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Toxicity assessment and feasible recycling process for amorphous silicon and CIS waste photovoltaic panels

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ABSTRACT

End-of-Life (EoL) photovoltaic (P/V) modules, which are recently included in the 2012/19/EU recast, require sound and sustainable treatment. Under this perspective, this paper deals with 2nd generation P/V waste modules, known as thin-film, via applying chemical treatment techniques. Two different types of modules are examined: (i) tandem a-Si:H/μc-Si:H panel and, (ii) Copper-Indium-Selenide (CIS) panel. Panels' pretreatment includes collection, manual dismantling and shredding; pulverization and digestion are further conducted to identify their chemical composition. A variety of elements is determined in the samples leachates' after both microwave-assisted total digestion and Toxicity Characteristic Leaching Procedure (TCLP test) using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis. The analysis reveals that several elements are detected in the two of panels, with no sample exceeds the TCLP test. Concentrations of precious and critical metals are also measured, which generates great incentives for recovery. Then, further experiments, for P/V recycling investigation, are presented using different acids or acid mixtures under a variety of temperatures and a stable S/L ratio, with or without agitation, in order to determine the optimal recycling conditions. The results verify that chemical treatment in P/V shredded samples is efficient since driving to ethylene-vinyl acetate (EVA) resin's dissolution, as well as valuable structural materials recovery (P/V glass, ribbons, cells, P/V intermediate layers). Among the solvents used, sulfuric acid and lactic acid demonstrate the most efficient and strongest performance on panels' treatment at gentle temperatures providing favorably low energy requirements.

1. Introduction

1.1. P/V waste generation

Global energy crisis, as a result of the sharp overuse of conventional energy resources combined with the increasing risks of upcoming depletion of fossil sites, has led to massive production and prevalence of photovoltaic systems over the last decades. This promising technology generates concerns regarding the management of the new waste stream involved when their predicted operation time will be completed. Based on estimations (Tao and Yu, 2015; Ashfaq et al., 2014; Kang et al., 2012; Klugmann-Radziemska et al., 2010; Doi et al., 2001), the technical lifetime of modules is approximately 25 years denoting that massive waste volume is expected in the next years (Tao and Yu, 2015).

For the time being, the implementation of feasible P/V recycling practices in the P/V industry is considered to be troublesome due to the temporarily limited generated quantities of P/V waste. Most of today's waste P/V modules originate from defect units during production or damaged units during transportation, installation or operation (Tao and Yu, 2015) (e.g., cracks in the front glass, delamination due to UV or humidity, etc.). Thus, the recycling issue will be necessarily addressed in the near future due to the exponential increase in waste. In numbers, P/V waste quantities in Europe are estimated to verge on 33,500 tons in 2040 instead of 290 tons produced in 2010 (Müller et al., 2005). A more recent estimation reveals that in 2035 the expected mass of waste PV panels will amount to 3,000,000 tons, whereof about 45,000 tons belong to the Copper Indium Gallium (Di)selenide (CIGS) category (Rocchetti and Beolchini, 2015).

In order to tackle this serious issue, EU attempts are directed to the development of a sustainable framework which introduces producer's responsibility according to Directive 2012/19/EU. In Annex III of the Directive 2012/19/EU, it is stated that photovoltaic panels are included in large equipment with a long life cycle. Furthermore, Annex V establishes percentages and deadlines for recovery and recycling that should reach the minimum of 80% and 70% of the panels' average weight until 14 August 2018. In

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Nomenclature

Types of modules used
a-Si:H/μc-Si:H amorphous hydrogenated/microcrystalline hydrogenated silicon panel
CIS Copper-Indium-Selenide panel

Samples examined
a-Si:H/μc-Si:H_{panel} amorphous panel area
a-Si:H/μc-Si:$H_{junction\text{-}box}$ amorphous junction box and cable mixture
a-Si:H/μc-Si:H_{total} amorphous panel area homogenised with junction box and cable mixture at a ratio based on modules' typical composition
CIS_{panel} CIS panel area
$CIS_{junction\text{-}box}$ CIS junction box and cable mixture
CIS_{total} CIS panel area homogenised with junction box and cable mixture at a ratio based on modules' typical composition
$CIS_{panel\ edge}$ CIS panel area on the edge sides

parallel, non – profit associations, such as PV cycle, produce an industry-wide take back and recycling system for the waste modules (PV CYCLE, 2013). In terms of industry, Deutsche Solar has designed a process for the recycling of crystalline modules, First Solar has developed a recycling process for CdTe modules, while the recycling of the rest P/V types remains in a pilot scale. EU has further investigated some alternative strategies of P/V recycling through two research programs: SENSE (Sustainability Evaluation of Solar Energy systems) and Resolved (Berger et al., 2010).

