Photovoltaic panel recycling: from type-selective processes to flexible apparatus for simultaneous treatment of different types

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Photovoltaic (PV) technology for renewable energy utilisation is constantly growing throughout the world. Many recent efforts were devoted to the treatment of end-of-life panels, but only two full-scale processes were developed for crystalline silicon modules (Deutsche Solar) and CdTe panels (First Solar). Furthermore, recent developments concerned with new technologies designed for treating together more kinds of PV panels by automated processes. In this work, a picture of the PV world in terms of market, typology, waste dynamics and recoverable materials was given. A description of full-scale processes will be reported evidencing products and yields of recovery. A case study of process development for the simultaneous treatment of different kinds of PV panels was presented. In particular, experimental results in lab and pilot scale were described regarding the development and optimisation of a process including both physical pre-treatment and hydrometallurgical treatment for the recovery of target metal.

Keywords: Photovoltaic panels, Secondary raw materials, Physical pre-treatment, Hydrometallurgy, Metal recovery

Introduction

Photovoltaic (PV) installations during the last years have been growing exponentially especially in Europe with a PV market share equal to the 80% of world demand. Recent reduction (in 2011) in subsidy levels across the major European markets did not affect significantly the overall demand due to the increased importance gained by emerging markets such as India, USA, Canada and Australia. The dramatic increase of PV installation could be a solution to fossil fuel depletion in terms of renewable energy source. Nevertheless, PV energy production will give rise to an environmental problem related to the generation of huge amounts of end-of-life panels. PV panels have been installed since 1980s with the first appreciable PV power dated to the beginning of 1990s. According to an average life time of 25–30 years, a sudden and sharply growing amount of end-life panels is expected starting from 2035 (about 3 000 000 t/year in EU).

PV panels can be classified according to three main categories or generations as reported in Fig. 1a. First-generation panels are based on crystalline silicon both in monocrystalline and polycrystalline form. Second-generation panels are thin film based on different materials such as amorphous silicon, cadmium telluride (CdTe), copper indium gallium and copper indium gallium selenide (CIS and CIGS, respectively). Third-generation panels include concentrator PVs and emerging technologies such as dye-sensitised solar cells, organic solar cells and hybrid cells. First-generation panels are the most diffuse (globally mono and polycrystalline are about 80% of the total market), while thin-film panels cover a little portion of the rest of the market. These three generations differ for size, weight, energetic performances and composition. In Fig. 1b, details about the composition of multilayer structures for the different panel types are reported. Glass is the predominant material in all types, while specific elements are used as active photoelectric materials in the different types.

Taking into account panel composition, the main environmental concerns arise for possible pollutant release due to leaching of heavy metals such as lead and cadmium. In addition, there are environmental impacts related to the loss of conventional resources (such as glass and aluminium) and rare metals (silver, indium, gallium, germanium, tellurium).

European Directive 2012/19/EU included PV panels as Waste of Electric and Electronic Equipment (WEEE) of type 4 (Monier and Hestin 2011). The Directive established target recycling rate (65% by 2012 and 70% by 2015) and minimum recovery target for dedicated processes (75% in weight by 2012 and 80% by 2015). Accordingly each European Country adopted national regulations in order to fulfil EU directive objectives. Also consortia were promoted for take back and recycling promotion: as an example the PV Cycle association was founded in 2007 by the PV industry to put in place and promote a take back and recycling programme at European level.
Scientific literature and patent survey denoted the use of different kinds of treatments for PV panel treatment: mechanical treatments (crushing, attrition, density separation, flotation), thermal treatments (incineration, pyrolysis, melting) and chemical treatments (acid/base treatment and solvent treatment) (Menezes, 2001; Takuya et al. 2001; Radziemska 2009; Berger, Simon, Weimann and Alsema 2010; Klugmann-Radziemska et al. 2010; Pagnanelli et al. 2016).

