Sustainable urban electricity supply chain – Indicators of material recovery and energy savings from crystalline silicon photovoltaic panels end-of-life.

Fabiana Corcelli[a], Maddalena Ripa[a,1], Enrica Leccisi[a], Viviana Cigolotti[b], Valeria Fiandra[b], Giorgio Graditi[b], Lucio Sannino[b], Marco Tammaro[b], Sergio Ulgiati[a,c]

[a] *Department of Science and Technology, Parthenope University of Naples, Centro Direzionale – Isola C4, 80143 Naples, Italy*

[b] *ENEA, Italian National Agency for New Technologies, Energy and the Environment, Portici Research Centre, P. le E. Fermi, 1, Portici, 80055 Naples, Italy*

[c] *School of Environment, Beijing Normal University, 19 Xinjiekouwai St., Haidian District, 100875 Beijing, China*

Keywords: Si photovoltaic panel, Thermal treatment Recycling, Life Cycle Assessment

Abstract

Solar photovoltaic (PV) electricity has the potential to be a major energy solution, sustainably suitable for urban areas of the future. However, although PV technology has been projected as one of the most promising candidates to replace conventional fossil based power plants, the potential disadvantages of the PV panels end-of-life (EoL) have not been thoroughly evaluated. The current challenge concerning PV technology resides in making it more efficient and competitive in comparison with traditional fossil powered plants, without neglecting the appraisal of EoL impacts. Indeed, considering the fast growth of the photovoltaic market, started 30 years ago, the amount of PV waste to be handled and disposed of is expected to grow drastically. Therefore, there is a real

[1] Corresponding author. Tel.: +39 081 5476666. *E-mail address:* maddalena.ripa@uniparthenope.it (M. Ripa).

need to develop effective and sustainable processes to address the needed recycle of the growing number of decommissioned PV panels. Many laboratory-scale or pilot industrial processes have been developed globally during the years by private companies and public research institutes to demonstrate the real potential offered by the recycling of PV panels. One of the tested up lab-scale recycling processes – for the crystalline silicon technology – is the thermal treatment, aiming at separating PV cells from the glass, through the removal of the EVA (Ethylene Vinyl Acetate) layer. Of course, this treatment may entail that some hazardous components, such as Cd, Pb, and Cr, are released to the environment, therefore calling for very accurate handling. To this aim, the sustainability of a recovery process for EoL crystalline silicon PV panels was investigated by means of Life Cycle Assessment (LCA) indicators. The overall goal of this paper was to compare two different EoL scenarios, by evaluating the environmental advantages of replacing virgin materials with recovered materials with a special focus on the steps and/or components that can be further improved. The results demonstrate that the recovery process has a positive effect in all the analyzed impact categories, in particular in freshwater eutrophication, human toxicity, terrestrial acidification and fossil depletion indicators. The main environmental benefits arise from the recovery of aluminum and silicon. In particular, the recovered silicon from PV waste panels would decrease the need for raw silicon extraction and refining in so lowering the manufacturing costs, and end-of-life management of PV panels. Moreover, the amount of the recovered materials (silicon, aluminum and copper, among others) suggests a potential benefit also under an economic point of view, based on present market prices.

1. Introduction

1.1. *PV in the urban systems*

The electricity market has revealed unprecedented and widespread growth of distributed sources of power generation in recent years (EPIA, 2014), in particular photovoltaic (PV). In several countries, the PV contribution to electricity demand

was beyond1%, with Italy in first place with 7.92% and the overall European PV contribution amounting to around 3.5% of EU electricity demand. Worldwide, 19 countries already produce at least 1% of their electricity needs with PV (IEA, 2015).
In urban systems, PV plants can be installed on top of roofs
– namely Building Adapted PV systems (BAPV) – or can be integrated into the roof itself or building façade – namely Building Integrated PV systems (BIPV). Generally, PV devices on the rooftop can be residential (<10 kWp), commercial (10–100 kWp), or industrial (100 kWp–1 MWp).

The world's cumulative installed PV capacity in 2014 was more than 178 GW and the European Union leads the way with more than 82 GW; the rooftop segment represents around 17% of total PV installations (EPIA, 2015). Furthermore, the growing market penetration of PV technologies was also associated to incremental improvements in their environmental performance (Fthenakis and Alsema, 2006; Fthenakis and Kim, 2011; Held and Ilg, 2011; Raugei et al., 2012).

On one hand, the total constructed area in Europe occupies over 22,000 km^2 of land, out of which 40% of all building roofs and 15% of all façades in Europe are suited for PV applications; on the other hand, the European population is over 490 million units and the expected electricity demand in the short term is about 3.5 TWh/yr. According to EPIA (2011), over 1500 GWp of PV could technically be installed in Europe, which would generate annually about 1400 TWh, representing 40% of the total electricity demand by 2020.
PV technologies are classified as first, second or third generation in which the first one is the basic crystalline silicon (c-Si); the second one is composed by thin film technologies such as amorphous silicon (a-Si), multi-junction thin silicon film (a-Si/μc-Si), cadmium telluride (CdTe), copper, indium, gallium, (di)selenide/(di)sulphide (CIGS) and copper, indium, (di)selenide/(di)sulphide) (CIS); whilst the third group includes concentrator PVs, organic and others. Moreover, each PV technology has own cell and module[2] efficiency and different area needed per kWp_{el} in installed rooftop plants (EPIA, 2011; Paiano, 2015).

[2] It has to be highlighted that in this paper, the term 'module' is equivalent to the term 'panel', which is much more frequently used. Both of them refer to the same unit – that is, a unit composed of solar cells.

Historically, c-Si PV has dominated the market for the last 30 years and both monoand poly-crystalline cells are produced in fairly equal proportion (EPIA, 2011).

1.2. *End of life (EoL)*

Most often PV is considered as an energy technology that has very minimal waste generation because no emissions are released during the operation phase, while traditional electricity sources are characterized by large flows of airborne released chemicals (McDonald and Pearce, 2010). Although PV-related solid waste is negligible in comparison to the waste generated by traditional energy sources, there is still a material flow of solid and airborne waste that cannot be ignored, associated to the decommissioning of the solar modules at the end of their useful life (McDonald and Pearce, 2010), to be added to the waste released in the production phase. The PV related waste flows are in direct correlation with the growth of the PV market. The rapid expansion of the PV industry will translate into a large amount of modules to be disposed of in the next years. In fact, considering PV modules are foreseen to last about 25–30 years, a large amount of the already installed modules are now very close to the end of their useful life and will have to be decommissioned and disposed of or re-used in some way (Fthenakis, 2000). In 2008, the amount of PV waste generated in the EU was around 3800 tons (corresponding to 51 MWp) and by 2030, this is expected to rise to 130,000 tons (Larsen, 2009). Furthermore, several important factors affect the amount of PV waste generated, such as production quantities, weight per Wp, production waste during various stages of production, proportion of premature waste (during transport and installation), failure rate during use, and useful life (Sander et al., 2007).

One of the major concerns regarding the PV EoL treatment and disposal is the emission of hazardous metals, as chromium and lead, and toxic gases, as hydrofluoric acid that may be released in the environment if special requirements for their handling and disposal are not adopted (Fthenakis, 2003). Appropriate EoL management of PVs may offer a sustainable solution to resource availability, economic feasibility and EoL related environmental risks (Choi and Fthenakis, 2014).

In order to achieve this goal, the PV Cycle association (http:// www.pvcycle.org) – established by the European PV industry in July 2007 – promotes the photovoltaic industry's commitment by setting a voluntary take-back and recycling program for EoL panels and by taking the responsibility for PV modules throughout their entire life cycle (PV Cycle, 2011). According to last report of PV Cycle (2015), over 13,000 tons of PV waste have been treated throughout Europe from 2010 to 2015.

To tackle this issue, the European Commission proposed in December 2008 to recast the Directive 2002/96/EC on waste electrical and electronic equipment (WEEE) so as to include PV panels. The Bio Intelligence Service study, ordered in the 2011 by the EU Commission (Bio Intelligence, 2011), significant for the development of the new Directive 2012/19/EC, concluded that including PV panels in the WEEE directive will generate economic benefits by limiting the quantity of PV panels improperly disposed of, avoiding toxic chemicals leaching into the environment, and allowing the recovery of valuable resources and rare metals.

Moreover, the Global Data report (2012) details the economics of the PV recycling process. This study foresees that the value per watt of a recycled PV module will reach \$0.58 by 2025, increasing to \$1.21 per watt in 2035. With a 100% collection rate, 278 MW of PVs are expected to be recycled in 2025 with that rising to 17,000 MW by 2035. By then the value per watt of a recycled PV module is predicted to reach \$1.21, depending on the market price variations of the materials. For crystalline modules, the expected recycled product value is predicted to increase from \$122 million in 2025 to \$12,908 million by 2035. In 2025, the recycled values of glass and aluminum are expected to account for \$105 million and \$11 million of the \$122 million, respectively, and \$11,066 million and \$1,131 million, respectively by 2035 (GlobalData, 2012).

According to the literature, the hypothetical power curve for a PV energy facility, from construction to operation and final decommissioning of the plants, shows that major impact is attributed to the construction phase in comparison with the energy required during the operation and the decommissioning phases

(Herendeen and Cleveland, 2004).

Several studies have shown the environmental feasibility of PV electricity in comparison to conventional fossil-based electricity by means of different sustainability assessments (Brown et al., 2012; Hadian and Madani, 2015; Pearce, 2002; Raugei et al., 2012, among others). Indeed, a comprehensive analysis should consider the contributions of each phase of the life cycle (Fthenakis et al., 2009). The problem of achieving a suitable electric source in support of urban sustainable development is thus an important challenge. The development of a method for assessing the status of urban sustainable development requires the definition of scientific and effective assessment indicators (Zucaro et al., 2014). Life Cycle Assessment (LCA) has been demonstrated to be an appropriate tool for this aim and its application in this field has rapidly expanded over the last few years (EC, 2010). LCA has been widely applied to compare the environmental performance of PV panels production and operation worldwide (Held and Ilg, 2011; Sherwani et al., 2010; Stoppato, 2008, among others) whilst very few studies have been dealt with the end-of-life PV panels (Berger et al., 2010; Giacchetta et al., 2013; Müller et al., 2006, among others).

1.3. *State of the art of PV panels recycling*

The recycling of PV modules involves both silicon-based (mono and poly-crystalline (c-Si), amorphous (a-Si)) and thin film (CIGS and CdTe) solar cells. In general terms, the PV panels recycling process can be divided into three macro-steps: (i) mechanical, chemical or thermal de-lamination, (ii) chemical de-coating and

(iii) chemical extraction/refining (Granata et al., 2014; Radziemska et al., 2010). However, these phases generally differ depending on the PV panels technology. In particular:

- the recycling of mono and poly-crystalline solar cells involves incineration or pyrolysis, for the recovery of crystalline silicon wafers (Fthenakis, 2000);

- the recycling of CIGS solar cells entails a thermal or chemical process to recover critical metals (e.g. Se, In and Ga) (EC, 2014) and glass (Fthenakis et al., 1996);
- the recycling of CdTe solar cells involves a chemical process to strip metals and Ethylene Vinyl Acetate copolymer (EVA) and additional steps of chemical treatments to separate and recover critical metals (e.g. Cd and Te) (Fthenakis et al., 2006);
- the recycling of a-Si solar cells entails a mechanical process (Sander et al., 2007).

A number of laboratory-scale or pilot industrial recycling processes have been developed recently by private companies and public research institutes to demonstrate the potential benefits offered by the recycling of PV panels (Giacchetta et al., 2013). With regard to the treatment of crystalline silicon modules, a pilot study, based on thermal and chemical processes, was carried out by Deutsche Solar AG (2003) to assess the environmental effects of such recycling process, as well as the Energy Pay Back Time (EPBT) of new PV modules versus the ones created using recycled solar cells. The study underlines that the recycling process reduces the environmental burden of processing new silicon as well as the burden associated with disposing of the PV modules through more conventional means. Furthermore, the use of recycled wafers for wafer production instead of new ones can halve the EPBT of a module (Müller et al., 2006, 2008). The same conclusion is achieved by PV Cycle in cooperation with Maltha Glass Recycling (Belgium): the PV module recycling process, as applied at Maltha Recycling by physical operations, contributes to a further reduction of the environmental profile of the crystalline silicon PV module life cycle. Specifically, the latter study shows how the recycling of 1 ton of silicon-based PV modules saves approx. 800 kg of CO_2-eq. and up to 1,200 kg of CO_2-eq. compared to those modules made 100% of primary materials (Held, 2012).

