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Physical and chemical treatment of end of life panels: An integrated automatic approach viable for different photovoltaic technologies

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ABSTRACT

Different kinds of panels (Si-based panels and CdTe panels) were treated according to a common process route made up of two main steps: a physical treatment (triple crushing and thermal treatment) and a chemical treatment. After triple crushing three fractions were obtained: an intermediate fraction (0.4-1 mm) of directly recoverable glass $(17\%_{w/w})$; a coarse fraction (>1 mm) requiring further thermal treatment in order to separate EVA-glued layers in glass fragments; a fine fraction (<0.4 mm) requiring chemical treatment to dissolve metals and obtain another recoverable glass fraction. Coarse fractions ($62\%_{w/w}$) were treated thermally giving another recoverable glass fraction ($52\%_{w/w}$). Fine fractions can be further sieved into two sub-fractions: <0.08 mm ($3\%_{w/w}$) and 0.08-0.4 mm ($22\%_{w/w}$). Chemical characterization showed that 0.08-0.4 mm fractions mainly contained Fe, Al and Zn, while precious and dangerous metals (Ag, Ti, Te, Cu and Cd) are mainly present in fraction ($22\%_{w/w}$). The process route allowed to treat by the same scheme of operation both Si based panels and Cd-Te panels with an overall recycling rate of 91%. © 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Photovoltaic panels are the emerging technology converting solar radiation into electrical energy, which is expected to provide a fundamental contribution to the shift from traditional fossil fuels to renewable energy-based economies.

Photovoltaic panels have been installed since eighties with the first appreciable photovoltaic power dated to the beginning of nineties. During the past decade, photovoltaic market has grown exponentially with a world cumulative installed capacity that reached 140 GW in 2013 (EPIA, 2014). Europe remains the top region in terms of cumulative installed capacity, but a rebalancing between Europe and the rest of the world is ongoing, closely reflecting the patterns in electricity consumption. In Europe, Germany covers about 50% of the global European photovoltaic capacity, followed by Italy and Spain.

As for the Italian case, an estimate of waste flux was performed assuming a fixed life-time of 25 years: in this case about 2 million tons of photovoltaic wastes will be generated in the period 2012–

* Corresponding author. *E-mail address:* francesca.pagnanelli@uniroma1.it (F. Pagnanelli). 2038, and up to 8 million tons within 2050, with significant amounts (>40.000 ton/y) since 2032 (Paiano, 2015). Disposal of this flux of wastes by land filling is unsustainable because leaching and dispersion into the environment of toxic elements (such as cadmium), and loss of conventional resources (mainly glass and aluminum) and high-value elements (such as silver, titanium and tellurium).

In line with the analysis illustrated above, European community has extended regulations for the treatment of end-life electrical and electronic wastes in order to include the disposal of photovoltaic panels. The legislation currently established collection rates for photovoltaic modules up to 85% and recycling rates up to 80% (Directive 2012/19/EU).

This requires the implementation of efficient collection programs and the development of processes enabling almost the integral recovery of materials. The elevated dynamism and competitiveness of photovoltaic industry determined a very rapid modification of employed technologies and recourse to different panel solutions. This last aspect can considerably limit the impact of processes tailored to a single panel technology (type-tailored processes). Proposed recycling processes should be flexible and offer the possibility to treat panels characterized by different com-







position and structure. Combination of physical and hydrometallurgical processes seems to be a feasible and flexible approach even for the exploitation of such kind of e-wastes (Tuncuk et al., 2012).

Currently the dominant photovoltaic technology uses crystalline silicon (monocrystalline and polycrystalline) as semiconductor, but thin film photovoltaic modules using cadmium telluride (CdTe), amorphous silicon, Copper Indium Gallium Selenide (CIGS) and Copper Indium Selenide (CIS) recently get much more importance due to their lower production costs and higher efficiency (Fthenakis and Wang, 2006; Raugei et al., 2007).

