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Review

Technological Advancement in Solar Photovoltaic Recycling: A Review

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Abstract: This review examines the technological surveillance of photovoltaic panel recycling through a bibliometric study of articles and patents. The analysis considered the number of articles and patents published per year, per country, and, in the case of patents, per applicant. This analysis revealed that panel recycling is an increasingly prominent research area. However, the number of patents filed annually has varied in recent years, averaging fewer than 200 per year. The state-of-the-art review identified three main types of treatment for photovoltaic panel recycling: mechanical, chemical, and thermal. Among these, mechanical treatment serves as a preliminary stage before the recovery of valuable elements, which is achieved through chemical or thermal processes. The articles reviewed cover a range of processes, including hydrometallurgical and pyrometallurgical methods, and explore various classification processes, solvents, and oxidizing agents. In contrast, patents predominantly focus on pyrometallurgical processes. This analysis is supplemented by a survey of market-ready technologies, many of which include stages such as size reduction or delamination followed by pyrometallurgical processes. Additionally, the review highlights the collection processes implemented by some companies, noting that the volume of panels considered waste is currently insufficient to maintain a continuous and year-round operational process. This study identifies key challenges such as (i) reducing solar panel size due to the EVA polymer complicating conventional machinery use, (ii) high process costs from the need for high temperatures and costly additives, (iii) the environmental impact of thermal treatments with high energy consumption and air pollution, and (iv) the necessity for environmentally friendly solvents in hydrometallurgical treatments to reduce contamination during recycling. Future directions include developing specific machinery for panel size reduction, either creating or modifying a polymer to replace EVA for easier treatment, adopting hydrometallurgical treatments with green solvents proven effective in recycling minerals and electronic waste, and addressing the lack of detailed information on industrial processes to make more precise recommendations.

Keywords: solar panel recycling; technological surveillance; solar energy; hydrometallurgy

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1. Introduction

In recent decades, energy demand worldwide has increased, primarily due to substantial population growth. At the same time, as the effects of global warming and CO_2

emissions intensify, renewable energies are playing a more significant role in mitigating the environmental impact of conventional energies. Due to low CO_2 emissions, electricity generated using photovoltaic panels (PV) are a high priority option, because it is one of the cleanest forms of energy [1]. While emissions generated by fossil fuel-based electricity emit 400–1000 g CO_2-eq/kWh, electricity generated by crystalline silicon PV panels emits 23–81 g CO_2-eq/kWh, which is 5 to 8% of fossil fuel-based emissions [2].

According to the 2024 Renewable Capacity Statistics report from the International Renewable Energy Agency (IRENA) by the end of 2023, a total capacity of 3870 GW was reached in the deployment of renewable energies in the energy sector globally, registering a considerable increase of 473 GW of new renewable energy capacity added. The report highlighted the participation of solar energy, which contributed an increase in installation of 345.5 GW of photovoltaic solar energy [3]. The increase in renewable energy in Asia totaled 237.7 GW, to which China, India, and Japan contributed 216.9 GW, 9.7 GW, and 4.0 GW, respectively. On the other hand, the United States contributed 24.8 GW, while Germany and Brazil added 14.3 GW and 11.9 GW, respectively, to the total expansion in 2023. Thus, 1419 GW of photovoltaics was reached, which is equivalent to 73% of growth of renewable energies compared to the year 2022. This implies that China has become the most influential country in the development of photovoltaic solar energy, increasing its competitiveness against coal and gas. The global installed solar capacity of photovoltaic panels at the beginning of 2022 was 1 TW. Global photovoltaic capacity is forecast to exceed 2 TW by 2025, 2.3 by the end of 2026, 3.5 by 2027 and 6 TW by the end of 2030 [4].

Chile has one of the largest solar energy potentials in the world, due to its climatic conditions and high solar radiation [5]. According to the National Electric System (SEN), Chile's installed electricity generation capacity was 33,339 MW as of December 2023, and its installed solar energy capacity was 25.4%. On average, 64% of the installed capacity in the SEN was generated with renewable technologies, and 36% with fossil fuel plants [6].

Photovoltaic panels are devices capable of converting sunlight energy into electrical energy without the need for a heat engine or rotor equipment. Among the different types of photovoltaic panels, silicon panels are the most common worldwide, comprising 85%–90% of the PVs on the market. Such panels are generally composed of 77.41% glass, 1.6% metal filaments, 6.77% solar cells, and 14.06% polymers [7]. Elements such as copper (0.8 mg/g), silver (2.2 mg/g), zinc (12% by weight), aluminum (10% by weight), and silicon (20% by weight) are present in the different types of panels [8,9]. The range of current technologies for the manufacture of photovoltaic modules is divided into three generations. First-generation photovoltaic modules contain crystalline silicon (c-Si) (monocrystalline or polycrystalline). Second-generation thin film (a-Si) photovoltaic modules contain amorphous silicon, cadmium telluride (CdTe), multi-junction cells (a-Si-μc-Si), copper indium gallium diselenide (CIGS), and copper indium diselenide (CIS). Third-generation photovoltaic modules include concentrator photovoltaic (CPV) and emerging technology such as dye-sensitized solar cells, organic solar cells, hybrid cells, a back contact cell with a Passivated Emitter Contact Cell (PERC) and Passivated Emitter Back Contact Cell (PERL), Tunnel Oxide Passive Contact Cells (TOPCon), Perovskite Solar Cells, and Heterojunction Technology (HJT) [6–8]. The most promising solar energy technologies are TOPCon and Perovskite photovoltaic cells. TOPCon are like PERC cells but contain a thin layer of silicon dioxide and a layer of polycrystalline silicon mixed with phosphorus, while the Perovskite photovoltaic cells highlight the potential for high energy conversion efficiency, which could achieve an efficiency of 38%. Currently, its biggest drawback is its lead content and the stability of the material [7–10]. For the new second- and third-generation photovoltaic technologies, which do not use crystalline silicon as a base material, some researchers such as Marwede et al. [11] and Kuroiwa et al. [12] have presented methods for recycling thin film panels (CdTe, CIS and CIGS). The common approach in these methods is the delamination of the modules by grinding, the stripping of the substrate, the extraction and refining of metals (because the removal of toxic metals is required before recycling), and the decomposing of metals in an initial step before their processing in decomposition stages.

