

RECYCLING OF PHOTOVOLTAIC CELLS – A REVIEW

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ABSTRACT

The growth of solar energy has been remarkable between 2013 and 2022 on EU level, with a doubling of capacity from 80 GW to 197 GW. To recover valuable materials and mitigate environmental impact, it is imperative to have effective waste management practices in place. While recycling technologies are still in the experimental phase, the EU has put in place legal frameworks for manufacturer liability. There are continuous efforts being made to develop commercially viable technologies for the management of end-of-life PV module waste. An important part of the system of renewable sources is the establishment of a high-quality and efficient waste management system, which is contained within the concept of the circular economy. PV modules will at some point reach the end of their life cycle, which is estimated to be around 25 years, and become waste, therefore a lot of effort is currently being put into research and development of different waste treatment technologies of PV modules. They are still in the experimental phase, and few technologies become commercially available. Also, the management of waste generated at the end of the life cycle of photovoltaic technology is not yet fully regulated. However, at the level of the European Union, there is a legal framework for the liability of PV module manufacturers according to Directive on electric waste and electronic equipment. This paper is a detailed review of recycling technologies based on existing literature.

1. INTRODUCTION

1.1 Renewable energy and European Union policy

Renewable energy sources are energy sources that naturally replenish and do not deplete like fossil fuels. Renewable energy sources include hydroelectric power, wind energy, solar energy, marine energy, geothermal energy, and bioenergy. The total global capacity of renewable energy sources in 2013 was 1,567 TW, and in 2022 was 3,382 TW (IEA PVPS, 2023).

The ultimate goals of the growth share of renewable energy sources are reduction of harmful gas emissions, the impact on the environment and the prevention of resource depletion. Their use can help decrease the reliance on fossil fuels and increase energy sustainability, which will be beneficial for the environment and economy in the long run. According to (Isherwood, 2022) solar energy occupied 8,5% of the total capacity of all renewable sources in 2013, and more than 30% in 2022. Therefore, solar photovoltaic (PV) technology is widely recognised as key to achieving fully decarbonised energy generation, and as such is a vital tool in combatting climate change. Still, the production process of PV modules may involve some greenhouse gas emissions, but they do not produce any greenhouse gas emissions during their use.

Also, a new look at the energy strategy of the European Union (EU) is also a consequence of the Russian-Ukrainian war conflict that has been ongoing since February 2022. Therefore, the EC's REPowerEU plan was adopted in May 2022, where the EU proposes to end the energy dependence on Russian fossil fuels. Now it is the time for the European Union to turn to a rapid increase in renewables to establish energy independence from Russia. Hence, some member countries increased the targets for renewable electricity, introduced higher auction volumes and improved remuneration for distributed PV, reduced permitting timelines for solar and wind plants, increased grid capacity for new renewable energy projects etc. (RES Croatia, 2022).

If capacities of different types of renewable energy sources are compared in the period 2013-2022 in the EU, it can be seen a significant growth primarily in solar energy, followed by wind energy, while the other resources have almost the same capacities (Figure 1). In a period of 9 years, solar energy capacities have more than doubled, from 80 GW in 2013 to 197 GW in 2022.

It is important to emphasize that a significant part of the system of renewable sources also includes the establishment of a quality and efficient waste management system. Therefore, it is necessary to establish effective and



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sustainable waste management mechanisms and move away from the traditional practice of landfilling waste without treatment, which is contained in the circular economy of the European Union. The circular economy advocates an industrial economy that is consciously renewable, aims to use renewable energy sources, reduces, and strives to eliminate the use of chemicals and waste generation, and creates new jobs and green technology. Considering that the technologies of renewable energy sources are relatively new and that the transition is still at an early stage, the management of waste generated at the end of the life cycle (EOL) of photovoltaic (PV) technology is not yet fully regulated (Heath et al., 2020). However, all PV modules eventually reach the end of their life. Ensuring that the materials contained within modules at the end of their life are not confined to landfills has been an initial policy focus in the EU and other regions. Hence, PV modules are sorted based on the power of their installation facility and the time they entered the market, thus permitting differentiated processing according to technical and economic criteria. This uses an approach known as extended producer responsibility (EPR), which now represents one of the most important meta principles of environmental policy (Sica et al., 2018). The biggest challenge is likely to come from PV systems that were manufactured before the extended producer responsibility policy and from systems manufactured by manufacturers that no longer exist.

The EU has pioneered waste electric and electronic equipment (WEEE) regulations including PV waste specific collection, recovery, and recycling targets Directive on Waste Electrical and Electronic Equipment, according to end-of-life PV modules are hazardous waste belonging to the category of WEEE since 2012. The WEEE legislation has set up the minimum rules and targets for the dispos-

al of photovoltaic modules in EU member states. Revised Directive 2012/19/EU from 2019 suggests the minimum collection rate annually shall be 65% of the average weight of WEEE generated on the territory of that member state concerned, or alternatively 85% of WEEE generated on the territory of that member state. Minimum targets applicable to PV modules from 2018: 85% of weight shall be recovered, and 80% shall be prepared for re-use and recycled (European Union, 2012). However, every European country must transform this EU legislation into national law and can further refine or strengthen the rules behind the collection and recycling process. The main problem arising from this type of waste is the presence of environmentally toxic substances and the poor biodegradability of waste, which takes up significant space when deposited in landfills.

Currently, there is no pressure to ensure recycling capacity for photovoltaic panels since their lifespan is relatively long (25-30 years), they are still relatively new technology, and significant quantities of panels have yet to reach end-of-life stages which is anticipated by the early 2030s. . EoL processing technologies for photovoltaic panels are not yet green, but scientists and engineers around the world are working on improvements in terms of efficiency, environmental friendliness, and low-cost technology. As the quantity of waste photovoltaic panels increases, countries will have to establish their own disposal structures or hand over their photovoltaic waste to other countries, incurring high costs and without reclaiming the materials obtained through recycling. Currently, damaged photovoltaic modules covered by warranties mostly end up with the manufacturers who ensure proper disposal by handing them over to processors (Salim et al., 2019). All products should be designed and engineered for reuse after EoL. Thus, a closed loop implies a circular industrial system within a cir-

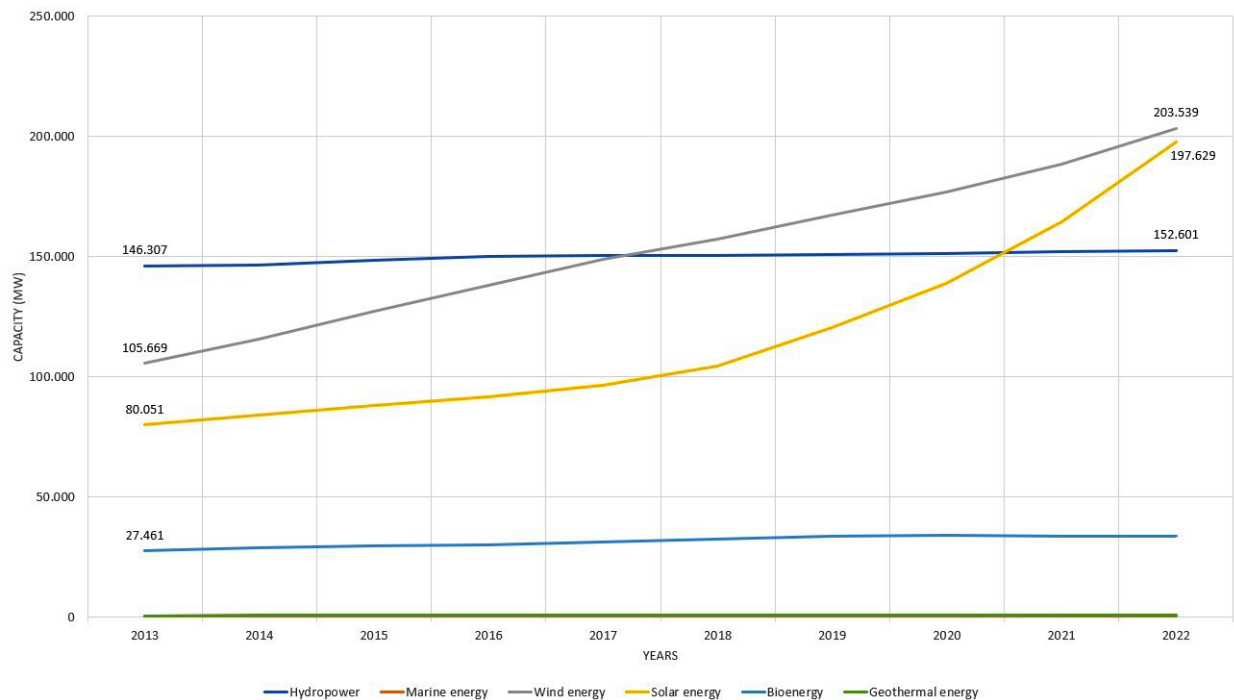


FIGURE 1: Total renewable energy capacity in the European Union 2013-2022. Data according to (IRENA, 2023).

cular economy, where the photovoltaic panel is designed in such a way that all the materials used for its production in the EoL can become a primary resource without creating waste and sacrificing quality, the whole process can be observed by up-cycling (Contreras-Lisperguer et al., 2017).

Researchers have placed focuses more on the PV waste in the countries where PV was initially installed or PV installation has kept rapid growth, such as Mexico, Italy, Spain, Australia, the OECD countries, USA, Belgium, India, and China (Song et al., 2023) Since the PV power capacity is increasing widely industrial-scale disposal or recycling is a vital economic and environmental aspect to consider (A. Omar et al., 2023).

Although waste management in accordance with the circular economy is covered, the work is focused on the review of PV module recycling. The introduction of the article provides an overview of the current installed capacity of renewable energy sources as well as solar energy. Trends in the installed capacity of individual renewable sources in the period 2013-2022 are presented. Then the shares of individual PV technologies on the market are presented. Later, a description of PV technologies is given with the specified materials used for individual components and a comparison of the technologies. The greatest emphasis is on the recycling process of PV technologies, so different recycling processes and the obtained results are listed.

1.2 Market and quantities of PV panels

PV module market can also be tracked through PV module capacity. The global picture of the growth of the capacity of PV modules is shown in Figure 2. For the period 2013-2022 an intensive growth of capacity is visible, especially for the area of Asia.

Although different types of PV cells are under development, only technologies that meet the criteria for service

life (> 15 years), efficiency (> 14%) and cost (< 0.3 USD/Wp) and that are not significantly constrained in resources can represent a major technological trend in solar energy application (Benda & Černá, 2020). This is also confirmed by the representation of each PV technology on current market. Therefore, the market share of silicon-based panels is projected to decrease to 44,8% until 2030, while third-generation PV panels are predicted to reach 44,1% in 2030 (IEA International Energy Agency; International Renewable Energy Agency, 2016).

Currently, c-Si technologies account for more than 95% of the overall cell production. Therefore, this review article focuses mostly on silicon PV module recycling techniques, although the main characteristics of other solar module technologies will be mentioned hereinafter. In 2015, technology of polycrystalline silicon PV module dominated the market with a share of 69,5%, and in 2019 monocrystalline silicon PV technology with a share of 65,5% (Figure 3). Amorphous silicon cells are dominant type of thin film solar cells and accounts about 13% of market share (Sander et al., 2007).

Regarding the estimation of PV waste, Figure 4 shows an estimation of cumulative PV waste up to 2050 for regular and early-loss scenarios on global level. The early-loss scenario gathers following assumptions, according to (IEA International Energy Agency; International Renewable Energy Agency, 2016):

- 0,5% of PV panels (by installed PV capacity in MW) is assumed to reach end-of-life because of damage during transport and installation phases.
- 0,5% of PV panels will become waste within two years due to bad installation.
- 2% will become waste after 10 years.
- 4% will become waste after 15 years due to technical failures.

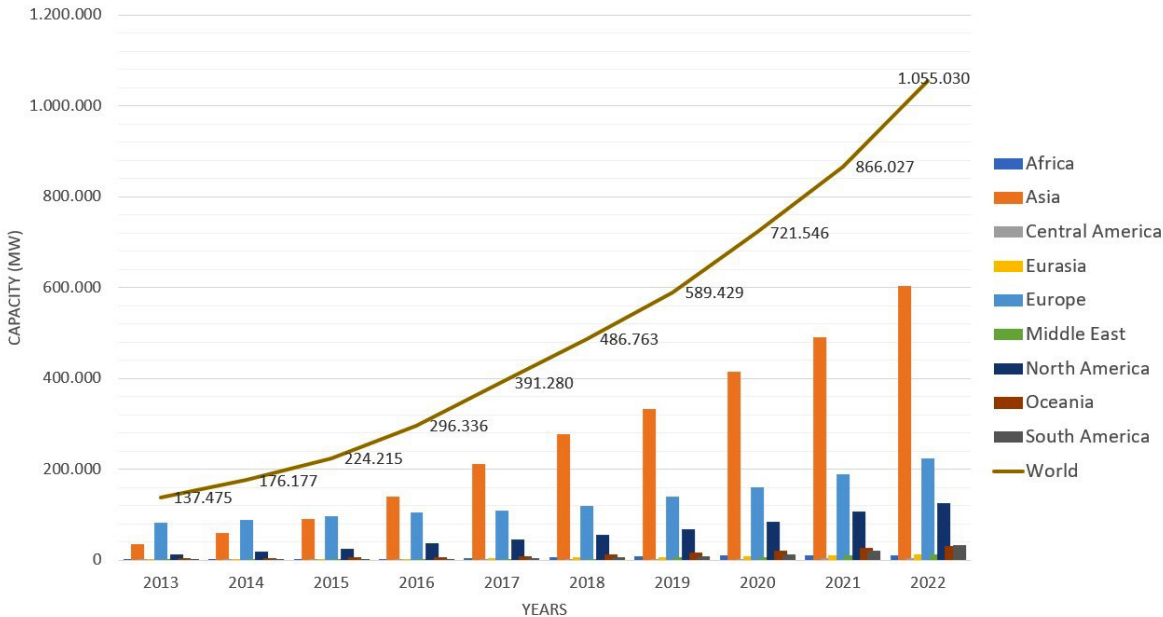


FIGURE 2: PV technology installed capacity globally 2013-2022. Data according to (IRENA, 2023).

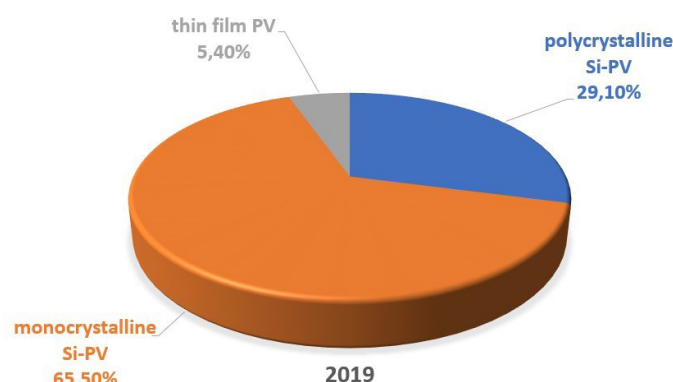


FIGURE 3: PV technology market share in 2019. Data according to (Benda & Černá, 2020).

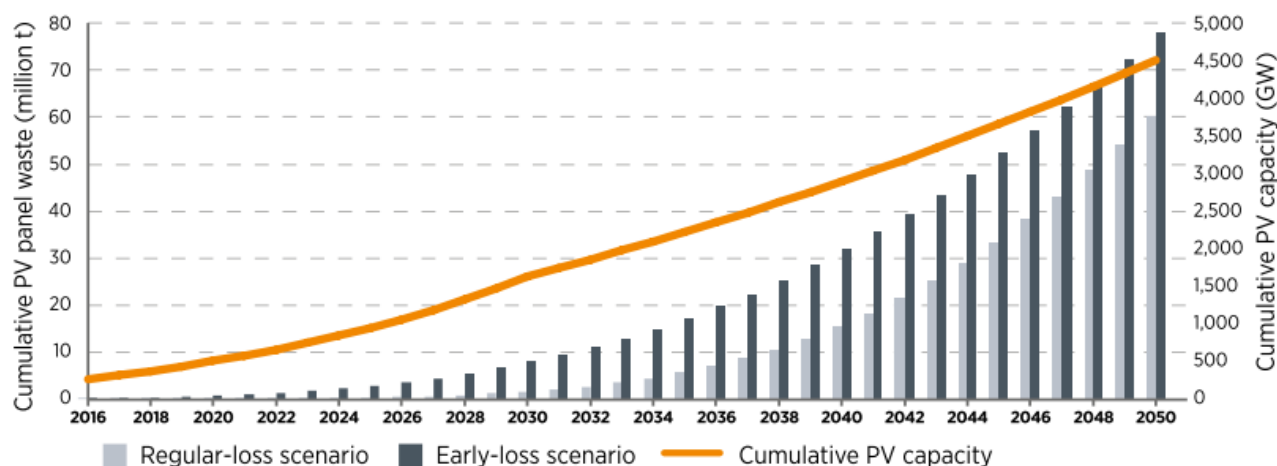


FIGURE 4: Estimated cumulative global waste (million t) of EoL PV panels. (IRENA & IEA-PVPS, 2016).

The early-loss scenario projection estimates much higher total PV waste streams, with 250.000 t alone by the end of 2016. This estimate would rise to 8 million t in 2030 and total 78 million t in 2050 on global level. The early-loss scenario assumes a higher percentage of early PV panel failure than the regular-loss scenario. In the regular-loss scenario, PV panel waste amounts to 43.500 t by the end of 2016 with an increase predicted to 1,7 million t in 2030. An even more drastic increase to approximately 60 million t could be expected by 2050 (IEA International Energy Agency; International Renewable Energy Agency, 2016).

The capacity of CPV modules in the world in 2022 was <1% of the total capacity of solar energy sources, which was 6,6 GW. A similar share of CVP module capacity was in the European Union in 2022 and amounts a little more than 1%, which was 2,3 GW (IEA PVPS, 2023).

2. TECHNOLOGY OF PHOTOVOLTAIC PANELS

2.1 Classification

Solar radiation is converted into direct current electricity by photovoltaic cell often called solar cells. When a material absorbs photons (the unit of electromagnetic radiation) with energy above a certain threshold, the photovol-

taic effect caused electrons to move within semiconductor material. Solar cell technology is based on this basic physical mechanism called photovoltaic effect (Voudoukis, 2018).

Interconnected PV modules make-up a solar panel or module, which can then be further connected into solar arrays or fields (Figure 5). It is important to note that solar panels perform best when exposed to direct sunlight, but they can still generate electricity even in cloudy weather, although in smaller quantities (Y. Xu et al., 2018). Typically, PV modules are rated from 290 W to 600 W, depending on the technology and the size (International Energy Agency, 2022).

The most used classification of solar cells is the one where they are divided according to the cell production technology. Therefore, there are three generation of photovoltaic cells presented in Table 1.

2.2 1st generation of solar panels

Wafer based crystalline silicon cells are classified as first generation of solar cells. There are two main types: monocrystalline silicon and polycrystalline silicon solar cells. Figure 6 shows wafer based crystalline silicon cell design.

Silicon is environmentally safe and the second most abundant chemical element in the Earth's crust. However, it

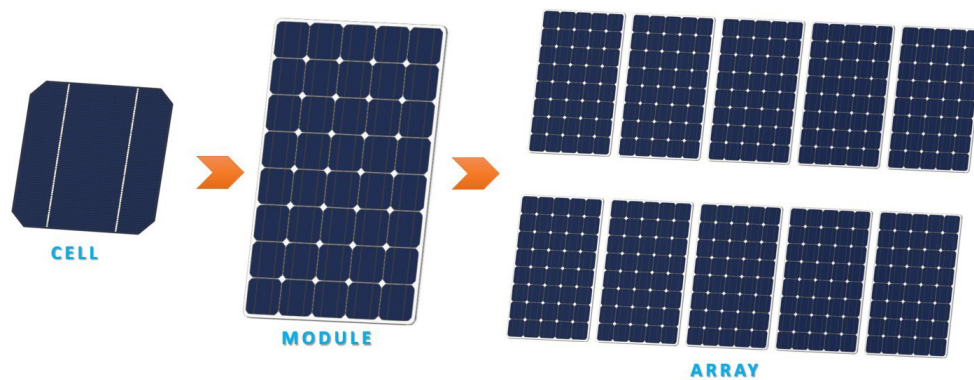


FIGURE 5: PV cell - module - array.

