

Recycling of end-of-life PV panels - a review of technologies

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Abstract. A number of documents have been launched by the European Commission in recent years to increase the amount of renewable energy and reduce the dependence on energy sources (and CRMs) outside of European Union. Solar panels are a great source of renewable energy, and their installed capacity in EU increases each year. The lifetime of a solar panel is approximated to be 20 years, and they are starting to represent a significant group of multimaterial waste to be disposed of in the near future, therefore their recycling aimed at the recovery of valuable and critical materials becomes a crucial part of EU energy transformation. The paper presents the overview on the existing technologies used to recycle end-of-life photovoltaic panels.

1 Introduction

The strong need to increase the share of renewables in the energy mix of European countries and reduce the dependence on energy sources (and CRMs) outside of European Union is reflected in a number of documents and regulations published in recent years, including the WEEE Directive (2012) [1], European Green Deal (2019) [2], Fit for 55 (2021) [3] and REPowerEU (2023) [4]. In order to achieve the goals described in those documents, EU countries need to accelerate their efforts to reduce their dependence on the combustion of fossil fuels. Photovoltaic (PV) panels can be a great alternative to the technologies based on the combustion of fossil fuels, however their production and utilization is also associated with certain environmental burdens [5]. At the end of 2021, the total installed PV capacity in EU was 158 GW, what translates into 15% increase of total PV capacity installed in EU countries [6].

Recycling of end-of-life and/or damaged photovoltaic panels is considered to be a crucial part of the EU energy transformation. It is estimated that by 2040, the PV waste will amount to as much as 27 million tonnes per year, whereas the share of recovered materials will be 6%, compared to only 0.08% recovered currently [7]. According to IRENA and IEA-PVPS, the cumulative PV panel waste will be 1.7-9 mln tonnes in 2030, with a value of 450 mln USD for raw material recovery, and as much as 60-78 mln tonnes by 2050, with an estimated value of 15 billion USD [8–10].

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2 Types of PV panels

Silicon-based photovoltaic panels are currently the most commonly used, and represented as much as 73.3% of all the PV panels worldwide in 2022 [12]. Based on the structure, material composition and the production technology, three main generations of photovoltaic panels can be distinguished [11].

2.1 1st generation

Currently, the market is dominated by photovoltaic panels constructed from silicon wafers approximately 0.2 mm thick. Each silicon wafer contains a P-N junction made of boron- and phosphorus-doped silicon. The silicon-based panels can be divided into two types:

- Polycrystalline – made from silicon that has crystallised into multiple monocrystals. They are characterised by their light blue colour and square or rectangular shape,
- Monocrystalline – made from monocrystalline silicon. They range in colour from dark blue to black. They are more efficient than polycrystalline panels and have a lower rate of power loss with increasing temperature, and a higher price. It is estimated that around 80% of the panels available on the market are monocrystalline [11].

2.2 2nd generation

Produced by plasma-assisted deposition of Si thin films from the gas phase. Thin-film (approx. 1µm) modules also feature a P-N junction. Among the thin-film panels, the following subcategories can be distinguished:

- Amorphous – made from silicon in an amorphous form. Their colour is maroon or black. Their advantages include a low power drop rate, while the main disadvantage is lower efficiency than models made from crystalline silicon,
- CIGS/CIS – a type of thin-film panel in which a mixture of copper, indium, gallium and selenium (CIGS) or copper, indium and selenium (CIS) serves as the semiconductor. Their main advantage is their relatively high efficiency in winter,
- CdTe – the role of the semiconductor here is played by cadmium telluride. Due to their very low power drop, they are characterised by high efficiency at high temperatures,
- CZTS – in this type of panel, copper zinc tin sulfide acts as the semiconductor. The main advantage of this technology is the use of low-cost and accessible materials, which translates into lower production costs [11].

2.3 3rd generation

This type of photovoltaic panel does not have a P-N junction. They are mainly characterised by their simple design and low production costs, but their key disadvantages include low efficiency and shorter lifetime compared to earlier generation modules. Third-generation technologies include [11]:

- InGaP / GaAs tandem cells – multi-junction cells,
- Dye-sensitized solar cells – manufactured using technology that uses low-cost materials and/or natural dyes. Their manufacturing process is simpler than silicon cells and they also work in less intense lighting [13],
- Perovskite cells (PSC) - hybrid organic-inorganic cells, with potentially low production costs and high efficiency [14],

- Quantum dot solar cells (QDSC) - use quantum dots a few nanometres in size to absorb incident photons from sunlight in order to generate a photovoltaic effect,
- Organic cells - these are mostly polymeric solar cells composed of conjugated polymers or small organic semiconductor molecules. They represent the combination of the properties of polymers and semiconductors and low production costs [11].