On the other hand, Pagnanelli et al. [8] presented an automated process for the treatment of CdTe panels, consisting of a mechanical treatment of the panels through crushing, sieving, the thermal treatment of the coarse fraction, and the chemical treatment of the fine fraction. For the recycling of perovskite solar cells, it is necessary to establish a viable recycling process because of its lead content, focusing mainly on organic solvents to achieve high metal solubility and recyclability. Park et al. [13] investigated the use of iron-containing hydroxyapatite as a new adsorbent for recovering lead from perovskite-containing organic solvents. In a recent laboratory-scale study, the recycling of perovskite solar cells was efficiently carried out by Le Khac et al. [14] using a single-step chemical treatment and recovery of glass substrates coated with ITO (Indium Tin Oxide). They achieved high levels of purity in useful elements and a high recovery of heavy metals including lead from perovskite devices.

Despite their low environmental impact, solar panels have a useful life of 20–30 years, and in the north of Chile, this can be as short as 15 years [15,16] due to climatic conditions. With the high projection of future installations, it is anticipated that there will be an accumulation of solar panels due to failures or the end of their useful life in the upcoming years [17,18]. Consequently, many countries have enacted various decrees, laws, regulations, and initiatives to control Waste Electrical and Electronic Equipment (WEEE) [19–24]. In Chile, the Extended Producer Responsibility (REP) law [25] is in force, establishing goals for the management, recovery, and valorization of post-consumer waste, including photovoltaic panel waste. This regulation is recognized as a key tool in waste treatment [26].

Currently, recycling companies such as Veolia (Rousset, Bouches-du-Rhône, France), Rosi-Solar (Grenoble, France), NPC Incorporated (Tokyo, Japan), and Loser Chemie (Freiberg, Germany) are working or planning to recycle photovoltaic panels globally, using thermal, physical, and/or chemical processes. There can be found published articles or patents on the recycling of PV, in which combinations of processes are applied to recover valuable materials. However, they are not very comprehensive or lack details.

The aim of this study is to outline the current progress of PV-recycling processes, identifying the main advantages and disadvantages of the developed processes, aspects that require attention in future processes, and the maturity of the technologies. This review provides a technological overview of photovoltaic panel recycling. It analyzes the status of solar panel recycling through an evaluation of articles, patents, and technologies under study and/or applied on a pilot or industrial scale.

2. Methodology

The methodology and the selection of studies were designed according to the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) method [27], which has been used in other similar investigations [28]. The procedure is summarized as follows:

- The identification of studies in the database: The search for studies was performed in the Web of Science (WoS) database in December of 2021 using the keywords "solar panel recycling" as presented in Figure 1. The management of these articles was performed through the Mendeley software (2.74.0) to eliminate duplicate articles and multiple studies by the same author.
- Narrowing the search: the second screening of articles was performed using "solar panel", "recycling", and "process" as key words. The screening of the studies was analyzed considering articles that contain details on the processes involved during the recycling of solar panels.
- The primary review of studies: All identified studies were initially reviewed by an examination of their titles, abstracts, and keywords to discard studies that did not fit the topic of analysis.
- Study reading: The selected studies were read in full. This step was taken to discard studies that were not written in English and articles with restricted access.

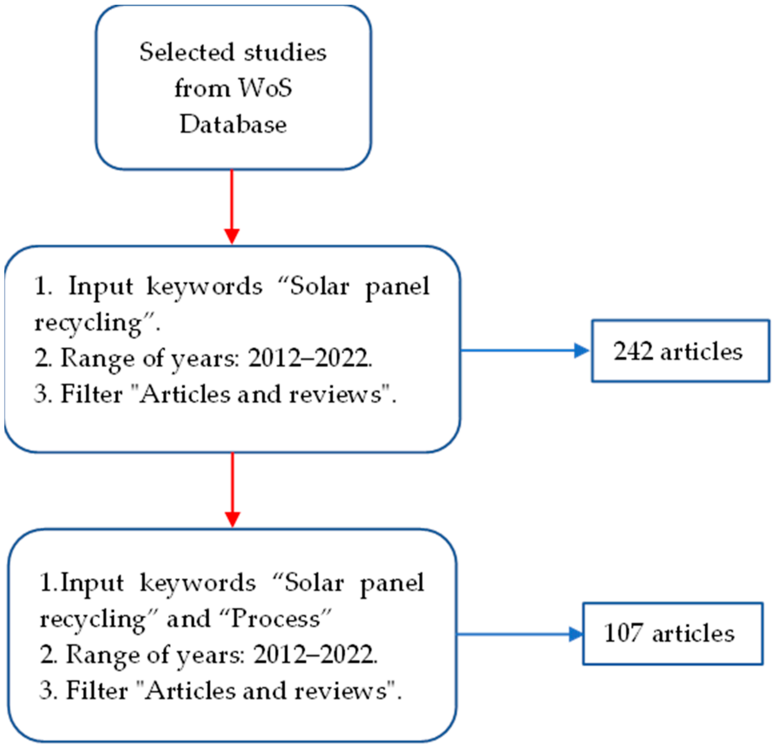

Figure 1. Sequence of the methodology used in this review based on the PRISMA method.

Figure 1 shows a graphical scheme of the search for published papers and the keywords used.

For the search of patents, a search was conducted for methods of recycling photovoltaic panels. The information was extracted from the PATENTSCOPE database. The search was performed using the following keywords: "recycling", "photovoltaic panels", "modules", "method", "process", and "solar cells". The results are organized by number of patents published by country, by year, and by application.

3. Results and Discussion

3.1. Distribution of Articles and Patents on Photovoltaic Panels Recycling

The first bibliometric analysis was conducted to search for articles related to the photovoltaic panel recycling process. It found 242 articles and reviews published between 2012 and 2022. The information analyzed was sourced from the Web of Science and the World Intellectual Property Organization database.

From the second search 107 results were obtained, which were then analyzed. Basically, two approaches were considered, the first one consisting of the number of articles published per country; Table 1 shows the 10 countries from which most of the published articles originated.

