Stabilization / Solidification of First Generation End-of-Life Photovoltaic Panel Waste in Cement Mortar

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Abstract

Photovoltaic Panels (PVP) have been widely used as an alternative of fossil fuels to produce power. However in order for PVP to be a completely environmentally friendly alternative, planning for their end-of-life cycle is also required. This work addresses the need to establish a safe disposal plan by stabilizing 1st generation PVP waste that use Si as semiconductor in cement mortars.

Silicon PVPs were initially mechanically and thermally pretreated (550 °C for 30 min), in order to remove the polymer sheets. A mixture of glass, silicon, electrodes and ash were recovered and separated in a trommel. Experiments were carried out with 3 materials; recovered semiconductor (silicon), glass and mixed waste. The mixed waste consisted of glass, silicon and ash as retrieved after only electrode removal from the material generated by the pretreatment. A series of 8 mortar samples containing 1-20% of the aforementioned fractions as aggregate substitute were prepared according to EN196-1 and their flexural and compressive strength was measured at ages of 2, 7 and 28 days. After 28d of curing, the samples were subjected in Toxicity Characteristic Leaching Procedure (TCLP) and leached metals were measured by ICP-OES.

The presence of Al on the surface of the semiconductor resulted in gas production and air encapsulation in samples containing semiconductor and mixed waste aggregate, leading to 31.1- 41.8% lower compressive strength in comparison to a reference mortar sample. TCLP results indicate that stabilization was successful since no significant metal amount was detected.

Sample containing 1% mixed waste achieved compressive strength of 27.6MPa at 28d, 31.1% lower than reference (39.5MPa). However, this compressive strength value indicates that it could be used in some constructions after further examination of mortar's physicochemical properties.

1. Introduction

Over the past decades the use of photovoltaic panels (PVPs) to harness solar energy has been widely expanded. As installed PVPs reach the end of their lifespan, recycling, reuse and safe disposal of PVP waste are becoming a critical and global challenge. Ways to recover valuable materials such as silver and semiconductors are studied, as well as potential ways to reuse semiconductors [1-5].

However, in order to establish a safe disposal plan, it is important to prevent PVP waste to end up in landfills. Stabilization / solidification in cement mortars, concrete or other binding materials is a technique commonly used to prevent metal containing waste from leaching toxic elements to the environment and could be applied in the case of PVP disposal as well[6-9].

The scope of this work is to evaluate the potential of 1st generation PVP waste to be used as aggregate in mortars and assess the stability of the waste containing mortars in case of their safe disposal in a landfill as well as to check their potential utilization in constructions by testing their mechanical performance.

2. Materials and methods

2.1. Silicon recovery

First generation PVP was cut into pieces and placed in a furnace in porcelain crucibles at 550 °C for 30 min to remove polymer sheets, ethylene vinyl acetate (EVA). The resulting mixture of Si flakes, soda lime glass, electrodes and ash was separated in a trommel screen. Silver electrodes were collected separately due to their high value and the rest of the mixture was treated as mixed waste sample to be stabilized. The process is displayed schematically in Figure 1. Glass and semiconductor (Si) fractions were also tested separately in order to assess their suitability as recovered components. Samples were ground and their grading was measured.



Figure 1: Material recovery process from 1st generation PVP

2.2. Mortar sample preparation

Prismatic mortar samples with size of 40x40x160 mm were prepared according to EN 196-1with a water to cement ratio (w/c) equal to 0.55 and sand to cement ratio(s/c) equal to 3.0. CEM II 32.5R Portland cement and calcareous sand were used. Prepared samples consisted of a reference with no added waste (R), samples with sand replacement by only glass in 10, 20% w/w (G10, G20), mixed waste in 1, 2.5, 5, 10, 20% w/w (M1, M2.5, M5, M10, M20) and a sample containing 5% w/w of the semiconductor fraction (SC).

2.3. Mechanical strength

The Compressive and Flexural strengths of the samples were measured at 2, 7 and 28 days of curing, according to EN 196-1. Measurement and recording of the values was conducted on a Matest Servo plus evolution 300/15 kN system. Performance of the prepared samples over the aging period was examined in order to evaluate the effect of the aggregates' presence in the mortar mix.