1. a PV panel classification as crystalline Si, thin film and emerging technologies including concentrators PVs; b multilayer composition of PV panels for crystalline Si, CdTe and CIGS technologies

2. Block diagrams for Deutsche Solar process for crystalline Si recycling a, for the First Solar process for CdTe panel recycling b and for the treatment of end-of-life panels according to the here presented process scheme valid for different kinds of PV panels c
Klugmann-Radziemska and Ostrowski (2010). Even though a number of treatments were tested for PV recycling in laboratory scale, there are currently only two processes that have been tested in large scale: the Deutsche Solar process and the First Solar process.

Deutsche Solar process was launched in Germany in 2003 and halted due to its costliness for the low quantities of PV panels at that time and the low automation level of the process.

Deutsche Solar process was designed for crystalline silicon panels to recover silicon wafer in intact solar cells by manual dismantling according to the process scheme reported as Fig. 2a.

Main process steps are:
- Heating and manual separation of panels.
- Manual separation of intact solar cells.
- Chemical treatment of solar cells for the removal of metallisation layer.
- Chemical treatment of solar cells for the removal of antireflective coating.
- Chemical treatment of solar cells for the removal of n-doped layer.

Glass and metals manually separated after initial thermal treatment were recycled according to conventional process routes. Main disadvantages of the process are the manual treatment of panels, the use of sequences of thermal and chemical operations involving mineral acids for solar cell treatment, the use limited to crystalline silicon panels.

First Solar process is currently used in the USA, Germany and Malaysia for CdTe panels treatment according to the process scheme reported as in Fig. 2b.

The process consists of the following steps:
- Crushing and grinding.
- Removing the semiconductor film by leaching with sulphuric acid and hydrogen peroxide.
- Physical separation of ethylene vinyl acetate (EVA)–glass aggregates through mechanical operations: classification and vibrating screen.
- Precipitation of metals by addition of sodium hydroxide.

In this process, there is the recovery of 90% of the glass and about 95% of cadmium and tellurium which must still be subjected to a purification step. Main disadvantages of First Solar process is the treatment of the whole amount of waste by hydrometallurgical treatment and the use limited to CdTe panels.

In this work, experimental results were reported for an innovative process aiming at the treatment of different kinds of panels (crystalline Si, amorphous Si, CdTe) according to the same process scheme including a physical pre-treatment section and a hydrometallurgical section (Fig. 2c). All physical pre-treatments were performed in conventional equipment easily available for waste collectors not requiring specific design and high investment costs making easily available and economically feasible the valorisation of different kinds of PV panels in the same plant.

The specific sequence of physical operation was determined trying different combinations of crushing (single and multiple), milling (hammer mill and attrition mill) and thermal treatment (Granata et al., 2014).

The process here discussed includes:
- Manual dismantling of all electronic equipment (printed circuit boards) for the integral recovery of plastics and of precious metals therein (such as Cu, Au, Ag and Pd).
- Manual dismantling of frames for the recovery of aluminium.
- Physical and chemical pre-treatment of panels for glass recovery: automatic shredding of panels gives three fractions: a coarse fraction (containing EVA agglomerates), an intermediate fraction (directly recoverable as glass), a fine fraction (sent to hydrometallurgical section for metal recovery). The coarse fraction was thermally treated for EVA dissolution, then sieved giving further portions of intermediate fraction and fine fraction.
- Hydrometallurgical section for glass cleaning and/or metal recovery: fine fractions are treated by acid and/or alkaline leaching for metal extraction giving a residual solid as recoverable glass and/or a concentrate of metals (Ti, Ag and Si or Cd and Te depending on the input type of panels).

This approach has the advantage that only small fractions of treated wastes (about 10–20% in weight) is treated by hydrometallurgical operations, requiring small units for such treatment and then low cost of investments.

Si recovery was not specifically addressed for different reasons:
- very low % of this constituent in PV panels (less than 1% still decreasing in new commercial products),
- recent dramatic diminution of electronic Si price (from 400 $/kg of 2008 to the current 200–40 $/kg),
- recent development in electronic Si production estimating 8 $/kg as final price.

Over all these reasons it should be also evident that the cost of electronic Si used in panel construction is not due to the cost of raw material but to the cost of production. Then except when a manual dismantling of Si cells is performed on intact panels (which is only a part of end-of-life panels), the recovery of reusable electronic Si cannot be technically and economically feasible.

