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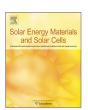
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Life Cycle Assessment of an innovative recycling process for crystalline silicon photovoltaic panels



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ABSTRACT

Lifecycle impacts of photovoltaic (PV) plants have been largely explored in several studies. However, the end-of-life phase has been generally excluded or neglected from these analyses, mainly because of the low amount of panels that reached the disposal yet and the lack of data about their end of life. It is expected that the disposal of PV panels will become a relevant environmental issue in the next decades. This article illustrates and analyses an innovative process for the recycling of silicon PV panel. The process is based on a sequence of physical (mechanical and thermal) treatments followed by acid leaching and electrolysis. The Life Cycle Assessment methodology has been applied to account for the environmental impacts of the process. Environmental benefits (i.e. credits) due to the potential productions of secondary raw materials have been intentionally excluded, as the focus is on the recycling process. The article provides transparent and disaggregated information on the end-of-life stage of silicon PV panel, which could be useful for other LCA practitioners for future assessment of PV technologies. The study highlights that the impacts are concentrated on the incineration of the panel's encapsulation layers, followed by the treatments to recover silicon metal, silver, copper, aluminium. For example around 20% of the global warming potential impact is due to the incineration of the sandwich layer and 30% to the post-incineration treatments. Transport is also relevant for several impact categories, ranging from a minimum of about 10% (for the freshwater eutrophication) up to 80% (for the Abiotic Depletion Potential - minerals).

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1. Introduction

Photovoltaic (PV) is one of the renewable technologies that has been gaining importance globally in the last decade. The International Energy Agency (IEA) estimates a total installed power of PV of around 136.5 GW at the end of 2015 [1]. Among the different technologies, crystalline-silicon PV technology still dominates the market, accounting for 85–90% of the technology share [2].

Europe still holds the biggest PV installed capacity, representing 70% of the total installed capacity worldwide [3]. The annual PV Installation in Europe rose from 58 MW/year in 2000 up to 10,975 MW/year in 2013 [3]. In 2012, the electricity produced from PV technology in the European Union (EU) accounted for 2.2% of the total electricity generation [4]. This rapid increase has been largely boosted by European policies and regulations. For example, the European Union (EU) strategy for climate and energy that

imposes member states to achieve a target of 27% of the share of renewable energy to be consumed in the EU by 2030 [5].

Given the quantity of the already installed PV panels and its predicted growth, the amount of waste PV panel is estimated to reach 9.57 million tonnes in 2050 [6]. The recycling of waste PV panels will represent a challenge for waste treatment plants in the future. Difficulties related to the end-of-life (EoL) management of the panels (including dismantling of the plant, collection and transport) will be higher and higher, especially considering the large heterogeneous distribution of panels at urban scale [7].

However, the issue on how to properly treat the PV waste raised public attention only recently. For example, the first version of the EU Directive on the "waste of electric and electronic equipment (WEEE)" in force until 2012 excluded PV waste from its scope [8]. In the recast of 2012, the new Directive 2012/19/EU included PV among the list of electric and electronic equipment (EEE) which requires dedicated treatment at their EoL [9]. As regards to the minimum requirements for the treatment of PV panels, the European Commission (EC) also recently requested the European Standardisation Organisations to develop specific

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standards for the treatment of WEEE, which are still under development [10].

Several reasons can be related to this late inclusion of PV waste within the waste legislation and, in general, to the low attention to the potential burdens of the EoL of PV. First of all, PV panels have a potential very large lifetime, up to 25–30 years [11]. Therefore there was a limited interest into investigating EoL aspects so far.

Secondly, the amount of waste PV panels reaching the recycling facilities nowadays is still negligible compared to the amount of other WEEE [6]. Current WEEE recyclers have not yet developed the know-how to process such new waste. According to our interview with two recyclers in Italy, the amount of waste PV reaching their plants is in the order of few panels per month, which are partially dismantled and then treated, together with other WEEE (i.e. by shredding plus post-shredding sorting), without any dedicated plant.

Moreover, policy makers have been trying to promote the diffusion of PV technologies in the last years. In this context, the setting of mandatory requirements for the EoL treatment could have been seen as an obstacle to the effective uptake of this emerging technology.

Furthermore, the lack of scientific evidences about the potential impacts and benefits related to the PV waste treatment did not stimulate policy makers to intervene. As declared by some authors (e.g. by [12,13]), the EoL phase was generally excluded from the studies on the lifecycle of PV technologies because the installations were relatively new and no data or few information were available, mainly referring to small-scale recycling processes. Other studies roughly assimilated the impact of PV recycling to the recycling of other products, as automobiles [14].

However, a study by BiolS [6] already highlighted potential environmental problems related to the improper disposal of waste PV panels, as: leaching of hazardous substances (as lead and cadmium), losses of conventional material resources (as aluminium and glass), and losses of precious and scarce metals (as silver, gallium, indium, germanium). The recast of the WEEE Directive in 2012 intended to regulate this aspect and avoid such future environmental problems to occur. As highlighted by the PV-cycle, the largest pan-European Producer scheme for solar technologies, under the WEEE Directive "PV companies will not only have to ensure the collection and recycling of their discarded EoL products but are required to also guarantee the financial future of PV waste management" [15].

In the last years the interest upon new technologies for the PV panels recycling raised, as proved by the innovative treatments developed by 'Deutsche Solar' for the recycling of crystal silicon panels, and by 'First Solar' for the recycling of cadmium-telluride (CdTe) panels [6].

However, a detailed analysis of the impacts related to such treatments in a lifecycle perspective is still missing in the literature.

A recent research project has been financed by the EU "LIFE programme", titled "Full Recovery End of Life Photovoltaic project-FRELP", aiming at maximising the recycling of the different material fractions embodied into silicon PV panels [16]. This project was developed during the period 2013–2015 in partnership with "PV Cycle Italy". The FRELP project had the objective of developing an innovative recycling process (successively defined as 'FRELP process') for c-Si PV waste aiming at maximizing the recovery of all the material fractions contained into the panels.