China has the highest percentage of publications related to the photovoltaic panel recycling process, accounting for 16% of worldwide publications. Italy and Australia follow with 14.9% and 13.8%, respectively. This high percentage is attributed to China's significant advancements in the implementation of photovoltaic energy. In Chile, the field of photovoltaic recycling is still developing. According to the search performed, there is only one article published by Chile in 2020. This represents both a challenge and an opportunity for the national scientific community, especially since the north of the country has favorable conditions and great potential for the generation of photovoltaic energy.

The second focus of the analysis was the number of articles published per year. Figure 2 shows a clear exponential increase in publications, indicating a substantial rise in the number of articles over time. Between 2017 and 2021, there was an increase of more than 200% in publications related to PV panel recycling. This trend highlights the growing interest in solar panel recycling within the scientific community. For example, the United

States ranks fourth among countries with the most publications, but in the last three years, it has published seven articles. This gives the USA the highest number of publications after China between 2020 and 2022, likely due to its significant generation of energy through photovoltaic panels.

Table 1. Number of published articles regarding PV-recycling treatments by country (based on the country of the corresponding author).

Country	Number of Articles	Percentage
China	15	16.0%
Italy	14	14.9%
Australia	13	13.8%
USA	10	10.6%
UK	9	9.6%
India	6	6.4%
Japan	6	6.4%
Spain	6	6.4%
Brazil	5	5.3%
Republic of Korea	4	4.3%

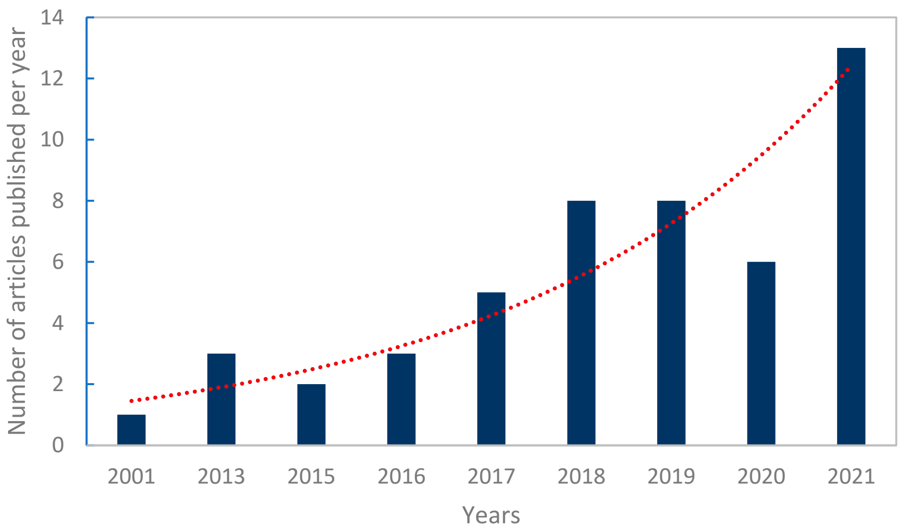

Figure 2. Trend in the number of articles published per year on photovoltaic recycling treatments.

A patent search was conducted for methods of recycling photovoltaic panels. The information obtained was extracted from the PATENTSCOPE database, which provides access to international Patent Cooperation Treaty (PCT) applications. The search was performed using the following keywords: "recycling", "photovoltaic panels", "modules", "method", "process", and "solar cells", yielding 2108 results.

Most of the selected patents fall under the classification H01L, which deals with basic electrical elements, specifically semiconductor devices. The subclassification H01L 31/00 pertains to semiconductor devices sensitive to light radiation and specially adapted to convert such radiation into electrical energy. It also includes processes or apparatus specially adapted for the manufacture or treatment of their parts.

In 2022, the American recycling company SolarCycle opened (Odessa, TX, USA), developing patented technology and a scalable business model that can profitably extract up to 95% of valuable materials and return them to the supply chain. In 2023, a new patent for the recycling of solar panels stood out (publication number WO2023205732), which refers to the use of one or more techniques that can be used separately or combined, specifically in the restoration or recycling of used solar modules. This a method that encompasses the following steps: grinding a photovoltaic module, which includes a glass sheet and a polymeric encapsulant; separating the broken glass resulting from the crushing step from a first phase, including the polymeric encapsulant; after separation, performing a second grinding on the first phase, including the polymeric encapsulant. All this within the International Patent Classification (CIP): Destruction of solid waste or transformation of solid waste into something useful or harmless that involves mechanical treatment [29–31].

As in the analysis of articles, for patents two approaches were considered. The first approach focused on the number of patents published by country, and the second approach on the number of patents per year. Table 2 shows the countries in which concentrate most of the published patents originated.

Table 2. Number of patents published on PV recycling treatments by country. There is a significant difference between the country with the highest number of patents and the other countries.

Country	Number of Patents	Percentage
USA	1096	70.7%
European patent office	151	9.7%
Australia	111	7.2%
India	97	6.3%
Canada	70	4.5%
UK	15	1.0%
Singapore	4	0.3%
South Africa	4	0.3%
New Zealand	2	0.1%

Unlike the analysis of the previous section, the predominance of patents related to photovoltaic panel recycling is concentrated in the United States, which accounts for more than 50% of all published patents on the recycling of PV panels. This can be attributed to the fact that photovoltaic solar energy is one of the most active industries in the U.S. global photovoltaic market. The growth of this industry needs the development of technologies and methods to recycle photovoltaic panels at the end of their useful life, thus preventing potential large-scale contamination in the future.

Regarding the number of patents published per year, there is a significant difference between the trends in article publication and patent filings. The previous section observed an increasing number of articles over the years, reflecting the need to develop new methods for PV recycling. However, the same trend is not observed in the number of patents published each year. Figure 3 shows that the highest number of patents were registered in 2014 and 2020, with 160 and 230 patent publications, respectively. Over the past two decades, the number of patents has fluctuated between 113 and 230 publications per year.

Figure 4 shows that the largest number of patents granted to applications corresponds to PIXTRONIX INC (Andover, MA, USA), a company that develops optimized visualization technologies for multimedia devices, accounting for 32% of the patents obtained. This is followed by companies such as BASF SE (Ludwigshafen am Rhein, Germany) (chemical company), FLEX LIGHTING II LLC (Chicago, IL, USA) (manufacture of electric lighting equipment), SOLEXEL INC (Milpitas, CA, USA) (solar photovoltaic technology), and NANOSYS INC (Milpitas, CA, USA) (development and manufacture of nanotechnology materials), among others, each accounting for 10% of the patents obtained in the search.

