

Silicon-PV panels recycling: technologies and perspectives

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Millions of photovoltaic panels have been installed in Europe in the past twenty years. The average life of a panel is about 25 years and, for this reason, in Italy there will be soon more than 50 million panels that will require disposal. In order to recover the materials that they contain, various treatment technologies are available nowadays, even if most of them have not yet been industrialized.

The panels installed are mostly (> 90%) based on mono- or poly-crystalline silicon and they are composed, apart from silicon, also of glass, copper, aluminum, tin and silver. The methods of treating photovoltaic waste can be divided into: mechanical, thermal and chemical or a combination of these.

In this paper, the existing methods are analyzed and compared. Nowadays the mechanical method is the most implemented as it is the less expensive. Nevertheless, the silicon cannot be valorized because it is recovered in powder with high contamination due to the mechanical grinding. On the other hand, pure chemical treatment cause also great damages to the silicon because of EVA swelling. The use of the thermo-chemical treatment, is therefore the most promising in order to recover and reuse the silicon. This process has been tested during 2019 on a pre-industrial scale (ReSiELP project) and comprise a heating treatment to burn polymeric fraction combined with materials separation and chemical treatment of the silicon cells. The results of the constructed pilot plant, that are briefly reported, showed the feasibility of recovering several raw materials as well as different issues in the silicon purification process. Finally, the Life Cycle Assessment (LCA) of the studied process, pointed out the importance of the proper heat treatment design and the advantage of silver and silicon recovery, from an environmental point of view.

KEYWORDS: SILICONX, PHOTOVOLTAIC, RECYCLING, LCA, RESIELP PROJECT;

INTRODUCTION

In 2020, the prices of raw materials were upset, from those for manufacturing and construction to those for electronics, defense and aerospace. The main reasons for this derangement were: i) High speed of recovery of manufacturing activities, especially in emerging economies and in China; ii) Low speed of recovery in the extraction of raw materials (copper in Chile, iron ore in Australia); iii) Logistic difficulties, both for restrictions and for the lack of availability of containers.

This crisis evidenced the importance of the raw materials supply, in particular in European Union (EU). In fact, only a minor amount of the European consumption of metals is mined in the EU [1]. Therefore, among Europe's ambitions, there is reducing dependence on third country stocks, increasing the resilience and strategic autonomy and, this optics, the EU periodically produces a list of critical raw materials for European industry on the basis of two parameters: economic importance and risk of supply disruption asses-

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sment [2]. This list of strategic raw materials seems to continuously increase and it contained 14, 20, 27 and 30 materials respectively in 2011, in 2014, in 2017 and in 2020.

Metallic silicon is on this list since 2014. Silicon is hard and brittle crystalline solid with a blue-grey metallic luster, and it is a tetravalent metalloid and semiconductor [3]. It is by far the most important and popular semiconductor material since the emergence of solid-state electronics in the late fifties and the early sixties [4].

The most important property of silicon which determines its application is its degree of purity. In fact, silicon is classified according to its purity: 98% (metallurgical grade), 99.9999% (six nines or 6N) and 99.999999% (eight nines or 8N).

Silicon with 98% purity is used directly in metal industry and, for this reason, it's called "metallurgical grade" silicon. The silicon used for solar photovoltaic (PV) panel wafers must be purified to at least 6N purity and it is usually called "solar grade" silicon. Finally, a small portion of silicon, with purity 8N or higher, is used in the electronic/semiconductor industry as electronic chips (such as transistors, liquid crystal displays, diodes, etc.) and it is referred to as "electronic grade" silicon. The purity of silicon highly affects its price: metallurgical-grade silicon costs 4 US\$/Kg, solar-grade silicon costs between 15 US\$/Kg and 50 US\$/Kg whereas the purest form of silicon costs more than 50 US\$/Kg [5].

More than one million metric tons of metallurgical silicon are produced per year worldwide [6] and most of this production (ca. 70%) is used for metallurgical applications. Applications in a variety of chemical products, such as silicone resins, account for about 30% and only 1% or less of the total production of metallurgical grade silicon is used in the manufacturing of high-purity silicon [7]. The market for this high purity silicon, which has been traditionally dominated by microelectronics applications, has changed due to

the expansion of the photovoltaic industry: nowadays 30% is used by the electronic industry and 60% in the photovoltaic (PV) industry [5].