Regarding the thin film panels, only few technologies are applied for the recovery of high value materials, as recently reviewed by Giacchetta et al. (2013). Sasala et al. (1996) reported that mechanical treatments, based on water blasting and chemical processes followed by precipitation, electroplating or ion exchange, were suitable for the recycling of CdTe PV panels. The company First Solar (2003) industrialized a process for the recycling of CdTe PV panels based on hydrometallurgical processes. Furthermore, First Solar is the first company to implement an unconditional prefunded Collection and Recycling Program for damaged and EoL modules (http://www.firstsolar.com/). Fthenakis et al. (2006) developed hydrometallurgical processes based on leaching, ion exchange separation, precipitation and electrowinning to recover cadmium and tellurium from CdTe panels. Moreover, in the framework of two European projects, two different combinations of recovery processes for the copper indium selenide (CIS) and CdTe panels were developed: the "RESOLVED" project, testing a process based on thermal/wet-mechanical and hydrometallurgical treatment (Berger et al., 2010), and the "SENSE" project, analyzing a combination of thermal and chemical treatments (SENSE, 2008). However, nowadays, neither technologies have been designed for treating together more types of photovoltaic panels nor completely automated processes have been developed yet.

Considering the fast growth of the market of PV panels and the related EoL environmental issues, European Union calls for a longterm sustainability of the PV industry. Indeed, decommissioned PV panels are included, for the first time, in the list of WEEE in the EU Directive 2012/19/EC. The Directive, become effective on 14 February 2014, aims to improve the collection, re-use and recycling of used electronic devices to contribute to the reduction of waste and the efficient use of resources. Annex V of the Directive provides minimum recovery targets applicable by category and by time frame. In particular, with regard to PV panels: from 13 August 2012 until 14 August 2015, the targets for recovery and recycling are set to 75% and 65%, respectively; from 15 August 2015 until 14 August 2018, these targets shall become 80% and 70%, respectively; from 15 August 2018, these percentages shall increase to 85% and 75% (EC, 2012; Paiano, 2015). Moreover, the Commission Mandate M/518 requested the European standardization organizations to develop European standards for the treatment, including recovery, recycling and preparing for reuse of WEEE (EC, 2013). In addition to these goals each EU Member State could adopt more ambitious targets.

In Italy, as a consequence of the directive's provisions and in accordance with the Ministerial Decree on 5 July 2012, the manufacturers of panels have to adhere to a system or consortium for PV panels recycling at the end of life to demonstrate the sustainability of these systems. The national (Italian) Agency for the Management of Energy Services [GSE, Gestore Servizi Energetici], has published information on procedures to be followed and documents to be submitted by the recycling entities in order to ensure that the requirements are addressed (GSE, 2012).

As a follow up of a wider project, entitled F.E.R.G.E. ("Devices, Techniques and Enabling Technologies for Renewable Energy Sources toward Green Economy") (http://uttp.enea. it/index.asp?p=108&t=Progetto%20F.E.R.G.E.), funded by the Italian Ministry of Education, University and Research [MIUR] in 2013, this paper presents the results of a Life Cycle Assessment of a thermal recovery process for EoL c-Si PV panels. The overall goal of this paper is to compare different EoL scenarios, focusing on the evaluation of the environmental advantages of replacing virgin materials with recovered resources. The aim of the present study is also to explore to what extent the thermal treatment is capable to provide considerable amounts and high quality of recovered materials; in addition, this research would contribute to the development of a suitable know-how and technology to meet the recent EU directives for PV decommissioning.

2. Materials and method

2.1 Life Cycle Assessment of waste flows

LCA is a method that attempts to quantify the environmental impacts associated with a product or service throughout its life cycle. It is defined as a technique for the compilation and evaluation of inputs, outputs and potential environmental impacts of a product system throughout its life cycle – from the extraction of resources, through the production of materials, parts and the product itself, the use of the latter, and the management after it is discarded, either by reuse, recycling or final disposal of ('from cradle to grave', according to a very common definition of LCA). This methodology comprises four phases such as the goal and scope definition, inventory analysis, impact assessment and interpretation (ISO, 2006a). Although LCA has traditionally developed for environmental assessment of products, there are several examples where LCA was used for other more complex functions, such as improvement of industrial production steps, evaluation of strategies for treatment of solid waste (Finnveden et al., 2005) or performance evaluation of wastewater systems (Tillman et al., 1998; Weiss et al., 2008) and more.

LCA models of waste management generally calculate environmental burdens per unit amount of waste treated without considering how the latter was generated. Hence in the evaluation of waste management, instead of the traditional approach 'from cradle to grave', the starting point of the analysis will be the point where the waste is generated. This approach is called 'zero-burden', and suggests that waste entry into the system is considered as free from the impacts of the process that has contributed to its production (Ekvall et al., 2007).

In this study, the methodology and concepts developed for LCA – defined by ISO standards and ILCD Handbook guidelines (EC, 2010, 2011; ISO, 2006a,b) – are used for the evaluation of the innovative recovery process of c-Si PV panels, as designed within the framework of the F.E.R.G.E Project.

2.2 System description

Within certain limits determined by technological requirements, the composition of the crystalline silicon panels is highly variable. In fact, the structure of panels has undergone several modifications over the past years due to the evolution of technology and materials used (e.g. the solder paste whose composition is covered by patent). A crystalline silicon photovoltaic panel (c-Si) is mainly made in layers: the PV cells are wrapped with materials such as EVA (ethylene-vinyl-acetate), PVB (poly-vinyl-butyral) or TPO (thermoplastic polyolefine elastomer) and then tempered glass on the upper surface, and PVF (polyvinyl-fluoride) or glass as back sheet. The EVA layer is used like an adhesive between the tempered glass and PV cell (Wenham et al., 2013). In Table 1, the typical composition of a crystalline silicon panel, manufactured before 2007, is reported.

In general, the recovery and recycling of the c-Si PV panel requires the panel disassembling in its main components: the process begins with the disassembly of the aluminum frame and junction box. The frame is frequently disassembled manually because of the size, profiles and fastening varies between manufacturers (Olson et al., 2013). The next step is the removal of the EVA layer to separate the glass from the silicon cell (Kang et al., 2012). The most common method used to decompose the EVA layer is the thermal treatment (Allen et al., 2000).

Table 1

Typical composition of a crystalline silicon panel.

Component	Weight percentage (%)
Aluminum (frame)	10.30
Glass	74.16
Silica cell	3.48
EVA	6.55
PVF (back sheet film)	3.60
Electrical contacts	0.75

Source: Sander et al. (2007).

The technical feasibility of this process was tested at the laboratory scale by the Italian National Agency for New Technologies, Energy and the Environment (ENEA). The experimental tests were performed on three samples of 10 cm 10 cm, obtained from three Poly-Si panels with some difference in their composition. In fact, one panel had a back sheet film made of PVF (panel A) and the other two (B and C) made of glass. Besides, the thicknesses of panel A and B are almost four times larger than panel C. Considering that results did not differ by a large extent, this paper only discusses the results of the treatment of panel A (with PVF), in order to include also the emissions from incineration of fluoropolymer materials. In fact, the research focus is placed on the treatment technology, temporally disregarding the influence of module thickness. The panel A characteristics are shown in Table 2.

After manually removing the aluminum frame and the junction box from the panel, a representative sample that included a single cell was identified, cut and carefully cleaned in order to avoid any contamination due to use of saw. Then, it was heated from the initial temperature of 20 °C up to 600 °C and kept at this temperature for 30 min. The heating ramp had the duration of 45 min corresponding to a heating rate of 12.8 °C/min. Throughout the test, i.e.75 min, an air flow rate of 1 L/min was blown into a furnace and then bubbled through the acid solutions in Drechsel traps, in order to verify the presence of metals in the gas phase (Tammaro et al., 2015).

Table 2

Technical features of c-Si panel used in the experimental test

Origin	Italian
Technology	Poly-Si
Fabrication year	1986
Dimensions (cm)	130 × 68
Total weight (kg)	12.694
Frame weight (kg)	3.294
Layers type (thickness)	Glass-cell-PVF (43 mm)
Cell: shape; size; thickness	Square; $l = 10$ cm; 0.48 mm
Total numbers of cells	72

The final temperature and the duration of the test have been chosen to ensure that the thermally degradable parts of the panel were fully eliminated (PVF and EVA decompose around 450 °C and 350 °C, respectively).

A blank test, without the sample, was performed under the same experimental conditions in order to assess the content of metals in the environmental air. After the thermal treatment a coarse-grained residue was left. This solid was passed through a 0.5 mm sieve and the filtered mass (ashes) collected for further characterizations. The coarse portion which remained on the sieve was mainly composed by silicon, glass and metal electrodes and these were further manually separated and weighed (see Table 3).

It should be noted that all the subsequent phases involving the recovery of thermally treated materials have, as input flows, the materials coming from thermal treatment and weighing steps. Thus, each inflow carries to the recovery step a fraction of impacts of the thermal treatment depending on the allocation procedure. The recovery process ends with the production of semifabricated products such as shapes and ingots (for recovered metals) and packaging glass (for recovered glass), to be returned to a new production cycle.

Table 3

Amount of recovered material from c-Si PV panel referred to a functional unit of 1 m^2.

Process	Recovered materials	(kg/m^2)
Thermal treatment	Aluminum (frame)	3.72
	Glass	8.14
	Silicon	0.98
	Metal electrodes[a]	0.07
	Ashes (metals, inert)	0.05

Tammaro et al. (2015) – modified.

[a] 50% of metal electrodes is assumed to be made of copper (Jungbluth et al., 2012).

2.3 Goal and scope

The ISO standards describes the goal and scope step as the phase in which the intended uses and users of the LCA results are identified and the overall context is framed (functional unit, quality of data, regional boundary, etc.). The goal of this study is to evaluate the environmental impacts of a high-rate recovery solution of end-of-life (EoL) c-Si PV panels, with a special focus on the environmental advantages of replacing virgin materials with recovered resources in processes for which the quality of the recycled materials fits the technological needs. Furthermore, the high-rate recovery scenario is compared with a low-rate scenario, where the not recovered fraction is disposed of in landfill.

This study is aimed at providing decision-makers with potentially useful recommendations for c-Si PV panels EoL since by 2030 more than 40% of PV panels in the future PV waste stream will be c-Si panel (Bio Intelligence, 2011).

The functional unit chosen was 1 m^2 of EoL c-Si PV panel treated, in order to compare with similar studies, according to the International Energy Agency Photovoltaic Power Systems Program (IEA PVPS) Task 12 guidelines for LCA of PV (Fthenakis et al., 2011).

A 'zero-burden waste' approach is adopted in this study, not including the upstream generation of waste (i.e. only the processing inputs – recovery and recycling – are accounted for, disregarding the upstream production chain of the PV modules the cost of which is not attributed to the final waste material) (Bala Gala et al., 2015). According to the ILCD Handbook (EC, 2010), the analyzed context can thus be identified as a micro-level decision support (so-called situation A) and an attributional LCI modeling framework was therefore applied.

Since during the waste treatment processes more than a single valuable product is produced (e.g. electricity from waste incineration and/or a secondary good after some additional cleaning and treatment steps, etc.), an allocation procedure, based on the current market value criterion, was applied (EC, 2010). Therefore, during the inventory analysis, an economic allocation, based on average market prices of the co-products, was performed to partition the input and output burdens between the different co-products (e.g. semiconductor, aluminum frame, glass, copper, ashes, energy in the case of thermal treatment).

As it can be observed in Table 4, about 60% of the total economic value of the product is allocated to the recovery of aluminum, 8% to the recovery of glass, 11% to the recovery of silicon, 3% to the recovery of copper and 19% to the recovery of heat from the thermal process. In relation to ashes, no allocation has been made since they have no market value, being collected by specific companies which do not pay anything for the recovered material, thereafter destined to clinker production.