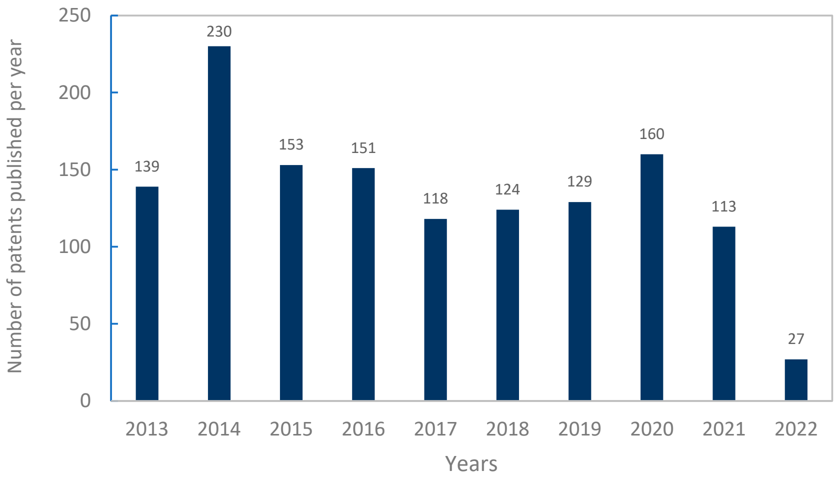

Figure 3. Number of published photovoltaic recycling treatment patents by year, from 2013 to 2022.

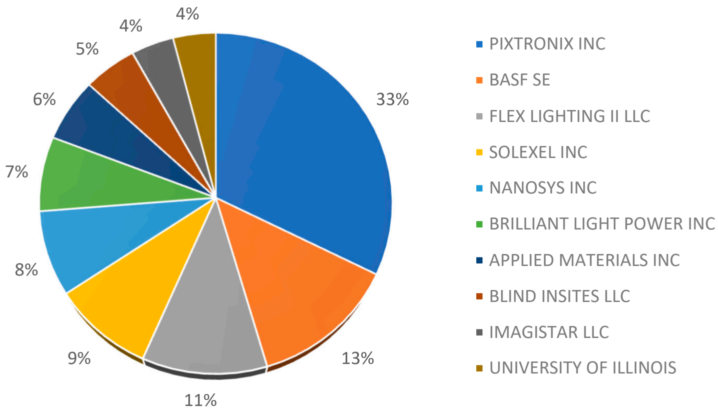

Figure 4. Distribution of the patents granted to companies in solar panel recycling applications.

Table 3 summarizes the main companies that handle or recycle monocrystalline, polycrystalline, and new-generation photovoltaic panels, as well as an overview of the processes involved.

Table 3. List of companies and processes for photovoltaic panel recycling.

Company	Recycling Process	Type of Module Recycled	Reference
Veolia (Rousset, Bouches-du-Rhône, France)	The process starts with the use of robotic automation to disassemble and classify solar panels. Junction boxes, cables, and aluminum frames are removed. The remaining laminate is then crushed, and the resulting pieces are sorted by size, including glass, EVA (Ethylene Vinyl Acetate), backsheet, coated copper connections, and solar cells. These sorted materials are processed and packaged for shipment to various industries, where they are reused.	c-Si	[32]
ROSI-Solar (Grenoble, France)	Ultra-pure silicon and silver fingers are recovered from solar cells using physical, thermal, and soft chemistry processes. The first step involves thermal pyrolysis to separate polymers binding glass and solar cells. Next, mechanical sorting separates the materials, followed by a soft chemistry process that releases silver fingers from the cells without dissolving the metals. Fragments of high-purity silicon cells are recovered and reused in the industry.	c-Si	[33]

Table 3. *Cont.*

Company	Recycling Process	Type of Module Recycled	Reference
NPC Incorporated (Tokyo, Japan)	An automated line is used to dismantle solar panels, separating glass from other materials without crushing it using the "heated blade separation method". This approach enables efficient recycling by preventing glass contamination with metals. The separated materials are delivered to recycling companies, achieving complete glass recycling. In this method, a blade heated to 300 °C melts the EVA layer to separate the glass from other materials, thus achieving total glass recycling.	c-Si	[34]
Loser Chemie (Freiberg, Germany)	Optical technologies are employed to open the sandwich structure of solar panels without damaging the glass, unlike traditional methods such as crushing that can break the glass. Alkanesulfonic acid is used to clean the panels, removing photoactive layers and various metals in a short reaction time. This biodegradable acid enables hydrometallurgical extraction at room temperature, resulting in classified pure glass. Alkanesulfonic acid is recoverable and is also used for silver recovery without generating nitrous gases, unlike nitric acid.	c-Si and a-Si	
First Solar (Tempe, AZ, USA)	A two-stage crushing process is employed for recycling solar modules: in the first stage, the module is superficially broken to facilitate transportation, and in the second stage, glass plates are crushed into small pieces of 5 mm diameter using hammer crushers. Semiconductor films are leached with sulfuric acid and hydrogen peroxide to obtain a semiconductor solution. This solution is precipitated and subcontracted for refinement, later used in the production of new CdTe thin-film modules.	CdTe	[35]
SolarCycle (Odessa, TX, USA)	The present invention addresses the need for recycling solar modules, complex devices that harness solar energy but require technologies for end-of-life management. It describes a method to restore or recycle used solar modules, which involves shredding the photovoltaic module with a glass sheet and polymer encapsulant. Broken glass is separated from the initial crushing phase along with the polymer encapsulant, followed by a second shredding of the separated initial phase including the polymer encapsulant.	c-Si	[29–31]

3.2. Studies on Methods of Recycling

The International Energy Agency (IEA) reported that by 2050, approximately 11% of all the energy produced worldwide is expected to be generated through photovoltaic solar energy. However, it should be considered that photovoltaic (PV) panels have a lifetime of about 25 to 30 years [36]. After this period, PV panels become waste without a defined recycling treatment [37,38]. To mitigate the negative impact of PV waste due to its projected growth, the European Union (EU) commission has categorized PV panels as waste electrical and electronic equipment (WEEE), which includes legislation on e-waste recycling [39]. This mandates that all PV manufacturers, distributors, and retailers have a legal obligation to ensure the collection and recycling of their discarded products, including financing, reporting, and administration, within European borders [40].

