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ANALYSIS REPORT ON PHOTOVOLTAIC WASTE AS SOURCE OF VALUABLE MATERIALS

Overview on the current material recovery approaches

RT/2023/5/ENEA

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ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

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Abstract

End-of-life photovoltaic (EoL PV) modules are hazardous waste belonging to the category of WEEE. They contain environmentally toxic substances, poorly biodegradable materials but also valuable materials. The recovery of these last is the main goal of PV-waste treatments having the materials separation as initial stage conditioning the process. In order to facilitate the recovery and produce released fractions that are suitable for the recovery of glass, Si, Ag, Cu, Sn, Pb, and Al, the mechanical technics applied in the management of all WEEE without differentiation by type, are the most commonly used. However, a new and appropriate management strategy is required to create more profitable roads leading to the industrialization of environmentally and economically sustainable processes. The exponential increase in the volume of PV-waste imposes key challenges in the more efficient management of EoL PV modules. This paper aims to expand knowledge on critical point in the PV-waste management processes and provides information on types and trends for their treatment. It aims to help to formulate diversified management strategies and plans, shedding light on the usefulness of the adoption of a hybrid approach to optimize the recovery rate and recovered materials purity level to send to recycling.

Key words: *Photovoltaic waste; Materials recovery; Secondary source; Photovoltaic waste treatment; WEEE management.*

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1. Introduction

Waste from electrical and electronic equipment (WEEE) contains various valuable materials whose concentrations depend on the type and age of the equipment and on the manufacturing process from which it comes (Parajuly and Wenzel 2017). Therefore, WEEE can be considered such as a resource from which to draw scarce raw materials.

On the other hand, it also contains hazardous substances having negative effects on the environment and public health. Any treatment of WEEE has the purpose to reduce the hazardous substances and recovery the valuable materials contained therein (Awasthi and Li 2017). However, the heterogeneous composition of WEEE makes it difficult to find a unique and efficient recovering method for the different valuable materials.

In particular, in this waste there are some elements considered as critical by the for their scarcity and high price (Hofmann et al., 2018; Horta Arduin et al., 2020). Between these, some metals such as Cu, Ag, Fe, Al, Sn, Pb and Zn, are either in their elemental form or as alloys, embedded in non-metallic components (Sun et al. 2015). This may highly decrease their degree of liberation and the extraction efficiency, thus their recovery.

Actually, various technological processes are adopted to recovery components and valuable materials from WEEE in order to reuse or recycle them in other products (Chowdhury et al. 2020). Most of the recovering processes includes three main steps: disassembly, mechanical pre-treatment and end-refining (Chauhan et al. 2018).

Disassembly aims to separate the hazardous materials that have to be separately treated, the high value components, reusable as they are and the materials to be sent to subsequent recovering processes (Kuo, 2013; Bovea et al., 2016). Commonly, the most of the disassembly operations are manually performed (Alonso Movilla et al. 2016).

The mechanical pre-treatments consist of shredding to reduce the size of the components and separation of different materials fractions (Chancerel et al. 2009). The size reduction facilitates the release of the materials of interest from the other materials, thus helping the separation process downstream (Kaya 2016). During the separation step, the input material made up of mixed components is split into more fractions having different compositions, in each of which, the concentration of the material of interest is higher than the input material (Cesaro et al. 2017).

The end-refining processes, of chemical or thermal type, allow to obtain the target materials of very high purity that can be reused for new productions (Khaliq et al., 2014; Dodson et al., 2012; Rocchetti et al., 2013).

Most of the companies operating material recovery processes doesn’t work with treatment lines dedicated for each specific type of e-waste. For economic reasons, they use a single or few recovering lines without to differentiate between the diverse types of WEEE. The processes are batch, very rigid with respect to the high variability of materials, the process parameters aren’t dynamically modifiable and consequently their performances aren’t optimised (Baxter et al., 2016; Salhofer et al., 2016; Parajuly and Wenzel, 2017).

The actual WEEE treatment technologies allow to recover four groups of materials: ferrous metals, non-ferrous metals, plastics and glass/ceramics (Bovea et al. 2016).

For recovering metals, the vast majority of the industrial practices provide physical pre-treatments and pyrometallurgical processes, while the hydrometallurgical processes are less used (Ding et al. 2019). These methods not only have low recovery rate, but also a considerable impact on the environment.

The spent PV panels are part of the WEEE and their management follows the European regulations (European Parliament 2012).

The purpose of this work is to highlight the critical issues in applying to the PV-waste the treatments conventionally used for the material recovery from WEEE. We also focus on the need to adopt specific treatment programs for PV-waste. Appropriate strategic planning of the end-of-life PV panels will drive circular economy and enable more effective material recovery.

2. Global growth of PV-waste

Silicon-based PV panels represent the most consolidated PV technology. The average lifetime of a PV panel is about 25 years. Since the number of PV installations became relevant starting from the end of nineties and is actually growing, a dramatic increase of end-of-life PV panels can be expected in the next few years (Santos and Alonso-García, 2018; Mahmoudi et al., 2019; Paiano, 2015).

Several forecasts show that between 2025 and 2030, many PV modules installed will be reaching their end-of-life. The ratio of global PV-wastes to new installations is expected to increase over time, reaching 80% in 2050 (Sica et al. 2018).

Globally, the amount of cumulative PV-wastes could reach 8 million tons by the end of 2030 (Weckend and Heath 2016). In Fig. 1, the estimated amounts of cumulative PV-waste of top five countries at the end of 2050 are shown. China is forecast to have accumulated the greatest amount of PV-waste, United States of America (US) comes next followed by Japan. Moreover, by the end of 2016, cumulative PV-waste has accounted for 250,000 t, this represents only 0.6% of total waste but by 2050, the PV-waste could reach 10% of the global e-waste recorded today (Weckend and Heath 2016).

