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Are calcium silicate hydrates (C-S-H) present in alkali-activated glass cullet cement?

Baptiste Marchand [a], S. Lanier [a], C.A. Davy [a,b,*], C. Albert-Mercier [c], G. Tricot [d]

[a] Centrale Lille, LML, FRE CNRS 3723, and UCCS, UMR CNRS 8181, CS20048, F-59651 Villeneuve d'Ascq, France
[b] L2MGC, EA 4114, Université de Cergy-Pontoise, F-95011 Cergy-Pontoise, France
[c] LMCPA, Université de Valenciennes, F-59600 Maubeuge, France
[d] LASIR, UMR CNRS 8516, Université de Lille 1, Villeneuve d'Ascq, France

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ABSTRACT

This contribution analyzes the structure of sodium-lime-silica (SLS) glass alkali-activated with NaOH. The mix forms an alkali-activated cement (AAC), which has proven to be mechanically resistant when immerged under water. The aim is to determine whether the presence of calcium in the glass powder may have contributed, together with alkali-activation, to forming calcium silicate hydrates (C-S-H), which are responsible for water resistance in hydrated Portland cement pastes. This is investigated by SEM, where needles similar to C-S-H in Portland paste are observed, then by X Ray Diffraction (XRD), but the pastes are too amorphous to allow any phase identification. Finally, ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) shows that C-S-H are at most 2–3% in the 4 M and 8 M NaOH AAC pastes, so that they cannot be considered responsible for the water resistance of SLS glass AAC pastes and mortars. The latter are rather formed of sodium silicate hydrates and/or silica gel.

1. Introduction

1.1 Background

Soda-lime-silica (SLS) glass is an industrial "secondary raw mineral" of varied origins, e.g., for the greatest quantities, post-consumer beverage bottles or flat glass from construction and building works [1]. Among these, colored glass is economically difficult to reuse for the fabrication of new glass products, but its use as precursor of geopolymers is a promising alternative [2–4].

Currently, despite extensive research [1,3–7], promising prototypes and niche products, a number of issues remains regarding the extensive development of reuse routes for SLS glass.

Firstly, geopolymer manufacturing is not the sole route for reusing glass cullet. Several incorporation methods are proposed in the literature, ranging from asphalt to ceramics [8], and Portland concrete production [3–4,9–12]. Other routes include the use of glass cullet as a filtration medium, as a constituent in epoxy resins, in the production of glass fibers, for elastomeric roof coatings, aesthetic finishing materials (also called architectural mortars [9,10]), abrasive material for surface cleaning, and paint filler [13], or more simply as roadway construction aggregates or daily covers in landfills [14]. The economic advantage of these different routes (and particularly geopolymers) depends on the energy consumption, number and cost of the necessary operations to achieve a marketable product. In this context, the main asset of SLS glass geopolymers is their low energy consumption during manufacturing.

Secondly, when using SLS in alkali-activated cements (AAC), i.e. as a particular type of geopolymer according to J. Davidovits [15], the cement durability is still questioned, in particular as regards its water resistance, although heat curing may improve this aspect [3,4,16]. However, results in [17] testify of a limited loss in compressive strength when the AAC mortar is heat cured for 24 h at 65 °C, and then placed at 20 °C under water for six more days. This was observed for a formulation limiting the water-to-cement (W/C) ratio, with a sufficiently fine glass cullet, and optimized NaOH concentration. While [4,18] propose that the structure of similar glass cullet AAC consists in Sodium (Na) Aluminate Silicate Hydrates (abbreviated N-A-S-H), or sodium silicate gel [18,3], argue that it is a mix of N-A-S-H and Calcium Silicate Hydrates (C-S-H). The latter are the main hydrates responsible for the strength and water resistance (i.e. hydraulicity) of hydrated Portland cements [19]. C-S-H being stable under water, their presence would explain the water resistance of the glass cullet AAC measured in [17].

* Corresponding author at: Centrale Lille, LML, FRE CNRS 3723, and UCCS, UMR CNRS 8181, CS20048, F-59651 Villeneuve d'Ascq, France.
E-mail address: catherine.davy@centralelille.fr (C.A. Davy).

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1.2 Aims and originality of the work

This contribution focuses on the valorization of colored glass cullet as an AAC. Its formulation has been optimized in former research, to design prefabricated mortar elements [17]. Our aim here is to determine whether C-S-H are present, and in what amount, in this glass cullet AAC, in order to explain its limited strength loss when immersed under water. To this purpose, the structure of mortar and pastes are analyzed by a combination of experimental methods, ranging from X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-ray spectroscopy (EDX), and ^{29}Si MAS NMR. To our knowledge, compared to former research [3,4,16–18] using XRD, SEM, FTIR, or TGA/DTA, our originality is to deconvolve ^{29}Si MAS NMR spectra to determine the presence of C-S-H.

2. Material and methods

2.1 Materials

Green glass cullet from post-consumer beverage bottles is finely ground with d_{50} = 10 μm using a FRITSCH Pulverisette ball milling machine. As a matter of comparison, d_{50} is of 15 μm for the finest powder in [3], and d_{50} = 30 μm in [4]. Corresponding specific surface areas (SSA) of our glass cullet is measured by nitrogen adsorption at an average value of 1960 cm^2/g ± 170, which is in the lower range compared to [3] glass powders.

Using X-ray fluorescence, our SLS glass powders are made on average of 67 mol% ± 1 SiO_2, 16 mol% ± 1 Na_2O, 14 mol% ± 2 CaO, 2 mol% ± 1 MgO, 1 mol% ± 1 Al_2O_3 and 1 mol% ± 1 K_2O. This corresponds to a (Al/Si) molar ratio of 0.03, (Na/Si) = 0.5 and (Ca/Si) = 0.2. The most common type of beverage glass containers used in SLS glass contain 10–20 mol% Na_2O, 5–15 mol% CaO and 70–75 mol% SiO_2, and they are almost devoid of Al_2O_3 like ours [20]. These composition data also mean that our SLS glass has a lower SiO_2 content than what is most common (i.e. 70–75 mol%), although its molar ratios (Si/Al), (Si/Na) and (Si/Ca) are in the same range. According to the American standard ASTM C618 for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, the sum (SiO_2 + