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Photovoltaic's silica-rich waste sludge as supplementary cementitious materials (SCM)

G. Quercia[1, 2], J.`J. G. van der Putten[2] and H. J. H. Brouwers[2]

[1] *Materials innovation institute (M2i), Delft, The Netherlands*
[2] *Eindhoven University of Technology, Eindhoven, The Netherlands*

Abstract

Waste sludge, a solid recovered from wastewater of photovoltaic-industries, composes of agglomerates of nano-particles like SiO_2 and $CaCO_3$. This sludge deflocculates in aqueous solutions into nano-particles smaller than 1000 nm. Thus, this sludge is potentially hazardous waste when is improperly dumped. Due to its high content of amorphous SiO_2, this sludge has a potential use as supplementary cementitious material (SCM) in concrete. In this study the main properties of three different samples of photovoltaic silica-rich waste sludge (nSS) were physically and chemically characterized. The characterization techniques included: scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), nitrogen physical adsorption isotherm (BET, *t*-plot and BJH methods), density by Helium pycnometry, particle size distribution determined by laser light scattering (LLS) and dynamic light scattering (DLS). The effects on the hydration kinetics of cement pastes by the addition of nSS in the designed slurries were determined using an isothermal calorimeter. Finally, the compressive strength tests of standard mortars with 7% of cement replacement were performed to determine the puzzolanic activity of the waste nano-silica sludge. The results demonstrate the nSS can be utilized as SCM to replace portion of cement in mortars, thereby decreasing the CO_2 footprint and the environmental impact of concrete.

Keywords: Photovoltaic, Waste, sludge, nano-silica, SCM, pozzolanic

Corresponding authors's email: g.quercia@tue.nl

Introduction

Nowadays supplementary cementitious materials (SCM) are widely used in concrete either in blended cements or added separately in the concrete mixer [1]. The use of silica-rich SCM such as blast furnace slag, fly ash, metakaolin and micro-silica represents a viable solution to partially replace ordinary Portland cement. Other possible materials, which are under research worldwide, are silica fines. They are mainly composed of high purity SiO_2 with micron and submicron particles. Examples of this are silica flour (Sf), micro-silica (mS), fumed silica (FS) and nano-silica (nS). However, these products are obtained in complex processes which make their use non-feasible due to their price or in some case their availability for the construction industry [2][3]. In this context, another potential source of nano-silica particles is the waste sludge, generated during the polishing process of photovoltaic (PV) solar panels [4]. This waste sludge is collected during the filtering steps of the original slurries used in the polishing or finishing process of the silicon solar panels by chemical mechanical planarization (CMP) [5]. The polishing slurries are usually composed of a stable colloidal nano-silica, fumed silica, nano-$CaCO_3$ and other types of suspensions [4][5][6][7]. This sludge deflocculates in aqueous solutions into nano-particles smaller than 1000 nm. Thus, this nano-silica sludge (nSS) is potentially hazardous waste when is improperly dumped.

In addition to the need to improve the properties of concrete, the environmental impact of the cement used in concrete industry is becoming an important issue. The most environmentally damaging component used for concrete production in terms of energy and CO_2 emissions is cement. In general, 0.85 ton of CO_2 is released when 1 ton of cement is produced [8]. It is calculated that cement production contributes 5 to 8% to the total CO_2 emissions worldwide [8]. Consequently, the construction sector demands concrete with a lower environmental impact. Based on these premises, the aim of this research is to determine the potential use of photovoltaic silica-rich sludge as supplementary cementitious material (SCM) in concrete. In this study the main properties of three different samples of photovoltaic silica-rich waste sludge (nSS) were physically and chemically characterized. The final goal is to demonstrate that the nSS can be utilized as SCM to replace portion of cement in mortars, thereby decreasing the CO_2 footprint and the environmental impact of concrete.