This article aims at applying the Life Cycle Assessment (LCA) methodology, as harmonised by international standards [17], to the process developed by the FRELP project. The objective of the article is to provide detailed information about the EoL of the panels, which could be beneficial both to assess the impacts of the proposed recycling process and also to provide detailed lifecycle

inventory data potentially useful for other studies on the LCA of PV panels.

The article first illustrates the analysis of the state of art in the scientific literature of studies about the EoL of PV panels. Successively, the article analyses all the phases of the FRELP recycling process and accounts for the lifecycle impacts following the LCA phases set by the standard ISO 14040 [17].

2. State of art: end-of-life of silicon photovoltaic panels

A first study on the technical and economic feasibility of the recycling of crystalline PV modules was already presented in a photovoltaic technology conference in the 1990s [18]. However, the interest on PV recycling started to rise around one decade later. For example, the study by Fthenakis [19] identified the challenges and the possible approaches for PV recycling in USA, concluding that such recycling was technologically and economically feasible but not without careful forethought.

The methods adopted so far for the recycling of silicon PV panels have been based on physical treatments, chemical treatments or a combination of both. A description of these methods is provided in Table 1. In particular it was noticed that the Ethylene Vinyl Acetate (EVA) is the most commonly used material for a layer placed to protect the components of PV module from foreign impurities, moisture, and mechanical damage [20]. The removal of the EVA encapsulation layer has been recognised as one the most challenging steps in the recycling of crystalline silicon PV panels [21].

A completely different treatment to recycle crystalline-based solar cell into building material has been presented by Fernández et al. [22]. This treatment foresees the incorporation of grinded used solar cell to calcium aluminate cement matrix at maximum 5%.

Nevertheless, all these studies contain very little information about the environmental impacts of the proposed recycling processes. The study of Frisson et al. [23] estimated the energy consumption of a standard PV module (with 125×125 mm multicrystalline silicon cells) compared to a module using recycled wafers. The latter resulted in having 40% lower impacts per kWh of electricity produced. However the study did not provide disaggregated information on the recycling process considered. Klugmann-Radziemska and Ostrowski [26] observed that the acid etching mixtures used for the chemical treatments can contain high amounts of toxic substances (e.g. nitrogen oxides, fluorides and different silicon species), which require costly disposal measures. However, also in this case, no further detail was provided.

On the other hand, the lifecycle environmental impacts due to the production and use of PV technologies have been presented in a number of LCA studies available in the scientific literature, as emphasised by several recent reviews [31–34]. However, these reviews either did not consider at all the EoL stage of the panels, or simply highlighted the lack of information about the decommissioning of the PV plants and the EoL of the panels. In the review of Peng et al. [35] some LCA studies, which partially investigated PV recycling, were reported. In particular, this review reported some draft figures about energy consumption due to PV recycling, as calculated by Wild-Scholten [36]. The report estimated that 250 MJ, 240 MJ and 150 MJ were used for the taking back and recycling of mono-Si, multi-Si and CdTe PV systems, respectively. However the study is not clear in what functional unit was considered for these results.

Frankl et al. [37] studied the production of 1 kWh of electricity by different PV technologies and estimated that decommissioning and disposal of a ground mounted PV plant accounted for only 4% of the lifecycle greenhouse gas emissions. Lower impacts were estimated for other impact categories. However, this study did not

Table 1Processes developed for the recycling of crystalline PV panels.

Studied process	Outcomes	Reference
Pyrolysis (in a conveyer belt furnace or in a fluidized bed reactor).	Pyrolysis-based processes allowed to separate 80% for the wafers and almost 100% of the glass sheets.	[23]
EVA removed by dissolution in organic solvents.	The silicon cell was separated without any damage from a single cell module by dissolution in trichloroethylene at 80 °C for 10 days.	[18]
Pyrolysis process of EVA at different heating rates under different oxidising atmosphere.	The pyrolysis behaviour of EVA (e.g. melting point, pyrolysis gas amount) is strongly influenced by the content of acetate in the EVA.	[24]
Thermal and chemical process applied to a large sample of modules produced in the 80s (namely the Deutsche Solar's process).	The process achieved a separation yield of about 76% of the cells, suitable for reuse. This yield can be influenced by damages on the modules.	[25]
The first step is the separation of cells, comparing chemical process and thermal treatment and the second step is the refining of separated cells, comparing laser treatment and chemical treatment.	Thermal treatment was shown to be sufficient in the first step while the chemical was shown to be more advantageous in the second step.	[21]
Thermal process to remove the EVA layer, followed by a series of etching treatments to separate silicon and other metals.	The chemical processing is the most important stage of the recycling process. The chemical treatment conditions need to be adjusted in order to achieve a required purity level of the silicon.	[26]
Two-step heating process of EVA followed by chemical processes with acid and alkali	85% of copper and 62% of the silicon were separated.	[27]
Dissolution of EVA by organic solvents and treatment of the PV cell by chemical etching	The process allowed to recover up to 86% of the silicon with very high purity.	[28]
Two processes based on a two blade rotors crushing followed by thermal treatment and two blade rotors crushing followed by hammer crushing.	Results showed that the two blade rotors crushing followed by hammer crushing was the preferred option to recover 80–85% of the glass.	[11]
Prototype induction system to separate the glass sheet from displays screen and PV panels.		[29]
After removing the aluminium frame and the junction box, the panel is cut by a circular saw and then heated in a furnace. Successively, residues are separated by manual and mechanical treatments.	Process developed at the lab scale. Low efficiency in the recovery of some	[30]

provide information on what type of processes PV plant underwent at the EoL.

