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Recycling WEEE: Extraction and concentration of silver from waste crystalline silicon photovoltaic modules

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ABSTRACT

Photovoltaic modules (or panels) are important power generators with limited lifespans. The modules contain known pollutants and valuable materials such as silicon, silver, copper, aluminum and glass. Thus, recycling such waste is of great importance. To date, there have been few published studies on recycling silver from silicon photovoltaic panels, even though silicon technology represents the majority of the photovoltaic market. In this study, the extraction of silver from waste modules is justified and evaluated. It is shown that the silver content in crystalline silicon photovoltaic modules reaches 600 g/t. Moreover, two methods to concentrate silver from waste modules were studied, and the use of pyrolysis was evaluated. In the first method, the modules were milled, sieved and leached in 64% nitric acid solution with 99% sodium chloride; the silver concentration yield was 94%. In the second method, photovoltaic modules were milled, sieved, subjected to pyrolysis at 500 °C and leached in 64% nitric acid solution with 99% sodium chloride; the silver concentration yield was 92%. The first method is preferred as it consumes less energy and presents a higher yield of silver. This study shows that the use of pyrolysis does not assist in the extraction of silver, as the yield was similar for both methods with and without pyrolysis.

1. Introduction

1.1. WEEE

Waste Electrical and Electronic Equipment (WEEE) or e-waste, according to EMPA (Swiss Federal Laboratories for Materials Science and Technology), is the term used to describe old, end-of-life or discarded electrical appliances, including discarded computers, consumer electronics, and refrigerators (EMPA, 2009). The amount of WEEE generated worldwide seems to be underestimated, and there are no precise methods to determine the total amount. Globally, the upward trend in WEEE generation and production should continue to grow due to new technologies and affordable electronics (Ongondo et al., 2011). E-waste contains both valuable and hazardous materials, which require special handling and recycling methods. WEEE contains a significant number of precious metals, such as indium, silver and palladium. As these elements are often present in low concentrations and in complex components, their recovery is not easy (Nelen et al., 2014), and a large proportion of these precious metals is lost in the recycling process (Chancerel et al., 2009). Moreover, WEEE may contain heavy metals, brominated flame retardant (Wang and Xu, 2014) and a variety of toxic substances that can contaminate the environment and threaten human health, if the end-of-life phase is not meticulously managed (Kiddee et al., 2013).

The extraction of precious metals by mining is associated with negative environmental impacts due to significant greenhouse gas emissions and energy, water, and land usage (Ayres, 1997). The use of secondary raw material is becoming more important because the ore grade in primary production is decreasing (Simon et al., 2013). The environmental impacts of secondary production in state-of-the-art operations are much lower than in primary production (Hagelüken and Meskers, 2009). In addition to environmental protection and legislation, recycling is also driven by economic interests. The limited quantity of precious metals in reserve and their high economic value provide additional incentives to improve the recovery and research of precious metals from WEEE (Chancerel et al., 2009).

1.2. Photovoltaic modules

Solar modules convert energy from sunlight into electricity without using a rotor, heat engine or gears. Recently, they have

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attracted a great deal of attention due to their potential application for alternative energy generation. Many countries have already benefitted from the photovoltaic industry (Wang et al., 2008). The range of current technologies for manufacturing photovoltaic modules (or PV modules) is divided into three generations. First generation PV modules contain crystalline silicon (c-Si), which may be monocrystalline, polycrystalline or ribbon sheets. Second generation PV modules include thin film amorphous silicon (a-Si), cadmium telluride (CdTe), multi-junction cells (a-Si-μc-Si), copper indium gallium diselenide (CIGS), and copper indium diselenide (CIS). Third generation PV modules include concentrator photovoltaic (CPV) and emerging technologies such as dye-sensitized solar cells, organic solar cells, hybrid cells, passivated emitter rear contact cell (PERC) and passivated emitter rear-locally-diffused (PERL). Currently, the majority (approximately 80%) of worldwide production consists of crystalline silicon cells (first generation) (Paiano, 2015).

According to Radziemska (2014), crystalline silicon PV modules are made from the following materials, which are listed in order by decreasing mass: glass, aluminum frames, EVA (ethylene-vinyl acetate) copolymer transparent encapsulating layers, photovoltaic cells, installation boxes, Tedlar protective foil and assembly bolts. A typical cross-section of these modules, with several layers of distinct materials, is shown in Fig. 1. The metallic electrodes are placed in the front and the rear of the silicon cell. The front electrodes are typically made of silver and the rear electrodes of silver and aluminum (Pinho and Galdino, 2014).

1.3. Recycling photovoltaic modules

At the end of their lifespan, PV modules become solid waste (e-waste). The lifespan of first generation PV modules is approximately twenty years and approximately one million tons of PV modules are forecast to be disposed of in 2035, based on the growth in the solar industry (International Energy Agency, 2013). As the PV market continues to grow, so will waste, even if such waste appears with a long time delay (Kazmerski, 2006).