2.4. Toxicity characteristic leaching procedure

Effective stabilization of the waste was evaluated through US EPA 1311 - Toxicity Characteristic Leaching Procedure (TCLP) method after 28 days curing of samples. The leaching of PVP metals was carried out by acetic acid/NaOH extraction fluid with pH of 4.9 with extraction fluid to solid ratio 20:1. The samples were agitated in an end-to-end shaker for 18h at 30RPM. Concentration of metals found in PVPs (Pb, Cu, Zn, Ag, Sn, Al) in the extraction fluid was measured by ICP-OES after filtration. Pb and Ag are of particular importance, since they are enlisted among the 8 heavy metals to be monitored in a TCLP by Resource Conservation and Recovery Act (RCRA-8) regulations.

3. Results and Discussion

3.1. Mechanical strength

Grading of semiconductor, soda lime glass, mixed waste and sand that were used in the cement mortars is displayed in Figure 2. For all the aggregates 99.5% w/w is passing a 4mm sieve. Glass and mixed waste are the coarsest aggregates.

Flexural and compressive strength data measured for the 8 samples and the reference are displayed in Table 1 and are presented graphically in Figures3 and 4 respectively. The two samples containing only glass from PVP develop their strength similarly to the reference sample with slightly lower values, displaying satisfactory behaviour as aggregate, as expected [10]. Mortar containing mixed waste and semiconductor, however, developed lower flexural and compressive strength. This phenomenon can be attributed to the presence of Al in the backside of the semiconductor, which resulted in formation of hydrogen gas in the cement pastes [11]. Gas production caused air encapsulation in the paste and expansion of the occurring mortars, reducing their mechanical properties, which can be observed in Figure 5.



Figure 2: Grading of aggregates used in the cement mortar

	Sand replacement	Flexural Strength			Compressive Strength		
Sample	(%)	(MPa)			(MPa)		
		2 days	7 days	28 days	2 days	7 days	28 days
R	none	5.5	6.4	7.3	26.6	33.8	39.5
G10	10% glass	4.4	5.7	7.4	22.6	30.6	35.9
G20	20% glass	3.5	5.4	6.2	20.2	29.6	35.5
M1	1% mixed waste	1.7	3.9	5.8	6.8	19.1	27.6
M2.5	2.5% mixed waste	2.5	5.4	5.5	9.3	19.2	27.0
M5	5& mixed waste	-	3.5	6.4	6.9	17.3	23.3
M10	10% mixed waste	3.5	4.5	5.9	14.9	21.3	23.0
M20	20% mixed waste	3.0	3.7	5.7	11.9	17.2	23.7
SC	5% semiconductor	3.6	5.0	5.7	11.1	17.4	24.9

Table 1: Flexural and compressive strength of the prepared mortar samples after curing for 2, 7 and 28 days.



Figure 3: Flexural strength of the prepared mortar samples after curing for 2, 7 and 28 days.



Figure 4: Compressive strength of the prepared mortar samples after curing for 2, 7 and 28 days.



Figure 5: Reference sample without expansion (Left), semiconductor (SC) sample with air bubbles and expansion (Right)

All samples containing semiconductor (SC and M_x) developed their flexural and compressive strength at a much slower rate, through the aging period, in comparison with the reference and the samples containing the PVP glass fraction (R, G_x) due to the gas production mentioned above. The final compressive strength measured at 28d was also lower for these samples (23-27.6 MPa) in comparison to reference (39.5MPa). Reduction in compressive strength was consequently 31.1 to 41.8% (for samples M1 and M10 respectively). In mixed waste samples of low concentration (1, 2.5 % w/w) sample expansion was limited and the compressive strength developed was up to 20% higher than samples with over 5% mixed waste content (M1 compared to M10).

3.2. Toxicity characteristic leaching procedure

Metal concentration measurement in the extraction fluid was carried out using ICP-OES and the results are displayed in Table 2. All values for Ag, Cu, Pb, Al, Zn were below the quantification limit (50 μ g/L) while concentration of Sn was negligible. Ag and Pb (the two most important RCRA-8 metals) as well as trace metals originally present in the semiconductor were not detected in the extraction dilution indicating successful stabilization of 1st generation PVP waste in cement mortars.

Table 2: Metal concentration measurement obtained by ICP-OES for Ag, Cu, Pb, Al, Zn, Sn after TCLP.