Literature survey denoted that all research activities are typetailored, meaning that a specific sequence of operations was developed in order to treat a specific type of panels, and mainly crystalline silicon panels and CdTe panels. Then, the approach used differs according to the type of panels addressed. For crystalline silicon panels many efforts have been spent in the recovery of Si cells due to the high cost of this material also determining in previous years the development of alternative photovoltaic thin film technologies. Thermal and chemical treatment (Jung et al., 2016; Dias et al., 2016a; Gustafsson et al., 2014; Klugmann-Radziemska and Ostrowski, 2010a; Klugmann-Radziemska et al., 2010b) or treatment with organic solvents (Doi et al., 2001; Kanga et al., 2012) aiming to EVA degradation-dissolution were the core of these processes. As an example, also proven at pilot scale, the company Deutsche Solar (Solar World) developed a process for the manual dismantling of intact crystalline silicon modules (Bio Intelligence Service, 2011): panels are treated at 600 °C, manually dismantled for the recovery of intact crystalline Si cells, which are further treated by chemical leaching in order to be regenerated. This approach requiring manual operations aiming at Si cell recovery presents some drawbacks concerning economic feasibility due to low automation degree and recent dramatic diminution of crystalline silicon price (Bazilian et al., 2013).

As for thin film panels (CdTe, CIS and CIGS) the common approach consists of delamination of modules or grinding, decoating of the substrate, extraction and refining of the metals (Kuroiwa et al., 2014; Marwede et al., 2013; Giacchetta et al., 2013; Berger et al., 2010; Sasala et al., 1996). As an example, First Solar developed at large scale a recycling process dedicated to CdTe thin film panels including mechanical and chemical operations (Bio Intelligence Service, 2011) according to the following scheme: shredding, hammer crushing, leaching by sulfuric acid and hydrogen peroxide of the whole ground mass of waste, glass recovery by sieving and metal recovery from leach liquor.

According to this scenario, it is possible to note that many efforts have been spent on photovoltaic panel recycling, but no innovative technology for treating different kinds of photovoltaic panels in automatic way in the same plant according to the same process route was presented yet. Indeed the development of advanced and automated recycling seems to be the key to implement economically feasible processes able to treat the growing amounts of heterogenous photovoltaic wastes (Choi and Fthenakis, 2014; Granata et al., 2014). This could be achieved considering the common multi-layered structure of all photovoltaic panels, in which tempered glass is the dominant material (up to 90% in weight) supporting photoactive layers and conductive metallic grids encapsuled within a polymeric matrix (generally made up of ethylene vinyl acetate, EVA), with an inert polymeric back sheet (generally, polyvinylfluoride, PVF or Tedlar). In Fig. 1A of Supplementary material a schematic representation of the multilayered structure of a Si-based panel was reported.

In this work, a new process for the treatment of different kinds of panels was presented consisting of mechanical treatment of panels by crushing, sieving, thermal treatment of the coarse fraction, and chemical treatment of the fine fraction. The first novelty with respect to literature data is the application of this process route for treating different types of panels: crystalline Si, amorphous Si, and CdTe. In fact, all data reported in the literature refer to type-tailored processes specifically designed for Si crystalline panels (Kanga et al., 2012; Klugmann-Radziemska and Ostrowski, 2010a; Dias et al., 2016a) or CdTe panels (Fthenakis and Wang, 2006; Marwede et al., 2013; Sasala et al., 1996).

Another novelty aspect of this process is the selective treatment of distinct waste fractions produced in the plant. In fact, after mechanical crushing of the whole mass, sieving was performed in order to recover clear glass, plus other two fractions: the coarse fraction (>1 mm) and the fine fraction (0.08–0.4 mm). Each of such fractions was specifically treated by thermal treatment (coarse fraction) or chemical operations (fine fraction). In this way, a reduction of unit volume necessary for thermal and chemical treatment is achieved with respect to the nominal potentiality of the plant, thus reducing both capital investment and operating costs. Other processes reported in the literature performed thermal and chemical treatment for EVA degradation or metal recovery using the whole mass of grinded panels, and thus treating also fractions not specifically requiring such treatment.

Additional novelty of the process here reported is the final achievement of material recovery (90%) surpassing the 80% target established by EU Directive. Many recent papers focused on the recovery of metals and Si cells (Jung et al., 2016; Dias et al., 2016a) bypassing the problem of ensuring established resource recovery rate, which is a fundamental point of process sustainability.

Finally, another original aspect of the work concerns with the chemical characterization (both acid digestion and X-ray diffraction spectra) and leaching treatment of the fine fractions obtained by the selected process route. In this way, the complete process is addressed taking in consideration all the fractions emerging from physical pretreatment.