Besides, a comparison with a different allocation procedures based on mass and exergy, i.e. the useful work potential of the recovered products (Szargut et al., 1998; EC, 2010) was performed in order to verify if the results are sensitive to the chosen allocation approach. Hence, in order to convert energy and material flows to exergy, the following equation was applied to the recovered output:

Output Exergy (kJ) = y_{th} * Heat delivered (kJ_{th})+

$$+ \text{Chemical Exergy of recovered materials } (kJ_{chem}) \qquad (1)$$

where $y_{th} = 1 - (T_a/T_d)$ is the Carnot factor to convert thermal to mechanical exergy, T_a is the ambient temperature and T_d the temperature of heat delivered (assumed to be 293 K and 473 K, respectively). The chemical exergies (kJ/g) of recovered materials were calculated from the standard chemical exergies of pure substances (Szargut et al., 1998). In so doing, it is possible to calculate the percentage of exergy associated to each output flow.

As it can be observed in Table 4, the exergetic approach has produced similar results, with an average difference of 6%.

Conversely, when a mass allocation is performed, very different values are obtained, being glass the heaviest recoverable material (63% of total mass).

Actually, when dealing with end-of-life processes yielding secondary materials for recycling or recovered energy (incineration and sometimes landfilling), the recommended way to tackle them in LCA is by system expansion (EC, 2010). Basically, thanks to recycling and energy recovery it is no longer necessary to provide in input equivalent amounts of the same materials and/or energy by means of the mix of conventional technologies that would otherwise be employed; the analysis should therefore be extended to include those 'avoided' or 'displaced' systems (scaled accordingly), and then subtract their associated impact from that of the waste management system under analysis. For this reason, in the present study a system expansion based on average data (i.e. market mix) is chosen for crediting energy and materials recovery in order to highlight the potential benefits of the treatment under study.

Table 4

Mass, economic and exergetic allocation.

Recovered product	Amount (kg/m² panel)[a]	Price[b, c] (Euro/kg)	Mass allocation (%)	Economic allocation (%)	Exergetic allocation (%)
Recovery process by thermal treatment					
Aluminium (frame)	3.73	0.70	28.8	60.4	73.4
Glass	8.14	0.04	62.9	7.5	0.2
Silicon (cells)	0.98	0.47	7.6	10.6	17.8
Copper	0.04	3.50	0.3	2.9	0.1
Heat	37.7	0.02		18.6	8.5
Ashes	0.06	–	0.4	0	0
Ashes recycling process					
Ferrous metals	0.00002	0.11	0.04	0.004	0.1
Non-ferrous metals	0.02	d	30.37	99.4	99.6
Inert	0.04	0.01	69.59	0.6	0.3

[a] Except for heat, where MJ/m² panel is used.

[b] Except for heat, where D /MJ is used.

[c] Sources: www.metalprices.com, www.greengatemetals.co.uk, www.letsrecycle.com, www.scrapregister.com, www.ecamsrl.it, www.taufer.bz.it (accessed 09/2015).

[d] An average value of the prices of the main recycled non-ferrous metals was considered: copper (3.50 D /kg), lead (1.25 D /kg), zinc (0.70 D /kg), aluminum (0.70 D /kg), tin (6.23 D /kg), nickel (10.48 D /kg).

2.3.1 System boundary and scenario description

The boundary of the analyzed system includes two sub systems: the thermal treatment of the decommissioned PV panel and the subsequent recycling of the recoverable fractions. In particular, after the thermal treatment of the c-Si PV panel, two different scenarios can be designed:

- a high-rate (HR) recovery scenario (Fig. 1a), where the heat produced by the plastics thermal treatment is recovered and then exploited for hot water generation or for heating purpose within the plant where the process takes place. Several materials are recovered during the process: except for the aluminum – whose disassembling is done before the thermal treatment – glass, silicon and copper are recovered through manual separation after the thermal treatment; Fe and non-Fe metals are mechanically sorted from ashes thermal treatment. After the recovery, these materials are sent to recycling process to obtain secondary raw materials whilst the inert fraction of the ashes ashes is assumed to be used for the clinker production in cement plants, in accordance with the Italian and international literature (Grosso et al., 2010; Reuter et al., 2004).
- a low-rate (LR) recovery scenario (Fig. 1b): only the aluminum frame and glass are recycled and the not-recovered (hereinafter referred as residual) fraction of copper, silicon and ashes is disposed of in a sanitary landfill.

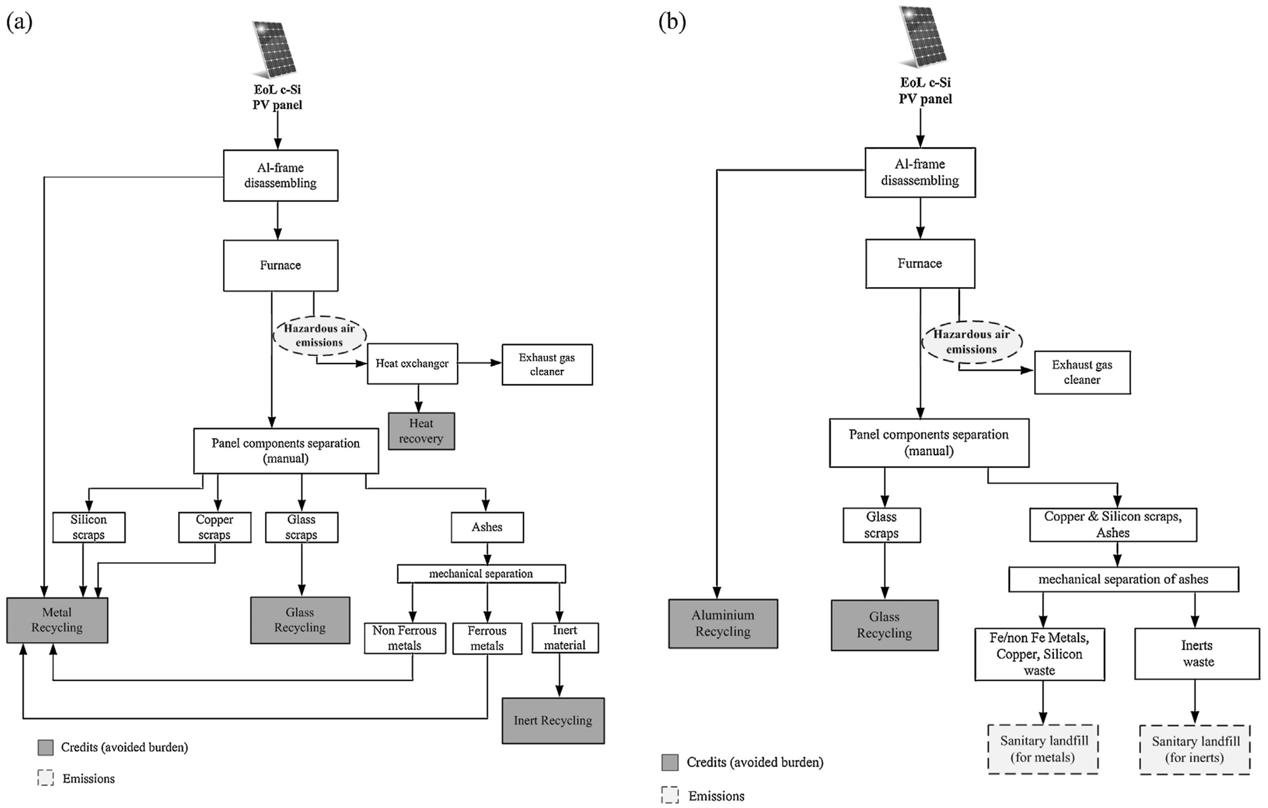


Fig. 1. (a) Flow chart of high-rate recovery scenario (HR). (b) Flow chart of low-rate recovery scenario (LR).

The transport of recovered materials to the recycling facilities is considered negligible as the sites for the collection of PV panels, treatment and disposal of are assumed to be in the same area, according to the European Union Directives of waste, that prescribe self-sufficiency of waste management at regional levels. In fact, the EU Waste Directive 2008 stated the proximity principle to be applicable also to the electronic waste (EC, 2008). Although this directive refers to urban waste, the increase of electronic waste, not only PV, is likely to require the same approach also for the EoL of these devices.

2.4 Life cycle inventory (LCI)

Tables 5a and 5b present the simplified inventory (LCI) of the inputs/outputs of the thermal treatment under study. All the flows are referred to 1 m^2 of PV panel treated (functional unit).

Primary data, e.g. specific information about furnace, recovered materials and heavy metals emissions related to the experimental thermal treatment, were provided by an Italian Research Center for Renewable Energy in the framework of F.E.R.G.E Project. The data related to the remaining emissions resulting from the burning of plastic components (EVA and PVF) and nitrogen oxides (NO_x) were modeled according to Hull et al. (2002) and Tewarson et al. (1994), respectively. Emissions of NO_x due to high temperature oxidation of nitrogen in the air, were calculated based on the data of the US Department of Health, Education and Welfare (U.S. Dept. of Health, 1970). Heat recovery from EVA and PVF incineration was also assumed, using respectively for calculation the values from Uçar et al. (2008) and Ecoinvent v3.1 database as heating values.

Table 5a

LCI of the main input flows of the thermal treatment referred to a 1 m^2 of c-Si PV panel.

Input flows[b]	Amount (kg/m^2 panel)[a]
Electricity, medium voltage	2.56E+01
Ammonia, liquid	2.76E−05

Cement	2.34E−02
Chemical inorganic	4.21E−05
Chemical organic	6.67E−06
Chromium oxide, flakes	1.61E−08
Hydrochloric acid	2.52E−05
Iron (III) chloride	1.25E−05
Quicklime	4.61E−03
Sodium hydroxide	2.62E−02
Titanium dioxide	7.91E-07

[a] Except for electricity (where kWh is used) and heat (where MJ is used).

[b] Except for electricity, the other inputs, referred to exhaust fume treatment, are modeled with reference to Ecoinvent database v.3.1 (process "treatment of waste polyvinylfluoride, municipal incineration").

Table 5b

LCI of the main output flows of the thermal treatment referred to a 1 m^2 of c-Si PV panel.

Output flows	Amount (kg/m^2 panel)[a]
HF	8.71E−04
NO	5.78E−06
NO_2	8.25E−07
CO	6.56E−05
CO_2	2.81E−04
VOC	4.32E−05
Hydrocarbons	2.34E−05
Al	8.60E−08
Cr	2.10E−09
Cu	1.76E−09
As	2.15E−10
Cd	4.42E−09
Pb	8.85E−08
Fe	8.20E−09

Sn	2.47E−07
Zn	3.16E−08
In	8.90E−10
Ba	1.37E−09
Ni	2.95E−10
Aluminum (frame)	3.29E+00
Glass	8.14E+00
Silicon (cell)	9.79E−01
Copper	3.62E−02
Inerts	3.81E−02
Non Fe-metals	1.66E−02
Fe-metals	2.27E−05
Heat from plastics	3.77E+01

[a] Except for electricity (where kWh is used) and heat (where MJ is used).

Dust emissions and solid emissions resulting from the subsequent treatment of exhaust fumes from thermal process are assumed to be negligible compared to the direct emissions of the thermal process. Furthermore, since at industrial scale the thermal treatment would require additional machineries and facilities to run the process (e.g. scrubber or the heat exchanger for the exhaust gases treatment), a scale-up scenario was designed in order to consider their impact and effects, using the most recent literature data on their consumption and abating efficiency.

Background data over the supply chain of energy and materials as well as all the data regarding waste treatments included in the proposed scenarios (such as treatment of waste in sanitary landfill or in incineration plant, also including wastewater treatment, airborne and waterborne emissions) were derived from the Ecoinvent v3.1 database. In particular, for the supply of electrical energy required by the thermal treatment, the Italian electric mix, medium-voltage, was selected.

Recycling costs related to materials and energy recovery and related environmental impacts were also included in the analysis. For crediting metals recovery, the avoided production of primary aluminum,[3] copper, and steel[4] was assumed. In the case of silicon, the avoided production of metallic silicon was assumed instead of EG silicon, given that it is not pure enough to be re-used for new solar cells manufacturing.

Since the recovered glass is a high purity material, it was considered suitable to be used for food packaging, although its re-utilization for glass sheets (float) production, thus being reintegrated in the same supply chain, should not be excluded. For crediting inert recovery, in accordance with Grosso et al., 2010, the avoided production of calcareous marl used as raw material for clinker production – was assumed.