3 Recycling of end-of-life photovoltaic panels

Recycling of end-of-life photovoltaic panels is now one of the most crucial issues related to the green energy transformation that needs to be solved. PV panels contain, on one hand, many valuable materials that might be recovered thus increasing the EU raw material independence. On the other hand, the waste panels might contain hazardous elements, that can potentially contaminate the environment, such as allium, arsenic, cadmium, lead and selenium, and polymers, such as ethylene vinyl acetate, polyethylene terephthalate, and polyvinylidene fluoride [5, 15]. Waste photovoltaic panels represent one of the fastest growing groups of the produced WEEE [16].

The vast majority of commercially available photovoltaic panels are crystalline silicon-based modules. Approximately 76% of their weight is made up of glass, 10% of polymers, 8% of aluminium, 5% of silicon, about 1% of copper, and silver and other metals (including tin and lead) in amounts below 0.1% [17].

The lifetime of photovoltaic panels is approximately 30 years. After this time, or after they have deteriorated or become beyond repair, they must be disposed of. As photovoltaic panels are a multi-material waste, it is challenging to recycle all fractions of them. In order to do so, many different techniques aimed at the recovery of different material fractions can be applied.

Among the biggest challenges in the recycling of photovoltaic panels is the removal of encapsulant from the laminated structures. To do this, the easiest approach is to use thermal methods, which, however, are not always environmentally beneficial. A combination of mechanical and/or thermal and chemical processes is also a possibility [10].

3.1 Mechanical processing

Mechanical processing of end-of-life photovoltaic panels mostly focus on mechanical removing of alumina frames (currently this process is fully automatic) [33-35]. Next step after removing alumina frames is cutting and crushing process which involve different types of crushers. As an example can be used chain crusher. To prepare smaller particles of damaged panels also as well is add another step of size reduction process by using shredders. It will help to receive small parts of material which include elements of copper wires, glass and silica [33, 34]. Next step include different methods of classification or separation to receive products which is interesting for us. As well here can be used different vibrating screens which reduce size of grain class delivered to separation process. For separation of different types of material can be used for example densimetric table. Products which still include EVA elements or other foils or coating fractions are sended to further thermal/chemical process [33-35].

3.2 Thermal processing

After the initial mechanical processing, the end-of-life photovoltaic panels can be subjected to further thermal and/or chemical processing. Thermal processes may include application of

elevated temperatures to soften the ethylene-vinyl acetate (EVA) adhesive layer and remove the remaining components, combustion, i.e. of the insulation board [18], or pyrolysis, which is a thermal process performed in an oxygen-free atmosphere in order to remove the polymers [19].

Thermal processing also includes metallurgical processes. In one of the studies [20], the authors evaluated the thermodynamic criteria for refining silicon wafers using oxidation refining, steam refining and solvent refining. It was found that it is possible to remove aluminium, beryllium, boron, calcium, gadolinium, hafnium, uranium, yttrium and zirconium into the slag and antimony, bismuth, carbon, lead, magnesium, phosphorus, silver, sodium and zinc into the vapour phase. Moreover, a solvent refining process performed with aluminium, copper and zinc as solvent metals was found to be effective in refining silicon wafers. The purification of n-type phosphorus-doped photovoltaic panels with metallic zinc and the purification of boron-doped photovoltaic panels using metallic aluminium are particularly favorable. The effectiveness of metallurgical processes for separating most impurities has been demonstrated.

In the study [21], the mass flow of Ag and In was investigated during the treatment of waste polycrystalline silicon and monocrystalline silicon, as well as CIS panels to produce valuable preconcentrates of these metals. The processing routes, used in various combinations, were thermal treatment and gravimetric separation, mechanical crushing, screening and thermal treatment, and chemical and thermal treatment of the panels.

3.3 Chemical processing

In many cases, the recovery of materials from end-of-life photovoltaic panels may involve several steps and processes, starting with mechanical processing followed by thermal removal of specific materials, with a chemical treatment as the final step. One of the studies [22] analyzed the heat treatment conditions in order to remove the EVA layer and determined the optimal conditions to be 30 min at 650°C. In order to separate silicon and metals, the composition of the HF/HNO₃ solution and the immersion time were adjusted accordingly.

Another publication [23] recovered silicon cells by mechanical processing and pre-screening to remove glass impurities, followed by hydrometallurgical treatment. The process involves an alkaline and an acid phase and produces the 3N silicon. Silver (AgCl) was obtained from the acidic waste solution by salt precipitation, followed by a reduction reaction in an induction furnace (Ag recovery step).

The composition of mechanical, thermal and chemical processes was also presented in [24], where the authors proposed a technological scheme for the recovery of pure crystalline Si and Ag from PV panels, involving thermal pretreatment and hydrometallurgical processes. The technology involves the removal of Al frames, junction boxes and copper cables and the fragmentation of PV modules to 4 mm, separation of the silicon cells from the reinforced glass by thermal treatment at 550°C for 15 minutes in excess air in order to decompose the encapsulating organic material. The next step was the separation of Si flakes and the ash residue and their subsequent sieving with a perforated rotary sieve. The Si flakes were further grinded with a ball mill and subjected to quantitative one-step leaching of Ag and Al from the Si flakes with HNO₃ at ambient temperature. The authors indicated that two-step acid leaching could also be used. Leaching of Si flakes with 2.5 M NaOH was used to remove the antireflection coating, recovering high-purity crystalline silicon. In the next step, Ag was separated and precipitated as AgCl or electrodeposited from nitrate solutions and Al was precipitated by neutralising the solution.