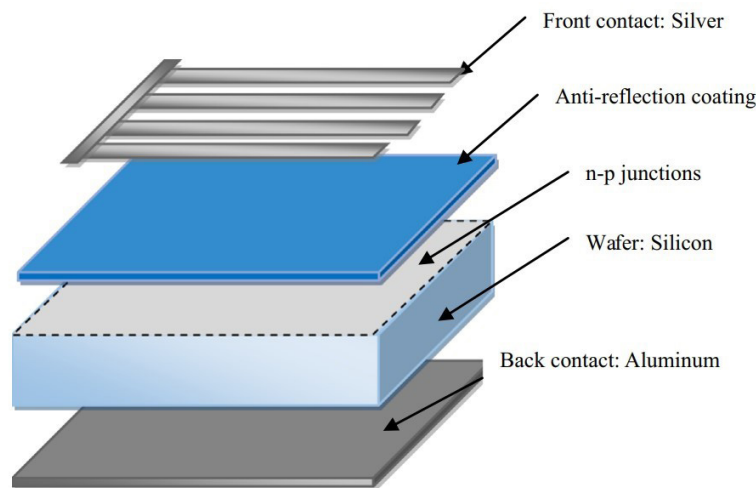


FIGURE 6: Wafer based crystalline silicon cells design (Tao & Yu, 2015).

is mainly found in the form of silicon dioxide and is therefore not suitable for direct use in photovoltaic modules. A significant portion of the costs associated with silicon goes to its extraction and processing to obtain a clean and uniform structure (Kumar et al., 2020).

TABLE 1: Most used classification of solar cells.

1st generation	Wafer-based crystalline silicon cells	Monocrystalline silicon (mono c-Si) solar cells Polycrystalline silicon (poly c-Si) solar cells
2nd generation	Single junction thin film cells	Amorphous silicon (a-Si) and Micromorph silicon (μ -Si) thin film solar cells Cadmium Telluride (CdTe) thin film solar cells Copper-indium-gallium-diselenide (CIGS) and Copper-indium-diselenide (CIS) solar cells
3rd generation	Devices with potential efficiency above the Shockley-Queisser limit (tandem cells) and emerging technologies using new materials	Dye sensitized (DSSC) solar cells or light absorbing dye* Concentrated solar cells Perovskite solar cells Quantum dot solar cells

* Also called organic cells

Only a few manufacturers control the whole value chain from quartz to solar cells. After production of 100% pure silicon rods, boron and phosphorus are added using a diffusion machine. Electrical contacts are then placed to connect each solar cell to another as well as to the junction box. The thinner the electrical contacts, the more sunlight the cell can absorb. After that, tin-coated copper strips are placed between the cells. Because pure silicon is still too shiny and can reflect up to one-third of sunlight, an anti-reflective coating is applied to the cell. Anti-reflective coatings are made of an oxide such as tantalum pentoxide (Ta_2O_5), titanium dioxide (TiO_2), silicon monoxide (SiO), silicon dioxide (SiO_2), silicon nitride (Si_3N_4), aluminium oxide (Al_2O_3), ITO (indium-tin-oxide), tin oxide (SnO_2). After these steps, the solar cells are usually sealed in ethylene vinyl acetate copolymer (EVA), placed in a frame that is sealed with silicone adhesive or polybutylene sealants and covered with a mylar back and a glass or plastic cover on the front. Other materials such as thermoplastic polyurethane (TPU), polyvinyl butyral (PVB) and silicone can also be used as encapsulating materials, the function of which is to bond the various layers and components together. The back layer or back sheet is usually made of Tedlar (trade name of PVF – polyvinyl fluoride) based or PET (polyethylene terephthalate) based. Chemicals and solvents like hydrochloric

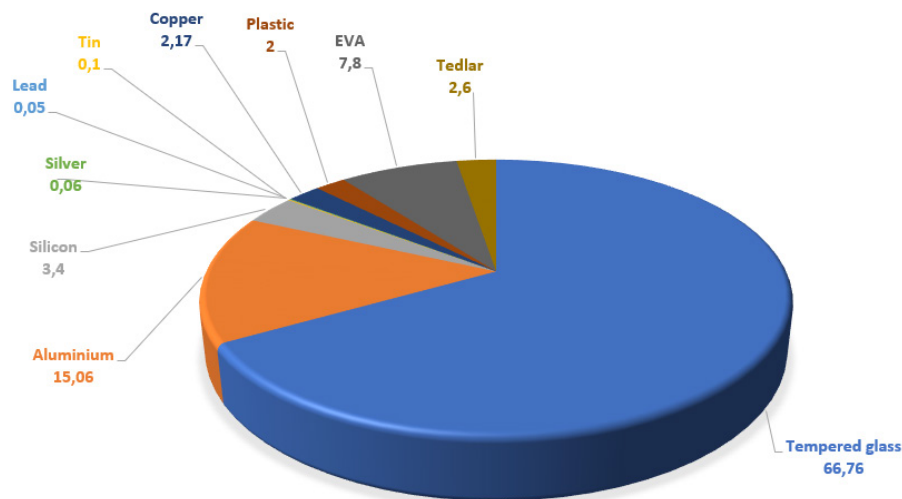


FIGURE 7: Average mass composition according to materials for c-Si module.

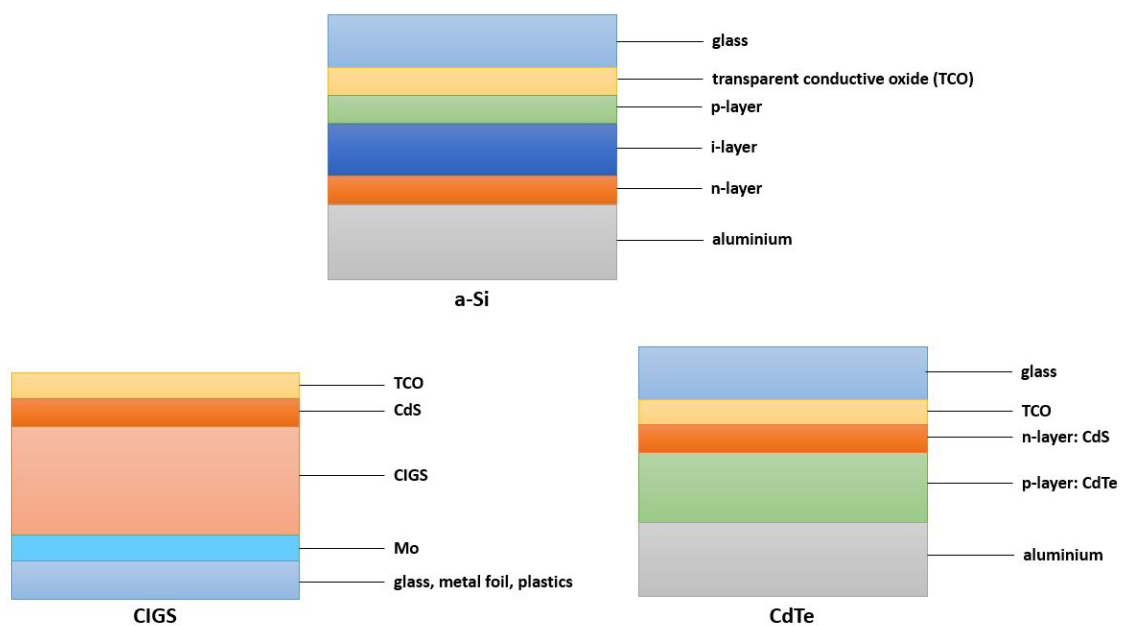


FIGURE 8: Thin-film cells (a-Si, CIGS, CdTe) design.

acid, nitric acid, hydrogen fluoride, acetone and ethanol are used for cleaning wafers and removing impurities during the fabrication process (MSK Instruments, 2024).

A typical crystalline PV panel with aluminium frame and 60 cells has a capacity of 270 Watt peak (Wp) and weights 18,6 kg (IEA International Energy Agency; International Renewable Energy Agency, 2016). When the average of the specified ranges is calculated, a pie chart with a grand total of 100% is obtained (Figure 7).

2.3 2nd generation of solar panels

Thin-film PVs are classified as the second generation of solar systems. Commonly used thin film solar cells are amorphous silicon (a-Si), micromorph silicon (μ -Si), cadmium telluride (CdTe) and copper-indium-gallium-diselenide (CIGS) and copper-indium-diselenide (CIS) thin film solar

cells. Some of the varieties of a-Si modules are amorphous silicon carbide (a-SiC), amorphous silicon germanium (a-SiGe) and amorphous silicon-nitride (a-SiN) (IEA International Energy Agency; International Renewable Energy Agency, 2016).

A thin-film module consists of several solar cells that are wired together, as shown in Figure 8. The module consists of thin semiconducting layer (CdTe, CIGS or a-Si) obtained using chemical vapor deposition techniques and a substrate - glass, polymer, or metal. Laser-scribing is used to delineate individual cells and make electrical connections between cells. Materials also used for thin-film PV cells are gallium arsenide (GaAs), copper and titanium dioxide (TiO₂). The typical structure of transparent conducting oxide (TCO) layer consists either of tin oxide (SnO₂) and indium tin oxide (ITO), or of zinc oxide (ZnO) (Savvilitidou

et al., 2017). The thickness of thin film cells varies from 80 nm – 0,5 μ m (Dhilipan et al., 2022).

For a standard CdTe panel, 110 Wp can be assumed on average for 12 kg. A CIGS panel usually holds a capacity of 160 Wp and 20 kg (IEA International Energy Agency; International Renewable Energy Agency, 2016).

Although there is no toxic material in the final product of a-Si modules, the manufacturing processes do involve toxic and pyrophoric gasses such as germane, phosphorus, trimethylborane, silane, hydrogen and so on (X. Deng & Schiff, n.d.).

2.4 3rd generation of solar panels

This is a generation that is still in the development and laboratory testing phase. Devices with potential efficiency above the Shockley-Queisser (S-Q) limit and emerging technologies using new materials are classified as third generation of solar cells. The S-Q model describes the efficiency limit for a single-junction solar cell under one-sun illumination. Efficiency beyond the S-Q limit can potentially be achieved for a single-junction solar cell by using the process of multiple exciton generation (e.g. in quantum dots), up or down conversion of incident light, or limiting radiative emission (raising the cell voltage (Polman et al., 2016). Theoretically, tandem modules composed of several single-junction cells can be used for efficiency above the Q-S limit. Some third generation PV modules are listed below.

Concentrating PV (CPV) module is a complex system that uses mirrors and optics to collect high levels of sunlight to concentrate incoming radiation using collectors and mirrors. They can be classified into three types according to the semiconductor material and the type of tracker used: high concentrator PV (HCPV) modules, low concentrator PV (LCPV) modules and compound parabolic concentrators (CPC). HCPV modules are made of multijunction cells with semiconductor alloys which contains elements from groups III and IV in the periodic table and are built with double-axis sun trackers. LCPV modules are composed of c-Si or other semiconductor materials and are built with double or single-axis sun trackers. Unlike the previous two types of CPV, CPCs are designed without sun trackers and are concave in shape so that the ratio of reflection of incident light to the absorber is very high.