2.5 Life Cycle Impact Assessment (LCIA)

The environmental assessment of the process was accomplished by means of LCA Professional software SimaPro 8.0.4.30 (Pre Consultants, 2014), integrated with Ecoinvent v3.1 database. The impact assessment was performed by means of one of the most recent and up-to-date LCA methods, the ReCiPe method (Goedkoop et al., 2009). The ReCiPe Midpoint (H) v.1.10 (http:// www.lcia-recipe.net/) was chosen, considering that it includes both upstream categories (i.e. referred to depletion of natural resources, such as fossil, metal and water depletion categories) and downstream categories (i.e. referred to impacts generated on natural matrices, such as terrestrial, marine or freshwater acidification) (Frischknecht et al., 2007). Moreover, the ReCiPe Midpoint (H) method assesses the environmental impacts in different impact categories of interest in waste management (e.g. global warming, abiotic depletion, acidification, eutrophication, human toxicity, among others). The ReCiPe method provides characterization factors to quantify the contribution of the different flows to and from a process to each impact category and normalization factors to allow a comparison across

[3] Non-ferrous metals, recovered from the ashes, are assumed to be recycled with the same costs and impacts as secondary aluminum.
[4] Ferrous metals, recovered from the ashes, are assumed to be recycled with the same costs and impacts as secondary steel.

indicators[5] (Goedkoop et al., 2009). Characterization quantifies the extent of the contribution of flows to each impact category (for example, expressing the contribution of CH_4, N_2O and CO_2 to the Global Warming category, by means of CO_2 equivalence factors). Normalization is a procedure used to express the characterized impact indicators in a way that allows comparison to each other. Normalization standardizes the indicators by dividing their characterized values by a selected reference value, translating into an assessment of how much the investigated process contributes to a given category with reference to a value considered acceptable or unavoidable in a given point in space and time (e.g. the average worldwide value in the year 2000). There are numerous methods of selecting a reference value, including, for example, the total emissions or resource use for a given area that may be global, regional or local (Sleeswijk et al., 2008).

In this study, the following indicators are considered: Global Warming Potential (GWP, in kg CO_2 eq), Photochemical Oxidant Formation Potential (POFP, in kg NMVOC), Terrestrial Acidification Potential (TAP, in kg SO_2 eq), Freshwater Eutrophication Potential (FEP, in kg P eq), Terrestrial Ecotoxicity Potential (TEP, kg 1,4-DB eq), Human Toxicity Potential (HTP, in kg 1,4-DB eq), Water Depletion Potential (WDP, in m^3), Metal Depletion Potential (MDP, in kg Fe eq), Fossil Depletion Potential (FDP, in kg oil eq).

3. Results

The performed analysis has two objectives: (1) to identify the flow(s) or steps that are most "responsible" of the environmental impacts in the PV panel thermal treatment and resources'

[5] According to ISO EN 14040 (2006), a category indicator is identified as the quantifiable representation of an impact category, being the object of characterization modeling, e.g. the category indicator for global warming is typically the increased radiative forcing and this radiative forcing is typically quantified with help of the Global Warming Potentials (GWP) as reported by the Intergovernmental Panel on Climate Change (Houghton et al., 1996).

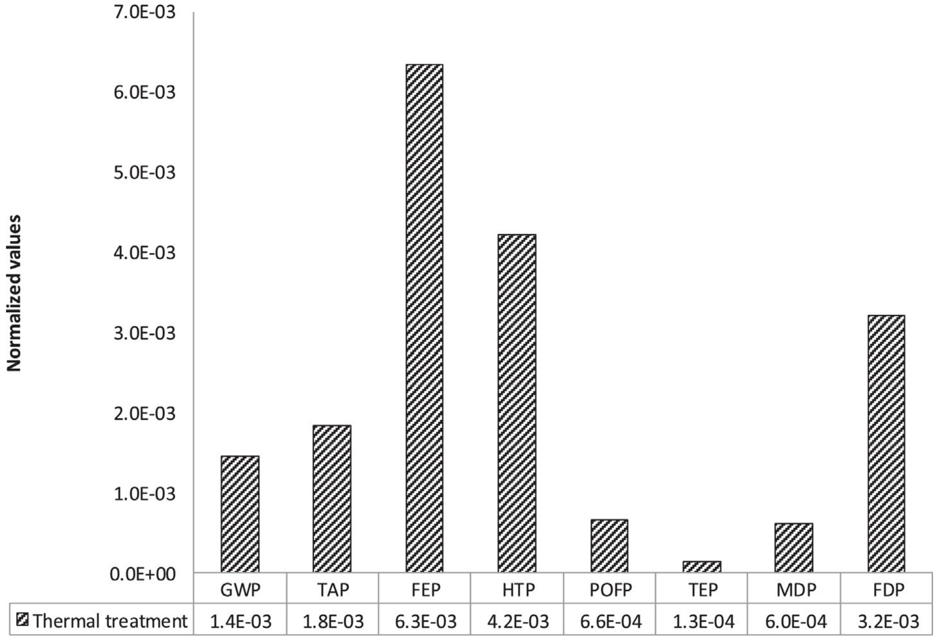


Fig. 2. Normalized impacts of the thermal treatment.

recovery; (2) to ascertain the environmental benefits of two different recovery scenarios, having in common the thermal treatment of the EoL panel and differing by the recovery rate (and likely the related costs and resources investment). The avoided costs, deriving from the possible recovery of materials in all scenarios were in any case considered (Ekvall and Andrae, 2005): in the present study, environmental savings of goods and energy (i.e. heat, metals, glass) were subtracted from the accounting of the system's impacts, considering that their production by means of conventional routes for later use in other processes is avoided. When the calculated impacts show negative values (see below), they suggest potential savings in the production of virgin materials and heat, and hint the amount of environmental benefits that can be achieved.

In order to ascertain the efficiency of the overall process (treatment and recovery) as well as the different performance of the HR and LR scenarios, it is worth taking into account firstly the actual impacts of each step, regardless of the inclusion of the benefits from the so-called "avoided products". The term "avoided product" refers to the use of recycled materials and energy to replace primary inputs to the process and avoid their production by means of new upstream processes. From an environmental point of view, an LCA accounting for avoided products (and related avoided impacts) highlights the actual benefits of recycling: the impact generated by the treatment and recycling phases (no process is exempt from impacts) is reduced thanks to the avoided production of new input flows. However, when focus is placed on understanding the actual impacts of the treatment or recovery processes, it is important to look at the process performance separate from the advantages provided by the recovered products, in order to avoid the risk that the latter hide the former.

3.1. *Thermal treatment*

Fig. 2 presents the normalized impacts of the thermal treatment phase (numbers are unit-less values that express a comparison with the chosen reference normalization standards). The most affected indicators are freshwater eutrophication (6.3E 03), human toxicity (4.2E 03) and fossil depletion (3.2E 03) and the major impact to all categories comes from the Italian medium voltage electricity mix (breakdown not shown in the figure, due to overwhelming percentage of electricity, around 98–99%), being electricity the only source of energy for thermal treatment. About 50% of this contribution is associated to the import of natural gas from foreign countries (24% from Russia, 16% from Algeria, 5% from the Netherlands, 5% from other countries).

3.2. *High-rate recovery scenario*

Table 6 shows the characterized impacts of the recovery process, with reference to the functional unit of 1 m^2 of c-Si PV panel treated, broken down into the different material recovery phases: aluminum and silicon recovery are the most impactful steps in almost all impact categories. In particular, concerning GWP, the impact generated by the recovery of aluminum accounts for 11.34 kg CO_2 eq/m^2 PV panel (43%), followed by the recovery of silicon (7.29 kg CO_2 eq/m^2 PV panel) (28%). If HTP is considered, the impact associated with aluminum recovery equals to 4.21 kg 1,4-DB eq/m^2 PV panel (56%), while silicon recovery contributes with 1.27 kg 1,4DB eq (17%). Regarding FDP, the impact generated by the recovery of aluminum accounts for 3.37 kg oil eq (42%), followed by the recovery of silicon (2.22 kg oil eq) (27%). Furthermore, in the water depletion category, the recycling phase of the silicon results to be the most impactful process, equaling 1.76 m^3/m^2 PV panel, 94% of total impact.

Fig. 3 shows the normalized contributions to the impacts, broken down into the contributions of each single phase of the high-rate scenario. Freshwater eutrophication and human toxicity categories are the more affected in comparison with others. In particular, with the exception of metal depletion, the aluminum and silicon recovery represent the most impacting phases in all impact categories. Regarding the silicon recovery, the impacts range from a minimum value of 5.55E−05 in TEP to a maximum value of 3.06E−03 in FEP, whilst the aluminum recovery contributes to the impacts with a minimum value of 1.45E−04 in TEP, to a maximum value of 6.69E+03 in HTP. WDP is not detectable at all, due to the normalization factor equal to zero, and it is not shown in Fig. 3.

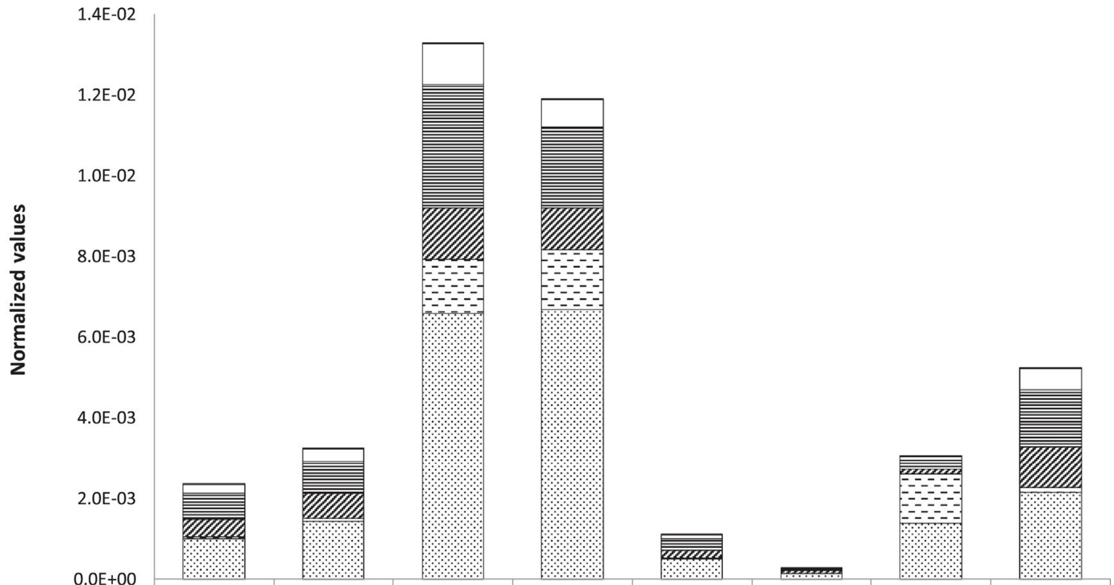
Table 6

Characterized impacts calculated for the high-rate scenario, broken down into different process steps, referred to a functional unit of 1 m^2 c-Si PV panel treated.

Categ. indic.	Unit/m^2 PV panel treated	Total	Aluminum recovery	Copper recovery	Glass recovery	Inert recovery	Silicon recovery	Steel recovery	Heat recovery
GWP	kg CO_2 eq	2.64E+01	1.13E+01	5.50E−01	4.64E+00	1.86E−04	7.29E+00	1.00E−05	2.59E+00
TAP	kg SO_2 eq	1.11E−01	4.91E−02	2.48E−03	2.19E−02	3.50E−06	2.71E−02	4.74E−08	1.01E−02
FEP	kg P eq	5.51E−03	2.74E−03	5.54E−04	5.26E−04	1.43E−08	1.27E−03	6.16E−09	4.22E−04
HTP	kg 1,4-DB eq	7.74E+00	4.21E+00	9.30E−01	6.42E−01	2.08E−05	1.27E+00	3.36E−05	4.24E−01
POFP	kg NMVOC	6.30E−02	2.85E−02	1.38E−03	1.10E−02	4.62E−06	1.62E−02	3.95E−08	6.01E−03
TEP	kg 1,4-DB eq	2.30E−03	1.20E−03	6.89E−05	4.04E−04	1.01E−08	4.59E−04	7.91E−09	1.68E−04
WDP	m^3	1.88E+00	9.36E−02	−1.39E−03	1.36E−02	2.06E−06	1.76E+00	−6.79E−07	1.34E−02
MDP	kg Fe eq	2.17E+00	9.85E−01	8.83E−01	8.81E−02	8.21E−06	1.46E−01	1.50E−06	6.88E−02
FDP	kg oil eq	8.11E+00	3.37E+00	1.67E−01	1.56E+00	5.67E−05	2.22E+00	3.24E−06	7.98E−01

Similar results and analogous trends are gained if the exergetic allocation is performed. Conversely, when mass allocation comes into play, although the most affected categories result to be the same, different values are obtained in each single recovery phase. In particular, the aluminum and glass recovery represent the most impacting phases in all impact categories, being aluminum and glass the heaviest fractions in mass terms: the impact of glass recovery ranges from a minimum value of 15% in MDP to a maximum value of 52% in FDP, whilst the aluminum recovery contributes to the impacts with a minimum value of 23% in

FDP to a maximum value of 45% in HTP (these results are not shown in the figure).