Process validation will be performed within the activities foreseen in Photolife project (LIFE13 ENV/IT/001033 co-financed by European Community in the LIFE+ program for Environment Policy and Governance), in which a pilot plant of 200 t/year capacity for EOL PV panel treatment will be designed and constructed.

Materials and methods

Experimental results reported in this work were obtained by using different kinds of PV panels: polycrystalline silicon module (BYD-230P6–30), monocrystalline silicon module (SHARP NT-175E1/NT-R5E3E), amorphous silicon PV module (Sharp NA-901 WQ), CdTe PV module (First Solar FS2).

The silicon devices were previously manually disassembled in order to separate the modules from external frames and then, in each test, around 2 kg of PV modules were used as input materials.

Crushing operations were carried out in a two-blade rotors crusher (DR120/360, Slovakia) without any controlling sieve and in a hammer crusher (SK 600, Slovakia) using a 5 mm sieve. Thermal treatment was performed at 650°C for 1 h in a silicate resistance furnace aiming to a complete degradation of cross-linked EVA (Granata et al., 2014).
After size reduction, a sieving analysis was carried out to evaluate size and products distribution as well as mass fluxes in the process. For this purpose, all samples were sieved by using five different sieves (8, 5, 1, 0.4, 0.08 mm) and an automatic shaker, then they were weighed. Coarse fractions \( (d > 1 \text{ mm}) \) were treated at 650°C for 1 h in a silice resistance furnace.

In order to test the purity of recoverable glass fractions, EVA presence was assessed by thermogravimetric analysis. 0.2 g samples of recoverable glass fractions \((0.4-5 \text{ mm})\) were tested by thermogravimetric analysis to evaluate residual EVA traces after thermal treatment.

As for CdTe panels, Cd concentration in recovered glass was also determined being Cd the most toxic metal present in PV panels. 0.2 g samples of recoverable glass fractions from CdTe panels were digested using sulphuric acid \((9 \text{ mL of a 96\% solution})\) and \(\text{H}_2\text{O}_2\) \((1 \text{ mL of a 35\%w/w solution})\) at 220°C in a microwave digester \((\text{Milestone Ethos 900 Microwave Digestor})\). Liquid samples were filtrated and analysed by Atomic Absorption Spectrophotometer \((\text{AAS: Analytik Jena ContrAA 300})\) for the determination of dissolved Cd.

Metal content in fine fractions \((d < 0.4 \text{ mm})\) was determined by acid digestion with aqua regia \((\text{solid to liquid ratio equal to 1 g in 20 mL})\) at 220°C in the microwave digester. Liquid samples obtained during digestion were analysed by AAS in order to determine the metal concentration released by solid dissolution.

As for the hydrometallurgical treatment, preliminary leaching tests in lab scale were performed. Acid leaching of fine fractions of monocrystalline, polycrystalline and amorphous Si were performed using 100 mL of a 5 M solution of \(\text{H}_2\text{SO}_4\) added with 5 mL of a solution of \(\text{H}_2\text{O}_2\) \((35\%w/w)\), using a solid–liquid ratio 1:3 for 3 h at 60°C. After solid–liquid separation by centrifugation the liquid was analysed by AAS and the solid was further leached by using a solution 75 mL of \(\text{H}_2\text{SO}_4\) \((10 \text{ M})\) and 25 mL of \(\text{H}_2\text{O}_2\) \((35\%w/w)\) at 100°C for 1 h.

Basic leaching tests of the fine fractions from CdTe panels were performed using 100 mL of a solution of \(\text{NaOH}\) \((5 \text{ M})\) added with 5 mL of a solution of \(\text{H}_2\text{O}_2\) \((35\%w/w)\) at 100°C for 3 h varying the solid–liquid ratio \((0.5 \text{ g 50 mL}^{-1} \text{ and 1 g 50 mL}^{-1})\) and leaching temperature \((40 \text{ and 80°C})\) according to a factorial design. Liquid samples after solid/liquid separation were analysed for extracted metals by AAS.