Materials and experimental methods

Materials

Photovoltaic silica-rich waste sludge

Three different CMP sludge cake batches from wet waste were obtained from DAE Pyung Ceramics Co., Ltd. located in South Korea. After drying at 105 °C for 24 h until a complete dry state (constant weight) the water content in sludges was determined to be between 33 to 39 wt.%. These cakes had ivory white color. The cement used was ordinary Type I Portland cement OPC (CEM I 52.5N) produced by ENCI Cement, the Netherlands. The OPC had an apparent density of 3.15 g/cm^3 and specific surface area of 0.90 m^2/g. Standard sand was used according to EN 196-1 [9], with the particles size between 0 and 4 mm. In addition, commercial type micro-silica slurry (mS) with 50% of solid was used as comparison.

Experimental methods

Characterization of the PV silica-rich sludge

The main characteristics were determined by different techniques included: Field emission scanning electron microscopy (FEG-SEM), X-ray energy dispersive spectroscopy (EDS), X-ray powder diffraction (XRD), X-ray fluoresce (XRF), TG/DSC thermal analysis, nitrogen physical adsorption isotherm (BET, *t*-plot and BJH methods), density by Helium pycnometry, particle size distribution determined using laser light scattering (LLS) and dynamic light scattering (DLS). Detailed characterization procedure is described elsewhere [10].

Slurry designs

The slurries were prepared using dried silica sludge (16.5 % m/m) from different batches. Each sample was pre-dispersed for 1 hour at 7000 rpm in water, using a glass stirred vessel coupled to an Ultramix® stirrer. Prior to the pre-dispersion step, NH_4OH and a polycarboxylate type SP were added to stabilize the slurries, and to modify the final pH value (9.1 to 9.6). Then the dispersions were transferred to the high shear mixer, but using a size reduction stator head for additional 30 min. The obtained slurries were stable in time. No gelling observed inclusive at longer time of static conditions (ex. 3 weeks).

Table 1: Proportioning of silica sludge slurries

Batch number	1	2	3
Water (g)	600	600	600
Powder nano-silica sludge (g)$^+$	200	200	200
NH_4OH (cm^3)	15	15	15
SP (PCE type) (g)	4.4	4.4	4.4
Final pH	9.27	9.58	9.12
Slurry density (g/cm^3)	1.070	1.103	1.102
Solid content (% m/m)*	13.06	16.48	16.32

(+): 30 to 35% content of H_2O, (*): Computed by drying 5 g of slurry at 110°C for 24 h.

Hydration kinetics of cement pastes with nSS

A calorimetric analysis of cement mortars with w/c ratio of 0.5 were performed, using the slurry prepared from the silica sludge batch 2. For this purpose, an 8-channel TAM® Air isothermal micro calorimeter from TA Instruments (U.S.A.) was used. In total 4 different cement pastes with 0, 3, 6 and 9% bwoc replacement were tested (in duplicate) during 72h at 20°C. The purpose of the calorimetric analysis was to assess whether the nSS particles exhibits an acceleration effect or any pozzolanic activity. The results were analyzed using the TAM assistance software for the determination of the dormant period, the relative setting time and the time to reach the maximum hydration peak, respectively. The dormant period was determined taking into account the time between the lowest point and the first inflexion point of the main hydration peak in the resulted head flow curve. Similarly, the relative setting time was defined as the time between the first and the second inflexion point in the heat flow curve after the dormant period. Finally, the time to reach the maximum peak was estimated as the time between the initial part of the dormant period (lower point) and the maximum point in the main hydration peak.

Compressive strength tests of cured cement mortars and puzzolanic activity

To determine the puzzolanic index or activity of the nSS, different cement mortars were prepared and tested following the procedure established in NEN-NE 196-1 [9]. A 7% bwoc replacement was selected based on the procedure described by Justnes and Ostnor [11]. In total 9 standard prisms per mix were tested following Table 2. The SP content in these mixes was adjusted to obtain a spread flow of 175 ± 15 mm (Hägermann cone). The flexural and compressive strengths of the mixes were determined at 1, 7 and 28 days. Finally, the pozzolanic activity index was calculated based on the results of the standard cement mortar (7 and 28 days). In addition, the pozzolanic index was compared to the results obtained for one commercial micro-silica slurry.