	GWP	TAP	FEP	HTP	POFP	TEP	MDP	FDP
Inert recovery	1.7E-08	1.0E-07	3.5E-08	3.3E-08	8.1E-08	1.2E-09	1.1E-08	3.6E-08
Heat recovery	2.3E-04	2.9E-04	1.0E-03	6.7E-04	1.1E-04	2.0E-05	9.6E-05	5.1E-04
Steel recovery	8.9E-10	1.4E-09	1.5E-08	5.3E-08	7.0E-10	9.6E-10	2.1E-09	2.1E-09
Silicon recovery	6.5E-04	7.9E-04	3.1E-03	2.0E-03	2.9E-04	5.5E-05	2.0E-04	1.4E-03
Glass recovery	4.1E-04	6.4E-04	1.3E-03	1.0E-03	1.9E-04	4.9E-05	1.2E-04	1.0E-03
Copper recovery	4.9E-05	7.2E-05	1.3E-03	1.5E-03	2.4E-05	8.3E-06	1.2E-03	1.1E-04
Aluminium recovery	1.0E-03	1.4E-03	6.6E-03	6.7E-03	5.0E-04	1.5E-04	1.4E-03	2.2E-03

Fig. 3. Normalized impacts of high-rate scenario, broken down into contributions from each single phase, with reference to 1 m^2 of c-Si PV panel treated.

3.2.1. *Recycling of aluminum and silicon*

Being aluminum and silicon the main responsible of the process impacts, their contributions to the impacts of the thermal treatment and subsequent recycling process phases were carefully evaluated and compared. The characterized results are shown in Table 7. Recycling of both aluminum and silicon contributes to the overall process impacts more than just their allocated fraction of thermal treatment. Aluminum recycling impacts are always 1.3–2.0 times higher than thermal treatment, except for metal depletion, that shows a four times higher impact. Silicon recycling impacts 2.6–3.6 times more than thermal treatment, except for water depletion that only shows a 1.5 higher impact. The different impacts of the two treatment phases for the two metals are graphically shown as percentages in Fig. 4, in so suggesting that efficiency improvements are much needed in the recycling phase (refining, purity upgrade, etc.).

Fig. 5 compares the normalized values, referred to the usual functional unit, of the aluminum and silicon recycling processes. The highest impacts generated by the aluminum recycling process affect freshwater eutrophication and human toxicity; in both cases the largest contribution (at least 90%) is associated to the use of alligants (breakdown not shown in the figure due to overwhelming percentage of alligants) whilst a much smaller contribute is attributed to electricity (1–3%). The silicon recycling process mainly affects freshwater eutrophication, the largest impact of which is associated to electricity, hydrochloric acid and sodium hydroxide for a share of 79%, 14% and 5%, respectively, and human toxicity, where the main impact comes from electricity (70%), hydrochloric acid (23%) and sodium hydroxide (5%) (breakdown not shown in the figure).

Table 7

Characterized impacts calculated for the two sub-processes (thermal treatment and recycling) of aluminum and silicon recovery.

Category indicator	Unit/m^2 PV panel treated	Thermal treatment		Recycling process	
		Aluminum	Silicon	Aluminum	Silicon
GWP	kg CO_2-eq	8.08E+00	2.26E+00	1.06E+01	7.77E+00
TAP	kg SO_2-eq	3.50E−02	8.82E−03	4.96E−02	2.90E−02
FEP	kg P-eq	1.47E−03	3.68E−04	2.76E−03	1.35E−03
HTP	kg 1,4-DB-eq	1.48E+00	3.70E−01	4.23E+00	1.35E+00
POFP	kg NMVOC	2.03E−02	5.26E−03	2.82E−02	1.73E−02
TEP	kg 1,4-DB-eq	6.04E−04	1.47E−04	1.23E−03	4.90E−04
WDP	m^3	4.89E−02	1.17E−02	9.65E−02	1.76E+00
MDP	kg Fe-eq	2.34E−01	6.02E−02	9.84E−01	1.59E−01
FDP	kg oil-eq	2.43E+00	6.98E−01	3.06E+00	2.37E+00

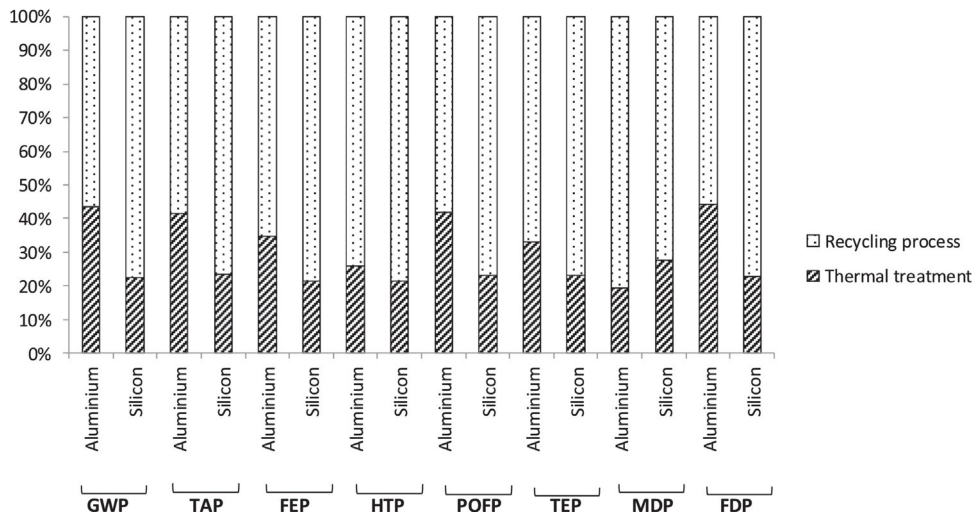


Fig. 4. Percent impact contribution of thermal treatment and recycling processes for aluminum and silicon recovery.

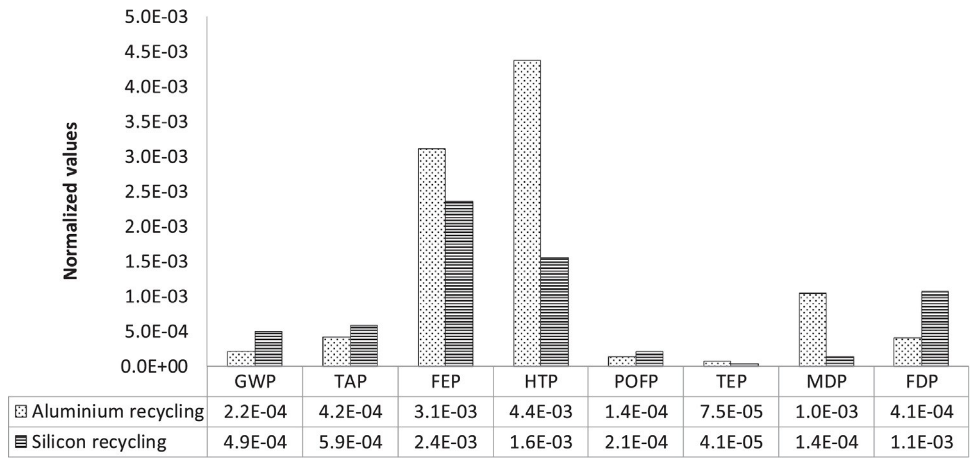


Fig. 5. Normalized impacts of the aluminum and silicon recycling processes.

3.3. *Comparison between high-rate (HR) and low-rate (LR) recovery scenarios*

Table 8 summarizes, for each single recovery process (which includes the thermal treatment phase), the characterized results related to the HR and LR scenarios. In the HR scenario, the environmental benefits – i.e. negative values – from recovery are much higher than the environmental loads in all impact categories, with minor impacts still associated to heat, copper, inert and steel recovery. In the global warming category, the most relevant benefits are achieved thanks to silicon and

aluminum recovery, amounting to 63.40 and 20.60 kg CO_2 eq/m^2 panel, respectively, whilst a smaller benefit is provided by glass recovery (3.65 kg CO_2 eq/m^2 panel). Silicon recovery and aluminum recovery also contribute to the largest avoided impacts in the human toxicity category, with 23.40 1,4-DB eq/m^2 panel and 16.60 1,4 DB eq/m^2 panel, respectively. Regarding the fossil depletion category, the most pronounced environmental benefits are provided by silicon recovery, corresponding to avoided impacts of 16.60 kg oil eq/m^2 panel.
In the LR scenario, the GWP environmental advantage of the aluminum recovery (18.50 kg CO_2 eq/m^2 panel) is greater than the recovery of glass (3.49 kg CO_2 eq/m^2 panel). Instead, a non-negligible GWP impact, around 2.79 kg CO_2 eq/m^2 panel, is generated by the landfill disposal of the residual fraction (including silicon, copper and ashes of the thermal treatment). In the human toxicity category, the aluminum recovery provides relevant benefits (16.20 1,4 DB eq/m^2 panel), with the glass recovery playing a minor role (1.61 1,4 DB eq/m^2 panel) as well.

In the remaining impact categories, contributions from the two scenarios do not differ markedly.

Fig. 6 shows the contributions of each single phase of HR and LR scenarios to the normalized impacts in all the investigated impact categories. In the case of HR, the environmental benefits overcome the environmental loads in all impact categories, but some burdens are provided by the recovery of heat, especially in POFP and MDP indicators, corresponding to impacts of 1% and 2%, respectively. Nevertheless, a net advantage (with the negative part much larger than the positive one) is reached in all the impact categories. In particular, environmental advantages from the silicon recovery are achieved in all the analyzed categories, ranging from a minimum of 56% in human toxicity to a maximum of 80% in freshwater eutrophication.

Beyond silicon recovery, the second main contribution to environmental benefits comes from the recovery of aluminum in all impact categories, except for terrestrial ecotoxicity and metal depletion. It is worth to point out that silicon and aluminum recovery are the main responsible of the negative values, equalling together more than 70% of the total avoided impact in all categories. In particular, FEP and GWP are the indicators where the avoided (i.e. negative) burden given by silicon and aluminum reaches 99% and 96%, respectively.

Table 8

Characterized impacts calculated for the high-rate and low-rate scenarios (broken down into different process steps), referred to a functional unit of 1 m^2 c-Si PV panel treated. Negative values correspond to avoided impacts thanks to recovery.