### Results and discussion

#### Physical pre-treatments

Experimental results denoted that the mechanical treatment gave similar results in terms of size fraction distribution obtained for the different kinds of panels (Fig. 3). This common behaviour in mechanical treatment can be explained by considering that the different types of panels have a common multilayered structure mainly made of glass glued using EVA. Main differences in panel types are in chemical composition of photoactive layers used in the cells being lower than 0.4% of the total weight in a panel.

This distribution is in turn strictly related to the specific type of mechanical treatment used \((\text{Granata et al. } 2014)\): optimal sequence of operations was chosen here in order to obtain sufficiently small pieces of fragments and simultaneously minimise the fine fractions emerging from the treatment. In particular, the treatment route involving the crushing by two rotors crushe plus hammer crushing was the best option to such aim \((\text{Granata et al. } 2014)\).

Fractions larger than 1 mm required further treatment in order to break down EVA aggregates still present as evidenced in Fig. 4a. On the other side, fractions 0.4–1 mm (about 20% in weight) are directly recoverable as glass fragments \((\text{Fig. 4b})\). XRD spectra of 0.4–1 mm samples denoted a completely amorphous nature according to the fact than glass is the main component present (data not reported here).

Fractions smaller than 0.4 mm contained significant amounts of metals, which can be extracted in a dedicated hydrometallurgical section. More specifically fine fractions can be treated chemically in order to extract metals thus giving a solid residue mainly made up of glass, and a leach liquor containing metals, which can be treated for instance by precipitation in order to obtain a metal concentrate. The solid residue of glass can be added to the rest of recovered glass, while the metal concentrate can be refined or inertised according to the specific composition and value.

Fractions larger than 1 mm were then thermally treated giving the size distribution reported as in Fig. 5, showing that after this treatment about 80% of directly recoverable glass was obtained not depending on the type of panels. Post thermal treatment recoverable glass fractions 1–5 mm was as represented in Fig. 4c for polycrystalline silicon as an example. Thermal treatment in the chosen conditions determined the complete removal of EVA and then the recovery of glass, which is covered by a layer of...
combustion products. This layer when necessary can be easily removed by washing with hexane thus obtaining clear recoverable glass (Fig. 4c).

During the thermal treatment, less than 10% of fine fractions was obtained to be sent to the hydrometallurgical section as that previously generated in the mechanical treatment.

The degree of glass–EVA separation was specifically addressed by performing thermogravimetric analyses (TGA) of directly recoverable glass fractions obtained for the three types of panels (crystalline and amorphous silicon-based panels and CdTe panel). TGA results showed (Fig. 6) no thermal transition nearby the EVA decomposition temperature (400–525°C) (Marín, Jiménez, López and Vilaplana 1996). Only very slight (<0.3%) weight increase was observed probably due to oxidation of some residual powders coming from physical pre-treatments. At this stage no explanation was found for the different trends observed for the three types of panels.

In the case of CdTe panels, the reduction of Cd content in recoverable fraction is a process target.

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4 a Fractions larger than 1 mm emerging from the triple crushing of polycrystalline Si (polySi), monocrystalline Si (monoSi) and CdTe panels (CdTe); b fractions ranging from 0.4 to 1 mm emerging from the triple crushing of polySi, monoSi and CdTe panels; c fractions larger than 1 mm emerging from the thermal treatment of polySi, and after a solvent treatment for cleaning (polySi_T)

5 Particle size distribution in mm for the different panel types after thermal treatment
Mineralisation tests on such samples showed Cd content of 0.01%, which is about one order of magnitude lower than the Cd concentration in the fine fractions as described below (Table 1). These metals can be extracted and valorised by hydrometallurgical operations including leaching and then recovery of metals or of their concentrates.