PV technology is based on the PV cell, the device that is able to convert sunlight into electricity and, although there are various types of solar PV cells, the crystalline silicon (c-Si) cell dominates 80% of the market globally [8]. Thin film solar cells are second generation semiconductor-controlled solar cells made from materials such as cadmium telluride (CdTe), and copper indium gallium (di) selenide (CIGS) but the diffusion of these technologies is still limited.

The silicon PV cells typically are made of 100–500 μ m silicon wafer [9]. In standard manufacturing process of p-type doped crystalline silicon based solar cell, the contacts are made with screen-printed aluminum and silver pastes [10]. Therefore, as it can be seen in Figure 1b, on the rear side of the cell there is an aluminum layer whereas on the other side there are silver contacts (fingers and busbars). Aluminum layer has a thickness of approximately 10 μ m and silver contact fingers have a width of about 0.1–0.2 mm and are 0.02 mm high. Fingers are perpendicular to the busbars with a pitch of typically 2 mm. Busbars, about 1.5–2.5 mm thick, run across the thin contact fingers [11].

Silicon-based PV panels are generally made up of 60 or 72 of these silicon PV cells joined together with copper ribbons and placed between a protective glass, lying on the silicon face exposed to the sun, and a polymeric sheet glued to the back face of silicon (backsheets), useful to protect the panel from atmospheric agents [12]. These elements are joined

SILICON PV-PANELS RECYCLING

Photovoltaic (PV) systems are regarded as clean and sustainable sources of energy [13] and for this reason the cumulative global PV capacity has a growth rate of 47% per year since 2001 [14]. Global installed capacity reached around 400 GW at the end of 2017 and is expected to rise further to 4500 GW by 2050 [8]. Initially the installations were mainly in Europe but the primacy of installed panels is now held by China. In Europe, Italy is in second position in terms of installed power, after Germany [15].

As the estimated life of a photovoltaic plant is around 20-25 years, million tons of PV waste are expected in the world in next 30 years.[16]

Much PV waste currently ends up in landfill. Given heavy metals present in PV modules, e.g. lead and tin, this can result in significant environmental pollution issues. Furthermore, valuable metals like silver and copper are also present, which represents a value opportunity if they are recovered. Hence, the landfill option creates additional costs and it does not recover the intrinsic values of the materials present in the PV modules.

By contrary, recycling end-of-life PV modules is environmentally favorable [17]. Compared with landfill, it effectively prevents toxic and hazardous substances from the PV modules such as lead to enter the soil and groundwater, cau-

sing many negative biochemical and physiological effects on human beings and other species. Effective recycling processes also conserve precious metals such as silver, conventional resources such as aluminum, copper and glass, and energy-intensive highly pure material such as the silicon wafer. Therefore, recycling end-of-life PV modules can significantly reduce the energy consumption and carbon emission, and alleviate lifecycle resource depletion [18]. For example, it was shown that GHG emissions can be reduced by 42% upon the use of recycled silicon material [13].

Nevertheless, only about 10% of PV modules are recycled worldwide [19]. EU has set up one of the main regulatory frameworks based on WEEE directives to address electrical and electronics waste [20]: PV waste are considered electronic waste and recycling End-of-life PV panels is mandatory. Moreover, WEEE Directive 2012/19/EU prescribes to recycle at least 80% of the materials [21].

For this reason, several recycling processes have been proposed to recycle PV panels with the aim to maximize the recovery yield. Unfortunately, they are typically not industrialized yet and, furthermore, insufficient attention has been paid to evaluate whether they fulfil the fundamental pre-requisites of economic and environmental sustainability[22]. The main processes developed for PV recycling are summarized in Figure 2.