With the projection of photovoltaic waste ranging from 1.7 to 8 million tons by 2030 and 60 to 78 million tons by 2050 [41], it is urgent to develop recycling methods that allow for the reuse of solar panel waste. Silicon photovoltaic panels (PV c-Si), both monocrystalline or polycrystalline, contain materials of interest such as Cu, Ag, Pb, Sn, Al, and Si and are the most widely used type of panels worldwide [42,43]. Several authors propose different methods for recycling photovoltaic panels, primarily focusing on the recovery of valuable metals and/or the solar cell, which can be categorized into three treatments: mechanical, chemical, and thermal treatments [44–46].

3.2.1. Mechanical Treatment

Material fragmentation treatments have been reported to facilitate the extraction process of valuable metals. Nevala et al. [47] proposed electrohydraulic shredding (EHF) as an alternative to conventional shredding. They reported that contamination is minimal compared to the residual dust from the conventional shredding process, which reduces the environmental impact. The method consists of introducing pieces of photovoltaic c-Si (12 cm $\times$ 18 cm) into the EHF reactor, which was filled with water causing the detachment and fragmentation of the photovoltaic layers using shock wave technology, which provides higher selectivity by concentrating the target metals into specific particle size fractions. This type of process is promising for the preparation of material for the subsequent extraction of valuable metals.

Song et al. [48] proposed a novel and environmentally friendly recycling process for polycrystalline c-Si photovoltaic panels by using high-voltage pulsed discharge in water, called high-voltage fragmentation (HVF), under different discharge conditions. The results showed that the discharge on the surface and inside the PV panels produced ablation holes, sputtered metal particles, and dendritic channels. With HVF, the average particle size was observed to decrease with increasing pulse number and voltage amplitude. At the end of the process, 95% of Cu and 96% of Ag had sizes less than 1 mm, 85% of Al was between 0.25 and 2 mm, and 85% of Pb and 87% of Sn had sizes less than 0.5 mm. HVF has a low cost with an energy consumption of 200 J/g (0.056 kWh/kg), only half that of mechanical treatments.

Other studies focused on the recovery of valuable metals, solar cells and/or ethylene vinyl acetate (EVA) copolymers. Li et al. [49] investigated the recycling of EVA by infrared fiber optic pulsed laser irradiation. The laser passed through the backside of EVA to reach the solar cell/EVA interface. The laser energy was absorbed by the back metal electrode (Al and Ag), which caused a temperature rise at the interface, which weakened the adhesive force between the solar cell and EVA. This facilitated the detachment of the EVA layer with mechanical peeling to recycle this back layer of the c-Si PV module. This process has the potential to greatly reduce the risk of environmental contamination compared to other recycling processes, as it does not present toxicity risks.

Lovato et al. [50] analyzed the efficiency of supercritical fluid technology in the delamination of photovoltaic panels, with the aim of recovering high value-added materials such as Ag, Si, and Pb, as well as polymers and glass. The procedure used $ScCO_2$ with toluene and ball milling. The samples were placed in a 304 stainless steel reactor, connected to a high-pressure pump, and attached to a carbon dioxide cylinder. Finally, 98.69% glass, 96.75% Pb filaments, and 99.35% back sheet were obtained. The recovery of Cell + EVA was 85.77%. Future research should seek to reduce the toxicity of solvents and find a better management of residual polymeric waste.

3.2.2. Chemical Treatment

Another treatment employed is chemical etching, in which the aim is to corrode and dissolve unwanted materials; this method is used when it is desired to recover mainly Si wafers from c-Si photovoltaic solar cells. Sah et al. [7] reported a simple process to recover metal contacts and silicon wafers using a KOH solution. The method consisted of immersing two parts in the solution (2M KOH) at temperatures of 383.15 $\pm$ 1 and 358.15 $\pm$ 1 K. The chemical etching succeeded in detaching the silver contact at the silicon–silver interface in its entirety. Moreover, the silver contact remained free of Pb, which allows its use in another application, and the lead was separated by the high reactivity of KOH. Silicon wafer and Ag contacts were obtained with 99% purity; therefore, the recovered wafer powder can be reused for the manufacture of ingots with very similar characteristics to the commercial wafer.

Shin et al. [51] studied a recycling process to recover silicon (Si) wafers using solvents for Ag and Al and an etching paste to remove the antireflective and emitter from the surface. This method consisted of sequentially dissolving Ag and Al metal electrodes in HNO_3 and KOH solutions, respectively, to recover the Si wafers. Impurities on the wafer surface were removed with an etching paste containing H_3PO_4. Although not specified, the results demonstrate that, if the etching process is carried out at 593.15 K, the recycled wafer still has an adequate lifetime value, which is acceptable with the new solar cell manufacturing guidelines and would justify the cost of the process.

Kang et al. [52] investigated the procedure for resource recovery from waste photovoltaic modules by using organic solvents and chemical etching. The organic solvent used to recover the tempered glass was toluene, which caused the expansion of the EVA resin, which was removed by thermal decomposition. The metallic impurities in the PV cell were removed by applying a chemical etching solution on the cell surface using a mixture of HF (48%) and HNO_3 (70%) with H_2SO_4 (97%). The result of these processes was 99.9% pure silicon and recovered tempered glass, achieving an optimization in the silicon recovery process by means of a surface treatment of the modules.

One way to recover various valuable metals such as Ag, Si, and Al from the photovoltaic c-Si is by combining different procedures that help to extract the different metals [53,54]. Dias et al. [55] characterized the materials used in photovoltaic panels and investigated techniques to separate these materials to allow for their recycling. They studied three different methods of component segregation. Mechanical crushing followed by screening and chemical separation with sulfuric acid succeeded in separating the semiconductor material by immersing the material in containers with 98% H_2SO_4 for 5 days. They also proposed that a pyrolysis prior to the separation of the material would decrease the toxicity of the chemical process, since it manages to degrade the EVA, thus detaching the layers bonded by the adhesive material. Thermogravimetric analysis showed that all the polymeric fractions present degraded at 773.15 K [56].