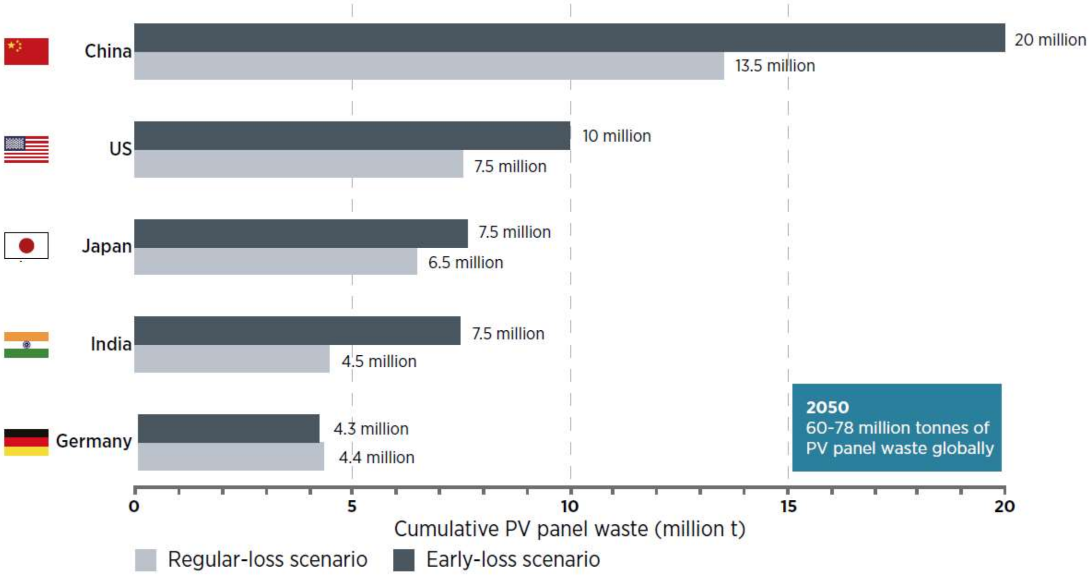

Fig. 1. Estimated volumes of cumulative PV-waste of top five countries in 2050 (Weckend and Heath 2016).

The experiences already acquired with e-waste management can be turned into opportunities for PV-waste management but can't be taken without to be modified and adapted to the specific case. The constituent structure of the PV panels requires the choice of dedicated treatments for the most effective recovery of some materials.

3. Composition of PV-waste

The PV modules are generally classified according to the solar cell type. The cadmium-telluride type modules contain metals such as Cu and Sn even in greater concentrations than Cd. Nevertheless, tellurium is considered as a rare strategic element and there could be a shortage of this metal in the future (Marwede and Reller 2012). Other valuable metals can be recovered from PV modules including gallium, indium and silver (Kuczynska-Lazewska et al., 2018; Savvilotidou and Gidarakos, 2020). However, until today, the absence of an interesting amount of valuable materials and the cost of the recovery treatments have been a limit to the development of the recovering processes, unless public incentives are given (D'Adamo et al. 2017). Nowadays, instead, the awareness of the future shortage of strategic elements and the considerations related to respect for the environment have led the scientific research on the topic to focus on the improvement of the recycling techniques.

Around 90% of the PV market is represented by crystalline silicon panels (c-Si PV panels) with a share of 40% monocrystalline Si panels and 50% of polycrystalline (Kusch and Alsheyab 2017). The remaining 10% of the market is divided among thin-film technology modules based on cadmium telluride, copper-indium-gallium-selenide and amorphous silicon (Azeumo et al. 2019).

The material composition of cumulative PV-waste is shown in Fig. 2 (Kim and Park 2018).

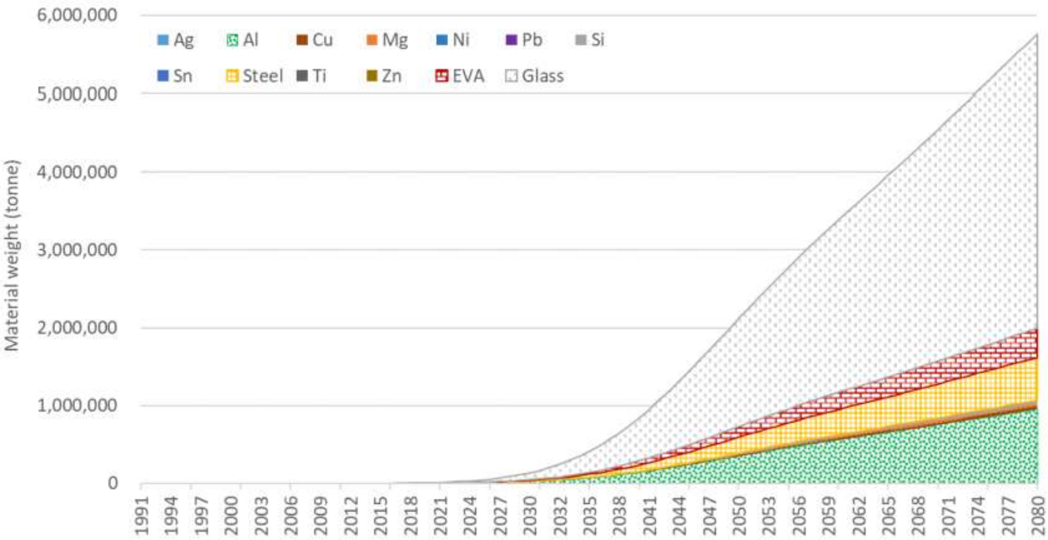

Fig. 2. Material composition of cumulative PV-waste (Kim and Park 2018)

Si-based panels are poor of high value materials and their recovering cost is often higher than the extracting one of the raw materials, making recycling an unfavourable economic route.

The main materials making up the c-Si panels are glass, aluminium (frames) and polymers. However, among the materials contained in low quantities, both hazardous and precious materials are to be found. The relative mass fractions for each component of a typical standard c-Si PV module have detailed in Table 1 (Peeters et al., 2017; Kusch and Alsheyab, 2017).

Table 1. Mass percentages of the main constituents of a typical c-Si standard module ($215W_p$) (Peeters et al., 2017; Kusch and Alsheyab, 2017; Farrell et al., 2020).

Materials	**Amount (wt. %)**				
	Ref[a]	**Ref[b]**	**Ref[c]**	**Ref[d]**	**Ref[e]**
Glass	70.00	74.16	74.00	67.40	74.16
Frame	18.00	10.30	10.00	15.80	10.30
Encapsulant (EVA)	5.10	6.55	-	7.40	6.55
Silicon cell	3.65	3.48	3.00	3.10	3.48
Backsheet	1.50	3.60	-	3.70	3.60

(Tedlar ®)					
Cables	1.00	-	-	-	-
Aluminium conductor	0.53	-	-	-	-
Copper	0.11	-	-	-	-
Silver	0.05	-	-	-	-
Tin& Lead	0.05	-	-	-	-
Contacts	-	0.75	-	-	-
Adhesives	-	1.16	-	-	-
Polymers	-	-	6.50	-	-
Ribbon	-	-	-	1.00	-
Junction box	-	-	-	1.60	-

[a](Gönen and Kaplanoğlu 2019); [b] (Peeters et al. 2017); [c](Farrell et al., 2020); [d](T.-Y. Wang 2016); [e] (Monier and Hestin 2011).

The amount of Pb present in c-Si modules is greater than that Cd in CdTe modules and it is estimated that, in 2050, the costs related to pollution caused by the improper disposal of these metals can exceeded € 2 billion and € 14 million for Pb and Cd respectively (Sica et al. 2018).

The main companies that are active in the management of the PV-waste use different technologies to recovery the materials present in the end-of-life panels and to reduce the environmental impact associated to an improper disposal (Francesca Pagnanelli et al. 2017).

Given the sandwich structure of the PV modules, the delamination of the various layers allows the separation of the different materials and extraction of the valuable materials. However, a unique way to process the different spent PV panels has not yet been identified. Moreover, the recycling practices of PV modules at end-of-life apply different technologies for each of the single stages of the whole recovering process (Chowdhury et al., 2020; Mahmoudi et al., 2021).

In particular, the waste of c-Si PV panels consists of three main streams: conventional materials such as glass and aluminium, rare materials such as silver and copper, hazardous elements such as lead and other heavy metals. While the recovering of conventional components such as glass and aluminium is useful to limit the environmental impact of the processes for obtaining the raw materials, the recovery of rare metals, including the elements which belong to the EU list of the 20 critical raw materials is indispensable also for positive performance of economies. Although rare materials form only 1% of the total panel mass, their economic value is significant enough to make even economically viable advanced recycling systems (Gautam et al. 2021).

Last but not least objective of the processes for the PV-waste treatment is the separation and appropriate management of the toxic and harmful materials they contain.

4. Spent Si-based PV panels as a secondary source of metals

Materials recovery from end-of-life PV panels can save scarce natural resources by limiting their consumption in new production processes. Nevertheless, the recycling of raw materials can reduce the production costs of new products. The valuable metals that can profitably be recovered from the silicon-based PV panels at end-of-life are aluminium, silicon, copper and silver (Xu et al. 2018). The percentage of recoverable aluminium used in the production of the modules, specifically in the frame, practically is 100% (Malandrino et al. 2017). Regarding the silicon, whereas around the 2000s, the recovery of the silicon cells was still considered promising for reuse in new PV panels, nowadays, it isn’t economically convenient due to the expensive processes to obtain it with the high degree of purity required and to the continuous change in the manufacturing processes of the cells (Klugmann-Radziemska et al., 2010; Smith and Bogust, 2018). Instead, the recovery of silicon to destine to different uses, for example metallurgical grade silicon, is interesting (Tao and Yu, 2015; Cucchiella et al., 2015).With current technologies, the range of recoverability of silicon is 76-86% (Paiano 2015). Regarding the copper, its recycling from the PV-waste may represent a valuable supply opportunity of this resource for many countries that haven’t the mineral reserves of this metal and are constricted to import it. The used amount of the primary resources of copper is very high, the reserves still available aren’t many and the global demand of refined copper exceeds the production. This disparity creates the need to reduce the use of primary resources and to encourage the recycling. Copper deriving mainly from the metal strips, can be recovered for 89 % from PV-waste (Paiano 2015).

The most valuable metal that can be recovered in the recycling processes of the silicon-based PV panels is the silver, which is present on the front and back sides of the solar cell as electrical contacts (Tao and Yu 2015). In the c-Si PV panels of first generation, the silver was used for the metallization of the modules. This leaded to a silver consumption of 10-42 g/m^2. Currently, silver consumption is estimated by the manufacturers to be approximately

10 g/m^2 (Feltrin and Freundlich 2008). Since silver is one of the main cost drivers in the cell manufacturing process, its consumption will be progressively reduced or replaced by a substitute.

The recovery percentage for the silver is 40 % of the silver contained in PV-waste (Paiano 2015). Silver belongs to the group of precious metals, which are naturally rare and have high economic value. About 65 % of the annual silver supply comes from the mining sector, but, since the silver demand exceeds the annual mining supply, the recovery from old jewellery, photographic wastewater, solar energy sector and electronics scrap is necessary (Grandell and Thorenz 2014).

The back contacts of Si cells are basically made of aluminum and are also recyclable by chemical etching (Zhang et al. 2013). Actually, the separation of silver, aluminum and lead from the front and back sides of the crystalline solar cells, is executed by chemical etching both to recover silver and aluminium, and to meet the demand of the environmentally friendly disposal of hazardous substances such as lead (Tao and Yu, 2015; Dias et al., 2016).

5. State of the art on materials recovering routes from PV-waste

Actually, the technologies and the best practice for the recovering of the valuable materials from PV-waste are not still defined and consolidated. No specific disposal system for the increasing stream of the PV-waste has been developed or implemented and the industrial plants for treating of the spent PV panels and materials recovering are few and based on energy-intensive and environmentally impacting technologies. Moreover, only few current research in the field of solar panels is focused on the dismantling of the spent panels and processes to recover valuable materials. Consequently, the environmentally sustainable management of the PV-waste still represents a problem requiring an urgent solution. With the aim of responding to the ever growing need to develop an efficient, economical and environmentally sustainable recovery process from spent PV panels, different routes have been taken (Granata et al., 2014; Tao and Yu, 2015; Strachala et al., 2017; Rubino et al., 2021).

To date, most of the PV-waste is delivered to plants that treat WEEE and managed by conventional mechanical processes. Globally, specialized companies handling the PV-waste, having different treatment lines dedicated to the modules, are very few. These all start from the manual or automatic dismantling of the frame and junction box for the recovery of aluminium and copper. Then, mechanical treatments are carried out for the separation of the glass from the rest of the panel. For recovering of the other materials or fractions, the used strategic approaches are of two types: fragmentation and homogenization of the product with subsequent recovery of fractions; delamination of the various layers with recovery of materials or fractions (Giacchetta et al., 2013; Pagnanelli et al., 2016; Deng et al., 2019). The subsequent treatments for the metal recovering often differ radically, based on the specific PV technology.

Currently, the most used industrial process for PV-waste deriving from c-Si panels provides a thermal treatment to eliminate the polymeric fraction and separate the materials. However, problems of contamination of the recovered materials, of environmental impact and energy expenditure are not negligible. Moreover, a subsequent chemical refining treatment is necessary (Dias et al., 2016; Jung et al., 2016; Huang et al., 2017).

Research on the materials recovery from this type of panels is still ongoing and various processes have been proposed on a laboratory or pilot scale (Xu et al., 2018; Sica et al., 2018). The main objective of them is to meet the material recovery targets established by the regulations, ensuring at the same time, economic and environmental sustainability. However, while the material recovery targets appear to be satisfactorily meet, insufficient attention has been paid to satisfy the fundamental pre-requisites of economic and environmental sustainability. These aspects are largely influenced by the different PV panels production technologies and therefore by their variety of composition and by the modifications of the PV panel compositions that are continuously introduced even for the same PV technology (Padoan et al. 2019). It has been demonstrated that the production techniques have led to a progressive decrease in the PV panel metal content, which ultimately caused a reduction into the value of recovered materials. In the case of Ag, its content in Si panels was found to be reduced from 0.14–0.2% on 2003 to 0.07–0.16% on 2023 (Peeters et al. 2017). Even if its concentration is very low, silver represents almost 50% of the economic material value of c-Si panels (Weckend and Heath 2016). Annually the PV industry consumes around 1,500 metric tonnes of silver, which is almost 6% of global Ag production in 2020 (Wirth 2021).

This study contributes to the literature on assessing the applicability of the e-waste management methods to PV-waste and offers to the researchers a tool to understand and overcome the complex issues involved in the development of a sustainable technology for the materials recovering sector from PV-waste.

6. Materials recovering routes from WEEE

Still today, the major part of the e-waste is treated by traditional or crude methods, mainly consisting in breaking, acid leaching and open burning which lead to the release of toxic gases into the atmosphere, heavy metals and other harmful substances into soil and ground water (Awasthi and Li 2017). Furthermore, these crude processing methods aren't sufficiently adequate for extracting the valuable metals with high efficiency due to the heterogeneous composition of WEEE.

Only recently, WEEE management has become an active research field, at global level, both from the point of view of the environmental pollution and human-health and the achievement of the recovery efficiency of resource materials (Ismail and Hanafiah 2020).

Different mechanical, chemical and thermal methods are already being applied to remove hazardous materials and/or recover precious metals from WEEE. However, the current technologies are not simultaneously cost-effective, eco-friendly and free of drawbacks. The mechanical treatments require important capital investments, the chemical ones require the management of acid and corrosive chemical products and the abatement of wastewater, the thermal ones are energy-intensive and the biological ones are slow.

In Fig. 3 a general flow sheet of the materials recovery processes from WEEE by traditional methods is shown.