Table 2: Mortars mix designs for the pozzolanic index determination

Materials	Reference	Batch 1	Batch 2	Batch 3	Micro-silica
CEM I 52.5N (g)	450.0	418.5	418.5	418.5	418.5
nSS slurry (16.5 wt%) (g)	0	196.9	196.9	196.9	0
mS slurry (50% wt%) (g)	0	0	0	0	72.3
Water (g)	225	59.6	59.6	59.6	184.2
Standard sand (g)	1350	1350	1350	1350	1350
SP (g)	0	2.01	0.93	0.93	1.07
SP (% bwob)	0	0.45	0.21	0.21	0.24
w/c	0.5	0.5	0.5	0.5	0.5
Spread flow (mm)	176 ± 4	176 ± 3	181 ± 4	180 ± 5	182 ± 7

Results and discussion

Characterization of the PV silica-rich sludge

Figure 1, shows the general characteristics of the different nSS particles from batch 1, 2 and 3 obtained using a FEG-SEM microscope. The nSS are characterized with a wide range of particle size distribution, having particles between micro and nano range. It shows a highly agglomerated state. Angular, irregular and spherical waste particles are also identified. The chemical analyses that were performed using an EDS detector demonstrate that the nSS batch 1 has a high content of SiO_2 (86 to 95%). Other elements that were identified were Na, Al and P. These elements probably originate from the stabilization agents that are normally used in colloidal silica products and the chemicals to treat the waste water as well. The analysis of nSS of batch 2, shows small angular and spherical particles (Figure 1b). The spherical particles are composed of SiO_2 (silica fume), commonly used in the preparation of CMP slurries [6]. In addition, small angular particles with a high content of Ca (detected by EDS) were also identified. The calcium rich particles are composed of $CaCO_3$ (validated by XRD and TG/DSC analysis), which is used for CMP slurries as well [5][6][7]. The chemical analysis, was performed using an EDS detector, demonstrated that the silica sludge batch 2 and 3 have a lower content of SiO_2 (46.79%) compared to batch 1. Other elements that were identified are C, Na, Cl, Ca, Mg, K, Al. Another observation is that the chloride content in the samples is high, reaching values of 0.56 to 1.86 wt %. The high chloride concentration most likely originates from the use of deflocculating agents during the waste treatments in the PV manufacture facility or from chlorates used as oxidizing agents [12]. Several authors reported [12][13][14] that water extracted from the sludge is normally treated with aluminum poly-chloride type compounds to deflocculate the nano-particles.

In order to obtain a more accurate chemical composition of the investigated nano-silica sludges, a quantitative X-ray fluorescence analysis was performed. The results were obtained by an external laboratory and it is demonstrated that the silica sludge batch 2 and batch 3 are rich in CaO and SiO_2, with an equivalent content between 41 and 45% by mass of SiO_2 and 45 to 52% by mass of CaO. In addition to the XRF analysis, X-ray diffraction (XRD) measurements were performed to verify whether the silica sludge samples had crystalline impurities. The XRD analysis showed that batch 1 is composed of high amounts of amorphous phases (more than 98%). On the contrary, the results for the silica sludge batch 2 and batch 3 revealed that in these two samples the content of crystalline phases (mainly $CaCO_3$ and α-quartz) was high. To complete the characterization of the different silica sludge samples, a combined TG/DSC analysis was also performed. Results demonstrated that batch 1 is mainly composed of physic-adsorbed water (42 to 45%) and amorphous SiO_2. In case of batches 2 and 3, the water contents were lower than batch 1, but both samples presented loses of weight between 420 to 750 °C. These loses of weight are caused by the de-carbonatation (CO_2 release) of the calcium carbonates. Taking into account the loss of mass (23 to 27% CO_2) and the molecular weight of each compound, it was possible to estimate that batch 2 and batch 3 have 55.99% and 48.63% of $CaCO_3$ respectively. A summary of the resulted characteristics of the PV nSS batches is shown in Table 3.

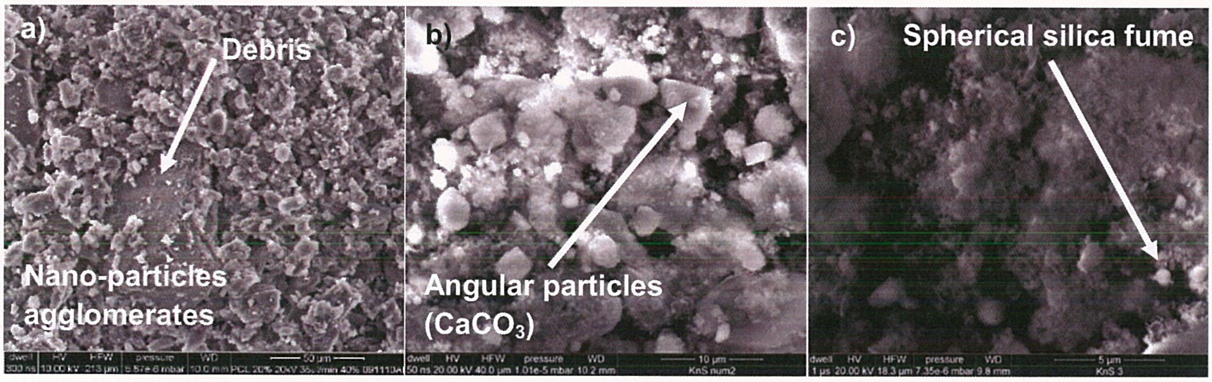

Figure 1: FEG-SEM photomicrographs of nSS, a) batch 1, b) batch 2 and c) batch 3

Table 3: Summary of the characteristic and properties of the PV nSS

Name	Batch 1	Batch 2	Batch 3
SiO_2 by XRF (mass %)	95.39	37.59	41.20
$CaCO_3$ by TG/DSC (mass %)	-	55.99	48.63
Na_2O+K_2O by XRF (mass %)	1.65	2.06	3.81
Cl^- by XRF (mass %)*	-	2.13	3.57
Loss of draying by TG/DSC (mass %)	39.3	33.06	35.26
Loss on ignition by TG/DSC (L.O.I.)	3.75	29.11	26.07
Specific density by He pycnometry (g/cm^3)	2.167	2.451	2.402
pH (16% m/m in H_2O)	7.18	8.05	8.08
Specific surface area by BET (m^2/g)	178	29	38
BET average particle size (nm)	16	84	66
PSD by FEG-SEM (µm)	<150	<50	<150
PSD by LLS (µm)	0.35 -110	0.28 - 30	-

Hydration kinetics of cement pastes with nSS

Studying the obtained curves (Figure 2), it is evident that the replacement of the cement with different concentration of nSS does not have a decreasing effect on the head flow of the blended paste. On the contrary, a higher heat flow was found due to the nucleation effects produced in the cement paste and due to the pozzolanic activity promoted by the presence of amorphous nano-silica and $CaCO_3$ particles. Nevertheless, the presence of SP in the silica sludge slurry caused an extension or retardation during the dormant period of the cement (Figure 2b and Table 4). Indirectly, when the amount of nSS slurry is increased the total content of SP increased as well (see Table 1). Despite the retardation effect on the dormant period (calculated as the time between the lower point of the heat flow curve and the first inflexion point in the main peak), the relative setting time (calculated as the time between the first and the second inflexion point in the heat flow curve), as well the time to rich the maximum hydration peak of the cement paste, were accelerated. The pozzolanic activity of the silica sludge is confirmed by the presence of an increase of the total heat shown in Figure 3. The total heat is the contribution of heat produced by the cement particles themselves and the heat contribution of the pozzolanic reaction between the nano-silica particles and the precipitated $Ca(OH)_2$ [15].