2. Materials and methods

2.1. Photovoltaic panels

The input waste material used in this work was taken from different kinds of PV devices in two successive campaigns performed in the same plant by different operators. Specifics about panels used in the different campaigns were reported in Table 1. Two samples (each one of 2 kg approximately) were taken from each kind of panel. Samples were obtained after manual dismantling of external Al frames, when present. Each sample was taken by cutting a piece of about 40 * 40 cm by using a diamond blade for glass incision and then a hammer for panel cutting.

Table 1

Photovoltaic panels treated in the two campaigns of crushing: type, brand, model, and year of fabrication for each treated panel.

Туре	Brand and model	and and model Year of fabrication	
Monocrystalline Si	SHARP NT-175E1/NT-R5E3E	2009	1
Polycrystalline Si	BYD - 230P6-30	2011	1
Polycrystalline Si	Lenus Solar 250 Silverine	2014	2
Amorphous Si	Sharp NA-901 WQ	2010	1
Amorphous Si	Sharp NA-E135L5	2013	2
CdTe	First Solar FS2-82.5	2012	1
CdTe	First Solar FS2-82.5	2012	2
CdTe	First Solar 380	2012	2

2.2. Mechanical pretreatment

Panels samples collected as described in Section 2.1, were submitted to mechanical treatment for size reduction. Three successive crushings (triple crushing) were carried out in a two blade rotors crusher (DR120/360, Slovakia) without any controlling sieve (the output of a crushing cycle is re-fed in the crusher for a successive cycle of crushing). A controlling sieving was avoided in order to reduce fine fraction formation due to continuous automatic recycling occurring when using a controlling sieving.

After size reduction, a sieving analysis was carried out in order to evaluate size and products distribution as well as mass fluxes in the process. For this purpose all samples were sieved by using an automatic shaker with 5 sieves (8 mm, 5 mm, 1 mm, 0.4 mm, 0.08 mm). Then all fractions obtained were weighed.

2.3. Thermal treatment

Thermal treatment experiments of coarse fraction were performed in a laboratory apparatus described elsewhere (Orac et al., 2015). All experiments were performed under air flux (30 l/ h). Coarse fraction (d > 1 mm) samples were weighted, put in ceramic boat-shaped crucibles, and fed into the furnace reactor. The rate of heating was 10 °C/min until reaching 650 °C, and then this temperature was maintained for 1 h.

After thermal treatment, the samples were cooled, sieved and particle size distribution determined as described in Section 2.2.

2.4. Fine fraction characterization by acid digestion

1 g of sample was treated with 3 ml HNO₃ ($69\%_{W/W}$ by Sigma Aldrich), 9 ml HCl ($37\%_{W/W}$ by Sigma Aldrich) and 0.6 ml H₂O₂ ($36\%_{W/W}$ by Sigma Aldrich) in microwave digester (ETHOS 900, Milestone) under the following conditions:

Step 1: 10 min from room temperature up to 220 °C at 1000 W.
Step 2: 20 min at 220 °C at 1000 W.

- Step 2. 20 mm at 220 C at 1000 W.

After filtration liquid solution was analysed by Atomic Absorption Spectrophotometer (AAS, contrAA[®] 300 - Analytik Jena AG). Residual solid was melted at 1000 °C for 20 min, digested at 1000 °C by HF (5 ml 48%_{W/W} Sigma Aldrich), H₂SO₄ (1 ml 96%_{W/W} by Sigma Aldrich) in distilled water (4 ml) and melted again at 1000 °C for 5 min. SiO₂ content was then determined by weight loss between two steps of melting.

2.5. Preliminary leaching tests of the fraction 0.08-0.4 mm

Fine fractions (0.08–0.4 mm) from campaign 2 were used for preliminary leaching tests in lab scale.

Acid leaching of fine fractions of the different panel types was performed using 100 ml leach solutions prepared using H_2SO_4 solution at 3 M concentration and adding H_2O_2 (5% in volume) with a solid/liquid ratio 1:3 for 3 h at 60 °C.

After solid/liquid separation by centrifugation the liquid was analysed by AAS in order to determine metal extraction yield.

2.6. Fraction characterization by X-ray diffraction

Obtained products (1–5 mm after triple crushing and thermal treatment, fractions 0.4–1 mm, 0.08–1 mm, <0.08 mm both after triple crushing and after thermal treatment) were analysed by X-ray diffraction (PANalytical X'Pert Pro, CoK α radiation) and X-ray fluorescence (SPECTRO XEPOS Spectrometer).