Metal concentration (µg/L)										
Sample	Ag	Cu	Pb	Zn	Al	Sn				
R	< 50	< 50	< 50	< 50	< 50	181				
G10	< 50	< 50	< 50	< 50	< 50	67				
G20	< 50	< 50	<50	<50	< 50	55				
M1	< 50	< 50	< 50	< 50	< 50	<50				
M2.5	<50	<50	< 50	<50	<50	<50				
M5	< 50	< 50	< 50	< 50	< 50	<50				
M10	<50	<50	< 50	<50	<50	58				
M20	<50	<50	< 50	< 50	<50	<50				
SC	<50	<50	< 50	< 50	<50	123				

4. Conclusions

End-of-Life 1st generation PVPs were pre-treated thermally and the resulting fractions were separated. Silver electrodes were recovered and the rest fractions were used as aggregate in cement mortar. Samples containing semiconductor, glass or mixed fractions were prepared. Results obtained by mechanical strength and leaching tests can be summarized in the following points:

- Mortars containing soda lime glass separated from PVP waste (G10, G20) developed mechanical strength close to that of the reference.
- Samples containing semiconductor and mixed fractions (M1, M2.5, M5, M10, M20, and SC) developed their flexural and compressive strength at a slower rate and lower final value than the reference due to the presence of Al on the semiconductor's back side, leading to gas production in the cement paste and expansion of the sample.
- Samples with low mixed waste load (M1 and M2.5) exhibited insignificant expansion in comparison to samples with higher waste load but their compressive strength at 28 days (27.6 and 27 MPa respectively) is still lower than that of reference sample (31.13% and 31.65% reduction respectively).
- TCLP measurements indicate that stabilization of 1st generation PVP waste in cement mortars is successful as for all prepared samples metal concentrations after leaching are negligible.

Thus, it can be concluded that cement mortar containing low aggregate substitution percentage of mixed waste from 1st generation PVP is effectively stabilized and can be potentially utilized in constructions like walks, patios, steps or as concrete fill [12] after further examination of its mechanical and physicochemical properties.

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References

- 1. Doi, T.; Tsuda, I.; Unagida, H.; Murata, A.; Sakuta, K.; Kurokawa, K. Experimental study on PV module recycling with organic solvent method, Vol. 67, (2001).
- 2. Granata, G.; Pagnanelli, F.; Moscardini, E.; Havlik, T.; Toro, L. Recycling of photovoltaic panels by physical operations. Sol. Energy Mater. Sol. Cells, 123, 239–248, (2014).
- 3. Masoumian, M.; Kopacek, P. End-of-Life Management of Photovoltaic Modules. IFAC-PapersOnLine, 48, 162–167, (2015).
- 4. Savvilotidou, V.; Antoniou, A.; Gidarakos, E. Toxicity assessment and feasible recycling process for amorphous silicon and CIS waste photovoltaic panels. Waste Manag., 59, 394–402, (2017).
- 5. Sica, D.; Malandrino, O.; Supino, S.; Testa, M.; Lucchetti, M.C. Management of end-of-life photovoltaic panels as a step towards a circular economy. Renew. Sustain. Energy Rev., 82, 2934–2945, (2018).
- 6. Baek, J.W.; Choi, A.E.S.; Park, H.S. Solidification/stabilization of ASR fly ash using Thiomer material: Optimization of compressive strength and heavy metals leaching. Waste Manag., 70, 139–148, (2017).
- El-Eswed, B.I.; Yousef, R.I.; Alshaaer, M.; Hamadneh, I.; Al-Gharabli, S.I.; Khalili, F. Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers. Int. J. Miner. Process., 137, 34–42, (2015).
- Ramos-Ruiz, A.; Wilkening, J. V.; Field, J.A.; Sierra-Alvarez, R. Leaching of cadmium and tellurium from cadmium telluride (CdTe) thin-film solar panels under simulated landfill conditions. J. Hazard. Mater., 336, 57–64, (2017).
- 9. Skripkiūnas, G.; Vasarevičius, S.; Danila, V. Immobilization of copper indium selenide solar module waste in concrete constructions. Cem. Concr. Compos., 85, 174–182, (2018).
- 10. Sikora P., Horszczaruk E., Skoczylas K., Rucinska T., Thermal Properties of Cement Mortars Containing Waste Glass Aggregate and Nanosilica, Procedia Engineering, Volume 196, Pages 159-166, (2017).
- 11. Paktiawal, A. Alam M., An experimental study on effect of aluminum composite panel waste on performance of cement concrete, Ain Shams Engineering Journal, (2021).
- 12. Gerald B. Neville, Concrete Manual, Chapter 3, pp. 24-27, International CODE Council, (2012).