

METHODS FOR RECYCLING PHOTOVOLTAIC MODULES AND ELEMENT RECOVERY PROJECTIONS IN SLOVENIA

METODE RECIKLIRANJA FOTOVOLTAIČNIH MODULOV IN PROJEKCIJE ZA PRIDOBIVANJE ELEMENTOV V SLOVENIJI

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Abstract

This paper aims to present different methods of recycling photovoltaic modules, which were researched by different institutes. Significant importance has been attributed to photovoltaic modules in the Renewable Energy sector, thereby contributing to the global transition towards sustainable energy sources. However, as the lifespan of these modules comes to an end, effective recycling methods will become crucial to minimize the environmental impact and resource depletion. This paper highlights recent advancements in photovoltaic module recycling technologies, focusing on predicting the potential mass of a specific element that could be recovered through recycling in Slovenia, considering the installed capacity of solar power plants, which is approximately 1105 MW. A projection of materials that can be obtained through the recycling process of photovoltaic modules was conducted based on current installed capacity, and it was discovered that up to 2150 tons of silicon and 1025 tons of copper could be obtained by the recycling process. The acquisition of various materials would have a significant role in the production of new photovoltaic modules, thereby enabling sustainable manufacturing and contributing substantially to the circular economy.

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Povzetek

V članku so predstavljene različne metode reciklaže fotovoltaičnih modulov. Fotovoltaični moduli so v sektorju obnovljive energije izjemno pomembni, saj prispevajo h globalnemu prehodu k trajnostnim energetskim virom. Čeprav imajo relativno dolgo življenjsko dobo, se tudi ta s časom izteče, zato je vse bolj nujno odkriti učinkovite metode recikliranja, saj so ključne za zmanjšanje okolijskih vplivov in izčrpanja virov. V tem članku so poudarjeni nedavni napredki v tehnologiji reciklaže fotovoltaičnih modulov, pri čemer je pomembna projekcija potencialne mase določenih materialov, ki jih je možno pridobiti v procesu reciklaže ob upoštevanju inštalirane moči fotovoltaičnih elektrarn, ki trenutno znaša okoli 1105 MW. Iz rezultatov projekcije materialov je bilo ugotovljeno, da bi lahko s postopkom pridobili do 2150 ton silicija in 1025 ton bakra. Pridobitev različnih materialov bi imela pomembno vlogo pri proizvodnji novih fotovoltaičnih modulov, saj bi omogočila trajnostno proizvodnjo in bistveno prispevala h krožnemu gospodarstvu.

1 INTRODUCTION

Photovoltaic (PV) technology stands out as a highly promising solution for bolstering energy security and combating climate change. Its market is experiencing swift growth, with projections indicating continued expansion globally. The anticipated global photovoltaic installed capacity is set to reach approximately 4500 GW by 2025 [1]. Beyond its evident benefits for energy security and climate resilience, PV technology distinguishes itself as one of the eco-friendliest options among all the energy and electricity generation methods. This is particularly evident when considering its entire life cycle, including end-of-life (EOL) handling. Therefore, ensuring proper management at end of its lifespan becomes imperative for maintaining the integrity of “clean” energy technologies [2].

One of the primary challenges in recycling PV modules is the lack of standardized recycling procedures, which underscores the importance of implementing appropriate regulatory and technological approaches tailored to the conditions of each country. The European Union (EU) is one of the associations that has already adopted specific Directives in this area, whereas, in other parts of the world, legislation is not defined or even developed adequately. The Waste from Electrical and Electronic Equipment (WEEE) Directive introduces laws pertaining to the recycling of electrical and electronic equipment aimed at enhancing sustainable production and resource efficiency to contribute to the circular economy. The Directive mandates that all WEEE, including PV modules, must be recycled and processed in accordance with specific Standards. Furthermore, it stipulates that manufacturers and importers of equipment are legally responsible for their recycling, and ensuring that their disposal aligns with the Environmental Standards. The first Directive that acknowledged detailed provisions for the EOL management of PV modules was 2012/19/EU. The law also stipulated that all European member states are required to establish systems for the collection and treatment of PV modules in compliance with this Directive. Manufacturers are also obligated to report monthly or annually on the number of PV modules sold. Within these reports, the result of waste management activities must also be presented, encompassing the mass of materials processed, recycled, or disposed of, such as glass, mixed plastic waste, metals, etc. Furthermore, accountability for informing customers about the management of PV modules at the EOL is also assigned to them [3].

Silicon (Si), as a semiconductor, is utilized most crucially in the production of PV modules, which are key for the generation of electricity. In general, three types of PV cells are distinguished:

monocrystalline, polycrystalline and amorphous solar cells.

Monocrystalline PV cells are made from a single crystal of high-purity silicon obtained from a cylindrical ingot. The ingot is sliced into wafers, each exhibiting a diamond-like crystal structure. Silicon extraction from silica sand begins in arc furnaces, and undergoes purification steps to remove impurities, resulting in polysilicon. The final production of monocrystalline silicon involves the costly Czochralski process, yielding an ingot. These ingots are cut into wafers used for solar cell production, known for their high efficiency ranging from 17% to 22% compared to other PV modules.

Polycrystalline PV cells are manufactured similarly to monocrystalline PV cells, but with a notable difference. Instead of bonding multiple grains of monocrystalline silicon together to form wafers, multiple grains of monocrystalline silicon are bonded together in polycrystalline cells. This variation earns them the designation of multi-crystalline PV cells. However, this configuration restricts the flow of electrons, resulting in lower efficiency compared to monocrystalline modules. Efficiency ranges typically from 15% to 17% in polycrystalline modules, although advancements in technology are narrowing the gap with monocrystalline PV modules.

Amorphous PV cells are manufactured similarly to integrated circuits, with thin semiconductor layers deposited on glass, plastic, or metal substrates. Various materials are used, including amorphous silicon, cadmium telluride, gallium arsenide, and copper indium gallium selenide. Despite varying efficiencies, ranging typically from 10% to 20%, they offer flexibility and reduced weight. Broad light spectra are absorbed effectively by amorphous silicon. Minimal risks are posed by cadmium telluride, despite its toxicity. Efficiency under temperature fluctuations is maintained by gallium arsenide, making it suitable for concentrator PV systems. Copper indium gallium selenide boasts the highest efficiency among thin-film materials, requiring thinner films due to its high absorption coefficient [4-8].

PV modules can be made from various materials; however, most of the market is based on monocrystalline silicon cell technology, which, typically, has a thickness between 150 and 180 μm . A monocrystalline PV module is composed of silicon cells, an antireflective layer of silicon nitride (SiN_x), with the front electrode made of silver and the back electrode made of aluminum [9].

Monocrystalline PV modules consist of the following mass fractions of materials, as presented in Table 1 [9].

Table 1: The mass friction of materials in PV modules [9]

Materials	Mass friction [%]
Glass	71,57
Polymer	12,68
Aluminium (Al)	10,30
Silicon (Si)	3,48
Copper (Cu)	1,77
Tin (Sn)	0,12
Lead (Pb)	0,07
Silver (Ag)	0,01

2 AN OVERVIEW OF METHODS FOR RECYCLING PV MODULES

Research and development in the technology focused on recycling monocrystalline silicon PV modules dates back to the 1990s, when the primary goal was to obtain Si cells without damaging them during the process. The recycling processes of PV modules are divided into thermal and chemical methods [10].

The thermal process, that has been known for several years, entails subjecting PV modules to heating in a furnace at elevated temperatures (between 500°C – 600°C) conducted in two phases. During the process, polymer materials undergo combustion or cracking, while Silicon cells, glass and metals are removed manually. All the obtained usable materials are subsequently processed through recycling, and can be employed in the manufacturing of new PV modules [11].

The chemical process involves the immersion of PV modules in solvents, after which the components are separated through various chemical reactions. The chemical process requires more time than the thermal process, but the percentage of undamaged silicon cells is higher. In the 1990s, BP Solar operated with nitric acid in the recycling process. After one day, ethylene-vinyl-acetate (EVA), a polymeric material that is used to protect PV cells, was dissolved, while the silicon cells and metals were separated and recovered. The silicon cells obtained can then be etched with sodium hydroxide, and reprocessed from silicon wafers into silicon cells. However, due to the formation of nitrogen oxide during the reaction, this recycling method was deemed not the most sustainable, and the disposal of waste acid posed another issue. The availability of organic solvents for separation was also explored as an alternative approach. It was found that many organic solvents could dissolve EVA, but, eventually, they were not suitable for thermal treatment [12, 13].