3. Results and discussion

3.1. Mechanical treatment

Photovoltaic panels were treated by multiple crushing operations in order to reduce the size of panel fragments. In Fig. 1 the evolution of size particle after sequential crushing is reported for polycrystalline Si panels as an example. It is possible to see that just one passage in the shredder leaves about 70% of panels with size >8 mm. This percentage falls to 50 and 40% after the second and the third crushing cycle, respectively. Reducing the size of fragments gives two main advantages. The first is the reduction of wastes to be further treated in the successive thermal treatment because only the coarse fraction requires such treatment. After triple crushing, only 62% of wastes has to be further thermally treated (coarse fraction), against 85% after just one crushing. The second advantage is the increase of glass recovery (fraction 0.4-1 mm) just by mechanical treatment. In fact, after triple crushing 17% of directly recoverable glass fraction is obtained, while after just one crushing this percent falls below 10%. Conversely there is a limit in increasing the number of crushing operations due to the simultaneous increase of fine fractions requiring further treatments to be re-used (20% after triple crushing and 10% after single crushing). At this stage triple crushing seems to be a compromise between these antagonist effects. Further process simulations also accounting for energy consumption will reveal the adequacy of such choice.

Particle size distributions for the different kinds of panels in the two campaigns were obtained by sieving as weight% (see Table 1A in Supplemental material). Experimental data showed very similar results in both campaigns for the different kinds of panels. In Fig. 2 particle size distribution as the mean values obtained for each kind of panel were reported. These data showed that all types of panels behaved in very similar way according to the common glassy multi-layered nature of all photovoltaic panels.

In fact, $62 \pm 6\%$ of fragments >1 mm (coarse fraction) was obtained after mechanical treatment by triple crushing for all types of panels. This fraction is characterized by fragments, in which the multi-layered structure is still present and glass, silicon wafers and back sheets are still glue together by reticulated ethyl vinyl acetate (EVA). This fraction required a further treatment in order to separate glass.

After mechanical treatment, $17 \pm 3\%$ of panels can be directly recovered as glass fragments with 0.4–1 mm size (intermediate fraction). In Fig. 3 these intermediate fractions were showed for the different kinds of panels: all samples are made up of clean fragments of clear glass directly, recoverable in the glass cullet industry.

After triple crushing, also a fine fraction emerged as $20 \pm 4\%$ weight of initial panels. This last fraction required further treatment to be exploited as explained in Section 3.4.

According to the previous data, it is possible to note that after the treatment of the mass of panels by crushing only selected fractions are further treated according to thermal treatment or chemical treatment. This aspect can give relevant advantages in terms of process feasibility allowing the reduction of the equipment for thermal treatment and chemical treatment with respect to the nominal potentiality of the plant. Then established the potentiality of the crusher, the consequent thermal treatment will be performed on a volume of wastes which is 60% of initial amount of wastes treated. In the same way, the leaching section and the wastewater treatment section will be designed for a capacity, which is 20% of the initial amount of panels treated in the plant.



Fig. 1. Particle size distribution (in mm) for polycrystalline Si panels after different cycles of crushing (crushing I: one crushing; crushing II: two successive crushing operations; crushing III: three successive crushing operations) and thermal treatment of the coarse fraction.



Fig. 2. Mean values and standard deviations of particle size distribution obtained after triple crushing for the different kinds of panels during the two campaigns (Poly Si: polycrystalline Si panel; Mono Si: monocrystalline Si panel; Amo Si: amorphous Si panel; CdTe: CdTe panel).

3.2. Thermal treatment

Thermal treatment of coarse fractions determined the destruction of EVA and then the release of glass fractions and metallic powders. Table 2A in Supplemental material reports the weight% obtained for the different panel types in the two campaigns.

It is possible to note that, even after this treatment, the different types of panels behave similarly (Fig. 4). In particular, $66 \pm 8\%$ of weight of the coarse fraction can be retrieved in the fraction 1–5 mm, which is made up of pure glass directly recoverable in glass culled industry (Fig. 5). Additional glass is also recovered in fraction 0.4–1 mm corresponding to $12 \pm 6\%$ of coarse fraction. Only for polycrystalline Si, amorphous Si and CdTe recoverable glass fractions >5 mm were recovered after thermal treatment (Fig. 1B in Supplemental material).

The weight loss showed different behavior for Si crystalline panels (mono and poly) and for thin film panels (amorphous Si and CdTe): the weight loss is about 15% for the first type and 5% for the second. These data are in agreement with the different content of EVA typically present in these kinds of panels.

Thermal treatment conditions were adopted in order to ensure complete degradation of EVA. EVA decomposition occurred according to a two-stage process consisting in deacetylation with acetic acid release ($300-400 \,^{\circ}$ C) and then in random-chain scissions giving mainly propane, propene, ethane, ethane, butane, hexane-1, butane-1 ($460-570 \,^{\circ}$ C) (Marín et al., 1996; Beyler and Hirschler, 2001). Dias et al., 2016a specifically investigated the problem of EVA degradation in panel recycling, showing that 1 h treatment at 500 $^{\circ}$ C is sufficient for complete polymer degradation. Similar results were obtained by Zeng et al., 2004 in a systematic study using the polymer itself: these authors found that every trace of residual coke was eliminated at 570 $^{\circ}$ C.

Accordingly, preliminary experimental tests of TGA (not reported here) performed on glass samples from thermal treatment did not show any thermal transition nearby the EVA combustion temperature.

At the end of thermal treatment, metallic contacts (busbars) resulted separated from the original multilayer structure due to thermal decomposition of EVA, and can be separated from glass by using physical operations. These metallic contacts (about 1% of the total weight of treated panels in the form of strips long up to 3 cm) are mainly made of Al with coatings of Cu, Ag, Sn and Pb (Dias et al., 2016a) and can be directly sold as scraps to smelters.

3.3. Fine fraction characterization

Characterization of fine fractions (0.08–0.4 and <0.08 mm) by acid digestion put in evidence that the same metals are present in both fractions but with different concentrations. In particular, the 0.08–0.4 mm fractions from Si panels are mainly characterized



Fig. 3. Intermediate fractions (0.4–1 mm) recovered after triple crushing from the different types of panels (Poly Si: polycrystalline Si panel; Mono Si: monocrystalline Si panel; Amo Si: amorphous Si panel; CdTe: CdTe panel).



Fig. 4. Mean values and standard deviations of particle size distribution obtained after thermal treatment of the coarse fractions for the different kinds of panels in the two campaigns. Percent weights are referred to the coarse fraction and not to the initial waste weight (Poly Si: polycrystalline Si panel; Mono Si: monocrystalline Si panel; Amo Si: amorphous Si panel; CdTe: CdTe panel).

by Fe, Zn, Al along with significant amounts of Si (about 20% in weight), while valuable metals (Cu, Ti, Ag) are present at very low concentrations in these fractions (Figs. 6A and 7A).

The finest fractions (<0.08 mm) from Si panels present similar concentrations of base metals (Fe, Zn and Al) and Si, but a content about 1 order magnitude larger of valuable metals (Figs. 6B and 7B).

For CdTe panels similar observations can be made about base metals and Si, while metals accumulating in the finest fractions are Cd and Te.

The different final concentration of metals in the different fractions, denoting enrichment in the finest fraction of these elements, could be explained taking in consideration the specific way metals are present in the panels.

A part from the busbars (which can be directly recovered at the end of the thermal treatment as discussed above) metals in photovoltaic panels are present in the form of coatings (as in the case of Al layer on the cell backside) and threads (as in the case of Ag grid) (Dias et al., 2016a). During crushing, busbars are broken in pieces 1–3 cm long, which can be directly recovered at the end of thermal treatment of the coarse fraction. The lack of grinding operations allowed the direct recovery of these metallic contacts thus avoiding their size reduction.

Metals in the form of coatings (as layers or threads) during shredding tend to detach from broken pieces and then, according to the micrometric thickness of deposits, tend to accumulate in the finest fractions.

This behavior is particularly interesting in the case of Ag.

SEM characterization of photovoltaic panels evidenced that Ag is deposited on the semiconductor as straight threads distributed throughout the photovoltaic module with an approximate thickness of 100 μ m (Dias et al., 2016a).

During shredding, the partial disruption of panel structure and cell release determined the detachment of such coatings, which are concentrated in the fine fraction after sieving.

This same result was achieved by Dias et al., 2016b, reporting that 81% of Ag in the module tends to concentrate at a particle size fraction smaller than 0.5 mm.

The concentration of Ag in the finest fraction can be interesting in view of its recovery. Ag content in panels strictly depends on the specific technology and manufacturing. Wide range of variability are reported in the literature: 0.04–0.06 mg/kg for Paiano (2015), 0.36 mg/kg for Jung et al., 2016, 0.6 mg/kg for Dias et al. (2016a). Chemical digestion using grinded Si panels denoted Ag concentrations ranging from 0.004 to 0.01 mg/kg (experimental data not reported here). According to this estimate the concentration of Ag in the finest fraction is at least one order of magnitude increased. This is another advantage of the proposed method avoiding milling of panels and then glass powder generation and recovery in the fine fraction.

According to these findings the most reasonable process option seems to be the following: the fraction 0.08–0.4 mm could be treated with the main aim of recovering another glass fraction due to the very low content of non-precious metals, hardly recoverable in an economically feasible process also including metal recovery operations (such as solvent extraction or electrowinning). In this



Fig. 5. Recoverable glass fractions (1–5 mm) after thermal treatment of the coarse fractions (Poly Si: polycrystalline Si panel; Mono Si: monocrystalline Si panel; Amo Si: amorphous Si panel; CdTe: CdTe panel).



Fig. 6. Mean values and standard deviations of the metal contents from acid digestion for the 0.08–0.4 mm fractions of the different kinds of panels in the two campaigns (Poly Si: polycrystalline Si panel; Mono Si: monocrystalline Si panel; Amo Si: amorphous Si panel; CdTe: CdTe panel).



Fig. 7. Mean values and standard deviations of the metal contents from acid digestion for the <0.08 mm fractions of the different kinds of panels in the two campaigns (Poly Si: polycrystalline Si panel; Mono Si: monocrystalline Si panel; Amo Si: amorphous Si panel; CdTe: CdTe panel).

Table 2

Glass recovery (%) for the different kinds of panels evaluated as the sum of the 0.4-1 mm fraction emerging from triple crushing (0.4-1 (3C)), the fractions larger than 0.4 mm from thermal treatment (>0.4 (3C + TT)), and the 0.08-0.4 fractions after leaching (0.08-0.4 mm (3C + TT + L)). Estimates of fine powder requiring further treatment (<0.08 (3C + TT)) and of weight losses.

	0.4-1 (3C)	>0.4 (3C + TT)	0.08–0.4 (3C + TT + L)	Glass	<0.08 (3C + TT)	Weight loss
Poly Si	16 ± 1	51 ± 5	22 ± 7	88 ± 1	4 ± 3	7 ± 2
Mono Si	17	49	22	88	2	10
Amo Si	20 ± 6	48 ± 5	25 ± 1	93 ± 2	3 ± 3	4 ± 1
CdTe	17 ± 1	56 ± 3	20 ± 5	92 ± 4	2 ± 1	5 ± 3

way the chemical treatment of fraction 0.08–0.4 mm for metal elution could give another $24 \pm 2\%$ of recovered glass, which can be add and mixed to the other recoverable glass fractions from mechanical and thermal treatment. On the other hand the fraction <0.08 mm could be used for the recovery of high value metals because these metals resulted concentrated in the finest fractions accounting for about $3 \pm 2\%$ of initial waste.

3.4. Preliminary leaching of fine fractions (0.08–0.4 mm)

Considering the chemical properties of metals contained in the fraction 0.08–0.4 mm (Fe, Al and Zn) an acid leaching can be performed in order to remove these metals and obtain clean recoverable glass.

Experimental results obtained in preliminary leaching tests of the fractions 0.08–0.4 mm denoted that the chosen conditions

were suitable for complete extractions of Fe, Al, Zn and Cd (when present) as evidenced by leaching extraction yields in Table 3A.

Considering dilution of chemically treated fractions in the total amount of recovered glass, the final concentrations of Zn, Fe, Al and Cd were estimated (Table 3A). The contribution of the fine fraction to the metal content in the final recovered glass resulted dependent on the type of panel. In particular the following ranges of concentrations in final recoverable glass were found: 0.1 to 0.16 g/kg for Zn, 0.04–0.76 g/kg for Fe, 0.01–0.1 g/kg for Al and 0.02 for Cd. In all these cases, the final amount of metals seems to be negligible. Nevertheless market investigation would give further insight about the economic advantage of adding chemically treated fine fractions to the other fractions of recovered glass.

A summary of the amount of glass recoverable for the different type of panels according to the process scheme here proposed is resumed in Table 2.