Müller et al. [38] provided so far one of the most detailed environmental analysis concerning the EoL treatment of multi-Si PV module according to the "Deutsche Solar" recycling process. The impacts referred to the treatment of a standard PV module, having 72 cells of dimension 125 mm x 125 mm, Tedlar as backside foil and an aluminium frame. As mentioned in Table 1, rather than material recycling, this process aims at separating PV wafers for their potential reuse in new panels. Müller et al. [38] estimated that the reuse of the above mentioned module implied an overall reduction of the global warming by 59.2 kg CO_{2eq}, of the acidification by 0.4 kg SO_{2eq}, and of the resource depletion by 6.1*10⁻⁸ kg Sb_{eq}. These reductions are due to the avoided production of new cells. However, the study did not provide details on the life cycle inventory with the input and output occurring in each process stage. Müller et al. [38] also compared the impacts of the PV recycling process to the treatment in a municipal incineration plant (with subsequent landfill) and to the shredding of the module (with subsequent sorting). In both the cases, the incineration and the shredding implied lower impacts, but also lower recovery yields. However, authors justifies this result with the different large scale of the incineration plant in comparison to the small scale of the recycling plant. No further details are provided about the yields of these processes.

The study by the Fraunhofer Institut [39] performed a screening LCA to analyse the impacts of the recycling of spent silicon PV modules. The functional unit was the processing of one ton of Si-PV module waste in a glass recycling line. According to this study, in the first step, aluminium frames and junction boxes are removed in a manual process. The prepared PV module waste is then fed into a shredder by using a wheel loader. The shredded PV modules enter the glass recycling line which includes a manual pre-sorting, crushing of the laminates, separation and extraction of materials. The output materials are separated according to their material fractions like ferro-metals, plastics, PV-cell/polymer foil laminate and glass cullet. The glass recycling line mainly requires electricity for running the processes (shredder, conveyors, hammer mill, compressor). The Fraunhofer study [39] estimated very

low impacts for the recycling compared, for example, to the potential environmental credits estimated for the recycling of valuable materials. Results have been presented only in an aggregated form. This study also evidenced the relevance of the transport distance for the eutrophication and photochemical ozone creation potential impacts. However, it is highlighted that this type of recycling was characterized by a low technological innovation and it did not focus on the recycling of precious material fractions, as silicon or silver.

Corcelli et al. [40] recently presented the preliminary results of an application of the LCA to a laboratory-scale recycling process for silicon PV panels (as illustrated by Rimauro et al. [30]). The considered functional unit was 1 m² of c-Si PV panel. These authors introduced different recycling scenarios according to lower and higher recycling and recovery yields obtained. Also in this case results have been presented as aggregated and normalised impacts, without the detail of each treatment step. Moreover, negative impacts have been estimated for all the considered impacts categories, due to the accounting of the potential credits for secondary materials productions.

It was observed also a lack of guidance on how to model the EoL phase of PV panels. For example, the International Energy Agency [41] developed some guidelines for the LCA assessment of photovoltaic electricity, aiming at supporting the development of LCA studies on the sector and also at assisting in identifying product-recycling issues. Nevertheless, the IEA guidelines did not provide detailed guidance on how the EoL of PV panels should be modelled, mentioning only that the system boundaries should clearly state if the disposal, the transportation and recycling stages have been included for both the PV modules and the balance-ofsystem [41]. Nevertheless, the International Energy Agency identified the need to develop and implement recycling solutions for the various PV technologies as short-term/mid-term research priority [42]. Guidelines should be also developed concerning the assessment of the potential benefits and burdens due to the distributed generation from PV panels, including also recommendations for the minimisation of impacts due to the dismantling and collection of the waste panels.

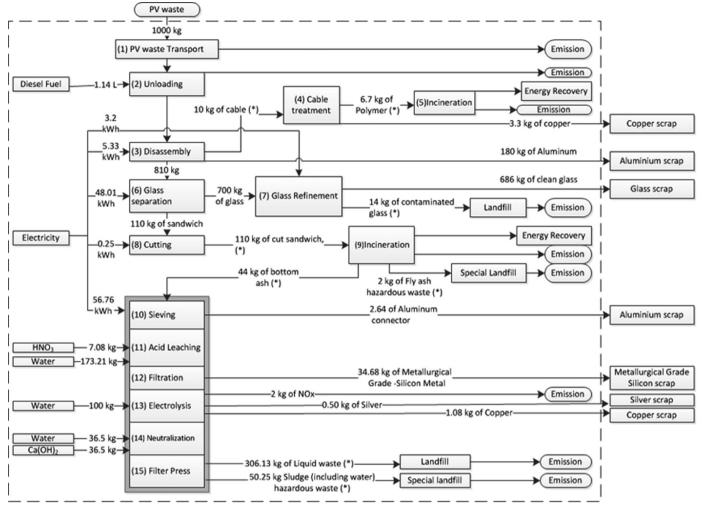


Fig. 1. System boundaries of the LCA of the silicon PV waste recycling process (transport between the processes is highlighted with an asterisk (*)).

Additionally, also LCA databases seem to be missing detailed information on the EoL of PV panels. For example, the Swiss ecoinvent database assumed that larger metal parts of the system and silicon are recycled, without considering any environmental impacts or benefits due to the recycling [43,44]. Jungbluth et al. [45] also highlighted that the environmental impacts caused by the dismantling, transport to recycling plant and further treatment of the PV panel should be investigated as soon as reliable data would be available.

Analogously, the GaBi LCA professional database does not include impacts of EoL of PV panels since, according to the authors, so far there are no common technologies to reuse/recycle them [46].

Few LCA studies were also available about the recycling of other PV technologies. The LCA of the recycling 1 m² of CdTe PV modules has been presented by Held and Ilg [47]. The recycling treatments were based on the "First Solar" process as a sequence of mechanical and hydrometallurgical treatments. Held and Ilg [47] found that such process implied, among the others: global warming: 6 kg CO_{2eq}; primary energy demand: 81 MJ; acidification potential: 9.1 kg SO_{2eq}.