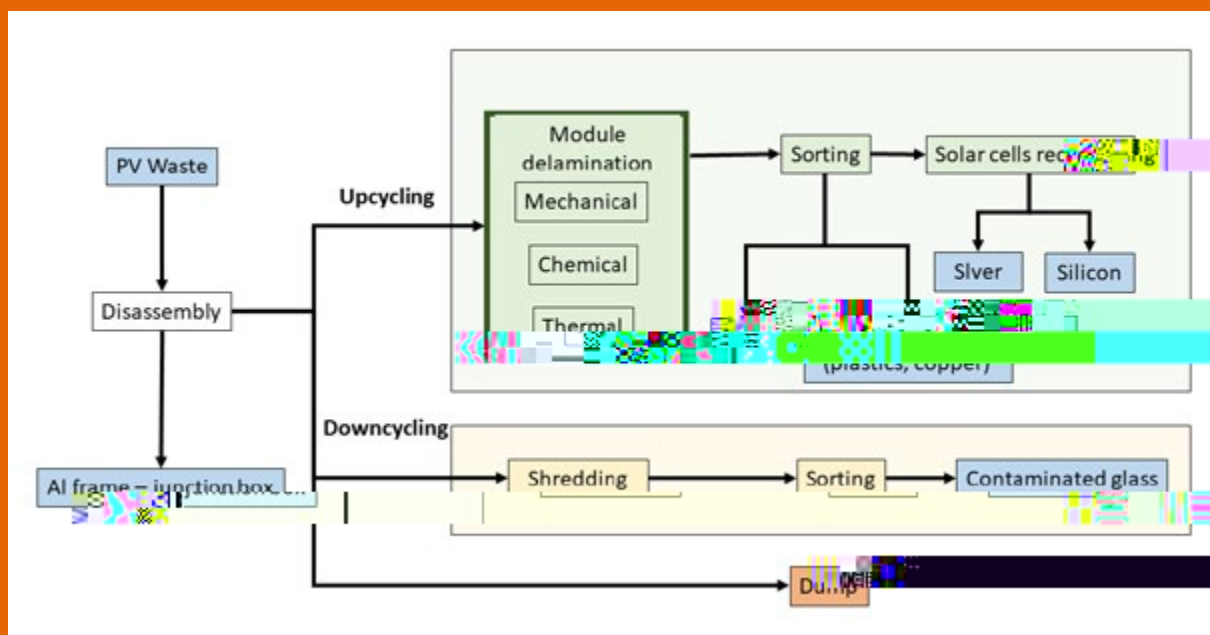


Fig.2 – Scheme of the methods for PV waste recycling/ Schema dei metodi per il riciclo dei rifiuti fotovoltaici.

Current recycling methods are based on downcycling processes, recovering only a portion of the materials and value [19]. Downcycling is typically performed by shred-

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requires a long period of swap-out for the swelling. Another process developed in Photolife research project, after grinding of PV modules, uses cyclohexane for the recovery of glass, copper ribbons and backsheets while performing pyrolysis on the EVA containing PV cells [33]. Its main advantage is the recovery of high-quality glass. Nevertheless, the crucial disadvantage of these chemical techniques is the use of toxic and hazardous chemicals.

THERMAL DELAMINATION

Thermal delamination was one of the first studied methods [34]. In fact, by heating EVA at 450°C it starts degrading and it completes combustion at 500°C [35]. The process can be performed with presence of oxygen (combustion) or not (pyrolysis).

RESIELP RESEARCH PROJECT

RESIELP TECHNICAL ANALYSIS

The possibility to recover solar-grade silicon have been

studied by University of Padova since 2014. In particular, there was investigated a method for silicon recycling that comprises: i) manual dismantling of aluminum frames and junction boxes; ii) combustion of polymeric fraction, iii) mechanical separation of the different components and iv) chemical purification of PV cells. This process, in fact, was able to recover 6N silicon at lab scale. During ReSiELP (Recovery of Silicon and other materials from End-of-Life PV panels) research project, the process was validated in a pilot plant with a capacity of 1500 panels/year specifically realized. The pilot was up and running on May 2019 and had been operating until May 2020, allowing to validate the technology at TRL 7.

The heating treatment in the plant, performed on 1 m² of PV panel per treatment, allowed complete delamination of silicon cells and glass: an example of a PV panel after combustion of polymeric part is showed in Figure 3.