The cost of HCPV and LCPV modules is very high, which makes them inaccessible for conventional PV application. Hence, they are mostly used for space application (Kumar et al., 2020).

Organic cells use dye or organic semiconductors as the active light-harvesting layer. These are photochemical cells that are based on chemical processes to produce electricity from light, not using standard semiconductors. Photoelectrochemical cells include dye sensitized (Grätzel) cells and polymer (plastic) cells. This technology has been researched a lot over the past few years and is currently the fastest growing solar technology. Despite the low production costs, stable products are not yet available on the market due to corrosion problems due to exposure to water (Polman et al., 2016).

Quantum dot solar cells are single-junction designs that use colloidal quantum dots (CQDs) with lead sulphide

(PbS) that have a bandgap that can be tuned into the far infrared, frequencies that are typically difficult to achieve with traditional solar cells. Half of the solar energy reaching the Earth is in the infrared, most in the near infrared region. Moreover, CQDs offer easy synthesis and preparation. While suspended in a colloidal liquid form they can be easily handled throughout production, with a chimney as the most complex equipment required. CQDs are typically synthesized in small batches but can be mass-produced (Polman et al., 2016).

Perovskite solar cells are derived from the ABX₃ crystal structure of absorber materials, which is called a perovskite structure, where A and B are cations and X is an anion. In 2021, the perovskite solar cell achieved an efficiency of 28% in the silicon-based tandem and 23,26% in the CIGS-based tandem (International Energy Agency, 2022). Although perovskite solar cells have become very efficient in a very short time, there are still many challenges before they become a competitive commercial technology. For example, they degrade faster than silicon solar panels, especially in a harsh environment, but their methods of production are low-cost.

2.5 Comparison of PV technologies

Photovoltaic panels directly convert solar energy into electricity without using mechanical moving parts that are prone to wear and tear. They do not contain liquids or gases that can unexpectedly escape from the production facility, and they do not pollute the environment (including thermal pollution). They do not require additional fuel or auxiliary energy sources to function and have a fast response time, reaching full power almost instantly. Due to their modular nature, they have a wide range of applications, from small standalone units with just a few watts of power to autonomous power sources of several kilowatts, and even centralized power plants in the megawatt range. They can be located wherever electrical energy is needed. However, they do not produce electricity continuously, so grid storage systems such as batteries or grid connections are required (Hossein Karami Lakeh, 2024).

Thin-film modules have lower power and durability than the first-generation c-Si solar panels (Kumar et al., 2020). However, a-Si modules use less raw material than crystalline silicon modules. Amorphous-Si PV modules are light, flexible and radiation resistant, making them desirable for energy and space applications. Still, they are more appropriate in micro-power applications such as a solar-powered calculator and high-temperature environments hence they are less sensitive to temperature than c-Si solar cells (H. Kang, 2021). Previously, a-Si and μ -Si had a significant market share but failed to keep pace with the cost of crystalline silicon cells and the increasing efficiency of other thin film technologies (IEA International Energy Agency; International Renewable Energy Agency, 2016).

In terms of module efficiency, crystalline silicon solar panels have the highest efficiency, which is confirmed by their wide use. Silicon has a band gap energy of 1.1 eV, meaning it can absorb photons with an energy of up to 1100 nm. Hence, most used PV cells utilize silicon var-

iations altered by doping process to make them suitable semiconductors (Ghazy et al., 2021).

PERC (Passivated Emitter Rear Contact) solar cells are designed with an extra layer on the bottom of the solar cell which adds an additional 5% efficiency. This additional layer is called a dielectric passivation layer which has become the dominant commercial technology. An additional dielectric passivation layer reduces electron recombination, which affects the increase in electric current production. It also increases the solar cell's ability to capture light due to the layer's reflective properties, so photons have more opportunities to generate electricity (backside passivation). And finally, PERC reflects wavelengths above 1180 nm. In the conventional Si-cell, such wavelengths are easily absorbed by backside metallization layer and converted into heat. Longer wavelengths are especially present during the morning and evening or during cloudy days (Ghazy et al., 2021).

Monocrystalline panels have higher energy efficiency and have gained the largest market share in the last few years, 85% of c-Si (International Energy Agency, 2022). The difference in efficiency depends on the TCO performance, semiconductor material quality, deposition uniformity, encapsulation loss, busbar shadow loss and electrical loss.

Regarding module efficiency, (Luo et al., 2017) reviewed potential induced degradation (PID) of c-Si and thin-film PV modules. The progression of PIDs in c-Si modules depends on the applied voltage, humidity, and temperature. Four types of test methods are available to assess cell and module level PID sensitivity. At the module level, chamber PID and AI PID tests are often used, while at the cell level, PID sensitivity can be tested by corona discharge PID set-up or bias voltage application on a module-like layer stack.

According to the prediction shown in Figure 9, by 2030 there will be a decrease in the mass share of materials in the PV module. This affects the reduction of production costs, resource conservation, reduced use of rare and hazardous substances, increased module efficiency and lower

module prices. However, the thinner the wafer, the more fragile it is and therefore breaks more easily during the recycling process, so if you want to preserve an intact wafer, the recycling process becomes difficult.

In the manufacturing of silicon PV modules, the production costs of monocrystalline and polycrystalline silicon PV cells are reduced. Therefore, material consumption for silicon cells has decreased significantly from about 16 grams/Wp in 2006 to less than 4 grams/Wp in 2016 (IEA International Energy Agency; International Renewable Energy Agency, 2016).

PV module manufacturers have introduced a wide variety of advanced module technologies to the market with higher electrical power output, more weather resistance and lower cost. So, there are frameless modules that effectively eliminate module current leakage, glass-glass modules replace the back sheet with heat-strengthened glass to ensure high performance in harsh environments, bifacial modules benefit from additional power generated from the rear, advanced module bonding reduces copper ribbon and lead solder of tandem modules for higher efficiency. Therefore, bifacial photovoltaic technology is considered a promising alternative, as it can generate more energy than conventional monofacial PV technology by absorbing sunlight from both sides. Compared to monofacial PV, bifacial PV module has an additional layer of anti-reflective coating and back contacts instead of a back surface on the back of the PV module. Moreover, to increase efficiency, there is module technology in tandem design (Gu et al., 2020). However, the cost of this technology prevents their widespread commercial use, (Nanayakkara et al., 2017) found that the cost of both tandem module structures (CdTe/CIS and CGIS/CIS) on an equal-area basis is approximately 30 USD/m² higher than single-junction alternatives, although their efficiency is 4% higher.

Except for the third generation of cells, c-Si panels have the lowest mass in relation to the energy produced (0,102

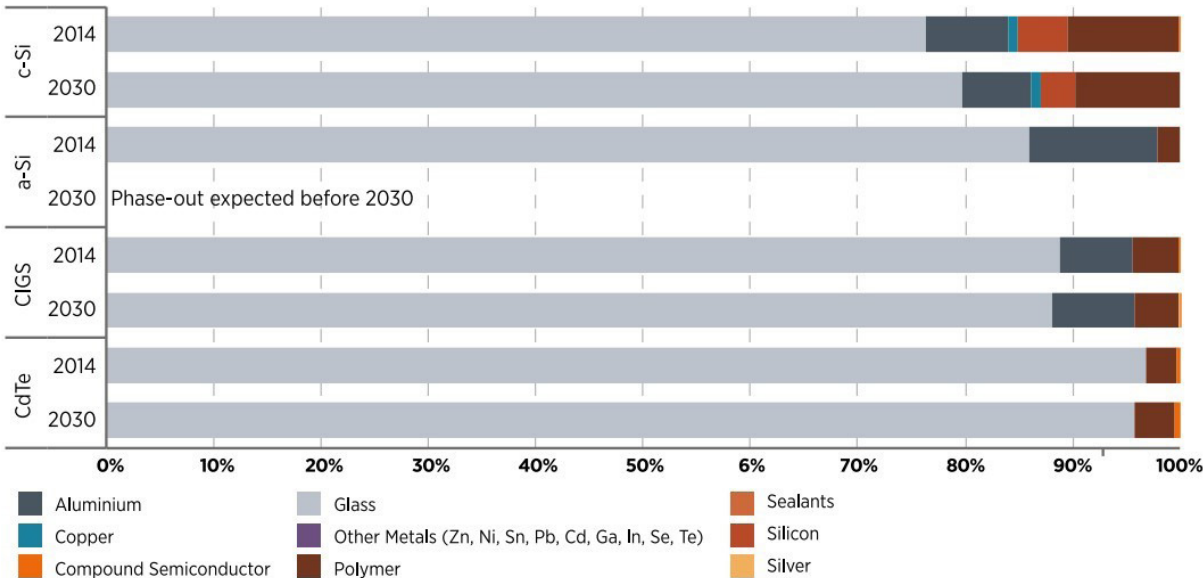


FIGURE 9: Total renewable energy capacity in the European Union 2013-2022. Data according to (IRENA, 2023).

kg/Wp), which is another reason why c-Si panels dominate the market (Divya et al., 2023).

3. EOL PV MANAGEMENT & CIRCULAR ECONOMY

As already emphasized earlier, the European Union provides a legislative framework for the extended responsibility of PV module manufactures at the European level through the Directive on waste electrical and electronic equipment (European Union, 2012). End-of-life management works on the principle of extended producer responsibility, which means that producers must be physically and financially responsible for the environmental consequences of their products until the end of their life cycle. This approach encourages the creation of more environmentally friendly products with a reduced environmental impact. Moreover, the EPR can be used to establish funds to support the financing of efficient collection, treatment, recycling, and disposal systems. Although producers bear the cost of waste management, these additional costs can, unfortunately, still be passed on to consumers, leading to higher product prices.