Fig. 8. X ray diffraction spectra (counts versus 2theta) of the directly recoverable glass fractions from polycrystalline Si module: fraction 1–5 mm after triple crushing and thermal treatment (1–5 (3C + TT)); fraction 0.4–1 mm after triple crushing (0.4–1 (3C)), and fraction 0.4–1 mm after triple crushing and thermal treatment (0.4–1 (3C + TT)).

In this computation, the recoverable glass fraction is evaluated as the sum of the following fractions:

- 0.4–1 mm fraction emerging from mechanical treatment (0.4–1 (3C));
- 0.4–1 mm, 1–5 mm and >5 mm fractions emerging from thermal treatment (>0.4 (3C + TT));
- 0.08–0.4 mm fractions from mechanical and from thermal treatment after leaching treatment (0.08–0.4 (3C + TT + L)).

According to these results $91 \pm 3\%$ of initial weight of panels (without accounting frames) can be recovered as glass, with a not negligible contribution of leached fine fraction $(24 \pm 2\%)$. Only $3 \pm 2\%$ of initial weight is stored as finest powder fraction which can be accumulated and directly sold or further treated to recover precious metals (Ag, Ti, Te).

3.5. Fraction characterization by X-ray diffraction

XRD characterization of the fractions emerging from the process for the polycrystalline panels have been performed (Figs. 8–10). XRD spectra of directly recoverable glass fractions (1–5 mm after thermal treatment, 0.4–1 mm after triple crushing, and 0.4–1 mm after thermal treatment) evidenced the predominant amorphous nature, which is typical of glass samples (Fig. 8). It follows from results of XRD qualitative analyses that the glass is present in the form of SiO₂. Generally this phase is amorphous and that is why it is not easy to confirm its presence based on XRD analyses. However, practically all measured samples showed increased level of background at lower values of Bragg's angle of diffraction pattern, revealing the presence of amorphous phase with indication to cristobalite SiO₂. For simplification in most cases the presence of this phase was not indicated in XRD patterns (Figs. 9 and 10). The shape of X-ray diffraction patterns also revealed the possible presence of organic materials, at least ethylene vinyl acetate (EVA), which are present in photovoltaic panels before thermal treatment.

XRD spectra of finest fractions (0.08–0.4 mm and <0.08 mm) denoted that due to grinding the metallic or metal bearing phases are concentrated mostly into these fractions (Figs. 9 and 10). These fractions presented a basic amorphous behavior (similar to that observed for directly recoverable glass fractions), but additional peaks due to metallic or metal bearing phases are also present. However due to the limited amounts of such metallic compounds in the samples, the detection of specific phases is critical as their diffraction lines are rather missing in the background of XRD pattern.

For both fine fractions (0.08–0.4 mm and <0.08 mm) after thermal treatment the amorphous character (increased level of back-



Fig. 9. X ray diffraction spectra (counts versus 2theta) of the fractions obtained from polycrystalline modules requiring acid leaching for heavy metal removal: fraction 0.08–0.4 mm after triple crushing (0.08–0.4 (3C)); fraction 0.08–0.4 mm after triple crushing and thermal treatment (0.08–0.4 (3C + TT)).



Fig. 10. X ray diffraction spectra (counts versus 2theta) of the fractions obtained from polycrystalline modules which could be exploited for metal recovery: fraction <0.08 mm after triple crushing (<0.08 (3C)); fraction <0.08 mm after triple crushing and thermal treatment (<0.08 (3C + TT)).

ground at lower values of Bragg's angle) tended to decrease denoting the major contribution of organic EVA residues to such trend. After thermal treatment (determining EVA destruction) the background decreased evidencing more distinct peaks related to metallic compounds.

4. Conclusions

In this work an improved process route for the mechanical treatment of different kinds of photovoltaic panels was presented. In a previous work (Granata et al., 2014) photovoltaic panels were treated according to two different schemes: single crushing followed by thermal treatment and single crushing followed by hammer crushing and thermal treatment. Single crushing followed by thermal treatment gave an overall glass recovery ranging from 50 to 70% depending on panel type. Introduction of hammer crushing after crushing improved the glass recovery to 80–85%, even though recovered products presented a significant presence of fine fractions (40–45% in weight depending on the type of panels).