Shibasaki et al. [48] analysed the production of 1 GJ of electricity produced by thin-film solar modules. This study analysed also the impacts of a recycling process based on: module delamination, removal of the EVA layer, and removal and recovery of the metals. Shibasaki et al. [48] concluded that the recycling of

thin-film PV is feasible, but this process contributes up to 4% of the life cycle impacts of the modules.

In conclusion, this survey highlighted that some recycling processes have been developed for silicon PV panels, but these are mainly at the pilot stage. However, the studies describing such processes did not investigate in details the life cycle inventories and the consequent potential life cycle impacts related to the recycling treatments. Information about the efficiency of the recycling and the achieved yields for different materials are generally lacking or incomplete. Nevertheless, EoL has been recognised as a potential critical aspect for the lifecycle of the panels.

Although several LCA studies applied to PV technologies have been discussed, the EoL stage was generally excluded from the system boundaries or roughly estimated. Few studies focused specifically on the EoL of crystalline-silicon PV panels. However, these either focused on potential reuse or have been applied standard WEEE recycling processes (i.e. focused on the shredding of the panel with the subsequent separation of the major mass fractions of the panels). Moreover, environmental impacts have been generally aggregated to the potential benefits due to the material recycling, making it difficult for any further assessment.

This article intends to continue the research on the EoL PV technologies and contribute to fill this lack of information in the LCA studies with a detailed analysis of a PV waste recycling process, mostly based on industry data.

Table 2Mass composition of 1000 kg of PV waste as input to the recycling process.

Component	Quantity	Unit	Percentage (%)
Glass, containing antimony (0.01–1%/kg of glass)	700	kg	70
PV frame, made of aluminium	180	kg	18
Polymer-based adhesive (EVA) encapsula- tion layer	51	kg	5.1
Solar cell, containing silicon metal	36.5	kg	3.65
Back-sheet layer (based on Polyvinyl Fluoride)	15	kg	1.5
Cables (containing copper and polymers)	10	kg	1
Internal conductor, aluminium	5.3	kg	0.53
Internal conductor, copper	1.14	kg	0.11
Silver	0.53	kg	0.053
Other metals (tin, lead)	0.53	kg	0.053
Total	1000	kg	100

3. Methodology

We applied the LCA methodology, according to the ISO 14040 standards [17], to a pilot process for the treatment of crystalline-silicon (c-Si) PV waste panels. The process has been developed by an Italian company, "SASIL S.p.A." within the project "Full Recovery End of Life Photovoltaic – FRELP" [16]. This project developed the 'FRELP process' in a pilot scale recycling plant and, subsequently, designed an industrial scale plant with a processing capacity of 1 t/h up to 8000 t/year of crystalline-silicon waste PV panels.

3.1. Goal and scope

The goal of this LCA was to assess the potential environmental impacts related to the FRELP recycling process and to identify its environmental hot spot (i.e. processing stages with the most relevant impacts).

The functional unit (FU) of the LCA was the recycling of 1000 kg of c-Si PV waste panels. This FU includes internal cables of the panel, while it does not include other PV plant components (e.g. inverter and external cables). The analysis followed a "gate-togate" approach, accounting for all the impacts occurring from the delivery of the waste to the recycling plant, up to the sorting of the different recyclable material fractions and the disposal of residues. The detail of the system boundaries of the LCA is shown in Fig. 1. Processes within the dashed area are those included in the study. These include: the transport of PV waste to the recycling plant; the impacts due to the treatments within the FRELP process (including the consumption of energy and auxiliary materials, and the emissions to the environment); the impacts due to the transport and disposal of residual materials to landfill. The recycling process also involved the use of a plant for the further treatment of electrical cables and the use of an external authorised incineration plant to treat the polymers layers inside the panel. The impacts of transport occurring during these treatments were also taken into account. The decommissioning of the PV plant was not considered.

The analysis also accounted for the energy (thermal and electricity) produced by the incineration process. These energy amounts have been modelled as co-product of the recycling process, and system expansion has been applied [17]. In particular, the FU has received the credits, in term of avoided environmental impacts, for the production of these energy amounts via conventional systems. Details on the credits applied are provided in the inventory phase (Section 3.2).

It is highlighted that the FRELP process separates various material fractions, such as metals and glass, in order to meet adequate purity and quality specifications needed for further processing downstream. These scraps (including aluminium, glass,

copper, silver and silicon) are, in fact, successively sent to additional plants for their further processing for the production of secondary materials. However, these processes are not directly related to the FRELP process, thus they have been not included within the system boundaries. Consistently, the LCA results did not incorporate the environmental credits derived for potentially substituted primary materials (as generally observed in the studies in the literature). However, the FRELP process includes some intermediate thermal treatments (i.e. incineration of the sandwich layer and of plastics from cables). Credits related to the energy recovered during these treatments have been included. The results of the Life cycle inventory and of the Life cycle impact assessment phases have been presented as disaggregated data, thus could be more easily used by LCA practitioners in future studies on LCA of PV panels.

3.2. Life cycle inventory

The FRELP process treats crystalline-based PV waste panels. The characterisation of the waste panels has been performed by the FRELP project based on a direct analysis of some waste samples [16].

The present study focused on the treatment of fluorine backsheet PV waste. Table 2 presents the mass composition of 1000 kg of crystalline-silicon PV panels as input to the recycling process. Information in Table 2 is based on industry data communicated by the responsible of the FRELP project.

3.2.1. Description of the PV waste recycling process

This section describes the processes for the recycling of the PV waste. The number used for each phase corresponds to the step's number in Fig. 1.

The first step of the process is the transport (1). The PV waste panels are expected to be collected in different locations in the northern and central regions of Italy. Because of the large heterogeneous distribution of the PV plant into the territory, it is not possible to exactly estimate the transport distances. Waste have been assumed to be initially transported to local collection points by trucks with a maximum capacity of 7.5 t. These local collection points could include some of the collection centres that already deal with the collection of WEEE in various regions. An average distance of 100 km from the PV plant location has been estimated for this transport step. Successively, the PV waste are supposed to be loaded into apposite large trucks (with maximum capacity of 32 t) and transported to the PV recycling site (located in the Piedmont region, in Northern Italy). The distance from the collection point to the PV recycling site is assumed to be 400 km.