Recycling processes must meet current, as well as anticipated, future requirements. They must adhere to Regulations for higher levels of processing, and reduce the environmental impact caused by waste PV modules and their processing methods. The current technological development focuses primarily on removing the EVA encapsulant from the laminated structure, separating the glass and other materials, and extracting metals from the Si cells and electrodes. In some cases, efficient removal of the aluminum (Al) frame and junction box is also included in the process before removing the encapsulant itself. Nevertheless, the extraction of the encapsulant remains the most formidable aspect of the PV module recycling procedure. Recent technological advancements in recycling procedures are categorized into thermal, chemical, and mechanical processes [2]. Figure 1 illustrates the scheme of currently researched recycling processes for monocrystalline silicon (Si) PV modules.

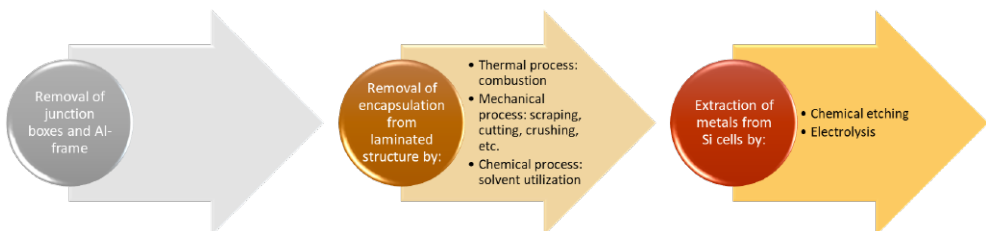


Figure 1: Diagram of current advancements in processes for recycling monocrystalline silicon PV modules

The technical potential of the thermal process has been confirmed through research in its preliminary stages. For example, the FAIS (Kitakyushu Foundation for the Advancement of Industry, Science, and Technology, Japan [14]) has developed PV module recycling technology which includes a process for removing the aluminum frames, back layers, and thermal degradation of EVA encapsulation. To manage PV modules, they employed a system controller that coordinated loading and unloading for PV modules, enabling automatic processing, from loading all the way to the recovery of valuable materials. The first step involves removing the Al-frame using an air actuator. The milling machine removes the back layer to prevent glass cracks in further cracks, and is disposed of as industrial waste. The PV modules, without the Al-frame and back layer, are heated, and the EVA encapsulation is degraded thermally in an oven, with the gas generated during the process being suctioned and incinerated. The oven is preheated to 350 °C, then heated to 500 °C, and, finally, cooled down to 250°C. The heat generated during the combustion of the EVA layer is utilized in the oven heating process. All components, including glass, silicon cells, and electrodes, are recovered after the three main steps. The technology is suitable for processing commercial modules on the market, with a processing rate of approximately 12 MW/year, depending on the module size. The recycling efficiency is nearly 95 %. The obtained glass can be processed into float glass without excessive fragmentation. The process of extracting metals from silicon cells and electrodes is not included in this type of technology. In addition, the technology developed by Chonnam National University [15] involves a thermal process for separating the laminated structure and a chemical process for metal recovery. Nitric acid and sodium hydroxide are used in the chemical process of ultrasonic treatment. After the process, the silicon is purified to 99.998 % purity using the CaO-CaF-SiO₂ compound at 1520 °C.

Currently, a mechanical process is employed in Europe for extracting glass from waste PV modules. The process involves crushing the glass, scraping off layers and cutting the encapsulating layer. Additionally, the procedures encompass the removal of the laminated structure, followed by steps to separate the glass and polymers. For instance, the Sapienza University of Rome [16] has developed an automatic crushing process, which involves manual removal of aluminum frames, automatic crushing of laminated structures and separation of glass for metal processing. Two different crushing methods were evaluated, the first involving crushing with a dual-rotor system, while the second method combined dual-rotor crushing with hammer milling, which appeared more suitable based on the analysis of the distribution of crushed module structures. Crushed particles can be processed in three ways, depending on the diameter (d), presented in Table 2.

