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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 fractions <0.08 mm. Acid leaching of 0.08–0.4 mm fractions allowed to obtain a third recoverable glass 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%.

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 2012–2038, 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-

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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 type-tailored, 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.

Type	Brand and model	Year of fabrication	Campaign
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