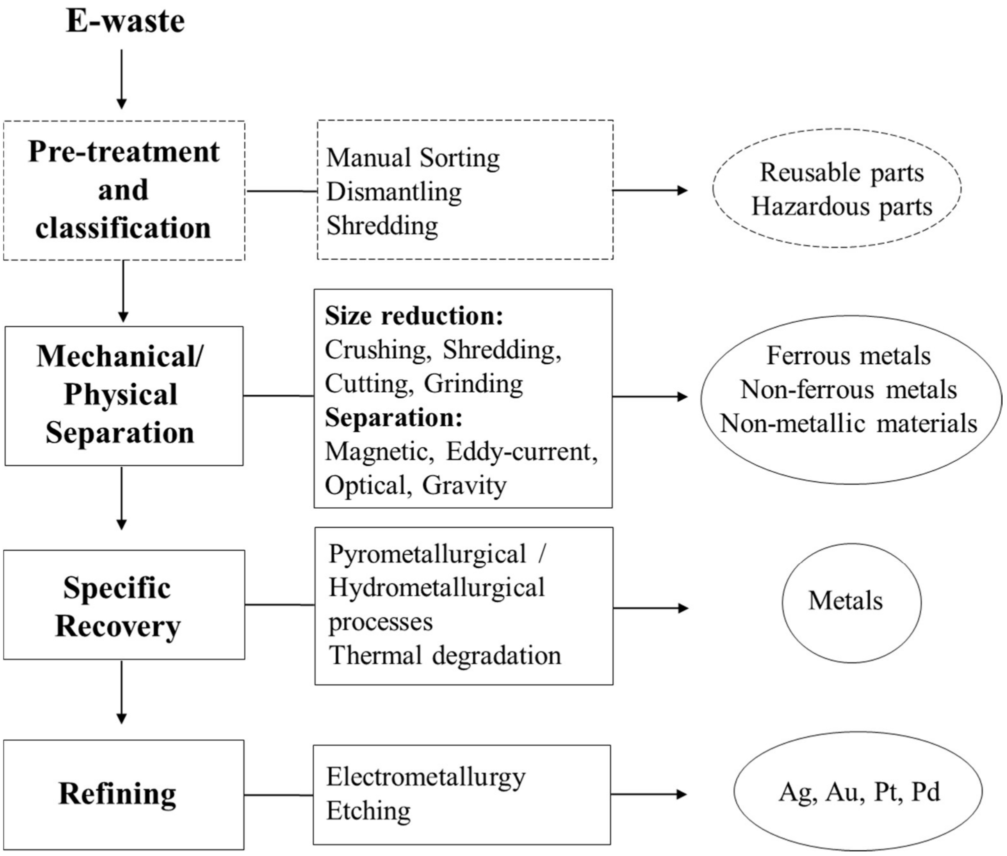

Fig. 3. Main steps of the materials recovery from WEEE by traditional processes.

The dismantling and sorting are the primary treatments, normally used to recover reusable components and separate hazardous components (Lu and Xu 2016). Following the dismantling, an effective liberation of non-metals from metals is required. For this purpose, the size reduction by crushing, cutting, shredding and the density-based separation are the popular methods employed in the second stage. More recently, the separation based on the difference in density and electrical conductivity between plastics, metals and ceramics is used and electrostatic, magnetic and optical methods are employed (J. Wang and Xu 2015). The next step is to screen and identify the specific treatment for the metals recovery, which is very important in terms of environmental and economic benefits and returns. The extraction of metals from WEEE can be carried out by specific methods based on hydrometallurgy, bio-hydrometallurgy or pyrometallurgy (Ghosh et al. 2015).

The last step is the refining to obtain precious metals. Although the current refining technologies have a relatively high recovery rate of precious metals, they are complex and have high economic cost. Hence, more suitable and lower cost approaches, which require simple operations and which are environmentally friendly, have to be investigated and developed to recover noble metals from WEEE.

To date, few studies have been done on the materials recovery from WEEE using a hybrid approach. This paper focuses on the opportunity of adopting a hybrid approach for the PV-waste, evaluating the various recovering methods that have been proposed both for WEEE and PV-waste.

7. Conventional materials recovering practice

7.1 Pre-treatment: dismantling and sorting

The pre-treatment is one of the fundamental steps in the recycling processes of WEEE (Ruan and Xu, 2016; Yoo et al., 2009). Typically, it is of physical type and is used to liberate the encapsulated metallic materials, glasses and ceramics. It can be carried out manually, automatically or with a semiautomatic process combining manual and automatic techniques. The main objectives of the pre-treatment are the sorting, the selective disassembly, targeted on differentiating between hazardous or valuable components, and upgrading to prepare the materials for the following process steps (J. Cui and Forssberg 2003).

The separation of the materials contained in the e-waste requires energy of different intensity depending on the material to be separated. In fact, same materials having to be liberated are locked through fastening by screws, clinks, rivets, other one by wrapping, inserting and packaging and can readily be detached. Instead, the materials locked by means of coating, binding, welding, alloying, filling and encapsulating are relatively difficult to be liberated by mechanical means and sometimes they need special treatments (Kaya 2016). The latter is the case of PV-waste in which, many of the valuable materials are embedded in polymeric materials. The most critical step in the separation process for their recovery is precisely the delamination of the module structure and the elimination of the encapsulant (C. Farrell et al. 2019).

Many dismantling systems have been developed to separate valuable materials making up the WEEE. The most commonly used type of disassembly is the manual separation even if it requires many time-consuming. The manual dismantling to liberate the materials includes manual handing, crushing and disassemble (Ruan and Xu 2016). Although, the recovery efficiency by manual treatment is higher than that of automatic systems, the risks for man and the environment of the manual practices are high. Just consider the exposure to the hazardous materials such as heavy metals and to the noise (Guo et al. 2015). Consequently, manual dismantling should be replaced by mechanical operations. Currently, for economic reasons, the manual dismantling is common in developing countries while the mechanical dismantling is common in developed countries where labour costs are very high (Chi et al. 2011).