However, the concept of a circular economy involves the reducing waste and closing the loops within industrial ecosystems. This is achieved by transforming goods at the end of their life into valuable resources (A. Omar et al., 2023). An appropriate EoL management strategy for solar photovoltaic systems is crucial, not only to prevent and/or mitigate future environmental issues but also to reduce the demand for rare materials (Salim et al., 2019). Waste management of PV modules at the end of their life offers options related to each of the 3Rs of sustainable waste management: Reduce, Reuse, Recycle. The solar panel industry is indeed developing rapidly, and the installed capacities are increasing every day, which makes it almost impossible to completely prevent or reduce the generation of waste at the end of their life cycle. Therefore, the focus should be on proper waste management in other segments of the waste hierarchy: reuse, recycling, energy recovery and, the last resort, disposal. The disposal option creates additional costs, and it does not recover the intrinsic values of the materials present in the PV modules (Lunardi et al., 2018). Thus, (Tao & Yu, 2015) provided an overview of commercially available PV modules and their waste management pathways that include waste recycling, remanufacturing, and reuse. The current design of PV modules makes it difficult not only to repair and maintain modules, reuse, and remanufacture components, but also limits the possibilities of recovering secondary materials (Fiandra et al., 2023). (Masoumian & Kopacek, 2015) pointed out that reuse refers to the further use of a worn or damaged PV module or its parts. The reasonableness of such reuse is strongly related to the expected lifetime of the module or part of a module. Some of the materials used to manufacture PV modules will either be disposed of or incinerated as they can neither be recycled nor reused (Contreras-Lispeguier et al., 2017). However, it has been estimated that about two-thirds of these PV modules can be repaired or refurbished, and only about 10% of PV modules are recy-

cled worldwide (Lunardi et al., 2018). Therefore, approximately 50% of PV waste can be diverted from the recycling stream. The ratio is likely to be even higher as functional photovoltaic modules that are retired also enter the waste stream. A report by (IEA International Energy Agency; International Renewable Energy Agency, 2016) estimates that up to 80% of the PV waste stream will consist of products with premature failures in next 10 years, such as manufacturing defects or damages caused during transportation.

During the production of PV modules, certain hazardous and toxic substances such as Cd and Pb are used in small quantities. These substances will be present even at the end of their lifetime, so this should be considered to avoid their harmful effects on people and the environment (Rathore & Panwar, 2022). Rare materials such as ruthenium, gallium, indium, and tellurium are essential components of some type of photovoltaic panels. Some materials contained in the PV modules are classified as hazardous. The main concern regards the presence of cadmium in thin film module, and of lead and chromium in crystalline modules (Tammaro et al., 2015). If special requirements for handling and disposal are not implemented, these hazardous substances could potentially be released into the environment at the end of the panels' life. Therefore, this transitional period should be utilized for financing and developing efficient and environmentally friendly recycling technologies to maximize the recycling of materials contained in solar modules in the future (Salim et al., 2019).

Although standards exist today to produce PV modules, there are only limited insights and hardly almost no standards on the characterization, reliability testing, certification or labelling for second-life PV modules (Tsanakas et al., 2020).

4. REVIEW OF PV PANEL RECYCLING METHODS

After increasing the installed capacity of PV modules, more and more attention is being paid to the end of life of PV modules, especially in the EU. As stated earlier, the minimum targets applicable to PV modules from 2018 are that 85% of the weight must be recovered and 80% prepared for reuse and recycled. This requires improvements of the recycling process because downcycling is no longer efficient enough. Despite the great potential interest of researchers in PV recycling, primary data on PV recycling is still very scarce (Ardente et al., 2019).

In this section, a detailed review of recycling technology is made according to the literature regarding mathematical modelling, software simulation, experimental tests, and practical application. There are different methods of evaluating the recycling process for different types of PV modules through energy, economic and environment/social analyses that can be confirmed by laboratory tests, pilot projects or commercial technology. (Lunardi et al., 2018) present a review of the recycling process of PV modules using examples of pilot and commercially used recycling procedures. A large part of these analyses remains only in the research and development phase, and a smaller part of the recycling process becomes commercial. There are

several different review articles. Some of them deal with a systematic quantitative literature review on the EoL of PV panels (Mahmoudi et al., 2019), some review the recycling status and different recycling methods of solar panels (Divya et al., 2023; Isherwood, 2022), the environmental impact (De Sousa et al., 2023; Divya et al., 2023b; Rathore & Panwar, 2022), or recycling policy (Chowdhury et al., 2020). (McDonald & Pearce, 2010) emphasized that the economic motivation for recycling most PV modules is unfavourable without appropriate policy. (Seo et al., 2021) concluded that the recyclability of c-Si PV panels is guaranteed by recycling technologies that can reduce the environmental burden. However, to promote the recycling industry, it is necessary to ensure a sufficient level of value-added opportunity.

With the development of the third generation of photovoltaic modules, whose goal is to increase the efficiency of the modules, tandem or multi-junction p-n modules appear, which require a more complex recycling process since they consist of several single-junction solar modules. The recyclability of PV module components can be determined by the materials from which these components are made (Figure 10). Recycling procedures for c-Si PV panels differ from those applied to thin-film PV panels due to their different module designs. There are also precious and rare metals such as silver (Ag), gallium (Ga), indium (In), germanium (Ge), cadmium (Cd) and tellurium (Te). As for thin-film panels, they use less material than c-Si panels, but there are concerns about the availability and toxicity of materials such as tellurium (Te), indium (In), and cadmium (Cd) (Savvilitidou et al., 2017). Tellurium has a harmful effect on the liver, while cadmium can cause lung cancer, and affects bones and kidneys. Indium compounds damage the heart, kidney, and liver, and may be teratogenic. Conventional ma-

terials in PV panels are aluminium (Al), copper (Cu) and glass, as well as high-purity energy-intensive material such as the silicon (Si). The great economic importance of silicon for Europe, together with the high supply risk, justified its inclusion in the list of Critical Raw Materials (CRMs) of the EU. The main global producers of silicon are China (66%), the USA (8%), Norway (6%) and France (4%), and the main sourcing countries are Norway (30%), France (20%), China (11%), Germany and Spain (both 6%) (Critical Raw Materials Resilience: Charting a Path towards Greater Security and Sustainability, 2020). Glass and aluminium production are also energy-intensive processes. Therefore, avoiding the disposal of these materials in landfills would contribute to significant environmental gains (Molano et al., 2022).

Figure 10 shows the typical structure of a Si-based PV module. Recycling of photovoltaic panels is a process that involves collecting, disassembling, and processing the various components of the panels for reuse. This presents a significant challenge, especially with the laminate encapsulant (typically EVA) used in PV modules, due to the high temperature processes (requiring significant energy consumption), the use of solvents, and treatment of fumes during encapsulate removal (Pagnanelli et al., 2016). Different materials for encapsulants such as PVB and EVA, or some unspecified materials can affect the behaviour of the module during the recycling process (S. Kang et al., 2012). Another important fact is that not all materials can be recycled, for example the EVA layer in the module has hardly been recycled so far. . Despite being a thermoplastic, the amount of vinyl acetate can cause the polymer to cross-link, which in turn makes its recycling unfeasible. Removing polymers using high temperatures will normally generate atmospheric emission that might be toxic according to the method and the polymers. The use of organic solvents

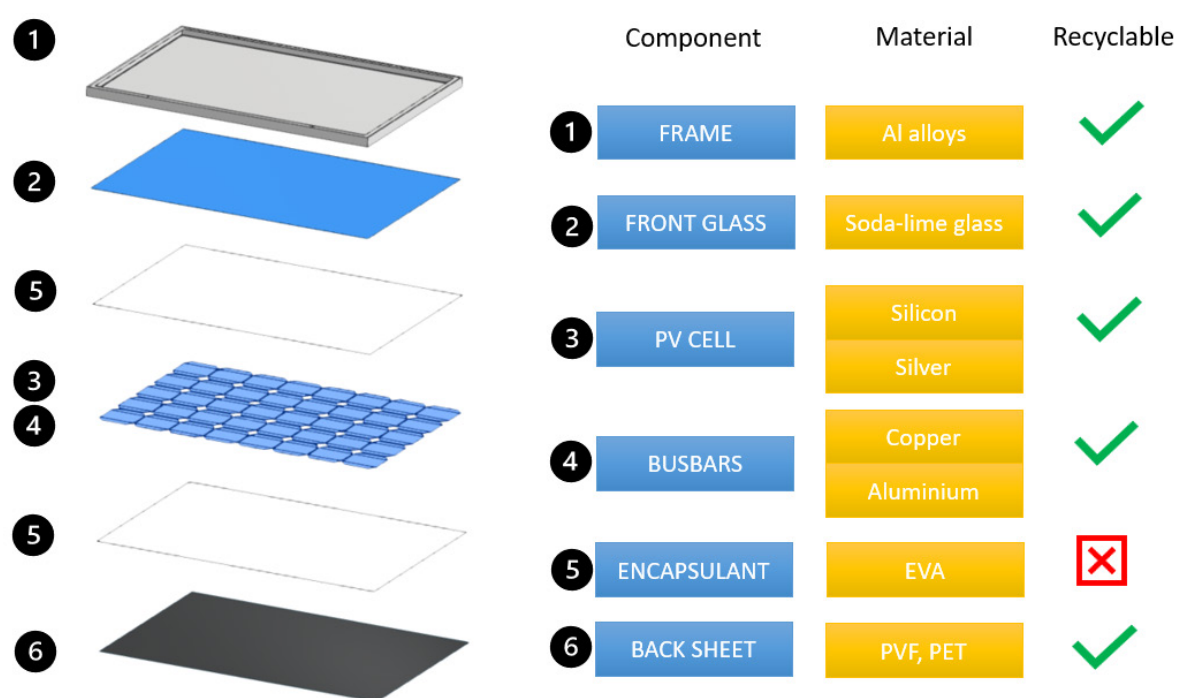


FIGURE 10: Recyclability of c-Si PV module's components.

can assist in the component separation phase with objective to separate or remove the encapsulant. This is most complex step of recycling PV modules. In industrial application, the use of organic solvents is hardly feasible because it requires a closed process (P. Dias & Veit, 2018). In contrast, recycling the aluminium frame, glass and plastic back is not technologically demanding. (Zhang et al., 2013) showed after testing that thermal separation, from an economic and ecological point of view, is a more favourable alternative compared to chemical processes that require the use of expensive and toxic reagents.

Various physical, mechanical, chemical, and thermal methods can be applied to recycle PV modules, depending on the composition of the module back sheet, but these methods often do not allow full recovery of all PV panel components (Chitra et al., 2020; Sica et al., 2018). Moreover, the procedures that can be used during processing and recycling of PV modules can be divided according to Table 2 with the corresponding references from the literature for a certain type of PV technology.