Table 2: Processing of crushed particles [16]

Diameter of particle	Process
$d > 1 \text{ mm}$	Incineration process at 650 °C to separate polymers.
$1 \text{ mm} > d > 0.08 \text{ mm}$	Direct glass recovery.
$d < 0.08 \text{ mm}$	Processing with a hydro-metallurgical method for metal recovery.

Chemical processes were already being utilized in the preliminary stages of research of procedures for recycling PV modules. However, it was found that many of them needed refinement, as they were found to impose significant environmental burdens with gas and liquid emissions, leading to the development of numerous new technologies. Chemical processes typically require prolonged treatment, which makes them unsuitable for mass processing.

The Yokohama Oils & Fats industry [17] has developed solvents and processes for removing the casing from laminated structures. Initially, aluminum frames and connection boxes are removed manually, while the casing is stripped away mechanically. The remaining laminated structure is then immersed in a neutral solvent, to separate the glass, EVA layer, silicon cells, and electrodes. If the separated glass is undamaged, it can be reused; however, if it is damaged, it undergoes the recycling process. The next layer is crushed and immersed in an alkaline solvent, from which the EVA layer, silicon, and electrodes are obtained after immersion. An additional process is required to obtain silver. The expected processing time is one day, due to the soaking process in solvents, which is the main drawback of this method. The main advantage is that the developed solvents are environmentally friendly, and the process could be made even more efficient by combining it with a mechanical process.

The Korean Research Institute of Chemical Technology (KRICT) and Kangwon National University [18] have developed a process for dissolving EVA by immersing modules in an organic solvent and subjecting them to additional ultrasonic (UV) irradiation. The aim of UV irradiation is to shorten the time of chemical separation. EVA plastic dissolves at 70°C and at an irradiation power of 900 W, while silicon cells are obtained without damage. In both technologies, after removing the casing from the laminated structure, an additional process is required to extract the metals from the silicon cells.

3 RESULTS

A review of the installed capacity of photovoltaic systems has been conducted, examining the main reasons for the growth or decline in installation. As will be evident later in the paper, photovoltaic power plants were initially installed with declarations, with self-sufficient installations only becoming active from 2015 onwards. Figure 2 presents the annual installed capacity and the total installed capacity of PV systems.

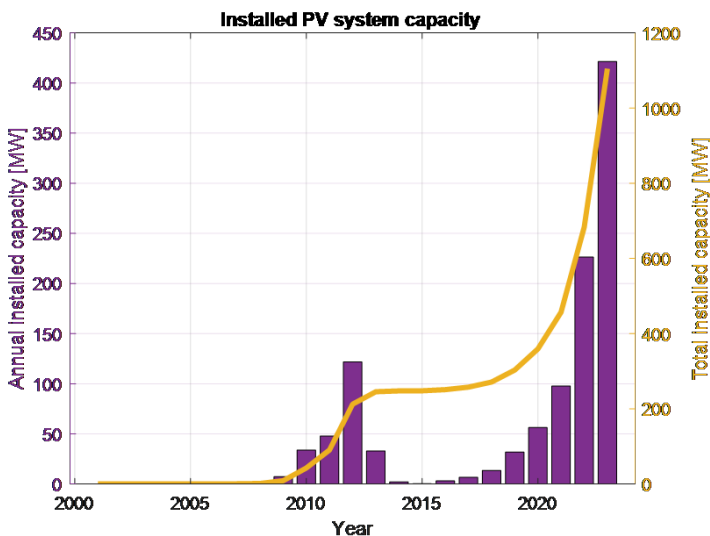


Figure 2: Installed capacity of PV systems by individual years in Slovenia

It can be observed that there has been an exponential increase in the installed capacity of PV systems. This growth is also driven by Slovenia's set target for the share of renewable energy sources in gross final energy consumption, with a goal of achieving 35 % renewable energy by 2030.

Figure 3 shows the installed capacity of PV systems with certification by individual years in Slovenia.

