminium frame	7.00	18.42
The largest pieces of fraction > 11.2 mm	5.30	13.95
The medium pieces of fraction > 5,6 mm	14.20	37.37
The smallest pieces of fraction > 1 mm	11.00	28.95
Connection boxes	0.50	1.31

To determine the composition of the crushed material, a spectral analysis of the fractions less than 1 mm was done (Fig. 12). Most of the sample consists of silicate glass, silicon dioxide and silicon, sodium calcium and aluminium, see Table 3. Other metals are not present in the crushed material according to the analysis because they were separated by the Galmet Company in the previous step by an electrodynamic separator and a chemical method. Data with metals are shown in the following chapter.

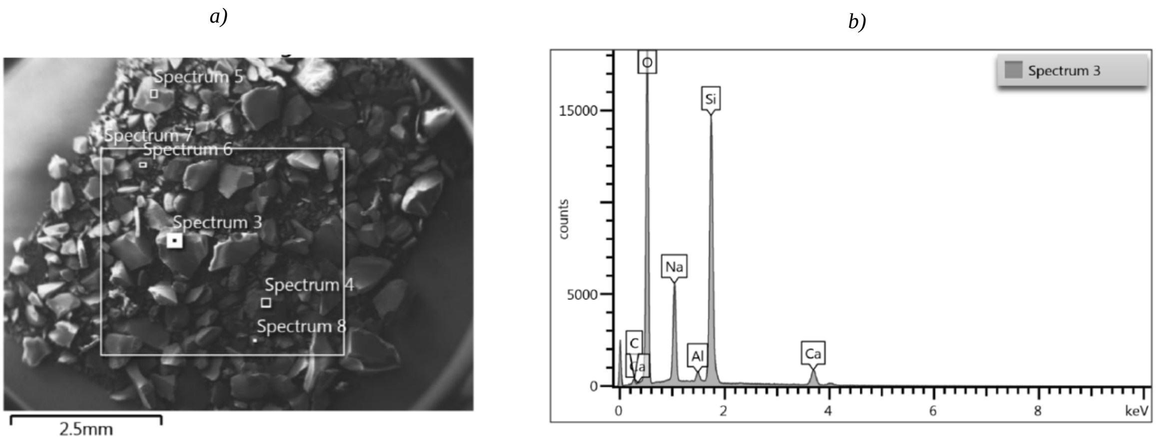

Fig. 12. a) Photo of crushed material with fragments less than 1 mm, b) Spectral analysis of fragments less than 1 mm.

Tab. 3. Parameters of spectrum 3.

Element	Weight percentage of total [Wt%]	Sigma – Deviation [Wt%]	Percentage of atoms [%]
C	3.06	0.21	4.89
O	53.81	0.17	64.63
Na	11.28	0.08	9.43
Al	0.88	0.03	0.63
Si	27.19	0.11	18.60
Ca	3.78	0.05	1.81

The next step in the recycling was chemical etching to obtain precious metals. Crushed material was already free of glass. The whole process took place in a stainless reactor with nitric acid.

The recycling of silver was interesting from the economic point of view. Obtaining aluminium and glass hardly paid the cost of mechanical operations. From an environmental point of view, however, it was advantageous. Silicon was very difficult to separate from the fine glass fraction (by wet flotation and electrodynamic dry method).

The amount of material saved by recycling PV modules

The following percentages of materials can be saved assuming that up to 500,000 tons of photovoltaic waste could be recycled by 2025 and the average weight of one PV module is 20 kg (Huang, 2017), see Table 4. Values in the table are averaged on the basis of data provided by the Galmet Company in our experiments. EVA, Tedlar and adhesive are not considered in the calculations.

Tab. 4. The amount of material saved by recycling PV modules.

Material	Glass	Al	EVA	Tedlar	Adhesive	Si	Ag	Sn	Zn	Cu	Pb	other
Percentage of material in PV module [%]	74	10.3	6.55	3.6	1.16	3.35	0.17	0.12	0.07	0.57	0.06	0.05
Amount of material in one PV module (max 20 kg.) [kg]	14.8	2.06	1.31	0.72	0.232	0.67	0.034	0.024	0.014	0.114	0.012	0.01
Material yield from PV module waste [%]	95	100	x	x	x	81	50	100	100	100	100	x
Theoretical estimation of saved material by 2025 [tons]	351500	51500	x	x	x	13567	425	600	350	2850	300	x

Discussion

The reason for the experiments described in this paper was the effort to solve the increasingly important recycling of an old and damaged PV modules and PV cells. The research was conducted in terms of minimal impact on the environment and with the ecologically and economically valuable emphasis.