4.1 Experimental study and real system operation

4.1.1 PV Cycle

PV Cycle was the first to establish a downstream PV module recycling process and waste logistics across the EU (Tsanakas et al., 2020). This recycling process of c-Si PV modules achieved a recycling rate of 96% in 2016 (Lunardi et al., 2018). The process starts with the separation of the aluminium frame and junction box of PV module. This is followed by mechanical processes (shredding and sorting by laser or vibration) that are used to extract the remaining module materials. Recovered materials are glass, aluminium, and silicon.

4.1.2 FRELP

In the early stage of research and development/pilot, Sasil, in Italy, within the framework of the EU LIFE project FRELP (Full Recovery End of Life Photovoltaic process), investigated a new PV recycling process line. The project did not achieve any of the set goals. However, partial results have been achieved with the design of a prototype for sep-

TABLE 2: List of procedures used during processing and recycling of PV modules.

Recycling procedure	Subprocess	Reference for c-Si modules	Reference for thin-film modules
Physical/mechanical	Cryogenic treatment	(Zhang et al., 2013)	
	Shredding/milling	(Azeumo et al., 2019; Fiandra et al., 2019; Granata et al., 2014)	(Berger et al., 2010)
	Cutting		
	Disassembling (physical disintegration)	(Azeumo et al., 2019; Belançon et al., 2022; Fiandra et al., 2019; Granata et al., 2014; Huang et al., 2017)	(Granata et al., 2014; Savvilotidou et al., 2017)
	Dry and wet mechanical processes: blasting, scribing, attrition, sieving, floatation	(Azeumo et al., 2019)	(Berger et al., 2010)
	Density separation	(Azeumo et al., 2019)	
	Electrostatic separation		
	Magnetic separation		
	Separation according different physical or chemical properties	(Lim et al., 2022)	
Chemical	Acid/base treatment	(Doi et al., 2001)	
	Solvent treatment	(X. Xu et al., 2021)	(Savvilotidou et al., 2017)
	Combination of organic solvents and heat treatment by an assisted ultrasonic method to improve the dissolution rate of the EVA	(Azeumo et al., 2019; Kim & Lee, 2012)	
	Chemical etching	(Cui et al., 2022; Huang et al., 2017; S. Kang et al., 2012; Klugmann-Radziemska & Ostrowski, 2010; Lim et al., 2022; X. Xu et al., 2021)	
	Precipitation		
	Hydrometallurgy: leaching	(Cerchier et al., 2021)	
Thermal	Pyrolysis		
	Burning	(Cui et al., 2022; Huang et al., 2017; S. Kang et al., 2012; Lim et al., 2022; Tammaro et al., 2015; Wang et al., 2012; X. Xu et al., 2021)	(Granata et al., 2014)
	Pyrometallurgy		
Electrometallurgical	Electrowinning	(Cui et al., 2022; Huang et al., 2017)	
	Electrolysis		

arating the EVA polymer back sheet from the glass and a robotic system for separating and restoring the aluminium frame and connectors from PV panels (LIFE Programme, 2016). The FREL P process is a combination of physical procedures, acid leaching and electrolysis where c-Si solar panels are economically justified in terms of waste disposal. The process is designed to increase the mass of the recovered material while reducing waste and considers the stages of transport and discharge, disassembly, cable treatment, glass separation, glass refining, cutting, sieving, acid leaching, filtration, electrolysis, neutralization, filtering, and incineration as well as waste disposal in sanitary landfills of hazardous waste and disposal of urban solid waste. A pilot project was implemented that processes around 1.300 modules per day (Cui et al., 2022), i.e. with a processing capacity of 1 t/h to 8000 t/year of waste c-Si PV panels (Latunussa et al., 2016). Expectations from that pilot project were high, which is confirmed by numerous LCA analyses. (Ardente et al., 2019) estimated a recycling rate for the FREL P process of 83%. Recovery rate for the FREL P process: insulated cables (100%), silver (94%) at 99% purity, copper (97%) at 99,993% purity, aluminium scrap (99,4%), silicon (97%) at metallurgical grade purity, glass cullet (98%) at 98% purity (Cui et al., 2022; Latunussa et al., 2016). The pilot project of FREL P process was interrupted in spring 2016 because of the small volume of waste panels currently collected. Secondly, mass incineration of large amounts of PV scraps with fluorinated plastics could become problematic for the plant which would risk exceeding legal limits for HF emissions. Finally, collection of the bottom ashes can be technically difficult and characterised by potential losses.

Some companies are working to formalize the recycling, repair/refurbishment and reuse segment in PV value chains and propose customized technical standards and regularity framework for EoL of PV modules.

4.1.3 ReSiELP

ReSiELP was a European project that aimed at recovery of valuable materials (aluminum, glass, copper, silicon, and silver) from EoL silicon PV modules. The recovery of silicon was carried out through thermo - mechanical and hydrometallurgical purification. Pilot plant was designed and built to upscale recycling technology to TRL 7, with a 1500 panels/year capacity by the group of metallurgy of Padova University (Cerchier et al., 2021). PV glass reuse for building materials production, sustainable mortar and concrete formulations were studied and seemed comparable with commercial products (Cerchier et al., 2022).

4.1.4 Veolia

In 2018, Veolia has opened their European PV module mechanical recycling plant in Southern France (in contract with PV CYCLE France). With a 95% recovery ratio, their recycling process isolates all PV component materials, from the glass to the aluminium frame, junction box and connection cables. The plant capacity is from 1.800 t in 2018 and will grow to 4.000 t. (Veolia Group, 2017). Recovered materials are then directed to various industries. The aluminium frame material is directed towards aluminium-based

refinery; polymeric materials are recycled to fuel used in cement industry; silicon cells to precious metal sectors; cables and connectors are crushed and sold in the form of copper shots; whereas glass, recovered as clean cullet, is used in the glass manufacturing industry. The glass recovered from such PV recycling process gets eventually contaminated with iron (Fe) due to the involved shredding process, and therefore cannot be considered as a low-Fe (i.e. high value) glass product (Tsanakas et al., 2020).

4.1.5 Solar World

Solar World is another pioneer in PV recycling c-Si panels based on the thermal treatment method, with which EVA is eliminated by burning at 600°C, followed by manual separation of metal, silicon cells and glass. The silicon cells are then etched again, and at the end of such a process the clean wafers can be reused, while the glass and metal are sent for recycling (Tao & Yu, 2015b). Solar World's recovery ratios typically exceeded 84% of the module weight, namely, 90% of the glass and 95% of the semiconductor materials. Solar World and its recycling subsidiary are no longer in business (Lunardi et al., 2018).

4.1.6 Loser Chemie

On the other hand, Loser Chemie's recycling process for c-Si PV starts with crushing and mechanical separation. Afterwards, chemical treatment is performed, followed by solid-liquid separation. As a last step of the recycling process, glass is chemically treated, whereas aluminium-based metallization is recovered. (Tsanakas et al., 2020) In 2019, they won an award for their Aqualux project, which uses water-jet technology to break down silicon-based PV modules into their individual parts. In doing so, the individual layers of the complex composite are separated using a special nozzle technique. Therefore, it is possible to detach the Tedlar and at the same time to obtain an EVA silicon cell mixture in which the former silicon cells with their contacts are present. Connecting lines containing copper are very clean and can be directly recycled. To separate the EVA from the silicon cell, they use an aluminium chloride solution to dissolve the aluminium back contact, destroying the bond between the silicon cell and the plastic. The silver is not lost by this process and can be recovered and poured into silver ingots by the hydrometallurgical process (PES Solar, n.d.).

4.1.7 Japan

In Japan, NPC Group has developed a recycling process for c-Si PV modules that can recover the glass without any destructive process. Recycling involves automatic separation of aluminium frames after PV module processing using a hot knife/cutter blade. Glass, solar cells matrix and EVA sheet can be directed to further recycling (Tsanakas et al., 2020).

4.1.8 China

In China, on the other hand, a PV recycling pilot plant recycles c-Si PV waste using cryogenic abrasive machining at -196°C and electrostatic separation. The mixture after abrasive machining, which contains EVA particles, Tedlar

particles and a mixture of silicon, silver and aluminium powder is separated by electrostatic separation. Mechanical processing does not involve a chemical process but cannot recycle silicon for reprocessing into new wafers due to its low purity (Zhang et al., 2013).

In the thin film PV segment, First Solar and ANTEC Solar are at the recycling technology forefront. They operate an advanced downstream program encompassing collection, transportation, and recycling of their CdTe modules (Tsanakas et al., 2020).

4.1.9 First Solar

Approximately 90% by mass of each collected First Solar PV module is recycled into new products (Tao & Yu, 2015). The EoL PV modules are shredded, and hammer milled into pieces small enough to break lamination bonds. Then, semiconductor films are removed by the leaching process with addition of acid and hydrogen peroxide in a slowly rotating, stainless steel drum. The remaining amount in the drum is then passed down to a classifier which separated the solid (including glass and laminate materials) from the metal-rich liquid. A vibrating screen separates the glass from the larger pieces to laminate material. The glass is further cleaned to remove any residual semiconductor material and then packaged for recycling. Meanwhile, the metal-rich liquid is pumped to the precipitation unit. The metal compounds are precipitated in three stages at increasing pH and then concentrated in a thickening tank. The resulting unrefined metal-rich material is packaged for processing by a third party to produce tellurium and cadmium products. This commercial process can recover 90% of the glass for use in new products and 95% of the semiconductor materials for use in new solar modules. First Solar is still operating and according to its web page recycle CdTe semiconductors (First Solar, 2024)

4.1.10 ANTEC Solar

ANTEC Solar has established a pilot plant based on the recycling process of thin-film photovoltaic modules CdTe/CdS. In this process, the modules are first physically dismantled into fragments. Subsequently, the module fragments are exposed to an oxygen-containing atmosphere at a temperature of at least 300°C, causing the pyrolysis of EVA. After that, the module fragments are exposed to a gas atmosphere containing chlorine at a temperature higher than 400°C, resulting in the etching process, where CdCl_2 and TeCl_4 are generated. The produced CdCl_2 and TeCl_4 are then condensed and deposited through cooling (Tao & Yu, 2015).

4.1.11 EVERP

Currently there is ongoing EVERP project funded by European Commission (HORIZON-CL5-2022-D3-03). The aim of project is to demonstrate two innovative technologies to delaminate the different layers of the PV panel. Through combination with recycling processes it will be possible to recover glass with less than 1% impurities, encapsulant and backsheet polymers with a purity over 99%, and silver with a purity of 99% (EVERP, 2024).