In the case of PV panels at end-of-life, the pre-treatment constitutes the primary phase of breakage of the module’s structure. Its purpose is to eliminate the frame and the junction box from the rest of the structure. In most industrial plants handling PV-waste, the disassembly and separation of the frame to recover the aluminium and of the junction box to recover metals from the cables for the electrical connection, are manually done (Giacchetta et al. 2013). The frame helps to keep the panel's structure, to provide mechanical strength and isolate the edges from weathering. It is composed around by 97% wt aluminium and for the remaining part by other elements contained in small quantities: iron, silicon, and nickel (P. Dias and Veit 2018). The latter are typical components of the aluminum alloys (P. R. Dias et al. 2016). Then no further refinement is needed to reuse the metal.

Copper too is recovered from the electric cables quantitatively (Deng et al. 2019).

7.2 Physical/mechanical treatment: size reduction

Usually, manual sorting and dismantling are followed by a size reduction step. This second step of the recycling process chain of the e-waste is a mechanical/physical treatment, in order to determine to which subsequent treatments the materials have to be fed. In fact, to optimize the recycle process economy, a specific material has to be sent to a treatment that is able to recover it, otherwise it is lost. The second step serves to determine the optimum operating conditions to achieve the best compromise between purity grade and recovered amount (Chancerel et al. 2009).

The main aim of the physical/mechanical treatment is to enhance the concentration of the precious metals in the metal fractions. Moreover, another and not secondary target is the removal of plastic to reduce or eliminate the generation of hazardous substances such as halogenated compounds during the thermal degradation treatments.

The step of size reduction is essential for the following step of metals recovery, because it allows to strip metals from non-metals and determines the efficiency of the recovering step in terms of selectivity towards the metals (K. Huang et al. 2009).

Various types of crushers, shredders, grinders and cutters are used for WEEE. Since WEEE are a mixture of glass, glass fibers, ceramic materials, polymers and multiple kinds of metals, they have high hardness and tenacity and hence conventional crushers operate poorly. Often, a two-step crushing is required. First, a shearing action is generated by a crude crusher to reduce the size of WEEE to small particles. Then, these small particles are subjected to a further crushing in a hammer grinder, specially designed for WEEE crushing (Li and Xu 2010).

Shredding or cutting are more effective methods (Wienold et al., 2011). After comminution, fractions of materials of 2–3 mm, 1–2 mm and 0.5–1 mm size are collected (Yoo et al. 2009). However, the conventional treatments for comminution and physical crushing are not optimized for the processing of all kind of e-waste, consequently, the loss of critical metals and the contamination with other metals or non-metallic materials is inevitable (Yoo et al., 2009; (Chancerel et al. 2009). During the mechanical treatment, about 10–35% of valuable metals is loss due to the insufficient liberation, generation of fine particles and inefficient separation.

In the case of PV-waste, the mechanical treatment for size reduction that is commonly carried out on e-waste, prior to the subsequent separation treatments, is not the most suitable treatment to recover the metals. It would produce such as output a fine blend of materials that would require subsequent sorting processes to separate the valuable materials from the scraps. The most profitable way for quantitatively recovering the metals is instead the disassembly of the module’s structure by delamination of its different layers. The preliminary grinding would not be profitable because the materials which were once concentrated, would disadvantageously disperse. The metals of interest recoverable from the modules in fact, mainly silver, copper and silicon, would disperse in the glass which constitutes about 80% of the weight of the module and in the plastic material whose content is around 10% of the weight of the module.

The c-Si PV modules have a typical sandwich structure, consisting of overlapping layers made of different materials (Strachala et al. 2017). The selective delamination of the layers would allow the recovery of different materials with a low degree of contamination.

The selective removal of the glass and the backsheet is certainly advantageous if carried out before proceeding with the grinding of the remaining metal layer. The recovery of the removed glass would allow it to be sold as it is. The removal of the backsheet would allow to avoid the dispersion in the environment of dangerous fluorinated substances, if it were made of the most commonly used material such as Tedlar, or the recovery of recyclable polymeric materials, if it were made of polyesters, used in the most recently manufactured panels.

7.3 Physical separation: materials recovery

Regarding the separation of materials, the high variety of WEEE components makes complex the liberation of the interesting metals. On basis of the physical and chemical characteristics of the various fractions separated by pre-treatment and first mechanical step, the subsequent approaches for the metals separation and recovering are different.

After dismantling and size reduction, the current state-of-the-art regarding the primary material separation from WEEE comprises technologies such as the separation for gravity, magnetic sorting, eddy-current separation and optical separation. Moreover, after the mechanical treatment, the enriched metal fractions are further treated by different metallurgical technologies for the recovery of precious metals. Consequently, the extent of the size reduction to achieve downstream of the pre-treatment depends on the subsequent recycling technologies.

For example, the crushing produces particles of different shapes but a mixture of particles with diversified shapes decrease the effect of the eddy current force and consequently the separation rate (Chancerel et al., 2009; Jujun et al., 2014; Duan et al., 2009).

Actually, among the procedures used for a clean recovery of metals and non-metals from e-waste, the separation in air current is commonly used. However, if the particles have similar size but not a great density difference, this method isn't suitable (Jujun et al. 2014).

In the case of PV-waste, the dry densimetric separation of materials risks leaving a non-negligible part of the silicon and silver in the polymeric fraction and further treatments could be needed. In fact, these separators always divide two fractions of materials with different densities. In the case of a mixture of several materials, the silicon, which has a lower density than metals, could be found in the fraction consisting of polymers and carries with it the silver of the electrical contacts. In such a case, several cascading separation steps are required.