Successively, the PV waste is unloaded (2) by using forklift and transferred into conveyor belt that will bring the modules to the dismantling process. The process is expected to unload 1000 kg of PV waste per hour. At the end of the conveyor belt, an automated system is used to dismantle the PV waste panel (3). First of all, a Cartesian robot will supply the PV waste into the dismantling part. Here, the edges of aluminium frame will be cut, followed by the tearing of the remaining aluminium frame. Afterward, the PV waste is transferred to the next process in which a mechanical arm will detach the cables from the PV waste. As a result, the aluminium frame and the cables/junction box are separated from the layer of photovoltaic cells, glass, and polymers. The aluminium frame is collected while the cables are sent to a separate plant for the further treatment (4). Plastic parts separated from cables are afterwards treated in an incineration plant with energy recovery (5).

The waste panels without frame and cable are introduced into a glass separation process (6). In this process the glass layer is detached from the remaining layers of polymers and cells (so-

called 'PV sandwich'). In order to facilitate the process, the PV panels are heated by mixed system for medium and short wave infra-red¹ prior to the mechanical detachment. The mechanical detachment of the glass is run by a high-frequency knife button, modulated in amplitude and speed [49]. The outputs of this process are pieces of PV glass and the PV sandwich.

Subsequently, these pieces of glass are brought to the glass refinement process (7). In this process, the pieces of glass are separated in different sizes (from 1 mm to 2.5 mm and from 2.5 mm to 5 mm, in diameter) by sieving. Afterwards, an optical-based separation system allows to remove pieces of glass with impurities (around 2% in mass), which are sent to disposal.

The sandwich layer is reduced in size (pieces of dimension $2 \text{ cm} \times 3 \text{ cm}$) by a cutting process (8), and later transported and treated by an authorized incinerating plant (9). This plant is supposed to be located 200 km away from the PV recycling site. The outputs of the incineration process are composed by the residual bottom ash (40% of the input). This high quantity is due to the large amount of silicon and other metals contained in the sandwich. Incineration produces also some fly-ashes (approximately 0.2% of the PV module weight) that are sent to a landfill for hazardous waste (assumed to be located 50 km away from the incineration plant). The energy produced during the incineration is assumed to be recovered in the form of heat and electricity. The emissions and energy outputs of the incineration plant have been estimated based on average data about the incineration of a mix of plastics (including fluorinated plastics) as available in the ecoinvent 3 database [50].

The bottom ash is sent back to the recycling plant to be further treated. This ash is sieved (10) to collect the aluminium connector residues. The efficiency of the separation of aluminium is approximately 50%. The residues of the sieving process are transferred to acid leaching process (11). The objective of this process is to separate the silicon from all the other metals in the ash. During the leaching process, the ash containing metals is mixed with the solution of water and nitric acid (HNO₃), which dissolves the metals (producing various metallic oxides) and leaves the silicon metal in the residues. The mixture containing the dissolved metallic oxides and the silicon metal residues is transferred to a vacuum filtration process (12), where the silicon metal is recovered and a part of the acid solution is recirculated (around 80%). The acid leaching is expected to recover 95% of the silicon as silicon metal at metallurgical grade.

The remaining silicon metal and the other dissolved metals in the acid solution are successively treated by electrolysis (13). Silver and copper are recovered, both with an efficiency of 95%. The electrolysis also emits NO_x gases at the anode of the electrolysis (estimated in 2 kg per ton of PV waste treated). The residues of the electrolysis remain in the acid solution to be successively neutralised by the addition of calcium hydroxide (14). The final output of the neutralization process is then filtered by a filter press (15), which separate a liquid waste (constituted by water and calcium nitrate) from a sludge containing the unrecovered metals with some residual water and calcium hydroxide (classified as hazardous waste). These wastes are finally transported to different landfills (assumed 100 km away) for the final disposal.

The detail of the energy and mass flows of each recycling step is illustrated in Fig. 1. Table 3 summarizes the overall inputs and outputs of the recycling process.

3.2.2. Life cycle inventory data

The foreground data used for the LCA were provided by the SASIL company's experts, which developed the FRELP recycling process [49].

Some background data, related to the use of electricity, auxiliary materials and impacts of the incineration and landfills have been derived from the ecoinvent 3 database [50]. Since an attributional modelling has been adopted for the accounting of the impacts of the recycling process, background processes have been referred to average processes in the market [52]. The detail of the background lifecycle inventory datasets is provided in Table 4. In particular the consumption of electricity refers to the Italian energy mix at medium voltage.²

As detailed in Table 3, energy quantities recovered from the incineration process of cable polymer and PV encapsulation layer are highlighted. These quantities have been credited to the FU in terms of avoided impacts for the production of electricity and heat from conventional sources. Consistently with the other background inventory data, average processes in the market have been used to model the credits (see Table 4 for the detail of the inventory data used).

3.3. Life Cycle Impact Assessment

The Life Cycle Impact Assessment (LCIA) of the FU has been modelled with the SimaPro software version 8.0 [51]. The midpoint impact categories recommended by the ILCD Handbook [52] have been selected for the LCIA, with two minor deviations:

- the "Mineral, fossil & renewable resource depletion" impact category was substituted by the impacts "Abiotic depletion, fossil" [53] and "Cumulative Energy Demand – CED [50]". This separation was adopted in order to distinguish the contributions of the impacts of energy sources from those of non-energy materials. The use of a dedicated indicator for energy consumption as the GER is particularly relevant since the study focuses on an energy related product;

- the "land use" and "water resource depletion" impact categories were not taken into consideration in this analysis due to their high uncertainty.