4.1.12 PHOTORAMA

Project PHOTORAMA was funded by European Commission (Horizon 2020) and lead by Italian research agency Enea and Italy-based heterojunction PV manufacturer Enel Green Power. Its objectives is a pilot line with established all needed interrelated successive steps: auto disassembly, smart separation and innovative recovery of metals from solar cells (Si, Ag, In, Ga). Project is based on new delamination technique based on a wire diamond technology, developed and patented by the CEA in order to separate a module's glass, backsheet, and cells in a single process, in such a way that the single parts of the module can then be treated individually for the recycling phase (Lovato et al., 2021; PHOTORAMA, 2024).

4.1.13 Experimental studies

(Azeumo et al., 2019) in their work processed polycrystalline-Si PV modules using a chemical and physical processes. The physical process involved disassembling the aluminium alloy frame and then cutting the modules into homogeneous samples to perform small-scale laboratory operations. Material separation in the PV module is achieved using a circuit consisting of operations like crushing/milling, sieving, and heavy medium separation. The plastics and most of EVA was recovered. After that, the sink (mainly composed of glass and metal) and the float (polymers and EVA residues) are sent to the recovery of the dense medium separator which is mainly pumped back to the dense medium separator after the first drainage screen, and partially regenerated after water spraying and magnetic separation. At the end of process, the sink is then milled and sieved to obtain the glass and metal fraction. The chemical process used solvents to separate the layers of glass, polycrystalline silicon, and polymer. The separation of EVA and the sheet of polymer was carried out using 99,8% pure toluene at different temperatures and with or without the use of ultrasound and thermal pretreatment. They concluded that the concentration of toluene for dissolving of EVA layer has a more important role during separation than the power of ultrasound. The type of solvent used to remove the EVA layer can mostly define the efficiency of the delamination (Savvilitidou et al., 2017).

After removing the Al frame, the recovery of the glass sheets of the c-Si PV panel was assisted by the thermal mechanical process (Belançon et al., 2022). Although the glass bottle has approximately the same composition as the cover glass in PV modules, the latter has higher purity and transparency. Therefore, it would be a waste to mix such a high-quality material with the glass of coloured glass bottles.

(P. R. Dias et al., 2022) also provided experimental part of study where they shredded c-Si module into a smaller than 2 mm parts, quartered homogenous mix. Ten such samples were prepared for the electrostatic separation of materials into electrostatic conductive and non-conductive fractions. For evaluation of metal distribution in each fraction, the outputs were digested in nitric acid (65% concentration), to leach silver and copper and then hydrochloric acid (38% concentration), to leach aluminium at room tem-

perature. The average mass distribution after the electrostatic separation had 3,34 wt% contained in the conductor fraction, while the remaining 96,66 wt% in the non-conductor fraction.

(de Oliveira et al., 2020) performed experiments in silver recovery and showed that is possible to recover up to 99.98% of the silver from photovoltaic cells by combining processes involving acid leaching by nitric acid followed by electroprecipitation process.

(Klugmann-Radziemska & Ostrowski, 2010) performed experimental recycling of c-Si PV cells (monocrystalline and polycrystalline). The process consists of chemically removing the Ag coating and chemically etching the rest of module with organic solutions with different concentrations and temperatures during the process to obtain a pure silicon wafer. Despite the efforts made to formulate the composition of a universal etching solution, the results showed that the solution must be modified according to the type of PV cells being recycled.

Chemical etching recipes must be adapted to different cell technologies. Numerous mixtures were tested, mainly based on the following compounds: hydrofluoric acid (HF), hexafluorisilicic acid (H_2SiF_6), nitric acid (HNO_3), acetic acid (CH_3COOH), hydrogen peroxide (H_2O_2) and distilled water (H_2O).

(Savvilitidou et al., 2017) in their experimental study disassembled Al frame, junction boxes and cables from CIS and tandem a-Si:H/ $\mu\text{c-Si:H}$ PV modules. Individual parts (panel, junction-box, and cables) were shredded and pulverized to study the toxicity of each part as well as the toxicity of the entire module for disposal. Most of the toxic elements in the junction box samples have high measured values. The absence of Cd in CIS PV panels, which is commonly used as CdS in the window layer of solar cells, is probably due to the replacement of Cd with Zn, which is less toxic. They also compared the measured concentration of toxic materials with Total Threshold Limit Concentration (TTLCL). This method determines the toxicity of the sample, if the samples exceed the threshold value they are classified as hazardous. For the CIS, all samples are hazardous for Se, one edge sample is characterized as hazardous for Cu, Hg and Zn, while the overall CIS sample and a-Si:H/ $\mu\text{c-Si:H}$ junction box sample are toxic for Cu. These results raise concerns about the potential risks of inappropriate module disposal and environmental risk may be underestimated or overestimated through a laboratory simulated scenario. Still, TCLP test proves that no sample leachate exceeds the threshold limits. They experimented with different treatments to successfully remove the EVA layer. They concluded that removing the EVA layer from the CIS panel is more challenging as it takes 4 days using lactic acid.

(Granata et al., 2014) in their experimental research used polycrystalline silicon PV module, a-Si and CdTe PV module. They concluded that, to obtain the highest mass recovery, for all three types of PV modules, the process scheme should be: crushing by two blade rotors crusher, crushing with a hammer, thermal treatment at 650°C of fractions larger than 1 mm and sieving with a sieve of 0,08 mm. With these procedures, about 85% of the total weight of the panel can be recovered as glass from frac-

tions $d > 0,08$ mm, while fractions $d < 0,08$ mm can be processed for further extraction of silicon, cadmium, tellurium, and zinc.

(Huang et al., 2017) proposed a three-step wafer-Si PV module recycling process with two new technologies in their experiment. The first technology was sequential electrowinning, which allows the extraction of multiple metals one by one from Si modules, Ag, Pb, Cu and Sn. The recovery rates of Ag and Cu were 74% and 83%, respectively, but they claim it can be increased to 95%. The purity of the recovered metals is over 99%. Another technology presented was sheet resistance monitoring which maximizes the amount of solar-grade Si recovered from the module.

(Tammaro et al., 2015) in their experimental tests heated three different c-Si panels in a furnace at 600°C and kept them at that temperature for 30 minutes. At the end of the thermal treatment, the PV cell and the glass layer are separated. Moreover, relevant amounts of hazardous metals, such as chromium and lead, have been released and may cause environmental concerns if the fumes are not properly treated.

(Cui et al., 2022) achieved the separation of silver, lead, tin, and copper in the laboratory (leaching, electrolysis, and etching from bare silicon solar cells). After removing the c-Si PV module frame and cables, organic compounds are burned in a furnace, leaving behind glass, silicon wafers and other residues. The recovered silicon is then leached with nitric acid to form soluble metal salts. The leach solution is treated with a two-stage electrowinning process to recover silver, copper, and lead oxide, while the remaining wafers are etched with hydrofluoric acid and sodium hydroxide sequentially to remove contact metallization and passivation layers to recover silicon.

(X. Xu et al., 2021) presented in their work a novel process that integrates solvothermal swelling and thermal decomposition for non-destructive Si-wafer recovery. First, the EVA swelling method is applied by exchanging organic vapours in a solvothermal reactor. This represents a significant saving of time and amount of solvent compared to previous processes in which the module was immersed in a solvent. In addition, the introduction of ethanol is effective for removing the back layer to accelerate EVA swelling and avoid emissions of fluorine-containing gases. The key to successful recovery from a non-destructive Si-wafer is to achieve rapid EVA release by placing the gas in a horizontal direction during thermal decomposition through pre-formed gas release channels by pre-swelling the EVA. Therefore, the proposed process provides to be a feasible method for widespread non-destructive recovery of Si-wafers.

Research by (Camargo et al., 2021) explained that the metal content of crystalline silicon PV modules can vary because of factors such as the PV panel brand, country of origin, year of manufacture, among others. The thermal degradation followed by manual segregation increased the silver concentration concerning the ground PV laminate due to the removal of polymers, the glass fraction and copper ribbons.

After reviewing the experimental recycling processes of different PV modules, the conclusion is that the delam-

ination process (removing of the encapsulant) most often takes place either mechanically (shredding/milling) or thermally (burn off EVA layer) or chemically (dissolving in organic or inorganic solvents/acids). In terms of material separation, the physical method of separating glass and aluminium is the most common approach, followed by dry and wet mechanical processes such as vacuum blasting, scribing, attrition, sieving and flotation. Of the electrometallurgical processes in the part of c-Si PV module material extraction, sequential electrowinning is used, which successfully recovers Ag, Cu and Pb. Moreover, regarding the recycling of thin-film PV modules, a combination of mechanical/physical and chemical processes is most often used.

The goal of recycling photovoltaic modules is to obtain valuable materials such as Ag, Al, Pb, Cu and Si. Chemical etching in different solvents and at different temperatures is most often used to remove various coatings or residues after material separation and recover valuable materials.

4.2 Analysis of PV modules – software simulations

There are many studies based on the EoL solar panel Life Cycle Assessment (LCA) methodology with the aim of obtaining an assessment of the efficiency of waste management system, the impact of different waste management options on the environment and human health, the efficiency of the system in relation to the recovery rate, energy savings and so on.

There is an initiative of the International Energy Agency under the Photovoltaic Power Systems Programme called Task 12 and several reports have been published based on LCA analysis of solar panels, and some reports are dedicated to EoL management of solar panels. Some of the objectives of Task 12 are the accurate quantification of the environmental profile of PV compared to other energy technologies which can be performed using LCA describing energy, material, and emission flows in all phases of the PV life cycle modules. The next objective of Task 12, EoL management options for PV modules, can be investigated using recycling analyses and other waste management options.

(Belançon et al., 2022) validated the simple manual removal of glass sheet as a proof of concept for the future reuse of glass sheets from c-Si PVs. They suggest developing some kind of mechanical separation machine to separate the glass from the rest of the PV module. Estimated energy savings could be around 10 TWh due to avoided demand for new cover glass production and carbon saving equal to half the weight of the glass. Limitation to this procedure is that was performed on unbroken glass.