Improper disposal of solar modules can generate significant environmental impacts. These devices contain cadmium and lead, which can leach into the soil and consequently pollute the environment. PV modules and other WEEE are composed of glass, aluminum, rare earths, brominated flame retardants (BFRs) and other hazardous substances (Widmer et al., 2005).

In general, the process of recycling PV modules starts with the removal of EVA resin. Several methods can be employed to remove the EVA, such as dissolution by nitric acid and thermal decomposition (usually pyrolysis) (Bruton, 1994). Most recycling research regarding PV modules aims to recover high-purity silicon and glass, leaving behind other materials such as silver, copper and aluminum. Table 1 presents a summary of experimental work conducted on the recycling of PV modules.

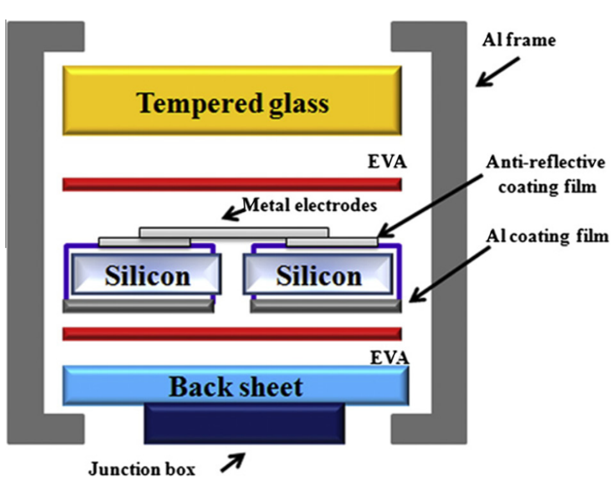

Fig. 1. Typical structure of c-Si PV modules: cross-sectional view (Kang et al., 2012).

1.4. Silver in photovoltaic modules

From an economic point of view, pure silicon, recoverable from spent cells, is the most important material due to its cost and scarcity (Radziemska and Ostrowski, 2010). However, given the high complexity of c-Si cell recycling, other useful materials such as glass, aluminum and silver are becoming increasingly useful for improving the economic viability of recycling processes (Tao and Yu, 2015). Table 1 shows that older studies focused on recovering silicon whereas the latest works tend to recover more materials.

Silver is a precious metal in high demand, and it is used in PV modules (Pinho and Galdino, 2014). Swerdrup et al. (2014) suggest that silver production will reach its peak in 2030, and because of its rapid usage and limited availability, the future silver supply will be soon at risk (2075). When mined, silver's concentration in the U.S.'s deposits must reach 700 g/t in order to be economically minable as a primary product (USGS, 2015). Despite the importance of this metal, the current high demand and its increasing market price, there are few published studies regarding the recovery of silver from PV modules. Authors such as Radziemska (2014) and Tao and Yu (2015) suggest that silver from PV modules can be extracted by nitric acid leaching followed by electrolysis. Palitzsch and Loser (2011) claim to recover aluminum in the form of poly-aluminum-chlorides through a demetallization process with an aluminum chloride and water solution while silver is extracted using nitric acid. Nieland et al. (2012) also aimed to extract silver from PV modules using hydrogen peroxide in combination with organic and non-organic catalyzers. All of these results, however, lack quantification and yield extraction analysis.

The objective of this study is to analyze the silver present in PV modules. This study aims to characterize the silver's distribution

Table 1
Summary of experimental work conducted on PV recycling.

Authors	Process	Materials Recovered
Frisson et al. (2000)	• Pyrolysis in a conveyer belt furnace and pyrolysis in a fluidized bed reactor • Etching using a sequence of 15% HF, 4–1 $H_2SO_4{\cdot}H_2O$ solution, 40% HNO_3 • Emitter etch in 20% NaOH	• Silicon
Radziemska and Ostrowski (2010)	• Removal of the aluminum coating by etching, using 30% KOH to remove Al metal coatings • Etching using a mixture of 250 ml HNO_3 (65%), 150 ml HF (40%), and 150 ml CH_3COOH (99.5%) 3 ml Br_2 for removing Ag coatings, AR coatings and n-p junctions	• Silicon
Kang et al. (2012)	• Recovery of glass using organic solvents • Thermal decomposition to remove the adhesive layer and recover the semiconductor • Obtainment of 99.99% pure silicon by immersion of the recovered cell in an etching solution combined with surfactant	• Glass • Silicon
Wang et al. (2012)	• Two-step heating process for PV module thermal delamination • Acid etching to remove tin-lead coating from copper and metal impurities from the silicon wafer	• Glass • Silicon • Copper

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