The LCIA results of the recycling of 1000 kg of silicon PV waste panels are illustrated in Table 5. Impacts due to the recycling process have been separated from the credits derived from the energy recovery. These credits can be particularly relevant for impact categories as: ozone depletion, ionising radiation ecosystems and ionizing radiation human health (around 30%); climate change, particulate matter and freshwater eutrophication (around 30%).

The contribution of the different treatments of the PV waste recycling to the overall lifecycle impacts is detailed in Fig. 2.

3.4. Life cycle interpretation and discussion of the results

The LCIA results show that for all the considered impact categories, the main contributions are related to the transport of the PV waste to the site, the incineration processes, and the further metal recovery from the bottom ash (including sieving, acid leaching, electrolysis, neutralization and filtrations). For example, the overall climate change impact of the process amounts to around 370 kg CO_{2eq}. This is mainly due to transport (29%), the incineration of the PV sandwich (34%) and the metal recovery treatments (24%).

¹ The infra-red system has been selected because more efficient compared to other alternative systems (based on the use of laser or microwave) [49].

² According to the ecoinvent 3 database, the electricity mix in Italy is constituted by [50]: 41% natural gas fired plants; 23% renewable energy sources; 15% coal fired plants; 6% oil fired plants; 15% import from other countries (mainly Switzerland and France).

Table 3Summary of input and outputs of the 'FRELP' process for the recycling of 1000 kg of silicon PV waste panels.

Input/output	Quantity	Unit	Note
Input			
PV waste panels	1000	kg	
Electricity	113.55	kW h	Required in various treatment processes as: disassembly, glass separation, module cutting, sieving, leaching, electrolysis.
Diesel fuel	1.14	1	Forklift work
Water	309.71	kg	Water consumption for acid leaching, electrolysis, and neutralization process
HNO ₃	7.08	kg	Acid leaching process
Ca(OH) ₂	36.5	kg	Neutralization of acid solution
Output, recovered materials			
Aluminium scrap	182.65	kg	
Glass scrap	686	kg	
Copper scrap	4.38	kg	
Silicon metal (Metallurgical Grade)	34.68	kg	
Silver	0.5	kg	
Output, energy recovery			
Electricity	248.84	MJ	Produced by the incineration of PV Encapsulation, back-sheet layer and polymers from cables
Thermal Energy	502.84	MJ	Produced by the incineration of PV Encapsulation, back-sheet layer and polymers from cables
Output, waste to landfill		-	
Contaminated glass	14	kg	Disposal in landfill
Fly ash (hazardous waste)	2	kg	Disposal in hazardous waste landfill
Liquid waste	306.13	kg	Disposal in landfill
Sludge (hazardous waste)	50.25	kg	Contains metallic residue, disposal in special landfill
Output, emission to air		-	
NO_x	2	kg	Emission from electrolysis

 Table 4

 Detail of the lifecycle inventory datasets used (derived from [49]).

Item	Used for the process phase	Datasets used
Electricity	Disassembly, cable treatment, glass separation, glass refinement, cutting of PV sandwich, sieving, acid leaching, filtration, electrolysis, neutralization, and filter press	Electricity medium voltage at grid/IT
Diesel fuel	Unloading	Diesel burned in building machine/GLO
Transport	Transport of PV waste to the recycling plant Transport of: PV waste to local collection point; cables to cable treatment plant and cable polymer to the incineration plant; glass residue to landfill; PV sandwich to incinerator; ash to the treatment plant; fly ash to special landfill	Transport lorry 16–32 t EURO5/RER Transport, lorry 3.5–7.5 t, EURO5/RER
	Transport of sludge from the recycling plant to landfills	Transport lorry 7.5-16 t EURO5/RER
Treatment for the recycling of cables	Cable treatment	Disposal, treatment of cables/GLO
Landfilling of the contaminated glass	Glass refinement	Disposal glass 0% water to inert material landfill/CH
Incineration of EVA	PV Sandwich Incineration	Disposal, plastics, mixture, 15.3% water, to municipal incineration/CH
Incineration of PVF	PV Sandwich Incineration	Disposal, polyvinylfluoride, 0.2% water, to municipal incineration/CH
Incineration of plastics from cables	Cable treatment	Disposal, wire plastic, 3.55% water, to municipal incineration/CH
Disposal of fly ash in a landfill	Incineration	Disposal average incineration residue 0% water to residual material landfill/CH
Production of electricity (avoided impacts from energy recovery during the incineration)	Incineration of cable polymer and PV sandwich, energy recovery	Electricity medium voltage at grid/IT
Production of heat (avoided impacts from energy recovery during the incineration)	Incineration of cable polymer and PV sandwich, energy recovery	Heat natural gas at industrial furnace > 100 kW/RER
Water	Acid leaching, electrolysis, neutralization	Water, completely softened, at plant/RER
Nitric acid	Acid leaching	Nitric acid 50% in H ₂ O at plant/RER
Ca(OH) ₂	Neutralization	Lime hydrated loose at plant/CH
Landfilling of inert sludge	Filter press	Disposal, limestone residue, 5% water, to inert material landfill/CH S.
Landfilling of sludge with metal residuals	Filter press	Disposal, sludge, pig iron production, 8.6% water, to residual material landfill/CH S

The contribution of the transport to the different impact categories is generally relevant, and it is ranging from a minimum of about 10% (for the freshwater ecotoxicity) up to 80% (for the abiotic depletion potential – minerals).

The incineration of PV sandwich and of plastics from cables, and the disposal of fly ash to a special landfill for hazardous waste are highly impacting for the freshwater ecotoxicity and human toxicity (cancer effect). Besides generating potential environmental impacts, the incineration process is expected to recover some energy derived from the combustion of polymers (about 250 MJ of electricity and 500 MJ of thermal energy). The credits for the energy recovery are observed as the negative values in Fig. 2 for the various impact

Table 5Life cycle impacts of the recycling process of 1000 kg of silicon PV waste.