(Daniela-Abigail et al., 2022) in their work provide environmental, economic, and social dimensions of PV waste for the Yucatan region of Mexico through life cycle environmental analysis and life cycle cost analysis. The analysis shows a reduction of 83% in the category of human toxicity (non-cancer effects) and freshwater ecotoxicity, while the depletion of mineral, fossil, and renewable resources show a 66% lower use of the FREL P recycling system compared to the system without recycling case. The categories of human toxicity (cancer effects), photochemical ozone forma-

tion, terrestrial eutrophication and marine eutrophication show reductions between 32% and 42%. Since the categories of photochemical ozone formation and terrestrial eutrophication are influenced by salvage mostly aluminium, and to a lesser extent glass, silicon, and silver. Regarding the categories of climate change, particulate matter and land use, the impact was reduced by 28%, 22% and 20%, respectively. The categories of water resource dependence and freshwater eutrophication show a change of 1%. (P. R. Dias et al., 2022) in their study proposed an economical and environmentally friendly processing method using LCA and LCC. This process consists of removing the module frame, laminate shredding and concentrating the material using electrostatic separation. The proposed technology is electrostatic separation to obtain an estimate of material separation efficiency. The latter gives two fractions: a valuable mixture (2-3% of total weight of module) of silver, copper, aluminium and silicon, and a mixture mainly of glass, silicon, and polymers. An economic evaluation shows that this process is more cost-effective than FREL P under some conditions such as: smaller amounts of waste (< 4 kt/y), if there is no market for recovered glass, and when the end-processing industry is located afar. They were also conducted an experimental part of recycling, described later in the experimental part of review.

There is a gap in the scientific literature when it comes to assessing the environmental impacts resulting from different methods of recycling and reusing PV module materials. (Contreras Lisperguer et al., 2020) conducted an LCA analysis using data for the FREL P process due to the lack of data for other types of processes. The LCA analysis was carried out for the scenarios of open material cycle and closed material cycle with the aim of assessing the impact on the environment.

In their study (Lim et al., 2022) analysed an optimal recycling process with high resource recovery efficiency first at the laboratory level, which consists of module delamination, acid etching and sequential electrodeposition. The obtained results are further applied in the LCA analysis where this recycling system is compared with waste disposal. The chemical they use are widely available and cost-effective, namely HNO_3 , H_2SO_4 , H_2O_2 and NaOH . High recoveries of 86%, 95% and 97% were achieved for silver, lead, and aluminium, respectively, representing a combined resource recovery of 86%.

(Contreras Lisperguer et al., 2020) used LCA methodology to assess the environmental impact of EoL c-Si PV panels in a closed-loop-material-cycle (CLMC) scenario and compared it with a CLMC scenario of CdTe panels. In this study, it was estimated that the transport of decommissioned panels has the greatest impact on the environment, and in the following categories - fossil fuel depletion, metal depletion, climate change, ozone depletion and particulate matter formation. Wafer recovery should be the optimal method of PV panel recycling at the EoL, and thermochemical processes must be avoided during the delamination process. The use of organic solvents can be considered as an alternative way to reduce emission of toxic gases, the formation of fly ash and sludge, and to avoid damage to the solar cell material in the delamination phase. For PV tech-

nology to be fully sustainable, the use of incineration, pyrolysis and toxic acids that generate harmful environmental impacts should be avoided.

The recoverable percentage of each material used to produce the modules is particularly high for glass and Al (97% and 100%, respectively), smaller but still significant for Cu and Te (around 80%), and less significant for rare metals such as In and Ga (75% and 99%, respectively), which only represent about 1% of the total panel weight (Sica et al., 2018).

In their study (R. Deng et al., 2019) presented a techno-economic review of three main recycling approaches: glass recycling, mechanical recycling and thermal recycling compared to landfilling of PV panels. Upcycling (high-value recycling) aims to recycle not only glass and Al frame, but also more valuable components, such as Ag, Si, Al, and Cu. This process is divided into module delamination (can be mechanical, thermal, or chemical), leaching/etching (to separate silicon and metal), metal extraction (electrolysis, metal replacement, chemical precipitation).

(Ardente et al., 2019) compared the FREL process and the recycling process currently used in Europe (baseline process) by applying LCA analysis. The overall recycling rate achieved by baseline process (according to visits to two recycling plants in Italy and Spain) is around 24%, well below the current minimum target of 80% reuse and recycling, as set by the WEEE Directive. The process consists of dismantling the panel frame and cables, which are subsequently sorted for recycling, then the glass is separated with a hammer or grinding, or it is directly shredded with other WEEE waste. The estimated basic process can separate up to 10% of glass, while PV cells and plastic are disposed of in landfill with shredding residues. In this study, the environmental impact of burning three types of different background layers (two fluorine plastics – TPT, KPK and fluorine-free plastic PPE) was evaluated. Compared to incineration of TPT back film, the FREL process applied to fluorine-free PV waste is characterized by lower impact on acidification, human toxicity, ozone depletion and cumulative energy demand (CED). Incineration of PV waste without fluorine has a slightly greater impact on climate change due to higher carbon content of PPE. Therefore, incineration of waste with KPK always has the greatest effects, due to the higher content of fluorine in the background layer. Hence, (Ardente et al., 2019) pointed out that the thermal treatment of PV modules must be carefully evaluated as they may be responsible for emissions of pollutants such as hydrogen fluoride that is potentially released by the combustion of halogenated plastics in the back sheet of PV panel. Unlike (Ardente et al., 2019), (Aryan et al., 2018) compared EoL management options (incineration and pyrolysis) for two types of back sheet materials that are typical for c-Si PV modules. They are PET based back sheet (fluorine free) and PVDF based (fluorinated). The results of the analysis, along with the assumptions made during the modelling, show that the fluorine-free back sheet shows a better environmental performance compared to the fluorinated back sheet in both incineration and pyrolysis scenarios.

(Latunussa et al., 2016) analysed by LCA a FREL process for recycling c-Si PV panels based on a series of phys-

ical (mechanical and thermal) treatments followed by acid leaching and electrolysis. The total impact of the process on climate change is about 370 kg CO_{2eq}. This is due to the incineration of PV sandwiches (34%), transport (29%) and metal recovery treatments (24%).

4.3 Mathematical models

(Molano et al., 2022) proposed a reverse logistics planning model for the collection of EoL PV panels, which is expected to support the integration of existing recycling technologies (FREL) and collection schemes using a holistic approach to ensure feasibility and reduce impact on environment. They emphasized that transport is one of the main activities that can put an additional burden on the environment. However, from the economic perspective the feasibility of reverse logistics highly depends on the price of commodities and recovered materials.

(Paiano, 2015) estimated waste production for the periods (2012-2038) and (2039-2050) with the aim of managing this waste to improve proper waste management of hazardous substances, as well as the importance of recovery and recycling of valuable resources. Given that the calculated amount of cadmium contained in EoL CdTe thin films is 877 t in 2050, its potential leaching due to nitric acid or rain is between 254-351 t. The amount of lead contained in the EoL of c-Si and CIGS modules in 2050 is 3381 t, so the relative value is between 439,5-3043 t.

(Choi & Fthenakis, 2014) developed a framework of mathematical modelling to evaluate economic feasibility of the macro- and micro-level planning of recycling process of c-Si PVs at the example of Germany. The yield of recovered cells is highly dependent on the type, design and condition of the modules being processed. Design-dependent factors that affect results of the thermal process are type of laminate, the crystal type and the dimensions of the embedded cells, the material and dimensions of the connections and solders.

4.4 Economic aspects of recycling technologies

Although the expected lifetime of PV modules is 25-30 years, based on several studies (Daniela-Abigail et al., 2022; Foles et al., 2020; M. A. Omar & Mahmoud, 2018) it can be concluded that the payback period of PV modules (without battery storage) for residential applications is between 5-12 years. The difference between the payback period of various locations is mainly because of the available solar radiation resource, ambient temperature, and the economic variables, especially inflation and the discount rate (Daniela-Abigail et al., 2022). Compared to other electronic products, silicon PV modules have a very low cost per kilogram, which makes them unattractive for recycling. Accordingly, the product price of new PV modules is sensitive to additional recycling costs (R. Deng et al., 2019). The recovered quantities of aluminium and glass cullets are much higher than the quantities of copper and silicon by weight. Therefore, Al and glass prices are relatively more sensitive to the recycling plant profits (Choi & Fthenakis, 2014). Also, whole glass has a higher economic value than broken glass (P. Dias & Veit, 2018).

(Molano et al., 2022) collected market prices of recovered materials in Australian dollars for 2022, here Australian dollars are converted to US dollars at the current exchange rate (for 2022) – data showed in the Table 3.

Additional interest in PV recycling is also shown by the recent high number of patents developed for the removal of encapsulant from the laminated structure of PV, which is one of most difficult and important goals for photovoltaic recycling technologies. A list of patents related to PV module recycling can be found in the literature (Padoan et al., 2019). To become economically viable (R. Deng et al., 2019) concluded that both mechanical and thermal processing of recycling should aim to reduce costs by at least 30%, reaching USD 400-500 per ton and USD 700-800 per ton, respectively, with improved material recovery. New technologies for PV modules recycling should aim to reduce the cost and complexity of recycling processing and improve the mechanical recovery of the intact silicon wafer. Furthermore, life cycle analysis for the Yucatan region indicated that the cost of electricity could be reduced by 2% to reach 0,146 USD/kWh. The only condition is that it is accompanied by a recycling incentive of 15% of the initial cost (Daniela-Abigail et al., 2022).

5. CONCLUSIONS

Photovoltaic panels have become a key technology in the production of clean-green energy, but as their use expands, it is crucial to consider the long-term environmental impacts. Proper management of photovoltaic panels at the end-of-life is of great importance. These modules contain materials that are recyclable and if properly recycled can be used to manufacture new panels or other products. However, no commercial recycling process can currently recover all valuable materials from photovoltaic panels, and there is no consensus on the best way to achieve that goal.

It often costs more to break down the panel and recover the raw materials than the actual value of those materials. Hence, if more materials could be recovered with higher purity, they would have a higher market value and make recycling more economically attractive. However, extraction of high-purity materials requires multiple processing steps, which increases recycling costs. Solving this dilemma could be key to the development of a sustainable photovoltaic panel recycling industry. What is important now is to extend the lifetime of photovoltaic panels as much as possible, to design modules with a long-term vision of processing module waste to enable the recovery of valuable materials to the circular economy loop. It is also im-

portant to use environment friendly materials, as well as to increase the efficiency of the module.

The development of new PV technologies alone does not guarantee their market acceptance, therefore new technologies must have adequate economic, environmental, social, and political support. Just as it took 25 years for PERC technology (Blakers, 2019) to move from development to widespread commercial use, it might take that long to commercialize new PV or recycling technology.

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TABLE 3: Prices (USD/kg) of recovered materials in 2022 (Molano et al., 2022).

Output – recovered material	Price (USD/kg)
Aluminium scrap	1,181
Glass scrap	0,0754
Copper scrap	5,27
Silicon metal (metallurgical grade)	1,428
Silver	786,19

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