In a study developed by Lee et al. [57] a hydrometallurgical procedure was proposed to recover Si, Ag, and Al from discarded silicon solar battery cells. Under optimum leaching conditions, the 100% recovery of Al and Ag was achieved. The aluminum was recovered by crystallization from a leaching solution with H_2SO_4 at 363.15 K. To recover silver from the leaching solution with HNO_3 reagent, HCl was specifically used as precipitating agent, and electrolysis was performed to recover part of the Ag by extracting the electrolyte at various time intervals. Then, a part of the Ag-containing solution was taken and placed in contact with Zn plates; the exchange reaction was developed for 3 h. Finally, silicon was the remaining solution; this study obtained a 100% recovery of valuable metals. Therefore, they conclude that these methods could be used to recover various valuable metals from solar panels to achieve recycling targets.

3.2.3. Thermal Treatment

Fisson et al. [58] developed and evaluated different recycling processes, from which they obtained two methods that yielded acceptable results. Pyrolysis was performed in a fluidized bed reactor filled with very fine sand at 723.15 K, followed by a general cleaning and etching sequence. For most of the recovered wafers, a 15% HF treatment was applied followed by a H_2SO_4:H_2O solution at 353.15 K and finally by a 40% HNO_3 solution at the same temperature. In conclusion, they obtained a mechanical yield of 80%, the 1 h treatment cycle delivered 576 wafers/h, and the total investment cost was 575,000 € for the complete process, while the cost per recovered wafer was 0.215 €. The recovered silicon wafers retained their initial high quality, resulting in high efficiency recycled solar cells, being a cost-effective recycling process.

Song et al. [59] proposed the recycling of PV CIGS (Cu-In-Cd-Ga-Se), using a sequential electrodeposition method to obtain the pure metal of the quaternary system Cu-In-Cd-Ga. They used $CuGa_{0.3}In_{0.7}Se_2$ from a CIGS PV panel which was exposed to a previous crushing process, followed by oxidative roasting and then leaching with HCl at 1073.15 K as pretreatments to separate the SeO_2. Electrodeposition was then carried out with a three-electrode configuration, one of saturated calomelane (Hg_2Cl_2) in front of a hydrogen electrode as reference and a platinum plate as counter electrode. The electrodeposition of In and Cd showed fast kinetics, followed by the electrodeposition of Cu, Zn, and Ga. This proposed recycling of CIGS could reduce the impact on global warming compared to virgin extraction processes, and the proposal has the advantage of reducing reagent consumption.

Other research, such as that by Pagnanelli et al. [8], proposed a separation of materials, where depending on the size of the material they are derived to a chemical or thermal treatment. Initially, the material is subjected to primary crushing, followed by secondary grinding and screening. The coarse fraction is sent to a heat or chemical treatment operation. Heat treatment is performed at the degradation temperature of the adhesive (923.15 K). Chemical treatment is performed by washing with a solvent to solubilize the adhesive, which results in the separation of the non-reflective silica-glass material. A 70%–30% cyclohexane–acetone mixture between 353–373 K was used. The intermediate fraction is directly recoverable as glass. The fine fraction contains mainly glass, Si, Cd, Te, Zn, Fe, Al, Ag, and Ti and is sent for chemical treatment. The final fraction concentrated in metals is subjected to alkaline leaching to take advantage of the different amphoteric properties of Te, Zn, and Al and of the same solution to precipitate Fe and Cd. Table 4 summarizes some studies (of the 107 found), their main objective, the technology implemented, and the authors.

Table 4. Studies reported in the literature on solar photovoltaic panel recycling, grouped by the method used.

Stage/Recovery	Technology	Author
Mechanical	Electrohydraulic shredding (EHF)	Nevala [47]
Mechanical	High-voltage fragmentation (HVF)	Song [48]
Mechanical	Waste is powdered and blended with recycled polypropylene (PP) and Low Density Polyethylene (LDPE) to make tiles.	Kokul & Bhowmik [60]
Mechanical	Eccentric stirring mill	Tokoro [61]
EVA recovery	Infrared fiber optic pulsed laser irradiation.	X. Li [49]
Metal/EVA recovery	Supercritical fluid technology.	Lovato [50]
Silicon	Thermal methods (923.15 K) Chemical methods (HF/HNO_3 solution)	Riech [62]
Si wafer recovery	Chemical etching with KOH	Sah [7]
Si wafer recovery	Solutions of HNO_3 and KOH	Shin [51]
Silicon and tempered glass	Solution of HF (48%) and HNO_3 (70%) with H_2SO_4 (97%)	Kang [52]
Metal recovery	Chemical process and sequential electrowinning	W.H.Huang [63]
Metal recovery	Chemical separation with sulfuric acid.	Dias [55]
Metal recovery	Leaching solution with H_2SO_4 and HCl. Crystallization	C.H.Lee [57]
Metal recovery	Pyrolysis, cleaning, and etching sequence.	Frisson [58]
Metal recovery	Sequential electrodeposition.	Song [59]
Metal recovery	Thermal treatment (923.15 K) Chemical treatment (alkaline leaching)	Pagnanelli [8]
Metal recovery	Leaching with nitric acid and an extraction with di-(2-ethylhexyl) phosphoric acid.	F.W.Liu [64]
Metal recovery	Leaching (HNO_3) and extraction (LIX84-I)	B.Jung [65]

3.3. Patents on Recycling Methods

In addition to the research reported in the articles, the processes reported in the patents which provide possible solutions to PV recycling are analyzed.

Pasin [66] proposed a glass recycling method for PV. Specifically, a load of PV is fed onto the conveyor belt and brought to the maneuvering zone between the two toothed rollers. These rotate in the opposite direction, and as soon as the end of the panel is inserted into the operating area the rollers drag the entire panel (PF), where the teeth of the pair of rollers form a first crushing, achieving the separation of the outer glass layer of the panel, thus removing approximately 25%–30% of the glass. Then, 70% of the remaining glass is removed in a third crushing stage.