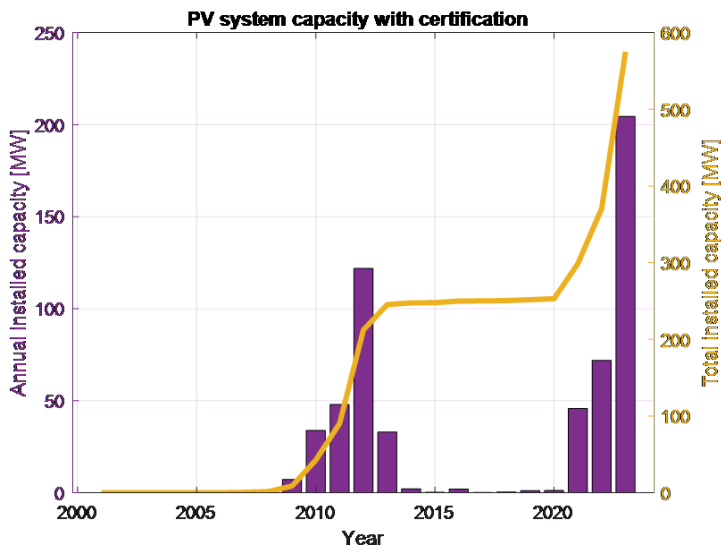


Figure 3: Installed capacity of PV systems with certification by individual years in Slovenia

In 2009, the government approved the installation of PV systems with certification (Figure 3), as the investment for installation was low, and the payout per kWh was favorable. The installed solar power plants were categorized based on capacity into:

- Micro power plants (up to 50 kW) – with an electricity purchase price of 0.41546 €/kWh;
- Small power plants (up to 1 MW) – with an electricity purchase price of 0.38002 €/kWh;
- Medium power plants (up to 5 MW) – with an electricity purchase price of 0.31536 €/kWh.

The state boosted interest in PV systems' construction significantly by offering investors higher purchase prices and extending the guaranteed purchase period. Regulations in 2011 proposed a reduction in production facility costs, affecting fixed and variable reference costs. Subsequently, in 2012, support for PV production facilities connected to the grid was reduced drastically, leading to a notable decline in solar power plant installations in 2013. The introduction of a tender system for promoting renewable energy sources through the 2014 Energy Act aimed to address this issue, alongside emerging initiatives for net metering to facilitate small private investments in PV systems, particularly concerning retirees facing pension repayment demands during operation [20 – 24].

At the end of 2015, the government adopted a new Regulation on self-sufficiency of PV systems (UL RS, No. 97/2015). This Regulation outlines the conditions for self-sufficiency with electricity generated from RES, the method of calculation, annual power limits for self-sufficiency devices, reporting requirements for the implementation of the measure, and the method of calculating the electricity produced by self-sufficiency devices. The Regulation defined the maximum rated power of a self-sufficiency device at 11 kVA, which could not exceed the connection power specified in the connection consent. Furthermore, the calculation method was established, whereby the amount of electricity credited to the owner of the self-sufficiency device corresponds to the difference between the consumed and delivered working electricity, as measured at the same metering point at the end of the billing period. Surpluses of produced electricity will not incur charges. If, at the end of the billing period, the amount of electricity delivered to the grid through the metering point exceeds the amount of consumed working electricity, the excess amount of working electricity is transferred to the supplier's account without charge. The Regulation came into effect on January 15, 2016 [20, 21, 22, 25].

In 2016, slightly over 3 MW of new PV systems were installed, with one-third of these systems being installed for self-sufficiency purposes. The government of the Republic of Slovenia issued the Regulation on Energy Infrastructure (UL RS, No. 22/2016), which eliminated the requirement for government approval for registration and deletion in the Infrastructure Registry. The most significant change introduced by this Regulation was for investors planning to install electricity generation devices, who would have previously been required to submit Appendix 2 before connecting the device, a requirement that is no longer applicable [20, 21, 22, 26].

Figure 4 presents a very dynamic market for PV systems in 2017, with the majority of installations intended for self-sufficiency, following a few years of quiet in the solar power sector.