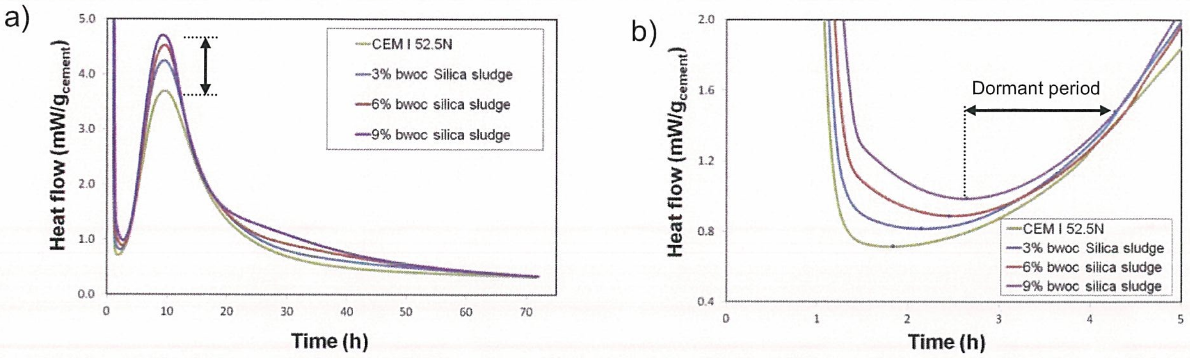

Figure 2: a) Normalized heat flow evolution of cement pastes with different silica sludge *batch 2* replacement based on the weight of cement (CEM I 52.5N), b) detail of the different dormant period stages of the differed cement pastes tested

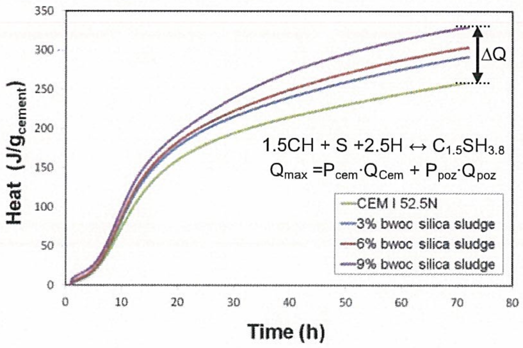

Figure 3: Normalized total heat evolution of cement pastes with different nano-silica sludge replacement based on the weight of cement (CEM I 52.5N)

Table 4: Hydration kinetics of the cement pastes with silica sludge batch 2

Paste type	Dormant period (h: min)	Relative setting time (h: min)	Peak time (h: min)
CEM I 52.5 N	0: 39	2: 03	7: 39
3% bwoc silica sludge	1: 03	1: 56	7: 20
6% bwoc silica sludge	1: 22	1: 45	6: 58
9% bwoc silica sludge	1: 35	1: 40	6: 35

Compressive strength tests of mortars and puzzolanic activity of nSS

The development of the mechanical properties of the different mortars tested is shown in Figure 4. Analyzing the development of the flexural strength in time (Figure 4a), several observations can be drawn. At early age (1 day), the flexural strength was influenced by the different doses of SP used in the mortars. The silica sludge from batch 1 showed the lowest flexural strength due to the high content of SP (0.45%) and probably due to differences in the chemical composition and presence of contaminants. On the contrary, batch 2 and batch 3 already at 1 day showed flexural strength values comparable to the reference standard mortar and higher than the strength of the mortar with micro-silica slurry comparing it with batch 3. At 7 days, comparable flexural strengths were observed for all the tested mortars, except batch 1. Finally, at 28 days, it is concluded that the flexural strength of batch 2 was similar to the reference mortar.

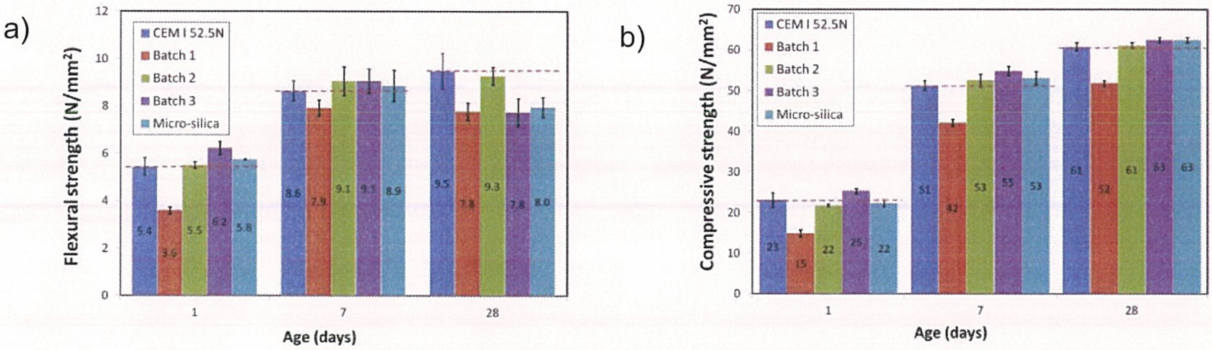

Figure 4: Development of the mechanical properties of the tested mortars (7% bwoc replacement), a) flexural strength, b) compressive strength