Impact category	Unit	Recycling process	Credit	Total
Abiotic Resource Depletion (Mineral)	kg Sb eq	4.36E – 03	-4.34E-05	4.32E – 03
Cumulative Energy Demand	MJ	3.15E + 03	-3.74E+02	2.78E + 03
Freshwater ecotoxicity	CTUe	1.33E+03	-2.15E+01	1.31E+03
Marine eutrophication	kg N eq	1.09E + 00	-4.18E-02	1.05E + 00
Freshwater eutrophication	kg P eq	5.58E – 02	-1.02E-02	4.56E - 02
Terrestrial eutrophication	molc N eq	1.21E+01	-4.43E-01	1.17E + 01
Acidification	molc H+eq	2.68E + 00	-2.63E-01	2.41E + 00
Photochemical ozone formation	kg NMVOC eq	3.00E + 00	-1.37E-01	2.86E + 00
Ionizing radiation Ecosystems (E)	CTUe	9.42E - 05	-2.46E-05	6.96E - 05
Ionizing radiation Human Health (HH)	kg U235 eq	3.05E+01	-7.67E+00	2.29E + 01
Particulate matter	kg PM2.5 eq	9.81E - 02	-1.62E-02	8.19E - 02
Human toxicity, non-cancer effects	CTUh	1.95E – 05	-1.06E-06	1.84E - 05
Human toxicity, cancer effects	CTUh	2.95E – 05	-1.26E-06	2.83E - 05
Ozone depletion	kg CFC-11 eq	3.21E-05	-8.66E-06	2.35E - 05
Climate change	kg CO2 eq	4.46E+02	-7.59E+01	3.70E+02

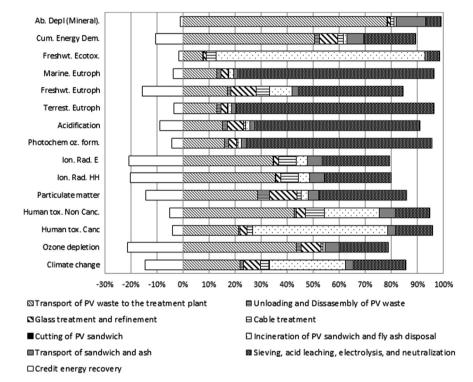


Fig. 2. Contribution of each phase to the overall environmental impacts of the recycling of 1000 kg of silicon PV waste.

categories. The negative values refer to the avoided impacts due to the generation of equivalent amounts of heat and electricity from alternative systems (see Section 3.2.2 for the details).

The treatments for the recovery of metals from the bottom ash are also highly impacting for the eutrophication impacts (freshwater, marine, terrestrials), acidification, photochemical ozone formation and particulate matter. For example, 80% of the impact category of terrestrial eutrophication (11.7 molc $N_{\rm eq}$) is due to the processes of sieving, acid leaching, electrolysis, and acid neutralization.

The phases of waste unloading, disassembly and thermal separation of the glass have a very low impact (below 10% for all the considered categories). The cutting of PV sandwich before the incineration has negligible impacts. However, all these phases are crucial to allow a high efficiency of the recycling process in terms of high quantity and quality of different recyclable fractions (glass, aluminium and copper).

A further detail of the impacts of the metal recovery treatments is illustrated in Fig. 3. It is noticed that the emission of NO_x during

the electrolysis are the main responsible for the photochemical ozone formation, acidification terrestrial and marine eutrophication, and for particulate matter. Waste disposal is the main contributor for human toxicity (cancer and non-cancer effects), freshwater eutrophication and freshwater ecotoxicity. The consumption of resources (electricity, nitric acid and calcium hydroxide) is the main contributor for the other impact categories.

Table 6 presents a summary of the impacts of the present LCA together with results of other studies available in the literature, as presented in Section 2. However, a direct comparison is not possible since other studies often presented aggregated results, referred to different impact categories and, in some cases, were not transparent or detailed enough on the assumptions (e.g. FU and system boundaries). A partial comparison can be performed with the impacts estimated by Held and Ilg [47] concerning the recycling of 1 m² of CdTe panels. Assuming that 1000 kg of PV waste corresponds to around 73 m² of panels (i.e. panels with a mass 22 kg and a surface of 1.6 m²) [6], it results that the recycling

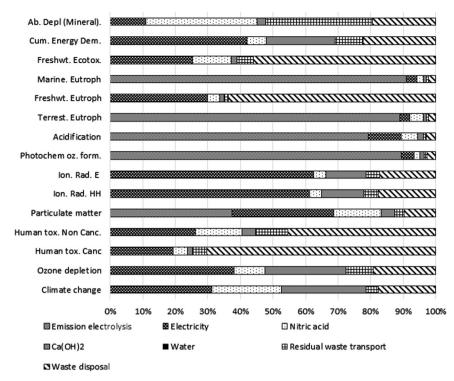


Fig. 3. Detail of the impacts due to the treatments of the bottom ash for the recovery of metals.

 Table 6

 Comparison of the results of the present LCA with other studies in the literature concerning the recycling of PV panels.

Process studied	Impacts	Reference
Recycling process of different types of PV panel (FU no specified):	t	[36]
– mono-Si	250 MJ	
– multi-Si	240 MJ	
– CdTe	150 MJ	
1 kW h of electricity by different PV plant	Recycling responsible of 4% of the GWP	[37]
Treatment of a silicon PV module with 72 cells (125 mm × 125 mm)	GWP: -59.2 kg CO _{2eq} ; acidification: -0.4 kg SO _{2eq} ; resource depletion: $-6.1 \cdot 10^{-8}$ kg Sb _{eq} . Aggregated results including also credits due to avoided primary materials.	[38]
Recycling of 1 m ² of CdTe PV panel.	GWP: 6 kg CO _{2eq} ; primary energy demand: 81 MJ; acidification potential: 9.1 kg SO _{2eq} .	[47]
1 GJ of electricity produced by thin-film solar PV modules.	Recycling responsible of 4% of the impacts	[48]
Recycling of 1000 kg of silicon PV panels	GWP: 370 kg CO_{2eq} ; acidification: 2.41 molc H_{eq}^+ ; resource depletion: $4.32 \cdot 10^{-3}$ kg Sb_{eq} ; GER: 2780 MJ. (other impacts illustrated in Table 5)	(Present study)

of 1 $\rm m^2$ of silicon panels according to the FRELP process would imply the emission of 5 kg $\rm CO_{2eq}$ of greenhouse gases and the consumption of 38 MJ of energy. These values are sensibly lower than those provided by Held and Ilg [47], which however referred to a different type of PV waste.