PV-waste delivered to WEEE treatment plants, are processed together with the other e-waste: aluminum frame and junction boxes are either removed manually or crushed and shredded with the entire panel. Then, the remainder of the panel is transported to the glass recycling line. After coarse crushing and shredding the modules, the ferrous metals are extracted and separated. Remaining waste is finely crushed and sorted out by screening devices into three separate fractions of glass, plastic and fine particles. A small fraction of non-ferrous metals is then removed by eddy current devices. The copper deriving mainly from the metal strips can instead be recovered by the common densimetric air separators used to treat WEEE. Lastly, the recovered fraction is sieved to remove impurities like stones, ceramic and plastic materials. The recovered materials at the output of laminated glass recycling facility are glass cullet, aluminum, and copper (Daljit Singh et al., 2021; Isherwood, 2022). In Fig.4 a diagram describing the system of materials recovery from PV-waste in a laminated glass recycling facility is shown. For PV-waste, novel strategies to liberate and separate the other valuable metals embedded in the non-metal components are necessary.

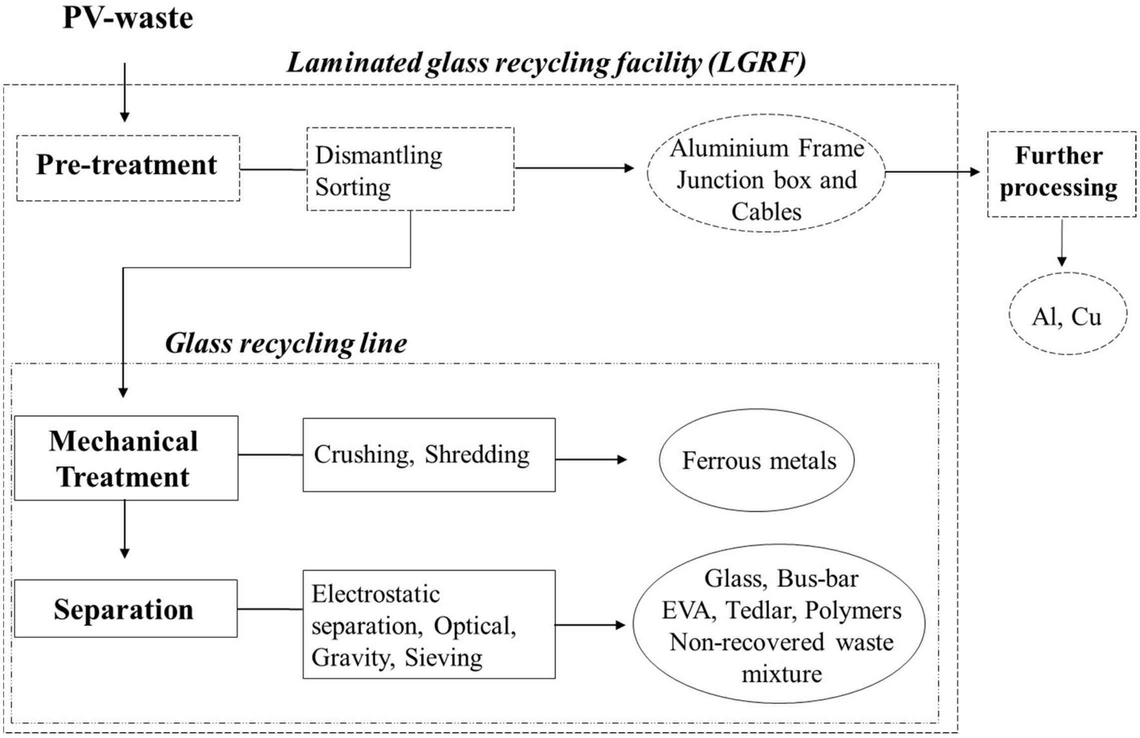

Fig. 4. Main steps of the materials recovery system from PV-waste in a current laminated glass recycling facility (Based on International Energy Agency Photovoltaic Power Systems Programme (IEA-PVPS 2017)).

In the case of large volumes of PV-waste, the electrostatic separation to recover the metals can be used. In fact, it is made of materials with different conductivity and electrostatic properties: conductive, semi-conductive, and non-conductive materials. The outputs of the electrostatic separation are three fractions: conductor, concentrated in glass; middling, in silicon; and non-conductor, in polymers. Even if, the glass isn't a nonconductive material, its particles fall into the conductive fraction because are too heavy. In fact, during the rotation, they gain a speed superior to the electrostatic forces acting, and in addition metallic particles can attach to they through the encapsulating material (P. Dias et al. 2018).

Corona-electrostatic separation and eddy current separation are the technologies generally adopted for separating aluminium and copper from plastic particles. Eddy current separation is not so efficient method to separate different kinds of non-ferrous metals present in PV-waste.

Since, they are firmly united to the inert materials, a more advanced crushing treatment is needed to free them completely.

8. New materials recovering routes from PV-waste

When the spent PV panels are recycled in general-purpose glass recycling facilities, only the glass, the aluminum frames and the copper from the cables are recovered while the remainder of the panels is often burned in ovens. In this way, other valuable materials aren't recovered and the specialty glass is mixed with other glass. Instead, in a recycling plant dedicated to the specific PV panels treatment, like that recently opened in Rousset, France, by Veolia group, the panels are disassembled to recuperate glass, silicon, plastics, copper and silver, which can used to make new products (Faircloth et al. 2019). Moreover, treating c-Si PV panels in laminated glass recycling facilities is promising when it is necessary to carry out small batches periodically. Nowadays, the amount of PV-waste reaching the recycling facilities for WEEE is still negligible compared to the amount of other e-waste. The lack of dedicated PV recycling plants is due to poor PV-waste flows (D'Adamo et al. 2017). Therefore, this poor amount of PV-waste reaching the WEEE treatment plants is treated together with other e-waste. The few panels are partially dismantled, shredded and then sorted, without any dedicated plant. To recover also the other materials, a dedicated PV recycling facility should be considered (Heath et al., 2020; Majewski et al., 2021; Jain et al., 2022). However, current WEEE recyclers have not yet developed the know-how to process PV-waste.