Due to experiments results, it is obvious that the PV modules recycling by the thermal method is more advantageous than the chemical method in term of process length and financial costs. From the environmental point of view, the disadvantage of thermal treatment is the formation of emission gases during evaporation of the EVA copolymer. The possible water damage is also disadvantageous. However, this method can be used for commercial recycling of PV modules, where aren't high-quality requirements for the output material components.

Other tests have shown that the chemical treatment is far more advantageous than laser method for obtaining reusable silicon for the manufacturing of PV cells. Laser method is expensive with removal time of layers about 1 min / cm^2. The whole PV cell can be chemically cleaned during this time.

Crucial in the mechanical recycling process are the used technologies. The key is to know which devices are suitable for creation of the crushed material. If the PV modules are bigger than 1 x 1 m, it is necessary to divide them into two parts because the chain crusher must be able to crush the material to the smallest possible pieces. Another important parameter for recycling itself is whether a chain or blade crusher is used. In a chain crusher, there is a risk that plastic pieces will remain together with silicon and silver. This will lead to a poorer extraction of the necessary materials.

In PV modules, several types of glass are used, and their shredding can cause damage to the crusher and higher operating costs. From the financial point of view, it also depends on whether there is a separator at the end of the line separating the glass or plastics from the crushed material. In cooperation with Galmet company, it has been found that it is very difficult to obtain metals from the mixture of recycled PV modules with glass. In the case of the mixture without glass, the entire process will be faster, easier and cheaper. Additionally, glass no longer has to undergo chemical etching steps and is directly delivered to the glassworks or building industry as a filler.

Conclusion

From all the analysed recycling methods, mechanical recycling, despite certain disadvantages, seems to be the most usable. In the mechanical recycling process, the silver-containing crushed material up to 0.07 % is not economically advantageous to process subsequently in a chemical way. The financial profit of the silver content does not even cover the cost of basic recycling operations. From the economic point of view, the final operation should be the mechanical separation of aluminium and glass. The biggest costs during recycling are crushing and sorting of PV modules, and disposal of wastewater and obtaining and refining of silver. Based on data provided by the Galmet company, the amount of saved material due to PV module until the year 2025 in the Czech Republic was also theoretically calculated. Recycling could save up to 351 500 tons of glass, 51 500 tons of aluminium, 13 567 silicon and 425 tons of silver – more in Table 4.

The process of PV modules recycling for reuse in PV module production is a burden on the environment, but production of PV modules from primary raw materials would be an even greater environmental burden. The results of the PV cell separation processes and the removal of unwanted layers indicate that PV module recycling is desirable and may lead to a reduction in environmental load and can reduce the extraction of raw materials.

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References

Ayres, R., Ayres, L., Råde, I.: The Life Cycle of Copper, its Co-Products and By-Products. *Eco-Efficiency in Industry and Science*, France: Center for the Management of Environmental Resources, 2012.

Alsema, E.A., de Wild-Scholten, M.J.: Reduction of the environmental impacts in crystalline silicon module manufacturing., *Ecn, p.8, 2015*.

Balomenos, E., Panias, D., Paspaliaris, I.: Carbothermic Reduction of Alumina: A Review of Developed Processes and Novel Concepts. *Proceedings of EMC 2011, p.16*.

Bechník, B., Bařinka, R., Čech, P.: Analýza životního cyklu fotovoltaických systémů. *Czech RE Agency, p.6, 2015*.

Dias, P.: Recycling WEEE: Extraction and concentration of silver from waste crystalline silicon photovoltaic modules. *Waste Management*, p.6., 2016. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0956053X16301015 .

Goe, M., Gaustad, G.: Strengthening the case for recycling photovoltaics: An energy payback analysis. *Applied Energy*, 2014(120), pp.41-48. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0306261914000555.

Granata, G., Pagnanelli, F., Moscardini., E, Havlik, T., Toro, L.: Recycling of photovoltaic panels by physical operations. *Solar EnergyMaterials&SolarCells*, p.10., 2014, Available at: http://linkinghub.elsevier.com/retrieve/pii/S092702481400018X .

Huang W., Shin W., Wang L., Sun W., Tao M.: Strategy and technology to recycle wafer-silicon solar modules. *Solar Energy, 2017*, p.10. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0038092X17300105 .

Hylský, J., Strachala, D. & Vaněk, J.: Analysis of Photovoltaic Modules after 20 Years in Service. *ECS Transaction, SCOPUS, 16th, p.8., 2015*

Choi, J.-K. & Fthenakis, V.: Crystalline silicon photovoltaic recycling planning: macro and micro perspectives. *Journal of Cleaner Production*, 2014(66), pp.443 - 449. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0959652613007865 .

Kang S., Yoo S., Lee J., Boo B., Ryu H.: Experimental investigations for recycling of silicon and glass from waste photovoltaic modules. *Renewable Energy*, 2012(47), pp.152 - 159. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0960148112002716.