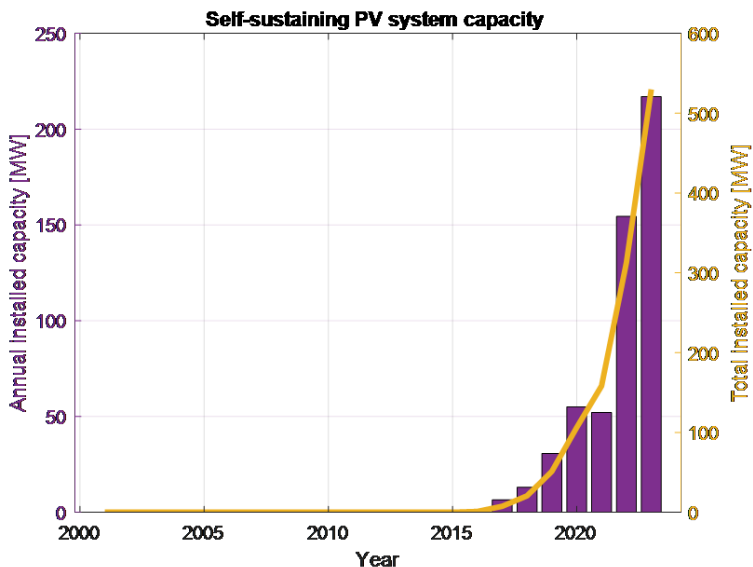


Figure 4: Installed capacity of self-sufficiency PV systems by individual years in Slovenia

In 2019, the rapid growth of self-sufficiency PV systems (Figure 4) continued under the self-sufficiency scheme, with an average and minimum offered price for electricity production from solar power plants at 75.71 €/MWh. The Regulation on self-sufficiency with electricity from renewable sources introduced the concept of "community self-sufficiency" for multi-apartment buildings and communities of renewable energy sources. In 2020, there was a further increase in small solar power plants for self-sufficiency, with almost 60% more installations than in 2019. The village of Luče in the Savinja Valley became Slovenia's first self-sufficient community, meeting its electricity needs fully from renewable energy. In 2021, approximately 56 MW of new solar power plants were installed, alongside a significant increase in electricity prices. In 2022, a total of 164 MW of solar power plants were installed, including the largest solar power plant to date, Prapretno, with an installed capacity of 3 MW. In March 2022, the Government of Slovenia issued a Regulation on self-supply with electricity from renewable energy sources, introducing new calculations for network charges, abolishing net metering for devices entering the self-supply system in 2024, simplifying procedures for devices up to 50 kW, and specifying that connections are considered approved if the distribution system operator does not issue decisions or rejections within one month. Self-supply consumers will be required to pay network charges for energy taken from the grid, but will not have to pay for energy fed into the grid [20-28].

Figure 5 shows the approximate number of PV modules in Slovenia, calculated based on the installed capacity of PV systems, and assuming that the average power of one module is 350 W.

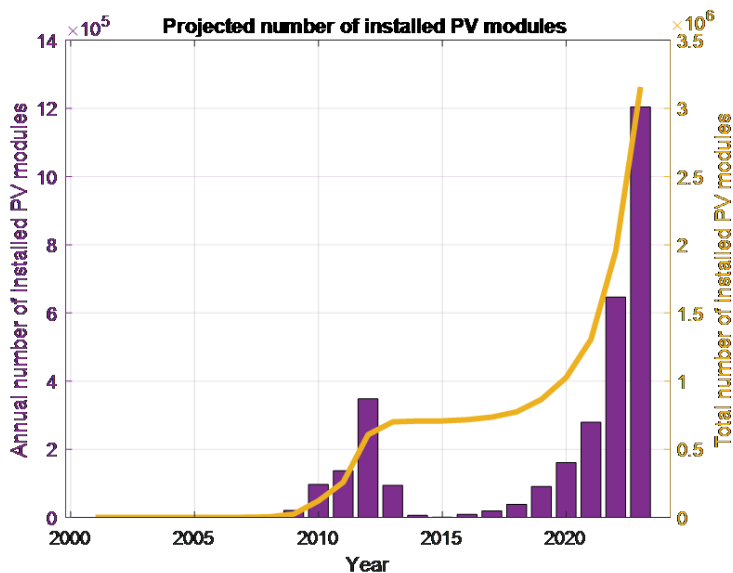


Figure 5: Projected number of installed PV modules

With the help of the projected number of modules (Figure 5) obtained by assuming that each PV module has an average power of 350 W, we aimed to illustrate the projected capacity of waste or recycled material in the future.