In the case of the compressive strength of the tested mortars (Figure 4b) at 1 day, it is also possible to observe the influences of the different additions of SP. At this age, only the mortar prepared using the batch 2 nSS showed the compressive strength slightly higher than the reference mortar. Batch 1 presented the lowest compressive strength. At 7 days, the strength of the samples batch 2, batch 3 and micro-silica reached comparable compressive strength than the reference mortar. The same trend was observed by the 28-day compressive strength of the mortars with silica sludge, batch 2 and batch 3. At this age, the mortar prepared with batch 1 silica sludge showed the lowest compressive strength (52 N/mm^2). The 7 and 28 days compressive strength values were used to estimate the relative pozzolanic activity index of the different silica sludges and the micro-silica sample. The pozzolanic index was calculated based on the compressive strength of the reference mortar (100%) and is shown in Figure 5.

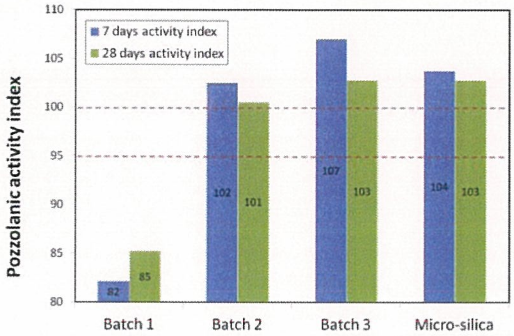

Figure 5: 28 days pozzolanic index of the different slurries tested
(nano-silica sludge and standard micro-silica)

The computed activity index demonstrates that the silica sludge has pozzolanic activity and this confirms the results obtained by the isothermal calorimetric measurements. The activity index varied from 82 to 107 for all silica sludges samples. Only the mortar with the sludge of batch 1 showed an index lower than 100. On the contrary, the mortars with silica sludge particles from batch 2 and batch 3 presented a pozzolanic activity index of 101 to 103. In general, the minimum pozzolanic activity index specified for micro-silica is 95 (lower limit) [16], which mean that it is possible to classify the nano-silica sludge as a pozzolanic material, like the tested commercial micro-silica.

Conclusions

The silica sludge samples studied are composed of highly agglomerated nanoparticles and micro-sized waste particles. Their chemical analyses reveal a high content of amorphous SiO_2 and $CaCO_3$ with some impurities related to the additives used to prepare the original polishing slurries. The dispersability study using a high-energy shear mixer demonstrated that it is possible to disperse the agglomerated particles of the original filter cake to a nano-size range and these stable slurries are easy to prepare for the application in concrete. The mechanical properties (flexural and compressive strength) of mortars with 7% bwoc of the silica sludge were similar and in some cases slightly higher than the reference. Therefore, the silica sludge batch 2 and batch 3 can be classified as a pozzolanic material with activity index higher than 100. The results demonstrate the photovoltaic's silica-rich waste silica can be utilized as SCM to replace portion of cement in mortars, thereby decreasing the CO_2 footprint and the environmental impact of concrete.

Acknowledgments

This research was carried out under the project number M81.1.09338 in the framework of the Research Program of the Materials innovation institute (M2i) and The European Community's Seventh Framework Program, ProMine: Nano-particle products from new mineral resources in Europe, FP7-NMP-2008-LARGE-2 under grant agreement 228559. The authors also wish to express their gratitude to P.R. Spiesz for his collaboration and following sponsors of the Building Materials research group at TU Eindhoven: Rijkswaterstaat Centre for Infrastructure, Graniet-Import Benelux, Kijlstra Betonmortel, Struyk Verwo, Attero, ENCI, Provincie Overijssel, Rijkswaterstaat Directie Zeeland, A&G Maasvlakte, BTE, Alvon Bouwsystemen, V.d. Bosch Beton, Selor, Twee "R" Recycling, GMB, Schenk Concrete Consultancy, Intron, Geochem Research, Icopal, BN International, APP All Remove, Consensor, Eltomation, Knauf Gips, Hess ACC Systems, Kronos and Joma International (chronological order of joining).

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