Klugmann-Radziemska, E. & Ostrowski, P.: Chemical treatment of crystalline silicon solar cells as a method of recovering pure silicon from photovoltaic modules. *Renewab. Ener.*,, 8(35), pp.378-387., 2010. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0960148109005199 .

Kreuger, L.: Overview of First Solar's Module Collection and Recycling Program. *First Solar*, p.27. Available at: https://www.bnl.gov/pv/files/PRS_Agenda/2_Krueger_IEEE-Presentation-Final.pdf [Accessed August 04, 2017].

Kudelas, D., Koščo, J., Tauš, P.: Document The potential of utilization and evaluation of polymetallic nodules bed in clipperton-clarion locality in pacific ocean, *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management*, (2014) SGEM 3 (5), pp. 485-492.

Kumar, S., Sarkar, B.: Design For Reliability With Weibull Analysis For Photovoltaic Modules. *International Journal of Current Engineering and Technology*, p.6, 2013.

Latunussa C. E.L., Ardente F., Blengini G., Mancini L.: Life Cycle Assessment of an innovative recycling process for crystalline silicon photovoltaic panels. *Solar EnergyMaterials&SolarCells*, 2016(156), pp.101-111. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0927024816001227 .

Meija, J. Coplen T., Berglund M., Brand A., De B., Gröning M., Holden N., Irrgeher J., Loss D., Walczyk T., Prohaska T.: Atomic weights of the elements 2013. *IUPAC Technical Report*. Available at: https://www.degruyter.com/view/j/pac.2016.88.issue-3/pac-2015-0305/pac-2015-0305.xml .

McDonald, N.C. & Pearce, J.M.: Producer responsibility and recycling solar photovoltaic modules. *Energy Policy*, 2010(38), p.7. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0301421510005537 .

McGraths.: Specifications for Limestone in Glassmaking. *Congcal.com*. 2013. Available at: http://www.congcal.com/markets/glass/ [Accessed August 04, 2017]

Müller, A., Wambach, K., Alsema, E.: Life Cycle Analysis of Solar Module Recycling Process. *Cambridge press* 2011. Available at: http://journals.cambridge.org/abstract_S1946427400045000 .

Park, Kim W., Cho N., Lee H., Park N.: An eco-friendly method for reclaimed silicon wafers from a photovoltaic module: from separation to cell fabrication. *Green Chem*, 18, p.8. 2015, Available at: http://xlink.rsc.org/?DOI=C5GC01819F .

Rocchetti, L., Beolchini, F.: Recovery of valuable materials from end-of-life thin-film photovoltaic panels: environmental impact assessment of different management options. *Journal of Cleaner Production*, 2015(89), pp.59 - 64. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0959652614011809

Shin, J., Park, J., Park, N.: A method to recycle silicon wafer from end-of-life photovoltaic module and solar panels by using recycled silicon wafers. *Solar Energy Materials & Solar Cells*, 2016(162), pp.1-6. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0927024816305591 .

Tao, J., Yu, S.: Review on feasible recycling pathways and technologies of solar photovoltaic modules. *Solar EnergyMaterials&SolarCells*, 2015(141), p.17. Available at: http://linkinghub.elsevier.com/retrieve/pii/S092702481500210X .

Tauš, P., Taušova, M.: Economical analysis of PV power plants according installed performance, *Acta Montanistica Slovaca*, (2009)14, pp. 92–97.

Tauš,P., Taušová,M., Šlosár, D., Jeňo, M., Koščo, J.: Optimization of energy consumption and cost effectiveness of modular buildings by using renewable energy sources, *Acta Montanistica Slovaca Volume 21 (2016)*, number 3, pp 171-179.

Wagner - Solar. Available at: http://www.wagner-solar.com/en/solar-power/products/solar-panel-recycling.html [Accessed December 01, 2017].

Wealthdaily., 2017. Special Report: Solar Technology. Wealthdaily. Available at: http://www.wealthdaily.com/report/solar-technology/1409 [Accessed August 04, 2017].

Yi, Y.K., Kim H. S., Tran T., Hong S. K., Kim M. J.: Recovering valuable metals from recycled photovoltaic modules. *Journal of the Air & Waste Management Association*, pp.797 - 807. 2014, Available at: http://www.tandfonline.com/doi/abs/10.1080/10962247.2014.891540 .

Zhang, Y. Hu Y., Zeng H., Zhong L., Liu K., Cao H., Li W., Yan H.: Silicon carbide recovered from photovoltaic industry waste as photocatalysts for hydrogen production. *Journal of Hazardous Materials*, 2017(329), p.8. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0304389417300353 .