Production of hydrogen and geopolymers from end of life photovoltaic panels

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Abstract. Photovoltaic panel waste is expected to rise rapidly as installed modules approach their end of life. Recovery and reuse of valuable components such as semiconductors is crucial. Crystalline silicon panel derived waste reacts with alkali producing hydrogen gas and metasilicate structures in the solution which can be used as geopolymerization activator. In this work the prospect of utilizing 1st generation crystalline silicon panel waste for geopolymer activation with simultaneous hydrogen production is examined. Preliminary test results show that 1.55±0.05L of hydrogen gas can be produced from 1g of recovered semiconductor (Si). The resulting metasilicate solution is used for fly ash geopolymer activation. After 7 days of curing, the compressive strength of the generated geopolymer samples reached 19.5±0.5 MPa, indicating that this zero-waste reuse pathway can be viable after optimization.

Keywords: end-of-life photovoltaic panel, hydrogen production, geopolymer activation, metasilicate precursor, silicon alkaline reaction.

1. Introduction

One of the most advanced and promising renewable energy production technologies is photovoltaic (PV) energy production [1]. Due to its environmental friendliness, PV technology has gained popularity as a power source. Thus, solar PV power has seen an upsurge in industrial and residential use over the last few decades. PV panels are currently quite popular and have the ability to generate sustainable energy on a worldwide scale. However, as more solar panels are installed, an increasing number of them will eventually approach the end of their useful lives (EOL) and will turn into a form of hazardous waste, if not retrieved and disposed properly. In order to limit the negative effects of the persistent development in PV waste volume and in order to implement solar module recycling, the European Union (EU) has added PV waste to the new Waste of Electrical and Electronic Equipment (WEEE) directive [2][1].Characterization of this upcoming type of waste has concerned researchers globally, who investigate possible environmental and economic impacts of solar PVPs after their EoL [3]-[5].

A typical crystalline silicon PV consists of soda-lime glass, Ethyl Vinyl Acetate (EVA), silicon solar cells, copper/silver electrodes and a Tedlar backsheet. Researchers have focused on material recovery from these types of PVPs. Physical and/or thermal treatment processes have surpassed chemical methods, as avoiding the use of organic solvents to dissolve the polymer sheets in the PVPs is more sustainable, both economically and environmentally [5]-[7].

Glass casing and silicon cells constitute the most voluminous wastes of the photovoltaic system. These solar panel parts can be recycled in technologies that can offer high added value products, following the circular economy principles [8]. Geopolymers, the most viable alternative to Ordinary Portland Cement (OPC) building materials [9], are such a technology, since they valorize massive amounts of industrial wastes and byproducts on manufacturing finished products of low embodied energy, fully aligned to 2030 Climate Target Plan [10]. Indeed, these materials are produced through geopolymerization reactions where a solid aluminosilicate precursor, such as fly ash, Construction and Demolition Wastes (CDWs) and slags, is activated by using an alkaline aqueous solution [11]. Conventionally, the preparation of the activation solution involves the use of commercial alkali silicates, the production process of which is significantly energy-intensive. Glass casing and silicon cell wastes, after appropriate processing, may be applied for the preparation of the activation solution of the geopolymer synthesis, since they contain significant amounts of the essential Silicon and Sodium ions [12].

Thus, the development of an activation solution based on solar panel wastes would further reduce geopolymers' carbon footprint and at the same time would enhance their recycling potential. Simultaneously, hydrogen gas can be recovered from this silicon-alkaline reaction [13]-[17].

This study concerns the development of the activation solution for geopolymer synthesis through the valorization of silicon solar cells and soda-lime glass with simultaneous hydrogen production.

2. Materials and methods

End-of-life first generation polycrystalline photovoltaic panel samples used in this study were provided by Polyeco S.A. after decommissioning from the field.

2.1. Sample preparation

The photovoltaic panel waste is manually cut into 40x30 mm pieces and reduced to fine powder through milling in an "LM2 Pulverising Mill". It is then characterized by XRD, XRF and Laser Granulometry. The semiconductor fraction (silicon solar cells) is also recovered through thermal treatment and tested separately. Thermal treatment of photovoltaic panels is conducted at 550 °C for 15 min in a furnace with air atmosphere. Separation of silicon solar cells, glass, ash and electrodes after the thermal treatment is performed with a trommel screen. Recovered silicon is also reduced in size and characterized.

2.2. Experimental procedure

Dissolution studies of the photovoltaic panel derived waste are performed under alkaline conditions, in order to determine their dissolution rate in terms of diluted Silicon and Sodium ions. The effect of parameters, such as the sodium hydroxide solution concentration and the temperature on the dissolution of wastes was investigated. The volume of the gas produced was measured and its composition was analyzed using Gas Chromatography (GC). The resulting sodium metasilicate solutions were characterized via Fourier Transformation Infrared Spectroscopy (FTIR).