The authors in [9] cited the following average recycling factors for the materials shown in Table 3.

Table 3: Average recycling factors for materials in PV modules [9]

Material obtained through the recycling of PV modules	The factor of successfully recycled material
Glass	0,96
Aluminum (Al)	1
Silicon (Si)	0,91
Copper (Cu)	0,85
Silver (Ag)	0,95
Lead (Pb)	0,96
Tin (Sn)	0,32

With the proportions of materials in PV modules considered from Table 1, the predicted mass was calculated of elements or substances obtained after recycling. The data sheet in [29], where it is stated that a 300 W solar module weighs 18.5 kg, was used to introduce the mass equivalent, which is 61.6667 kg/kW. Using the mass equivalent, the predicted mass of obtained elements after the recycling process for each year was then calculated separately, based on the estimated number of PV modules.

Figure 6 presents element recovery projections in Slovenia.

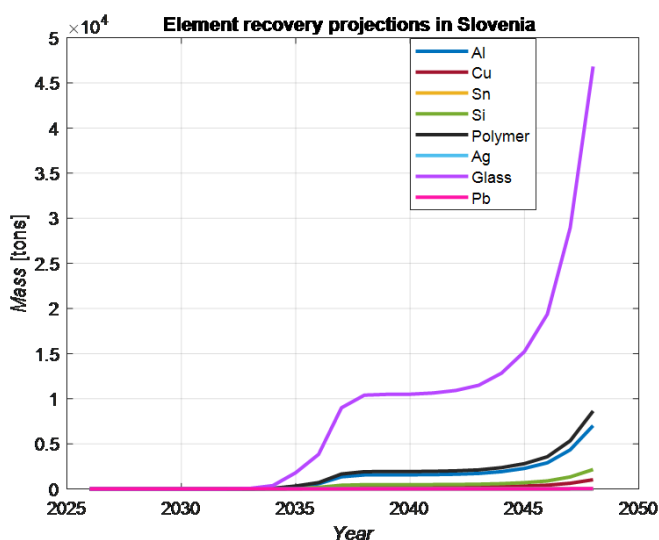
**Figure 6:** Element recovery projections in Slovenia

Figure 6 shows that the highest mass of glass, polymers, and aluminum can be yielded by the recycling process, as they constitute most of the PV module. With a 25-year lifespan assumed for PV modules and the first installations dating back to 2001, the initial modules eligible for recycling would be available in 2026. By 2048, approximately 46,818 tons of glass, 8,640 tons of polymers, and 7,018 tons of aluminum could be obtained, based on the current installed capacity

of 1105 MW. Elements such as silver, silicon, and copper will be crucial for the circular economy. According to our projection, based on the current installed capacity, 2,157 tons of silicon, 1,025 tons of copper, and approximately 6 tons of silver could be obtained for further use in production. However, significant optimization of the recycling processes is necessary, as the current purity of elements is not sufficiently high, and excessively aggressive chemicals are used in the process of obtaining silicon, copper, and silver.

4 DISCUSSION

This paper presented various methods of recycling PV modules. The main finding is the necessity for an effective recycling process, which includes mechanical, chemical, and thermal processes for optimal results. Currently, the most researched methods of recycling are those for monocrystalline PV modules, which are also the most widespread commercially. Despite the relatively recent emergence of recycling processes and associated legislation for PV modules, recycling technologies are already quite well-researched, but they will certainly be optimized further for improved efficiency, sustainability, and cost-effectiveness in the future. Additionally, the exponential growth of installed PV system capacity in Slovenia was described, along with the factors influencing it. A future decline in installed capacity is expected, due to economic factors. The acquisition of materials over 25 years was projected, based on data on the installed PV system capacity in Slovenia, factors of recycled materials, and known mass fractions of elements/materials in PV modules. The main finding was that significant quantities of useful materials could be obtained, such as silver, copper, and silicon. Additionally, a large amount of polymer, glass, and aluminum mass, which are the main constituent materials of PV modules, would be obtained as a result of recycling.

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Nomenclature

(Symbols)	(Symbol meaning)
PV	Photovoltaics
EOL	End-of-life
EU	European Union
WEEE	Waste from electrical and electronic equipment
EVA	Ethylene-vinyl-acetate