Shiyuan et al. [67] proposed another mechanical treatment to decompose and recycle PV panels. It consists of six steps: (1) remove the frame and junction box, (2) cut the PV cell into relatively small sizes (100 mm $\times$ 80 mm), then pass the PV cell fragments through an extrusion (3) and shearing (4) process, (5) remove the glass panel layer which is directly recycled, and (6) crush the material particles and sieve them into silicon particles, backplane particles, and EVA particles. The crushing process consists of a nitrogen cryogenic crushing module which generates the low-temperature environment and crushes the junction material particles into silicon particles, backplane particles, and EVA particles. The diameter of silicon particles is greater than 80 mesh, the diameter of backplane particles is greater than 20 mesh and less than 80 mesh, and the diameter of EVA particles is less than 20 mesh.

Xinjuan [68] introduced some mechanical methods such as crushing and rotary churning to disassemble and recover PV modules. As usual, the PV frame, junction box, and glass panel were removed manually. Then, using a shear, the initial distribution was cut into fragments; these fragments were placed in a closed threshing machine. Subsequently, in a metal trap at an electromagnetic transmission frequency of 100–500 KHz, the solder and bus bar were separated, the remaining mixture was placed on an antistatic vibrating sieve, and the silicon powder was sorted to obtain a mixture containing EVA film and back panel fragments. The mixture was sorted using a cyclone separator to obtain back sheet fragments and EVA sheet fragments. The valuable metals were arranged in a vacuum tight vessel to be heated to enrich silver in the gas phase. Tin and copper remained in the liquid phase, and after gas–liquid separation, the liquid phase was heated, tin is enriched was the gas phase, copper was enriched in the liquid phase, and gas–liquid separation was performed to obtain elemental tin and elemental copper.

There are studies that propose the combined use of treatments, such as the one by Zambon and Cerchier [69], who proposed a method that allows the glass to be separated from the silicon and the PV panel in an economical way, by mechanical separation and heat treatment. The PV panel was placed on a conveyor belt that took it through a furnace at over 773.15 K, sufficient to break the insulating junction plates and the back sheet, thus allowing for the separation of the PV layers, where the glass was separated from the PV cells. On leaving the furnace, it was transported to a gravity drop point. The fall caused the glass (usually in pieces), the metal contacts, and the elements of the silicon photovoltaic cells to separate from each other, falling into a collecting box located at the top with a grid. The mesh of the grid allowed for the passage of the pieces of glass and the silicon elements, while preventing the passage of the metal contacts. Below the conveyor belt there had to be a medium that generated air flow. Due to the morphological difference between the fragments and the fluid dynamic behavior, the air flow separated the materials and conveyed them into two collectors after the fall of the glass and silicon, respectively.

Finally, Schrijnemakers et al. [70] reported a method to recycle PV cells by hydrothermal treatment. When the cores of photovoltaic solar cells are subjected to hydrothermal treatment under oxidizing subcritical conditions with nitric acid at 423.15 K or oxygen at 463.15 K, the detachment of the core glass occurs, and residual fragments are generated. Simultaneously, the aluminum back sheet also detaches, and the depolymerization of the encapsulant layer progresses more rapidly, causing the back sheet to detach completely from the core of the module.

Figure 5 summarizes the main methods of treatment of the photovoltaic solar panels used, highlighting the mechanical, chemical, and thermal treatments analyzed in this study.

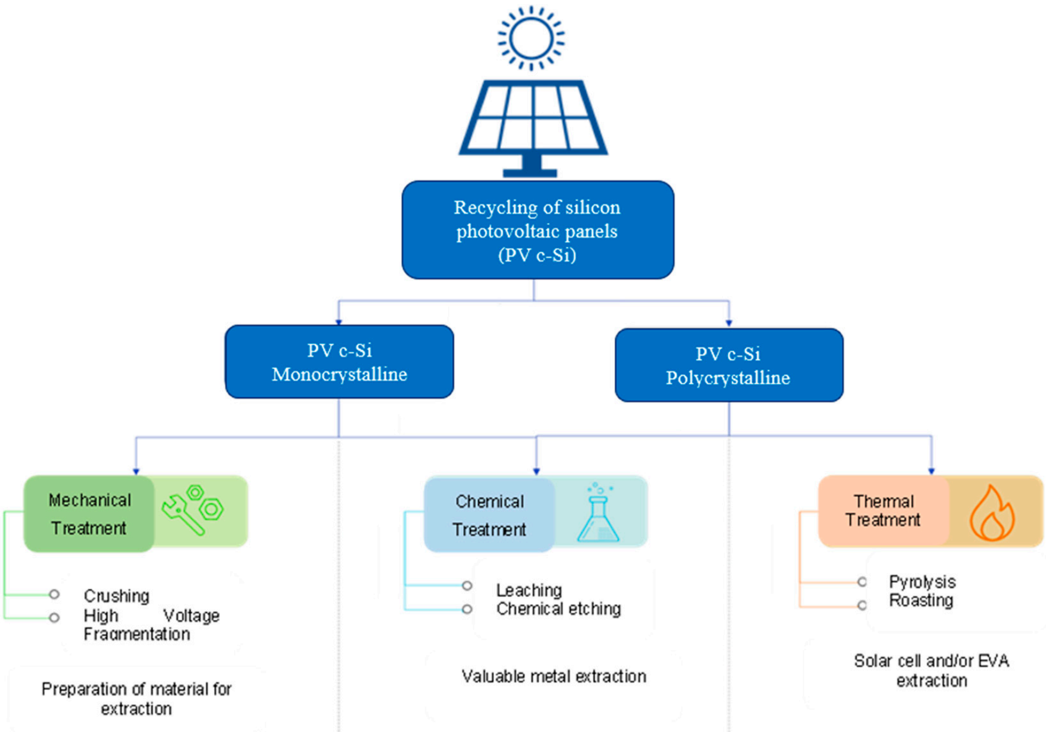

Figure 5. Main treatments used for disused photovoltaic solar panels and the most commonly used processes in each category.

4. Industrial Application Analysis

There are two paths for photovoltaic panels at the end of their useful life. On one hand, certain companies focus on the reuse of PVs that have lost efficiency through reconditioning. This method of giving a second useful life to the panels involves a simple and low-cost process. Second-hand panels can be marketed at a price of approximately $22 USD, which is less than half of the cost of a new panel. However, their value decreases because use reduces their capacity to generate electricity. Although the price of these second-hand panels is much lower than that of a new one, it may not be enough to merit their reuse.