Finally, the efficiency of the waste-based activation solution was evaluated by using it as an activation solution for geopolymerization of Greek fly ash, a thoroughly studied geopolymer precursor with its mineralogical content presented in Table 1. The solution was prepared and added in a mortar mixer (Controls 65-L0005) with the fly ash powder, and they were mixed until a homogenous slurry was formed. The prepared paste was casted in 50 mm × 50 mm × 50 mm cubic molds and cured at 70 ◦C for 2 days. Then, they were kept at room temperature until mechanical testing was performed (7 days after casting). The synthesis parameters of fly ash geopolymerization applied in this study, are Si/Al = 1.98[1] and Na/Al = 0.84[2].

Table 1. Fly ash' chemical composition (% w/w).

Fly Ash	%
SiO_2	48.05
Al_2O_3	24.40
Fe_2O_3	4.34
CaO	8.39
MgO	1.18
K_2O	0.88
Na_2O	0.00
SO_3	0.63
LOI	9.78

3. Results and discussion

Preliminary tests were conducted in triplicate using the recovered silicon solar cell fraction and 4M NaOH solution in a ratio of 50mL per 0.1g of solar cell, under stirring at room temperature. The generated gas volume was measured at 1.55±0.05 L/gSi and the GC analysis validated that this was hydrogen. This amount corresponds to 89% of the theoretical hydrogen generation calculated based on equation 1.

$$\mathrm{Si} + 2\mathrm{NaOH} + \mathrm{H_2O} \rightarrow \mathrm{Na_2SiO_3} + 2\mathrm{H_2} \qquad (1)$$

This deviation from the anticipated theoretical yield is expected due to impurities in the silicon solar cells such as anti-reflective coating, Al back sheet and metallic electrodes. Figure 1 displays the Si/alkaline solution at the starting point of the experiment and after dissolution. The FTIR spectrum after dissolution is presented in Figure 2 and its analysis in Table 2.

Figure 1. Si/alkaline solution at the starting point of the experiment (left) and after dissolution (right).

[1] The overall amount of Si involved in the geopolymerization process expressed as the Si/Al molar ratio.

[2] The alkalinity of the activation solution expressed as sodium to aluminium molar ratio Na/Al.

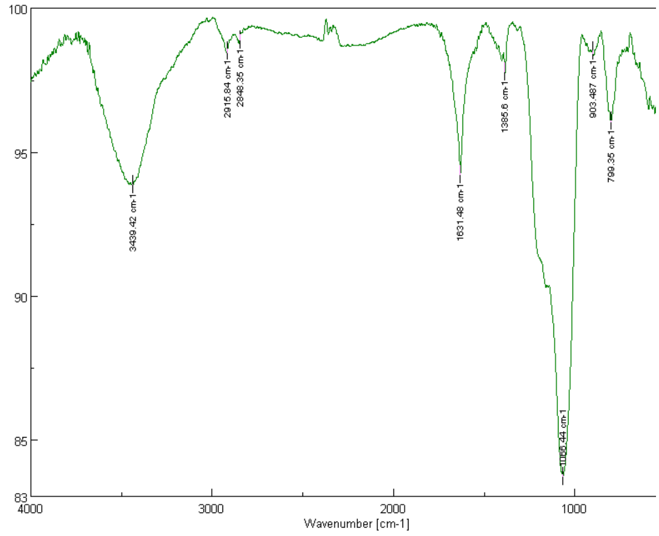

Figure 2: FTIR spectrum of sodium metasilicate solution from photovoltaic panel waste.

Table 2. FTIR peaks per observed frequency.

Frequences (cm^{-1})	**Assignments**
799.35	Si-O-Si symmetric stretching vibrations
903.487	Si-O-Na symmetric stretching vibrations
1066.44	Si-O-Na asymmetric stretching vibrations or Si–O–Si asymmetric stretching vibrations
1385.6	O-C-O
1631.48	-OH bending vibrations (H_2O)

Characteristic Si-O-Na stretching vibrations are present in the spectrum indicating the formation of sodium metasilicate as given in the literature [18].
The sodium metasilicate solution was used as activation solution for fly ash geopolymerization. Cubic 50x50x50 mm matrices were formed and resulting geopolymers (Figure 3) exhibited a uniaxial compressive strength of 19.5±0.5 MPa after 7 days of curing. Even though these are preliminary tests, the produced geopolymers achieved compressive strength suitable for a number of applications in the building sector.

Figure 3: Fly ash geopolymer samples using photovoltaic panel waste derived activation solution.

4. Conclusions

Results so far indicate that this alternative reuse pathway is feasible through simple reactions and methods. This process has zero waste, energy recovery in the form of hydrogen gas and a building material product, which is more environmentally friendly than regular OPC. More experiments are under way where the soda lime glass of photovoltaic panels is used alongside with the silicon solar cells as a precursor for sodium metasilicate formation.

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