Categ indic.	Unit/m^2 PV panel treated	Aluminum recovery		Copper recovery	Glass recovery		Inert recovery	Silicon recovery	Steel recovery	Heat recovery	Landfilling of ashes, copper, silicon
		HR	LR	HR	HR	LR	HR	HR	HR	HR	LR
GWP	kg CO_2 eq	−2.06E+01	−1.85E+01	4.63E−01	−3.65E+00	−3.49E+00	−2.00E−05	−6.34E+01	−3.01E−05	2.66E−01	2.79E+00
TAP	kg SO_2 eq	−2.03E−01	−1.95E−01	5.62E−04	−4.59E−02	−4.53E−02	1.49E−06	−3.34E−01	−8.75E−08	3.48E−03	1.10E−02
FEP	kg P eq	−1.33E−02	−1.9E−02	−1.97E−04	−6.35E−04	−6.09E−04	−3.65E−09	−3.01E−02	−8.19E−09	4.02E−04	4.59E−04
HTP	kg 1,4-DB eq	−1.66E+01	−1.62E+01	−4.88E−01	−1.64E+00	−1.61E+00	−2.66E−05	−2.34E+01	2.34E−05	2.64E−01	4.76E−01
POFP	kg NMVOC	−9.77E−02	−9.27E−02	5.52E−04	−2.43E−02	−2.40E−02	1.83E−06	−1.80E−01	−1.19E−07	3.65E−03	6.61E−03
TEP	kg 1,4-DB eq	−8.88E−04	−7.54E−04	2.27E−06	−1.76E−03	−1.75E−03	−5.05E−08	−5.02E−03	6.38E−09	4.74E−05	1.81E−04
WDP	m^3	−5.10E−01	−4.97E−01	−1.00E−03	−2.35E−02	−2.26E−02	−4.51E−08	−1.63E+00	−9.15E−07	2.74E−02	1.42E−02
MDP	kg Fe eq	−2.36E−01	−1.82E−01	−5.26E−01	−1.36E−01	−1.32E−01	−1.46E−06	−1.19E+00	−2.21E−05	4.72E−02	7.46E−02
FDP	kg oil eq	−3.28E+00	−2.65E+00	1.42E−01	−9.01E−01	−8.51E−01	−1.24E−05	−1.66E+01	−3.75E−06	−2.36E−02	8.61E−01

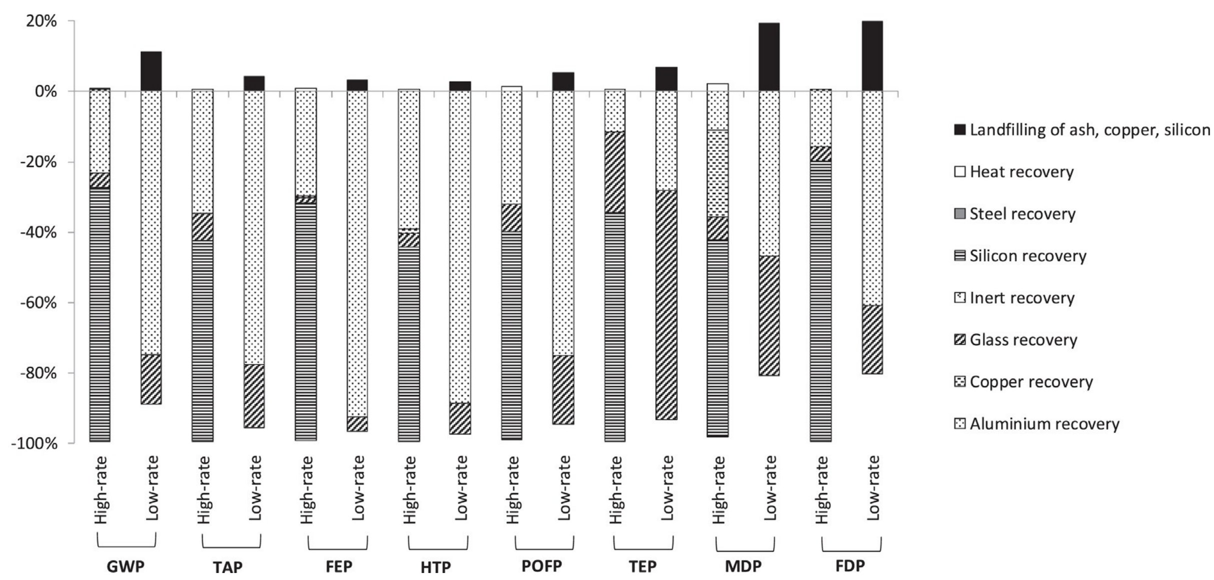


Fig. 6. Contributions to normalized impacts from each single phase of high-rate and low-rate scenarios.

Overall, a positive performance also in the LR scenario, thanks to the recovery of glass and aluminum is noticeable. In particular, the environmental benefits of the aluminum recovery are achieved in all analyzed categories, with values ranging from a minimum of 78% in terrestrial ecotoxicity to a maximum of 92% in freshwater eutrophication. However, unlike the HR, the impacts (i.e. positive values) of the process are more evident due to disposal of the residual fraction. Especially in the metal depletion and fossil depletion categories, the disposal phase contributes to the impact with a share of 20% approximately.

Table 9 compares the final characterized results achieved by applying the ReCiPe Midpoint (H) method to HR and LR scenarios, with reference to the usual functional unit. All the resulting values are negative, meaning that both scenarios turn out to be favorable (i.e. contribute to decrease impacts) thanks to the recovery of materials that can be reintegrated in the production chains.

In particular, HR scenario shows the highest avoided impacts, in comparison with LR scenario, in all the impact categories, especially GWP, HTP and FDP indicators, corresponding to 8.69E+01 CO_2 eq/m^2 panel (four times better than LR scenario), 4.18E+01 kg 1,4-DB eq/m^2 panel (two times better than LR scenario) and 2.06E+01 kg oil eq/m^2 panel (eight times better than LR scenario), respectively.

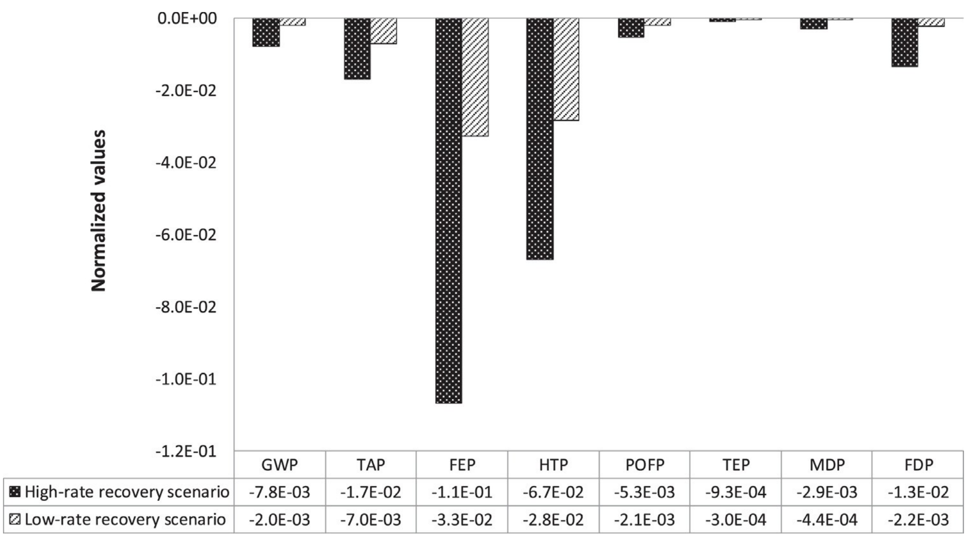


Fig. 7. Recipe midpoint (h) normalized impacts calculated for high-rate and low-rate recovery scenarios, with reference to 1 m^2 of c-Si PV panel. Results include avoided impacts due to recovery of energy and material flows.

Table 9

Characterized impacts calculated for the high-rate and low-rate scenarios, referred to a functional unit of 1 m^2 c-Si PV panel treated.

Negative values correspond to avoided impacts thanks to recovery.

Category indicator	Unit/m^2 PV panel treated	HR	LR
GWP	kg CO_2 eq	−8.69E+01	−1.92E+01
TAP	kg SO_2 eq	−5.79E−01	−2.29E−01
FEP	kg P eq	−4.39E−02	−1.31E−02
HTP	kg 1,4-DB eq	−4.18E+01	−1.73E+01
POFP	kg NMVOC	−2.98E−01	−1.10E−01
TEP	kg 1,4-DB eq	−7.61E−03	−2.32E−03
WDP	m^3	−2.14E+00	−5.06E−01
MDP	kg Fe eq	−2.04E+00	−2.39E−01
FDP	kg oil eq	−2.06E+01	−2.64E+00

If normalized values of impacts are taken into account (Fig. 7), according to Europe ReCiPe Midpoint (H) method normalization factors, a comparison across impact categories becomes possible. HR is the best performing scenario in terms of avoided burdens, in all impact categories. The most pronounced environmental benefits are achieved by HR in FEP and HTP indicators, corresponding to 1.1E 01 and 6.7E 02, respectively. WDP indicator is not detectable at all, due to the normalization factor equal to zero, and it is not shown in Fig. 7.

4. Discussion

The results of this study show that the recovery process of the poly-crystalline silicon photovoltaic panels displays non-negligible benefits from both energy and environmental points of view. In order to suggest solutions to improve the overall efficiency of the process, the system was analyzed also without considering the avoided products, so as to understand which of the different recycling phases has the greatest impact. As it can be observed in Fig. 3, if the economic and exergetic allocations are performed, the largest impact, overall higher by 70% in all indicators, is caused by the recovery of aluminum and silicon. Conversely, when a mass allocation is performed, very different values are obtained, being glass the heaviest recoverable material (63% of total mass). This result was the main motivation to orient the research toward a more detailed analysis of the most impacting steps and processes; therefore, the entire process was broken down into two sub-processes: thermal treatment, aimed at energy and material separation and recovery from the panel, and the recycling process, directed to the refining of recovered products to produce secondary raw materials.

In all impact categories, the impact of aluminum and silicon recycling processes is more than double relative to the thermal treatment. For this reason, the analysis was further detailed to identify the "responsible step" of the impacts in both scenarios. As for the thermal treatment and silicon recycling process, the most significant impact (larger than 70%) was generated by the Italian electricity mix, whose major contribution comes from fossil fuels gas (56%) and coal (14%) (Ecoinvent, 2014).

A similar result (with one main dominant flows responsible of the impact) is also highlighted in the case of the aluminum recycling process, in which more than 90% of the impacts is associated with the production of the alligants – i.e. metals such as zinc, copper and silicon. In fact, the environmental costs of the metal extraction processes, are very high due to the significant amount of slags that are produced and that need appropriate disposal, as they contain traces of toxic elements such as arsenic, mercury, cadmium, uranium and thorium (Norgate et al., 2007). According to Gardner and Sampat (1998), the annual world production of these trace elements is estimated at several hundred million tons, an amount greater than the mass of the Earth's crust naturally eroded by rivers.

Indeed, according to Table 9, the negative values achieved for the entire process mean that the avoided impacts are greater than the burden caused to the environment, thanks to the recycling process and to the recovery of secondary raw materials able to replace primary inputs. In particular, the comparison between high-rate (HR) and low-rate (LR) scenarios, shows important differences in terms of avoided costs: HR presents the highest avoided impacts in all indicators analyzed – with the larger environmental benefits arising from the recovery of silicon and aluminum (Fig. 6).

In the light of the findings of the present analysis, the thermal treatment tested by the Italian ENEA Research Institute, proved to be a good solution to remove the encapsulant (EVA) from Poly-Si PV panel, allowing the recovery of valuable resources. However, attention should be given to the flue gas treatment, because if they are not properly handled, they may release heavy metals (Tammaro et al., 2015) and fluorinated compounds resulting from the incineration of the plastic layer in PVF (Huber et al., 2009). Furthermore, in order to optimize the recovery process, future research is needed to modify the module design, for example by limiting the use of plastic polymers in their composition. In this way, also the dependence of the PV chain on fossil fuels would be decreased. Moreover, several technologies are being tested to replace the substrate and the layer of the front cover of the modules, such as bio-materials, having the same characteristics of strength, durability and transparency of the plastics.

In conclusion, this study shows that silicon recycling allows a net benefit in all impact categories (e.g. fossil depletion). In fact, the silicon wafer accounts for 76% of the embedded energy (Bennett et al., 2013), and it can contribute 60% to the costs of the module (US Dept. of Energy, 2012). A long-standing aim of European PV research has been to lower PV module costs. It has been articulated also in the goals of the Strategic Research Agendas and the Solar Europe Industry Initiative (SEII) PV Implementation Plans since 2007. The production cost issue has been tackled by improving efficiencies, device design and manufacturing processes (Reck and Graedel, 2012). In the most recent SEII plan (2013), improvement of recycling is also taken on as a research goal with the aim of improving the sustainability and competitiveness of EU PV products. It is conceivable that the production cost issue might also be addressed by re-using silicon wafers. After a lifetime of 25–30 years, the failure of a PV panel is due to de-lamination or other module architecture issues, and not due to the silicon solar cell itself. The reuse of silicon wafers, however, depends on the ability to de-manufacture the PV module so as to recover the solar cells intact and liberated from the crosslinked EVA polymer encapsulant. Current research on ways to recover the intact silicon wafer, including thermal and chemical methods, are still being tested (Klugmann-Radziemska et al., 2010; Wang et al., 2011). Additionally, since the main impact of a c-Si PV panel is due to the solar grade silicon production (Hough, 2007), recycling would represent both a significant environmental benefit, since it would avoid the energy intensive processes of extraction/purification of metallurgical silicon, and economic benefits, given the relatively higher market price of primary silicon (e.g. from 2010 to 2014 the price ranged between 2.5 D /kg and 3.2 D /kg) (USGS, 2015). At the same time the recycled aluminum and copper may also provide an economic benefit because of the primary raw material price ranged between 1.92 D /kg and 2.36 D /kg for the aluminum and 7.14 D /kg and 8.15 D /kg for the copper from 2010 up to 2014 (USGS, 2015).