Triple crushing operation addressed in the present work has different advantages with respect to previous ones. Comparing triple with single crushing, triple crushing operations allowed to reduce the amount of wastes to be thermally treated (only 62% against 85% after one crushing). Comparing triple crushing with single crushing plus hammer crushing, the obvious advantage is the use of a single equipment instead of two different ones with a reduction of the investment costs. In addition, glass recovered by triple crushing presented lower amounts of fine fractions in comparison with the scheme including hammer crushing.

The reduction of fine fractions is an advantage considering that, according to the metal content reported in the present work, a m etallurgical/hydrometallurgical treatment is necessary to recover these fractions as pure glass.

Photovoltaic panels are mainly composed of glass, whose weight ranges from 75% to 90% depending on photovoltaic technology. Then, the first aim of recycling processes should be glass recycling in order to maximize mass recovery and ensure process feasibility.

Nevertheless, other valuable metallic fractions can be recovered applying the proposed process. In the treatment of panels here proposed, metals were found in two different forms: as fragments of metallic contacts (busbars) recovered after thermal treatment of the coarse fraction, and as powder in the fine fraction submitted to leaching.

As for the first form, metallic contacts containing Al, Cu and Ag can be directly recovered after thermal treatment and sold as scraps to smelters. Metal distribution in the fine waste fractions (<0.08 mm and 0.08–0.4 mm) emerging from the process denoted that Fe, Zn, and Al are the most abundant metals in these finest fractions with concentrations lower than 5 mg/g. The low content, the low market value of these metals ($4.3 \in /kg$ for Cu, $2.0 \in /kg$ for Zn, $1.5 \in /kg$ for Al and $0.2 \in /kg$ for Fe) (https://www.metal-prices.com), and typical potentiality of photovoltaic panel recycling plants are points against the inclusion of a section for metal recovery in such plants.

The target of leaching of 0.08–0.4 mm fraction is then cleaning glass in order to increase the overall mass recovery of the process. The leach liquor containing Fe, Zn and Al can be treated in the wastewater section where primary treatment (precipitation) and secondary refinement (ion exchange resins) can be performed according to conventional route for metal-bearing wastewaters.

A different reasoning could be followed for the finest fraction (corresponding to <5% in weight of the panels treated) in which increased concentrations of all metals were found. Ag is the most interesting metal in this case taking in consideration both the intrinsic market value ($0.5 \in /g$) and the contents found in the finest fractions (ranging from 0.3 to 2 mg/g). According to these preliminary results, the Ag bearing fraction could be directly treated in the plant for photovoltaic recycling. Then conventional operations (leaching section, precipitation, and reductive melting) can be adopted according to the optimized conditions specifically developed for Ag recovery from photovoltaic panels (Jung et al., 2016; Dias et al., 2016a). Alternatively Ag-bearing fraction can be sold to refiners thus contributing to the overall feasibility of the photovoltaic panel recycling process.

Further economic estimates are still in course for this specific evaluation.

Experimental results reported in this work were used for the elaboration of mass and energy balances and then for a preliminary feasibility analysis by using a process simulation software (Superpro Design).

The process includes: shredding, sieving, thermal treatment of the coarse fraction, leaching of the fine fractions, wastewater treatment. Process simulations were performed assuming that Si-based panels were fed in the plant according to the predominance of this technology in the Italian market (Paiano, 2015).

The evaluation included the costs for plant, work force, raw materials, and energy consumption. Products recovered are glass (0.08 ϵ /kg) and aluminum (from frames and metallic contacts, 1 ϵ /kg), neglecting Ag recovery from finest fractions.

According to this preliminary analysis, the proposed process becomes economically feasible (Pay Back Time lower than 6 years) starting from a potentiality of 75.000 ton/y.

According to Paiano simulation of waste flux for the Italian scenario, this potentiality could be reached since 2034. Nevertheless, it should be noted that this preliminary estimate is conservative not taking in consideration the negative costs of waste panels (namely the fee payed for collection and treatment to the recyclers).

A demonstration activity in a pilot plant with a potentiality of 200 ton/y is now in course in order to finalize mass and energy balances on the base of relevant amounts of treated panels (3 tons).

These future data will be implemented in the already developed process scheme for economic analysis by process simulator and assessment of environmental impacts by LCA.

Acknowledgement

The process section related to mechanical pretreatment will be validated in pilot scale within the activities of the Photolife project (LIFE13 ENV/IT/001033) co-financed by European Community in the LIFE + program.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2016.11. 011.

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