In addition to glass, copper and aluminium, the new developing technologies aim to recover other materials and energy from PV-waste, in new dedicated recovery facilities.

In the Table 2, the materials that can be recovered with the technologies available today and their technological readiness are indicated (Kusch and Alsheyab, 2017; Sica et al., 2018).

Table 2. Valorization options for recoverable materials from spent c-Si PV panels

Component	% by weight	Valorization	Product	Status	Recycling rates (%)
Frame	10 - 12	Metal recycling	Aluminium, stainless steel	Well-established	100
Cables, junction box	1 - 3	Metals recycling	Copper	Well-established	78
Glass	70 - 95	Glass recycling	Flat glass, glass wool, foam glass, hollow glass	Well-established	97
c-Si solar cells components	4 - 6	Metals recycling	Silver, Silicon	Combination treatments required (physical and chemical)	85
Polymers	3 - 15	Heat recovery	Energy	Well-established	-

There is not an optimal process for the treatment of end-of-life modules so far. Among the new developed technologies, a promising process is based on the use of thermo/mechanical treatments to induce delamination by weakening and breaking the interfacial bond between the layers. By means of thermally induced cycles at cryogenic temperatures it is possible to induce the separation of the layers. The process allows materials to be separated and recovered through subsequent thermo/mechanical steps. After the mechanical dismantling for the recovery of the aluminum frame and the junction box, and the smashing of the module to recover the glass and busbar, the PV-waste is subjected to abrasion under cryogenic condition. Then, the fragments of mixed materials are subjected to electrostatic separation from which EVA particles, Tedlar particles and a mixed powder of Si, Ag and Al are obtained, which is sold to other companies (Zhang et al., 2013; Dassisti et al., 2020). Hybrid treatment routes for module recycling, like this one, make it possible to avoid the dispersion of materials that can be re-used and send only a small part of the original PV-waste to landfill. Recycling profitability of conventional mechanical processes can be increased through the development of technologies that enable to increase the recovery of the total mass of waste, in particular of silver, copper and silicon, and to obtain better quality materials, resulting in higher value and utility than those they have in the case of recovery with non-dedicated procedures. The Full Recovery End of Life Photovoltaic (FRELP) process, for example, allows to recover 20% more materials per treated module and to maximize profit with the recovery of silver and silicon (Walzberg et al. 2021).

However, the separation and recovery of the materials require the use of mixed thermo/mechanical techniques and the thermal treatment is not without environmental impact.

Among the innovative treatment processes for recycling PV-waste Loser Chemie has developed and patented a process using mechanical and chemical treatments. The first mechanical step is to crush and separate the materials. The next chemical step is to recover the semiconductor metal. Then, the aluminum metallisation and glass are also recovered (Lunardi et al. 2018).

One of the main obstacles to the growth of the PV recycling industry with the current technologies is the low purity level of the recovered materials, which decrease their market value. Some studies show that the thermal processes carried out to high temperature, chemical processes using solvents but also mechanical processes conventionally used for WEEE allow to recovering materials with a low purity level when used alone. Probably, in order to arise the efficiency and profitability of the current methods, the ideal solution is to use a combination of thermal, chemical or mechanical steps (Latunussa et al., 2016; Ardente et al., 2019). Furthermore, in order to reduce the production of waste and complete a circular economy, a trade-off exists among the cost of the material recovery process and the revenues deriving from the resale of the recovered materials. Silver, for example, has the greatest impact on the net value of the recovery process, hence the effective silver recovery is a way to maximizing revenue. A hybrid process that allows it to be recovered efficiently, compared to a traditional mechanical process that allows only the recovery of copper and aluminum, has a higher net value (H. Cui et al. 2022).

9. Conclusions

This paper discusses the status and trends of end-of-life PV module processing methods. To date, the thermal treatment to separate the module components and the chemical treatment to recover silicon and metals are deeply developed. Instead, the mechanical technology well-established for mixed WEEE, is not fully effective when applied to PV-waste because many value materials are lost. Moreover, it doesn’t allow the recycling of the recovered materials such they are due to their low purity.

New mechanical treatments specially designed for PV-waste are under development. They allow the separating and recovering of the materials by surface abrasion and electrostatic separation. Compared to the thermal and chemical processes, they are environmentally friendly and cost effective. However, the current mechanical technology is primary and needs to be quickly improved to face the growing PV-waste management demands.

The R&D of the new materials recovery processes from end-of-life PV panels indicate that the hybrid choice might be a most promising route.

This paper highlights specific gaps in the available mechanical technology for WEEE when adopted to the specific PV-waste treatment. Moreover, it points out the utility of an approach hybrid to solve the issues associated with the process efficiency, maximization of recovery, obtaining of materials with high purity.

Nowadays, for the development of new industrializable recycling technologies for PV-wastes, a few challenges such as the process complexity, energy requirements and economic feasibility, still remain to be resolved.

CRediT authorship contribution statement

Valeria Fiandra: Conceptualization, Writing- Original draft preparation, Writing- Reviewing and Editing; **Lucio Sannino**: Conceptualization, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability Statements

The authors confirm that the data presented in this study are available within the article in References Section.

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