Based on the above considerations, the targets of the WEEE European regulation should be revised in order to prioritize a quality material-related approach over a raw mass-related one (Reck and Graedel, 2012). In fact, the recovery/recycling of aluminum and glass only would be sufficient to meet the legislative objectives of recovery/recycling in terms of mass recovered (80% recovery prescribed), but revenues would not be able to cover the high costs of logistics and treatment (Cucchiella et al., 2015). Conversely, this would happen if all high value components are recycled, through the additional recovery of silicon, silver and copper, thus increasing both the economic and environmental benefits (Bio Intelligence, 2011). It is also worth to underline that since 2013 silicon has become a critical raw material according to the EC recent report on critical raw materials in the EU (EC, 2014).

Another important consideration relates to the source of energy required for the thermal process. The analysis of the Italian electricity mix, has pointed out that its larger component comes from fossil fuels (about 70%); moreover, the main impacts are generated by the disposal of tailings from fossil fuels extraction and refining processes. The existence of a waste generating process upstream of the actual PV treatment/recycling process lowers the whole performance. As a consequence, not only an improvement of the efficiency of the thermal treatment process is needed, in order to decrease the electricity demand, but also an improvement of the electricity supply chain, with a larger share of renewable energy sources, would contribute to a more sustainable processing. This would act as a feedback, with renewable sources supporting the environmentally sound management of renewable power devices. As for the development of renewable sources in Italy, in last years the sector has experienced a significant boost and more is expected in the next years also in accomplishment of international agreements and EU Directives. According to Terna (2013)[6] the share of renewable electricity compared to total gross production increased from 15.3% in 2007 up to 38.6% in 2013. This is due to the policies to reduce greenhouse gas emissions and increase renewable sources, in addition to the different incentives of renewable sources in the electricity sector and increased business opportunities arising (GSE, 2013).

5. Conclusion

A careful analysis of the environmental impacts of the photovoltaic technology (as with all other technological innovations) cannot be limited to considering only the production and operational phase of the PV panels, but the whole life cycle has to be considered, including the impacts associated with the "end-of-life" phase, namely their decommissioning and recycling. Moreover, with regard to the entire cycle of the production chain, an efficient recycling of the PV panels at the end of their life is likely to decrease the impacts and the economic costs associated with their production.

In this paper, the Life Cycle Assessment methodology turned out to be an excellent tool to assess the environmental impacts of an innovative recovery process of crystalline silicon PV panels based on thermal treatment and high-rate material recovery. Overall, the analysis shows that the recovery process of the PV panels has clear advantages from the energy and environmental points of view in all impact categories analyzed, in particular freshwater eutrophication, human toxicity, terrestrial acidification and fossil depletion. The main environmental benefits arise from the recovery of aluminum and silicon. Nevertheless, the other recovered materials (glass, copper) also provide non-negligible benefits. It is to be noted that the main impact of the PV module production is generated by the silicon wafer and its high embodied energy. Therefore, given the expected increase of the volume of the PV panels waste in the future, a well-designed recovery process has to be carried out; this has to include all high value materials such as silicon

[6] The Italian National Electricity Transmission Grid.

(feedstock, wafer or cell) and silver. Recycling would be facilitated by appropriate PV module design, for easier separation of components. Recycling of photovoltaic modules proves to be feasible at acceptable energy and environmental costs, thus reinforcing the claims for economic feasibility and large benefits. An appropriate EoL management of PV modules is a prerequisite for the sustainability of the entire PV electricity supply chain, which calls for increased efforts to assess and monitor impacts and benefits.

Acknowledgements

The authors Ripa and Ulgiati gratefully acknowledge the financial support received from the EU Project EUFORIE – European Futures for Energy Efficiency, funded under EU Horizon 2020 programme, call identifier H2020-EE-2014-2-RIA and to topic EE12-2014, Socio-economic research on energy efficiency. Sergio Ulgiati also acknowledges the contract by the School of Environment, Beijing Normal University, within the framework of the PR China Government "One Thousand Foreign Experts Plan". The author Graditi gratefully acknowledges the financial support received from F.E.R.G.E. Project – Dispositivi, tecniche e tecnologie abilitanti per le Fonti Energetiche Rinnovabili verso la Green Economy – PON03PE 00177 1 – funded under Italian Ministry of Education University and Research. The authors are indebted with two anonymous reviewers for their valuable comments.

References

Allen, N.S., Edge, M., Rodriguez, M., Liauw, C.M., Fontan, E., 2000. Aspects of the thermal oxidation of ethylene vinyl acetate copolymer. Polym. Degrad. Stab. 68, 363–371, http://dx.doi.org/10.1016/S0141-3910(00)00020-3.

Bala Gala, A.B., Raugei, M., Ripa, M., Ulgiati, S., 2015. Dealing with waste products and flows in life cycle assessment and emergy accounting: Methodological overview and synergies. Ecol. Model. 315, 69, http://dx.doi.org/10.1016/j.ecolmodel.2015. 03.004.

Bennett, I., Geerligs, B., Olson, C., Goris, M., 2013. Compatibility of copperelectroplated cells with metal wrap-through module materials. Photovolt. Int. http://www.sustainablepv.eu/fileadmin/sustainablepv/user/PVI21 Paper 08 ECN Modules v4.pdf.

Berger, W., Simon, F.-G., Weimann, K., Alsema, E.A., 2010. A novel approach for the recycling of thin film photovoltaic modules. Resour. Conserv. Recycl. 54, 711–718, http://dx.doi.org/10.1016/j.resconrec.2009.12.001.

Bio Intelligence, 2011. Study on photovoltaic panels supplementing the impact assessment for a recast of the WEEE Directive. Report for the European Commission DG ENV (Project No. ENV.G.4/FRA/2007/0067). http://ec.europa.eu/ environment/waste/weee/pdf/Study%20on%20PVs%20Bio%20final.pdf.

Brown, M.T., Raugei, M., Ulgiati, S., 2012. On boundaries and "investments" in Emergy Synthesis and LCA: a case study on thermal vs. photovoltaic electricity. Ecol. Indic. 15, 227–235, http://dx.doi.org/10.1016/j.ecolind.2011.09.021.

Choi, J.-K., Fthenakis, V., 2014. Crystalline silicon photovoltaic recycling planning: macro and micro perspectives. J. Clean. Prod. 66, 443–449, http://dx.doi.org/10. 1016/j.jclepro.2013.11.022.

Cucchiella, F., D'Adamo, I., Rosa, P., 2015. End-of-Life of used photovoltaic modules: A financial analysis. Renew. Sustain. Energy Rev. 47, 552–561, http://dx.doi.org/ 10.1016/j.rser.2015.03.076.

Ecoinvent, 2014. Swiss Centre for Life Cycle Inventories. Ecoinvent Centre, Dübendorf, Switzerland http://www.ecoinvent.org.

Ekvall, T., Andrae, A., 2005. Attributional and consequential environmental assessment of the shift to lead-free solders. Int. J. Life Cycle Assess. 11, 344–353, http:// dx.doi.org/10.1065/lca2005.05.208, 10 pp.

Ekvall, T., Assefa, G., Björklund, A., Eriksson, O., Finnveden, G., 2007. What life-cycle assessment does and does not do in assessments of waste management. Waste Manag. 27, 989–996, http://dx.doi.org/10.1016/j.wasman.2007.02.015.

EPIA, 2011. Solar photovoltaic electricity empowering the world. In: Solar genera-tion 6.

EPIA, 2014. Global market outlook for photovoltaics 2014–2018., http://dx.doi.org/10.1007/s10854-007-9177-9.

EPIA/Solar Power Europe, 2015. Global Market Outlook for Photovoltaics2015–2019. http://www.solarpowereurope.org/insights/global-market-outlook/.European Commission (EC), 2008. Waste Framework Directive 2008/98/EC.

European Commission (EC) – Joint Research Center – Institute of Environment and Sustainability, 2010. International Reference Life Cycle Data System (ILCD) Handbook – General Guide for Life Cycle Assessment – Detailed Guidance. First edition March 2010. EUR 24708 EN. Publications Office of the European Union, Luxembourg, LU.

European Commission (EC) – Joint Research Center – Institute of Environment and Sustainability, 2011. Supporting Environmentally Sound Decisions for Waste Management – A technical guide to Life Cycle Thinking (LCT) and Life Cycle Assessment (LCA) for waste experts and LCA practitioners. EUR 24916 EN. lications Office of the European Union, Luxembourg, LU.

European Commission (EC), 2012. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE).

European Commission (EC), 2013. Mandate to the European standardisation nisations for standardisation in the field of waste electrical and electronic equipment (Directive 2012/19/EU (WEEE)).

European Commission (EC), 2014. Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials. http://ec.europa. eu/growth/sectors/raw-materials/specific-interest/critical/index en.htm.

Finnveden, G., Johansson, J., Lind, P., Moberg, Å., 2005. Life cycle assessment of energy from solid waste—Part 1: General methodology and results. J. Clean. Prod. 13, 213–229, http://dx.doi.org/10.1016/j.jclepro.2004.02.023.

Frischknecht, R., Editors, N.J., Althaus, H., Bauer, C., Doka, G., Dones, R., Hischier, R., Hellweg, S., Köllner, T., Loerincik, Y., Margni, M., 2007. Implementation of Life Cycle Impact Assessment Methods. Am. Midl. Nat. 150, 1–151.

Fthenakis, V.M., Eberspacher, C., Moskowitz, P.D., 1996. Recycling strategies to enhance the commercial viability of CIS photovoltaics. Prog. Photovolt. Res. Appl. 4, 447–456, http://dx.doi.org/10.1002/(SICI)1099-159X(199611/12)4:6<447::AID-PIP147>3.0.CO;2-F.

Fthenakis, V.M., 2000. End-of-life management and recycling of PV modules. Energy Policy 28, 1051–1058, http://dx.doi.org/10.1016/S0301-4215(00)00091-4.

Fthenakis, V.M., 2003. In: Markvart, T., Castaner, L. (Eds.), Overview of Potential Hazards. Chapter VII-2, Practical Handbook of Photovoltaics: Fundamentals and Applications, General. Elsevier, http://dx.doi.org/10.1017/CBO9781107415324. 004, ISBN 1-856-17390-9.

Fthenakis, V., Alsema, E., 2006. Photovoltaics energy payback times, greenhouse gas emissions and external costs: 2004–early 2005 status. Prog. Photovolt. Res. Appl. 14, 275–280, http://dx.doi.org/10.1002/pip.706.

Fthenakis, V., Duby, P., Wang, W., 2006. Recycling of CdTe photovoltaic modules: recovery of cadmium and tellurium. In: Proceedings of the 21st European tovoltaic Solar Energy Conference, Dresden, Germany, pp. 4–8.

Fthenakis, V.M., Kim, H.C., Held, M., Raugei, M., Krones, J., 2009. Update of PV energy payback times and life-cycle greenhouse emissions. In: 24th Eur. Photovolt. Sol. Energy Conf, p. 4412, http://dx.doi.org/10.4229/24thEUPVSEC2009-6DO.10.5.

Fthenakis, V.M., Frischknecht, R., Raugei, M., Kim, H.C., Alsema, E., Held, M., de Wild-Scholten, M., 2011. Methodology Guidelines on Life Cycle Assessment of Photovoltaic Electricity. In: IEA PVPS Task 12, International Energy Agency Photovoltaic Power systems Programme, 2nd edition.