Distinct hydrometallurgical routes can be followed depending on the feed composition: if Si-based panels were preliminarily separated by CdTe panels, the fine fractions will be treated separately. Then fine fraction emerging from Si-based panels can be treated by mild acid leaching for the separation of Zn, Al and Fe and the obtainment of a concentrate containing Ag and Ti, which could be also further refined to give Ag and Ti as separated products. On the other hand, the fine fraction resulting from CdTe treatment can be treated by alkali for sequential extraction of Te, Al and Zn leaving a concentrated containing Cd, which can be further treated by acid leaching in order to extract Cd. Otherwise if no preliminary separation is performed between Si panels (crystalline and amorphous) and CdTe panels, the fine fraction can be treated in the hydrometallurgical section according to a sequential scheme of basic and acid leaching allowing the separation of the different metals.

Preliminary experimental results of sequential leaching performed using fine fractions emerging from pilot plant tests were reported here. Fine fractions emerging from monocrystalline, polycrystalline and amorphous Si panels were preliminary leached in mild conditions to extract Zn, Al and Fe (Fig. 7). Residual solid mainly containing Ti, Si and Ag was further treated in stronger leaching conditions in order to extract Ti (Fig. 7) leaving a residual solid containing Ag and Si.

Experimental results of basic leaching in different operating conditions denoted that Cd extraction is always zero, while a selective extraction of Te can be obtained working at 80°C (Fig. 8). After this step extraction, the residual containing Cd can be further treated by acid or directly inertised being 5–10% of initial waste. Inertisation (as encapsulation of solid wastes in cement matrices not allowing their dissolution and release in the environment) can be viewed as the last chance in waste disposal being an expensive treatment without any material recovery. Then reducing the final mass of wastes to be inertised according to the process scheme proposed here can be an economically and environmentally effective alternative in waste disposal and treatment.

Conclusions

In this work, a review of the status of the recycling activities for PV panels was reported along with pilot-scale experimental results for the treatment of various types of panels according to a new process route. This process allowed 70% recovery of the module weight (without frame and other equipment) as glass and the treatment by hydrometallurgical operations of only the 20% of the module weight.

A pilot-scale installation with a potentiality of 200 t/year is going to be constructed within the Photolife...
project (LIFE13 ENV/IT/001033) for the recovery of aluminium and glass from end-of-life panels of different kinds: Si-based panels, CdTe panels and innovative CIG and CIGS panels.

Fine fractions and electronic equipment included in PV installations will be treated according to hydrometallurgical operations in a mobile pilot plant already built within FP7 founding scheme (HydroWEEE project).

After fulfilling of targets related to PV panels, the same integrated units (physical pre-treatment and hydrometallurgical section) will be used to implement the pre-treatment section in other processes already developed for the hydrometallurgical section for similar wastes such as liquid crystal display (HydroWEEE DEMO project).

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| Table 1  | Chemical composition (%w/w) determined by acid digestion of the fine fractions (<0.4 mm) of the different types of PV panels (mSi, monocrystalline Si; pSi: polycrystalline Si; aSi, amorphous Si) |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Treatment            | Panel type | Ti  | Zn  | Al  | Fe  | Sn  | Ag  | Cu  | Cd  | Te  | SiO₂ |
|----------------------|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| After mechanical treatment | mSi       | 0.11| 1.21| 0.78| 1.67| ... | 0.05| 0.03| ... | ... | 40.8 |
|                       | pSi       | 0.04| 0.89| 0.51| 1.96| ... | 0.09| ... | ... | ... | 46.5 |
|                       | aSi       | 0.33| 0.69| 0.39| 1.03| ... | 0.01| ... | ... | ... | 46.8 |
|                       | CdTe      | ... | 1.50| 0.40| 1.79| 0.93| ... | 0.16| 0.19| ... | 47.7 |
| After thermal treatment | mSi       | 0.09| 0.99| 0.91| 1.78| ... | 0.09| 0.02| ... | ... | 42.3 |
|                       | pSi       | 0.06| 0.61| 0.43| 1.9 | ... | 0.08| 0.05| ... | ... | 43.5 |
|                       | aSi       | 0.35| 0.75| 0.35| 0.7 | ... | 0.03| 0.05| ... | ... | 49.8 |
|                       | CdTe      | ... | 1.36| 0.99| 0.93| 0.87| ... | 0.33| 0.21| ... | 49.3 |