The other option for discarded solar panels is to recycle their components, including glass, Ag, Al, Pb, Cu, Sn, and Si, which can be extracted by different processes. Some recycling facilities utilize mechanical methods such as crushing and grinding to reduce the size of glass, solar cells, and metals without separating them, resulting in what they call “waste glass”. This material can be utilized in industrial or construction applications [71]. Unfortunately, the value that can be obtained for this product is quite low, and there may not be a clear market demand [72].

For photovoltaic panel recycling to be profitable, the process must be able to separate the PV components, thereby increasing the value of the recycled products. Consequently, several companies have emerged that specialize in managing electronic waste and have developed processes for recycling solar panel components. Veolia associated with PV CYCLE is a company located in Rousset, France that dismantles cells and panels to recover glass, silicon, plastic, copper, and silver. These materials are then crushed into granules for reuse by the solar sector as raw material [73]. Another French company, ROSI Solar, operates a recycling plant for photovoltaic panels. The technology developed by this company enables the separation of encapsulated materials from the PVs, through the application of physical, thermal, and chemical methods. This process recovers pure silicon and metallic filaments from the cells without using aggressive reactions, and its reduced operating costs makes the recycling plant economically viable for photovoltaic panel recycling [74].

In Germany, Reiling GmbH & Co. KG has developed a solution for recycling silicon from solar modules on an industrial scale. This process utilizes physical methods to reduce the material and employs innovative technologies to separate the elements of the PV for subsequent use in manufacturing new PERC solar cells [75]. Additionally, Loser Chemie, another German company, has devised proprietary processes involving mechanical and chemical treatment of PVs for solar cell recycling. Like most processes, Loser Chemie begins by shredding the material to reduce its size and then separates it using mechanical methods. Subsequently, a chemical process is employed for the recovery of the semiconductor metals, followed by the metabolization of the aluminum, which can be utilized as aluminum oxide in wastewater treatment [76].

Compton Industriale, an Italian company, specializes in building and designing innovative machinery for waste recycling. In collaboration with companies in the WEEE recycling sector, Compton Industriale tests its prototypes for waste treatment. In terms of solar panel recycling, the company has developed the "Solar 4.0" machine. This equipment performs the delamination and recovery of the glass using special steel tools, allowing for the progressive recovery of all materials within the PV "sandwich" [77]. NPC Incorp is another company that manufactures equipment for photovoltaic panel recycling. They utilize rollers to move and hold the PV until it encounters a steel sheet heated to high temperatures (453.15–473.15 K), which cuts the glass and cells in just 40 s, a process known as the "hot knife" method [78,79].

5. Challenges in the Recycling of Photovoltaic Panels

After reviewing the articles and patents compiled in this study, it is evident that the processing of solar photovoltaic panels is still a developing area. The most challenging stage in this process is the size reduction of the solar panel, primarily due to the presence of the polymer inside (EVA), which provides flexibility and renders the machines typically used for this procedure ineffective [80]. While the selected studies offer several alternatives, there is a need to reduce the cost of this process by eliminating the use of high temperatures and other additives that contribute to its expense. Developing specific machinery for this task and exploring options to modify or create a polymer to replace EVA, which is easier to treat, are potential avenues for improving this stage [81].

Regarding thermal treatments, although they have excellent results, they are associated with significant energy expenditure and have a substantial environmental impact, particularly in terms of air pollution. Therefore, hydrometallurgical treatments hold an advantage in their application.

The challenges in hydrometallurgical treatment include utilizing more environmentally friendly solvents to recover the valuable metals present in the solar panels and minimize the risks of contamination during the recycling process. These green solvents have been successfully used in other studies to treat ore and electronic waste, indicating promising extraction percentages.

One of the limitations of this analysis or review is the scarcity or lack of information about companies, largely because the industrial secrets of their processes are of great interest. This clearly constrains the analysis, making it difficult to propose precise implementations based on available information. It is possible that advancements in research are being applied or could be complemented with what is already available on an industrial scale, but without detailed information, precise recommendations cannot be made.

6. Conclusions

It can be generalized that there are three main types of treatment for PV: mechanical, chemical, and thermal, which are investigated and mentioned in most studies related to panel recycling. On the one hand, mechanical treatment has been identified as one of the most complex stages of the process due to the flexibility of the panels. Processes such as electrohydraulic fragmentation (EHF) and high voltage fragmentation (HVF) have been studied; these reduce the size of the PV components and concentrate them in such a way that a greater selectivity of the components is achieved, improving and facilitating the separation process.

Chemical treatment, such as chemical etching, is mainly based on the dissolution of EVA by some reagents to recover the valuable materials of PV panels. These processes obtain high levels of recovery, but the high consumption of chemicals and/or both liquid and gaseous waste produced during treatment makes it difficult for them to be viable industrial processes. Additionally, they pose greater difficulty and cost in recycling processes.

The thermal method, such as pyrolysis, can separate the layered structure and facilitate the elimination of EVA, rendering it an efficient treatment. However, this process generates other undesirable gaseous products such as acetic acid and methane in the decomposition of EVA, which should be processed to minimize their environmental impact.

Regarding patented technological developments for PV panel recycling, most of them present mechanical separation plus another type of treatment (chemical or thermal) as the complete PV recycling process. However, these present one of the greatest uncertainties because there are parts of the process that remain a trade secret and are not disclosed in the published patent. This uncertainty could be reduced if there were greater access to this information. One way to overcome this obstacle is through cross-reference information, as was carried out in this study, which involves analyzing the three sources and finding patterns or trends. This approach allowed us to conclude that the biggest problem in recycling is the elimination of EVA and size reduction to release the material of interest, which is where most of the proposed works and processes were found.

Finally, as already mentioned, the number of photovoltaic panels that will be in disuse in the coming years is significant, underscoring the utmost importance of continuing research and patenting methods for PV recycling that are effective for resource recovery and have low environmental and economic impact.

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Abbreviations

PV	Photovoltaic panels
WEEE	Waste Electrical and Electronic Equipment
IRENA	International Renewable Energy Agency
REP	Extended Producer Responsibility
IEA	International Energy Agency
EVA	Ethylene vinyl acetate
EU	European Union

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