Fthenakis, V.M., Kim, H.C., 2011. Photovoltaics: life-cycle analyses. Sol. Energy 85, 1609–1628, http://dx.doi.org/10.1016/j.solener.2009.10.002.

Gardner, G., Sampat, P., 1998. Mind over matter: Recasting the role of materials in our lives, Worldwatch Paper.

GSE (Gestore Servizi Energetici), 2012. Rapporto statistico 2012. Solare rinnovabile. http://www.gse.it/it/Statistiche/RapportiStatistici/Pagine/default.aspx.

GSE (Gestore Servizi Energetici), 2013. Rapporto Statistico 2012. Impianti a fonti rinnovabili in Italia. http://www.gse.it/it/Statistiche/RapportiStatistici/Pagine/ default.aspx.

Giacchetta, G., Leporini, M., Marchetti, B., 2013. Evaluation of the environmental benefits of new high value process for the management of the end of life of thin film photovoltaic modules. J. Clean. Prod. 51, 214–224, http://dx.doi.org/ 10.1016/j.jclepro.2013.01.022.

GlobalData, 2012. “Solar Module Recycling – A Necessary Step to Maximize ronmental Benefits of Solar PV Industry”, Report Number: GDAE1003TR.

Goedkoop, M., Heijungs, R., Huijbregts, M., Schryver, A., De Struijs, J., Zelm, R.V., 2009. Report I: Characterisation. ReCiPe A life cycle impact Assess method which comprises Harmon. Categ. Indic. Midpoint Endpoint Lev., 132.

Granata, G., Pagnanelli, F., Moscardini, E., Havlik, T., Toro, L., 2014. Recycling of photovoltaic panels by physical operations. Sol. Energy Mater. Sol. Cells 123, 239–248, http://dx.doi.org/10.1016/j.solmat.2014.01.012.

Grosso, M., Rigamonti, L., Biganzoli, L., 2010. Separazione e recupero dei metalli e valorizzazione delle scorie di combustione dei rifiuti urbani, Rapporto per Federambiente e CiAl. http://www.cial.it/.

Hadian, S., Madani, K., 2015. A system of systems approach to energy sustainability assessment: are all renewables really green? Ecol. Indic. 52, 194–206, http://dx. doi.org/10.1016/j.ecolind.2014.11.029.

Houghton, J.T., Meira Filho, L.G., Callander, B.A., Harris, N., Kattenberg, A., Maskell, K., 1996. Climate Change 1995. The Science of Climate Change. University Press, Cambridge, United Kingdom.

Held, M., Ilg, R., 2011. Update of environmental indicators and energy payback time of CdTe PV systems in Europe. Prog. Photovolt. Res. Appl. 19, 614–626, http:// dx.doi.org/10.1002/pip.1068.

Held, M., 2012. LCA screening of a recycling process for silicon PV. http://www. pvcycle.org/pv-recycling/recycling-of-si/.

Herendeen, R.A., Cleveland, C.J., 2004. Net energy analysis: concepts and methods. Encycl. Energy 4, 283–289.

Hough, T.P., 2007. Recent Developments in Solar Energy. Nova Publishers.

Huber, S., Moe, M.K., Schmidbauer, N., Hansen, G.H., Herzke, D., 2009. Emissions from incineration of fluoropolymer materials. NILU (NILU OR, 12/2009), Kjeller. Hull, T.R., Quinn, R.E., Areri, I.G., Purser, D.A., 2002. Combustion toxicity of fire retarded EVA. Polym. Degrad. Stab. 77, 235–242, http://dx.doi.org/10.1016/S0141-3910(02)00039-3.

IEA (Internationa Energy Agency), 2015. Snapshot of Global PV Markets 2014, Report IEA PVPS T1-26., pp. 1–16.

ISO (International Organization for Standardization), 2006a. Environmental agement — Life Cycle Assessment — Principles and Framework. Standard ISO 14040, Geneva, Switzerland.

ISO (International Organization for Standardization), 2006b. Environmental agement — Life Cycle Assessment — Requirements and Guidelines. Standard ISO 14044, Geneva, Switzerland.

Jungbluth, N., Stucki, M., Flury, K., Frischknecht, R., Büsser, S., 2012. Life cycle tories of Photovoltaics. ESU-Services Ltd.

Kang, S., Yoo, S., Lee, J., Boo, B., Ryu, H., 2012. Experimental investigations for recycling of silicon and glass from waste photovoltaic modules. Renew. Energy 47, 152–159, http://dx.doi.org/10.1016/j.renene.2012.04.030.

Klugmann-Radziemska, E., Ostrowski, P., Drabczyk, K., Panek, P., Szkodo, M., 2010. Experimental validation of crystalline silicon solar cells recycling by thermal and chemical methods. Sol. Energy Mater. Sol. Cells 94, 2275–2282, http://dx. doi.org/10.1016/j.solmat.2010.07.025.

Larsen, K., 2009. End-of-life PV: then what? Renew. Energy Focus 10 (4), 48–53. McDonald, N.C., Pearce, J.M., 2010. Producer responsibility and recycling solar pho-tovoltaic modules. Energy Policy 38, 7041–7047, http://dx.doi.org/10.1016/j. enpol.2010.07.023.

Müller, A., Wambach, K., Alsema, E., 2006. Life cycle analysis of solar module recycling process. Mater. Res. Soc. Symp. Proc. 895, 1–6, http://dx.doi.org/10. 1557/PROC-0895-G03-07.

Müller, A., Schlenker, S., Wambach, K., 2008. Recycling of silicon, environmental footprints and economics. In: 23rd EUPVSEC, Valencia, Spain, pp. 1066–1070, http://dx.doi.org/10.4229/23rdEUPVSEC2008-2BO.1.3.

Norgate, T.E., Jahanshahi, S., Rankin, W.J., 2007. Assessing the environmental impact of metal production processes. J. Clean. Prod. 15, 838–848, http://dx.doi.org/10. 1016/j.jclepro.2006.06.018.

Olson, C., Geerligs, B., Goris, M., Bennett, I., Clyncke, J., 2013. Current and future priorities for mass and material in silicon Pv module recycling. In: 28th EUPVSEC, Paris, pp. 1–5, http://dx.doi.org/10.4229/28thEUPVSEC2013-6BV.8.2.

Paiano, A., 2015. Photovoltaic waste assessment in Italy. Renew. Sustain. Energy Rev. 41, 99–112, http://dx.doi.org/10.1016/j.rser.2014.07.208.

Pearce, J.M., 2002. Photovoltaics — a path to sustainable futures. Futures 34, 663–674, http://dx.doi.org/10.1016/S0016-3287(02)00008-3.

Pre Consultants, 2014. SimaPro 8 LCA Software: The Powerful Life Cycle Solution. http://www.pre.nl/.

PV Cycle, 2011. European Association for the Recovery of Photovoltaic Modules. Annual Report 2011., http://dx.doi.org/10.1017/CBO9781107415324.004.

PV Cycle, 2015. Operational Status Report. Europe – 12/2015. http://www.pvcycle. org/wp-content/uploads/2013/09/OPS-Status-Report-December.pdf.

Raugei, M., Fullana-i-Palmer, P., Fthenakis, V., 2012. The energy return on energy investment (EROI) of photovoltaics: methodology and comparisons with fossil fuel life cycles. Energy Policy 45, 576–582, http://dx.doi.org/10.1016/j.enpol. 2012.03.008.

Reck, B., Graedel, T., 2012. Challenges in metal recycling. Science 337, 690, http:// dx.doi.org/10.1126/science.1217501.

RESOLVED, 2008. Recovery of Solar Valuable Materials, Enrichment and Decontamination. http://www.resolved.bam.de.

Reuter, M., Xiao, Y., Boin, U., 2004. Recycling and environmental issues of gical slags and salt fluxes. In: VII International Conference on Molten Slags, pp. 349–356.

Sander, K., Schilling, S., Reinschmidt, J., Wambach, K., Schlenker, S., Müller, A., Springer, J., Fouquet, D., Jelitte, A., Stryi-Hipp, G.C., 2007. Study on the opment of a Take Back and Recovery System for Photovoltaic Products Funded by BMU. Components, Hamburg.

Sasala, R.A., Bohland, J., Smigielski, K., 1996. Physical and chemical pathways for economic recycling of cadmium telluride thin-film photovoltaic modules. In: Conference Record of the Twenty Fifth IEEE Photovoltaic Specialists Conference, Washington, DC.

SENSE, 2008. Sustainability Evaluation of Solar Energy Systems. http://cordis.europa.eu/project/rcn/67931 en.html.

Sherwani, A., Usmani, F., Varun, J.A., 2010. Life cycle assessment of solar PV based electricity generation systems: a review. Renew. Sustain. Energy Rev. 14, 540–544, http://dx.doi.org/10.1016/j.rser.2009.08.003.

Sleeswijk, A.W., van Oers, L.F.C.M., Guinée, J.B., Struijs, J., Huijbregts, M.A.J., 2008. Normalisation in product life cycle assessment: an LCA of the global and European economic systems in the year 2000. Sci. Total Environ. 390, 227–240, http://dx.doi.org/10.1016/j.scitotenv.2007.09.040.

Stoppato, A., 2008. Life cycle assessment of photovoltaic electricity generation. In: 19th Int. Conf. Effic. Cost. Optim. Simul. Environ. Impact of Energy Syst. ECOS 2006, vol. 33, pp. 224–232, http://dx.doi.org/10.1016/j.energy.2007.11.012.

Szargut, J., Morris, D.R., Steward, F.R., 1998. Exergy Analysis of Thermal, ical, and Metallurgical Processes. Hemisphere Publishing Corporation, New York.

Tammaro, M., Rimauro, J., Fiandra, V., Salluzzo, A., 2015. Thermal treatment of waste photovoltaic module for recovery and recycling: experimental assessment of the presence of metals in the gas emissions and in the ashes. Renew. Energy 81, 103–112, http://dx.doi.org/10.1016/j.renene.2015.03.014.

Terna, 2013., 2013. Dati statistici sull'energia elettrica italiana, 2013 – Nota di sintesi. Tewarson, A., Chu, F., Jiang, F.H., 1994. Combustion of halogenated polymers. Fire Saf. Sci. 4, 563–574, http://dx.doi.org/10.3801/IAFSS.FSS.4-563.

Tillman, A.-M., Svingby, M., Lundström, H., 1998. Life cycle assessment of municipal waste water systems. Int. J. Life Cycle Assess. 3, 145–157, http://dx.doi.org/10. 1007/BF02978823.

USGS (U.S. Geological Survey), 2015. Mineral Commodity Summaries. http:// minerals.usgs.gov.

U.S. Dept. of Health E. and W., 1970. Control Techniques for Nitrogen Oxide Emissions from Stationary Sources. http://www2.epa.gov/nscep.

US Dept. of Energy, 2012. SunShot Vision Study: February 2012. DOE/GO-1020123037. http://www1.eere.energy.gov/solar/pdfs/47927.pdf.

Uçar, S., Ozkan, A.R., Yanik, J., Karagöz, S., 2008. The influence of the waste ethylene vinyl acetate copolymer on the thermal degradation of the waste polypropylene. Fuel Process. Technol. 89, 1201–1206, http://dx.doi.org/10.1016/j.fuproc.2008.05.010.

Wang, T.-Y., Hsiao, J.-C., Du, C.-H., 2011. Recycling of Materials from Silicon Base Solar Cell Module. IEEE, ISBN 978-1-4673-0066-7, pp. 2355–2358.

Weiss, P., Eveborn, D., Kärrman, E., Gustafsson, J.P., 2008. Environmental systems analysis of four on-site wastewater treatment options. Resour. Conserv. Recycl. 52, 1153–1161, http://dx.doi.org/10.1016/j.resconrec.2008.06.004.

Wenham, S.R., Green, M.A., Watt, M.E., Corkish, R., Sproul, A., 2013. Applied voltaics. Published by Earthscan, United Kingdom, ISBN 978-1-84-407-401-3.

Zucaro, A., Ripa, M., Mellino, S., Ascione, M., Ulgiati, S., 2014. Urban resource use and environmental performance indicators. An application of decomposition analysis. Ecol. Indic. 47, 16–25, http://dx.doi.org/10.1016/j.ecolind.2014. 04.022.