1.2. State-of-the-art recycling on P/V processes

The main treatment stages include primarily panel's delamination and then separation of materials composing a typical P/V panel followed by metal extraction and purification (TaO and Yu, 2015). On this basis, according the newest scientific research, the relative lab-scaled recycling processes include (i) thermal treatment which results in EVA's removal/decomposition and recovery of the valuable materials (Corcelli et al., 2016; Granata et al., 2014), or (ii) chemical delamination with organic/inorganic solvents and then extraction/refining (Klugmann-Radziemska, 2013). Furthermore, other methods such as two-step heating process and mechanical treatment have been also investigated in P/V modules (TaO and Yu, 2015). Most of the aforementioned processes aim at the recovery of silicon and currently other precious (Ag) (Dias et al., 2016) and critical metals (In, Ga, Te).

Although the already obtained results offer clear recommendations for the decision – makers, the P/V treatment behavior is difficult to get generalized due to the constant changes in the P/V manufacturing techniques, the variety of P/V technologies (1st, 2nd and 3rd generation P/V modules) and its panel complex structure consisting of aluminum (Al) frame, junction box, glass, EVA resin, cells, electrodes, etc. More investigation is needed, therefore, to simulate the real conditions of such treatment techniques in large scale and achieve remarkably high recovery rates.

1.3. Literature overview of recycling approaches sustainability

Applying sustainable recycling approaches in waste modules can have a significant positive impact on the environment; however, the economic viability of such recycling policies should be verified to avoid any economical burdens and failures. Towards this route, Life Cycle Analysis (LCA) is one of the most plausible means to investigate and quantify the complex multi-dimensional impacts of a P/V module, or briefly its viability and sustainability. As the research interest is rapidly increasing for renewable energy, current studies assess the P/V life cycle in order to measure its environmental impact along with the accompanied economic cost (Gerbinet et al., 2014; Raugei et al., 2007), while some evaluate the benefits in case of P/V recovery process (Corcelli et al.,2016).

Specifically, the scientific community supports that even if thin-films recycling generates profits by selling the recycled materials at high price, the cost of recycling exceeds its benefit (McDonald and Pearce, 2010), including also high energy demand and CO_2 emissions. By the producer's point of view referring to the profitability of a recycling process, only 10% of the P/V unit is likely worth recycling since containing critical metals Te, In or Ga, but their recycling cost still remains higher than their market price (Cucchiella et al., 2015). In addition to this, P/V recycling viability is related to transformation costs, taking into account the geographical dispersion which constitutes an obvious difficulty in developing a comprehensive recycling system of P/V waste and makes P/V collection and transportation extremely challenging and expensive (Fthenakis, 2000). Despite the lack of obvious economic motivations, researchers still estimate that P/V recycling should be encouraged (McDonald and Pearce, 2010). It is, therefore, of great importance to identify the possibilities of favorable recycling processes in order to confirm or reject such concerns.

1.4. Why encouraging the recycling of thin-film modules?

Although the P/V technologies provide the environmental benefit of zero emissions during operation (Corcelli et al., 2016), the manufacturing techniques based on the use of toxic and valuable metals (e.g., in Cd, Pb, Te, Se, etc.) raise both health and environmental concerns regarding the EoL P/V panels disposal (Cyrs et al., 2014; McDonald and Pearce, 2010), as well as challenges regarding any benefits of reducing the criticality risks (e.g., In, Ga, Te, etc.) and recovering valuable materials in case of recycling.

In specific terms, the emerging thin-film, or 2nd generation P/V modules contain (i) amorphous silicon (a-Si), (ii) cadmium telluride (CdTe) and (iii) Copper-Indium-Gallium-(Di)selenide (CIGS) panels (Paiano, 2015). The main characteristic found in thin-film modules is the less semiconductor material used (width of a few nm to tens of μm) along with high-efficiency cells (Chopra et al., 2004) and low production costs (Granata et al., 2014). The aforementioned benefits have allowed the today's expansion of thin-films in P/V industry (Cyrs et al., 2014). Furthermore, a variety of valuable materials is embedded into thin-film modules since (a) the semiconductor material of CIGS/CIS, indium and gallium, are among the critical raw materials (Savvilotidou et al., 2014, 2015; Goe and Gaustad, 2014) and their recovery is of high importance (Rocchetti and Beolchini, 2015), (b) for a-Si, Si recovery still remains a challenge given that silicon cells' recycling has been studied mostly in crystalline photovoltaics (Kang et al., 2012) and therefore gap of knowledge dominates in a-Si recycling, (c) in case of CdTe, recycling is of great significance in order to limit Cd emissions (Marwede and Reller, 2012) and also to take back the rare Te (Rocchetti and Beolchini, 2015). Summarizing the above, thin – film solar panels are mostly selected for examination due to their composition consisting of valuable materials and crit-