Fig.3 – PV panel after heating treatment in ReSiELP pilot plant/ Un pannello fotovoltaico dopo il trattamento termico nell’impianto pilota ReSiELP

After the heating treatment, the glass and PV cells were separated using aeraulic method patented by University of Padova [37]. Then the silicon cells (2 kg per batch) were chemically treated so that aluminum and silver were removed.

The materials recovered during the project are shown in Figure 4. During this study, 10 tons of EoL PV panels was treated to produce: 1790 kg of aluminum frames (Fig. 4a), 88 kg of copper ribbons (Fig. 4b), 6980 kg of glass with

high purity (Fig. 4c), 140 kg of silicon (Si-cells based) with 2N purity (Fig. 4d) and 2 kg of silver with 2N purity (Fig. 4e) [38].

Silicon was the most difficult material to recycle because it is easily contaminated with other materials (e.g. glass) and was achieved with purity less than 3N, thus lower from the 4N expected. As a matter of fact, the removal of silicon nitride and phosphorous doped layer, to reach 6N, was not performed on this material.

Fig.4 – Materials recovered from the ReSiELP pilot plant: aluminum (a), copper (b), glass (c), silicon (d) and silver (e). / Materiali recuperati dall'impianto pilota ReSiELP: alluminio (a), rame (b), vetro (c), silicio (d) e argento (e).

A net environmental benefit is reached in all the impact categories (negative total values), thanks to the recovery of aluminum, most of all, and copper. Only for FRS, environmental loads are observed (5 t/kg oil eq), due to the fossil

depletion for electricity production, overcoming the benefits achieved by avoiding the investigated primary materials production.

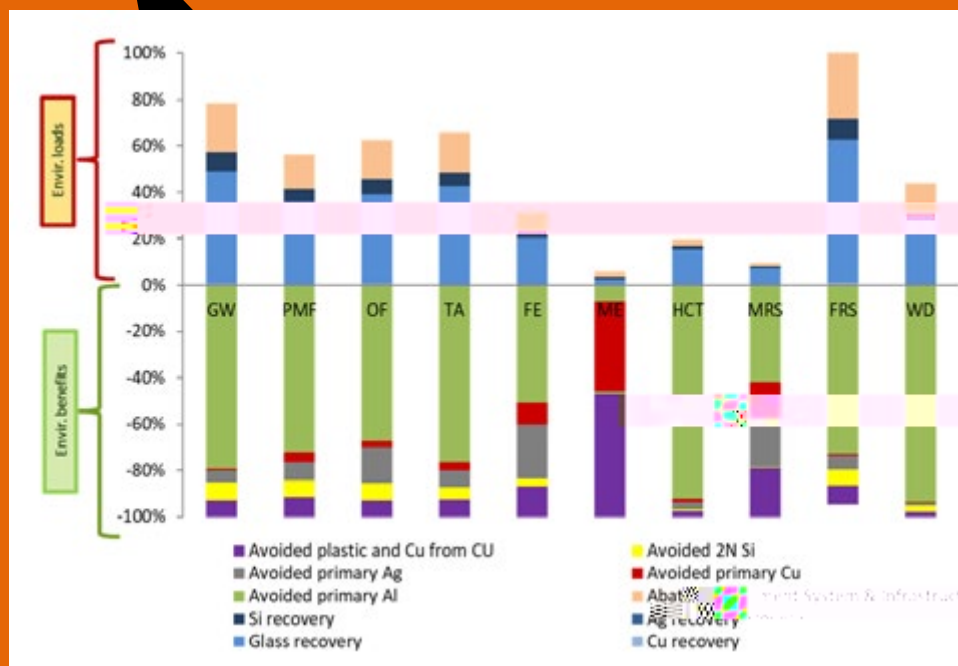


Fig.5 – Percentage contribution of each co-product to the overall environmental impacts of the Recovery line, referred to the selected FU (24 tons of End-of-Life c-Si PV panels). Results include avoided impacts (negative values) due to recovery of material flows [40].