The authors of the publication [25] describe a technology in which Pb-free solar panels can be produced from recovered modules. The recovered Si wafers showed properties almost

identical to those of commercial virgin wafers. Moreover, solar cells produced from the recovered modules showed an efficiency equal to that of the virgin cells.

The first step to recover Si wafers in the described technology is to dissolve silver (Ag) and aluminium (Al) using nitric acid (HNO₃) and potassium hydroxide (KOH), respectively. The next step is to remove the anti-reflective coating (ARC) and emitter on the surface with etching paste that contains phosphoric acid (H₃PO₄). The wafers to which the etch paste was applied were annealed for 2 minutes at 320, 340, 360, 380 and 400 °C.

In the study [26], the authors conducted an analysis of the recovery of silver from PV cells using leaching with HNO₃. The study shows that up to 6.87 kg of silver can be recovered per tonne of PV cells. With optimal parameters, it was possible to dissolve 100% of the silver contained in the PV cells. The authors indicate that the precipitation of silver by the addition of HCl and Na₂CO₃, as well as electrowinning, enabled the extraction of more than 99% of the silver in solution.

3.4 Other methods

Many publications also show electrohydraulic fragmentation as a method that can be successfully used for the separation of waste photovoltaic panels [27–30].

The exact description of the electrohydraulic phenomenon varies depending on the literature source. As reported by Nagashima et al [31], a material sample is placed in an aqueous environment. A high-voltage pulse is applied between two electrodes. A high voltage current is then passed through the metal layer. Part of the metal layer is vaporised by heating, and the pulsed arc discharge produces a plasma between the two electrodes. During this time, a shock wave is generated and the metal layer is separated from the plastic. No melting of the plastic occurs because the molten metal is immediately separated.

Another source [32] states that the phenomenon is induced by temporal power compression achieved by storing energy in a storage device for a certain period of time and then releasing this energy in a much shorter time. In its simplest form, the role of the energy storage element is played by a capacitor.

The communication [27] describes the EHF as the first step of the processing of waste PV panels leading to the further recovery of Si, Ag, Cu, Sn, Pb and Al. The results of the study suggest that, compared to traditional crushing, the dismantling of PV panels using EHF demonstrates improved selectivity by concentrating metals in fractions of a specific grain size. The method allows further recovery of metals from PV panels through simple operations such as screening.

4 Summary

The presented review shows that the methods of treating and recycling waste photovoltaic panels can be divided into:

- a) Mechanical,
- b) Thermal,
- c) Chemical,
- d) Mixed, and
- e) Other.

In the case of mechanical methods, two approaches to the management of used PV panels can be distinguished: one is based on the preparation of whole silicon wafers for further processing by, among other things, grinding the outer layers of the panel. In this case, the recovered silicon wafers are to be used to manufacture further panels. The second approach is based on mechanical grinding of the waste PV panels into fractions of the desired size and

subsequent mechanical separation prior to further recovery processes not covered in the patents and publications.

Thermal methods most commonly involve the use of heat treatment (incineration or pyrolysis) to remove the layers of plastic present in the panel. This is a form of preparation for further recovery and separation processes. The use of pyrometallurgical processes to remove aluminium, beryllium, boron, calcium, gadolinium, hafnium, uranium, yttrium and zirconium into the slag and antimony, bismuth, carbon, lead, magnesium, phosphorus, silver, sodium and zinc into the vapour phase is also described. The solvent refining process using aluminium, copper and zinc as solvent metals is effective in refining silicon wafers. The purification of n-type phosphorus-doped photovoltaic panels using metallic zinc and the purification of boron-doped photovoltaic panels using metallic aluminium are particularly beneficial. The effectiveness of metallurgical processes for separating most impurities has been demonstrated.

The reported chemical methods are most often based on the application of adequate chemicals in order to separate specific fractions of used PV panels. According to the analysis, the use of chemical treatments allows for the effective separation of the EVA layer and the structural elements of the panel. Highly effective solvents include sulphuric and lactic acids.

Mixed methods are usually a combination of mechanical, thermal and chemical methods. Thermal methods are primarily used to remove the EVA film layer. Chemical treatment aims to selectively remove selected elements.

Another described method is electrohydraulic fragmentation (EHF), which involves high-voltage pulsed discharges in an aqueous environment at different discharge conditions. It can be used as the first stage of the processing of end-of-life PV modules to produce fractions that allow the further recovery of valuable materials, i.e. Si, Ag, Cu, Sn, Pb and Al. Compared to traditional crushing, the dismantling of PV panels using EHF shows greater selectivity by concentrating metals in fractions of a specific grain size.

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