We highlight that the LCA study presented in this article had two main limitations related to the input data. First of all, the analysed recycling process is still at a pilot scale. The data regarding all the inputs and outputs flows and the related emissions of the recycling plant have been therefore estimated based on the information developed within the FRELP project. These data should be verified once the industrial scale plant will become operational.

A second limitation is related to the modelling of some phases not directly related to the pilot recycling process, as: the transport (collection of PV waste, delivery of the PV sandwich to the incineration plant, transport of the ash and other residuals); the incineration of the PV sandwich and of the plastics from the cables; and the disposal of residuals to landfill. Since primary data for these phases were not available, impacts have been calculated

based on average assumption and lifecycle inventory data as available in the LCA database (see Section 3.2.2 for the details). In particular, transport to the recycling plant and incineration were the processes that had a relevant incidence on various lifecycle impacts. For this reason, a sensitivity analysis (SA) was performed.

Concerning the transport, the base case analysis assumed 400 km distance between the collection centre of PV waste and the recycling plant. In the SA, this distance was supposed to vary between 300 km and 500 km. The results showed that some impacts categories (e.g. freshwater ecotoxicity, human toxicity-cancer, terrestrial/freshwater/marine eutrophication, acidification and photochemical ozone formation) have a limited variation (within the range \pm 3%). Climate change impact can vary up to \pm 5%, while other impacts (e.g. cumulative energy demand, ozone depletion and abiotic depletion potential – mineral) can vary up to \pm 11%.

Concerning the modelling of the incineration, inventory data for the incineration processes of various plastics have been considered in the base case (see Table 4 for details). In particular inventory data about incineration of plastics mixture was used to model the incineration of non-fluorinated plastics in the

sandwich. In the SA this inventory data was substituted with data concerning the incineration of plastics from consumer electronics [50]. The results showed a very large variation of the impacts "freshwater ecotoxicity" (30 times higher) and "human toxicity non-cancer effect" (4 times higher). The climate change impact value increased by 8%, while other impact categories had small variations (below 2%). The main reason for the large changes in the human toxicity and freshwater ecotoxicity was the larger emission of antimony in water, as accounted in the inventory data for the incineration of plastics from electronic waste. These emissions can be explained with the presence of antimony in electronics, generally used as flame retardant. However, based on the waste characterisation provided by the SASIL company [16], antimony was not detected into the sandwich of the analysed PV waste. Therefore we considered the results of the base case scenario more representative. However, more detailed information concerning the emission during incineration could be available only when the pilot process will be fully established at industrial scale.

4. Conclusions

The present article discussed the application of the Life Cycle Assessment methodology to an innovative process to recycling PV waste panels. The processes have been developed at a pilot scale under the 'FRELP' project co-funded by the European Life programme. The functional unit of the study was the treatment of 1000 kg of crystalline silicon waste PV panel.

This LCA study represents one of the few studies on the topic and aims to be one of the most detailed in the current literature. This article intends to contribute to the sustainability assessment of the recycling of PV waste, since it is expected that this type of waste will largely increase in the next decades. The presented results on the recycling of PV waste can be relevant also for policy makers and recyclers since this type of waste has been recently introduced within the European waste legislation for the treatment of WEEE.

The results presented here highlighted that the majority of the impacts for the recycling process are related to the transport of PV waste to the site, the plastic incineration processes, and the further treatments (including sieving, acid leaching, electrolysis, and neutralization) for the recovery of metals (including silver) from the bottom ash.

For example the contribution of transport to the different impact categories ranges from a minimum of about 10% (for the freshwater eutrophication) up to 80% (for the Abiotic Depletion Potential – minerals). Due to the heterogeneous distribution of PV plants in the urban areas, it could be interesting to explore in future the creation of decentralised recycling plants, at least for some pre-treatments of the PV waste.

Credits derived from the potential production of secondary raw materials from the recycling process (as aluminium, copper, silicon, silver) have been intentionally excluded from the system boundaries. Credits due to energy recovered during the thermal treatment of the sandwich layers and plastic from cables, have been accounted but separately illustrated. We aimed at providing transparent and disaggregated information on the recycling process suitable for future studies on silicon PV panel. LCA practitioners could use this information as inputs for their studies, to be modelled according to their goals and scope.

A comparison of the impacts presented in this article with the limited information available in other studies in the literature was not possible, mainly because these last have been generally presented as aggregated results.

Further analysis can be developed from this study to assess the potential benefits related to the recycling of the recovered

materials (e.g. in comparison to the impacts of the production the primary raw materials used in the PV panel) and to compare the impacts of the PV waste treatments with the impacts of the other life cycle stages. The presented results could be also relevant to assess how future PV panels could be designed in order to reduce the impacts due to the recycling and to maximise the recovery of different materials. New panels should be designed in order to reduce and/or avoid the use of fluorinated plastics in the sandwich layer and to simplify the disassembly of aluminium frames from the panel. Moreover, manufacturers should be encouraged to use recycled glass from PV waste treatment for the production of new panels, in order to recover also additives (as antimony contained in the glass scraps) which would be otherwise lost.

Disclaimer

The views expressed in the article are personal and do not necessarily reflect an official position of the European Commission.

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