In Figure 5, the contribution of each material to the total impacts of the Recovery line is depicted in percentage terms. Concerning the environmental savings (negative bars), it clearly appears that the avoided production of primary aluminum ranks above the other primary material productions in generating environmental benefits, with contributions higher than -90%, in WD and HCT. The ME impact category is mainly benefited by the recovery of copper from panels (-39%) and of plastic and copper from central units (53%), whereas the benefit gained for the MRS impact category is distributed among the recovery of aluminum (42%), copper (16%) and, at the same extent, of silver and central units plastic & copper (21%). The metallurgical grade silicon (mg-Si) recovery represents another advantage as its smelting plant requires ~20 MWh of electricity and releases up to 5 - 6 tons (t) of CO₂ (and CO) for every ton of mg-Si that is smelted from ore [41].

RESIELP ECONOMICAL ANALYSIS

ReSiELP process is probably the most recent examples of PV upcycling at pilot scale and, as described, it showed

technical feasibility and good environmental impact of the studied process. Nevertheless, at that stage, the process seemed not profitable from economical point of view.

The reasons were mainly due to the cost associated to: i) energy consumption from the furnace (460 eur/ton); ii) high amount of wastewater produced (550 eur/ton); iii) manpower required (1700 eur/ton).

The energy consumption of electric furnace was high due to the fact that it was not continuous, the insulation was poor and the maximum temperature that it can reach was quite low, which limits the treatment capacity. On the other hand, wastewater production was mainly due to the contamination of scrubber solution (130 eur/ton) and to the high quantities of basic wastewater produced for aluminum removal from PV cells (335 eur/ton) whereas the impact of acid WW produced for silver recovery was less significant (85 eur/ton). Finally, high amount of manpower was required because the recovery line, as a demonstrator, was not automatized.

All these issues were identified at the end of the research project and, in order to overcome them, after ReSiELP conclusion a booster project was financed by EIT RawMaterials

in 2020: "9PV". This project allowed the design and realization of a new pilot plant which comprises a continuous furnace and a machine for mechanical separation of treated material. This research is still in progress with the target of improving the efficiency of the process previously studied. The development and upscaling of recycling technologies for PV waste have huge importance because of the high quantity that will require disposal in next 20 years.

CONCLUSIONS

High amount of PV waste is expected in next years. A typical PV panels is based on silicon technology and contains important resources such as glass, aluminum, copper, silver and silicon. Silicon, in particular, is a critical raw material for European Union and EU directive prescribes recycling of PV modules. Therefore, it would be very important the implementation for PV waste of an upcycling process: a treatment able to recover and valorize all these materials.

Nevertheless, PV recycling is still an open challenge and, up to now, only downcycling process is performed at industrial scale. This process consists in grinding and sorting and only contaminated glass is recovered from PV waste. Upcycling of the material requires delamination of PV panels and this can be performed by means of mechanical, thermal or chemical treatment. Each delamination method has its

drawbacks: mechanical treatments provoke damages to the PV cells preventing pure silicon and silver recovery, chemical treatments require toxic chemicals and combustion/pyrolysis generates toxic fumes.

Among these techniques, thermal delamination seems the most promising route to valorize metallic silicon, because the PV cells are recovered with few damages and high yield and can be chemically treated for silicon purification. During ReSiELP research process, a thermo-mechanical and chemical process was studied and upscaled at TRL7 by University of Padova. This research proved the industrial feasibility of the idea and ENEA showed that the process can have positive environmental impact, due to the recovery of raw material with high embodied energy. However, in order to increase its economy, an optimization of the recovery line was necessary, which is now under studying.

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Riciclo dei pannelli fotovoltaici a base Silicio: tecnologie e prospettive

Milioni di pannelli fotovoltaici sono stati installati in Europa negli ultimi vent'anni. La vita media di un pannello è di circa 25 anni e per questo in Italia ci saranno presto più di 50 milioni di pannelli che dovranno essere smaltiti.

I pannelli installati sono per la maggior parte (> 80%) a base di silicio, mono o policristallino, e sono composti da vari strati laminati assieme (Figura 1) e contenenti, oltre al silicio, anche vetro, rame, alluminio, stagno e argento. Il silicio è uno dei materiali più interessanti da recuperare, in quanto è annoverato fra le materie critiche per l'Europa. D'altra parte, per trovare applicazioni che lo valorizzino, il silicio richiede una purezza molto elevata e ciò rende molto difficile il riutilizzo del silicio recuperato da rifiuti.

In generale il riciclo dei materiali presenti nel pannello fotovoltaico è benefico per l'ambiente in quanto da un lato evita la contaminazione del terreno con metalli potenzialmente pericolosi (principalmente piombo e stagno nel caso di tecnologia a base silicio cristallino), dall'altro contribuisce alla conservazione delle risorse con la conseguente riduzione delle emissioni di anidride carbonica in atmosfera.

Purtroppo ad oggi nel mondo solo circa il 10% dei pannelli viene riciclato e la maggior parte finisce quindi in discarica. In Europa il riciclo dei moduli fotovoltaici a fine vita è altresì obbligatorio, in quanto essi sono classificati come rifiuti elettronici. Attualmente il metodo di trattamento più utilizzato è di tipo meccanico, perché trattato del più economico: essenzialmente i moduli sono macinati recuperando un vetro contaminato di qualità piuttosto bassa. Questo processo infatti è definito come un "downcycling" del materiale. Il silicio, ad esempio, non può essere valorizzato perché viene recuperato come polvere molto contaminata con altri materiali.

Una valorizzazione del materiale, o "upcycling", è possibile solamente delaminando i diversi strati del pannello. A questo scopo sono state sviluppate negli anni diverse tecnologie di trattamento, anche se la maggior parte di esse non è ancora stata industrializzata.

Queste tecniche possono essere suddivise principalmente in meccaniche, termiche e chimiche.

I metodi meccanici si concentrano sulla rimozione del vetro attraverso coltelli o lame riscaldate. Questi metodi non riescono però a separare le celle fotovoltaiche ed i contatti in rame dalla parte polimerica che li ingloba (Figura 1).

Un trattamento chimico è possibile sia per mezzo di solventi inorganici (acidi forti) che organici (es: limonene o cicloesano) ed ha il vantaggio di consentire il recupero di un vetro di alta qualità nonché, eventualmente, del backsheet. D'altra parte, il trattamento chimico può provocare anche gravi danni alle celle fotovoltaiche, a causa del rigonfiamento indotto dal solvente, compromettendone un recupero efficiente. Inoltre ha la complicazione di impiegare solventi tossici e spesso infiammabili.

Infine un approccio di tipo termico, quali pirolisi o combustione, consente di delaminare le diverse parti del pannello eliminando la frazione polimerica, ma richiede un accorto trattamento delle emissioni prodotte, in particolare nel caso in cui il backsheet contenga fluoro.

carichi ambientali maggiori sono dovuti all'energia elettrica utilizzata per il trattamento termico e per il sistema di abbattimento (Figura 5). Lo studio ha quindi evidenziato l'importanza di una corretta progettazione di queste parti dell'impianto in modo che siano energeticamente efficienti, nonché ha confermato il vantaggio dal punto di vista ambientale del recupero di alluminio, rame, argento e silicio.

Nonostante i buoni risultati dal punto di vista tecnico ed ambientale, il processo non sembrava redditizio dal punto di vista economico. La ragione era principalmente dovuta ai costi connessi a: i) il consumo energetico del forno; ii) elevata quantità di acque reflue prodotte per l'operazione richiesta.

Tutte queste problematiche hanno portato, dopo la fine del progetto, alla successiva progettazione e realizzazione di un nuovo impianto pilota che comprende un forno continuo e una macchina per la separazione meccanica del materiale trattato. Questa nuova ricerca (9PV) è stata finanziata nel corso del 2020 con un progetto booster dall'EIT RawMaterials ed è ancora in corso con l'obiettivo di migliorare l'efficienza del processo studiato in precedenza. Studi come questi sono molto importanti affinché la grande quantità di rifiuti fotovoltaici prodotta nel prossimo futuro venga adeguatamente riciclata.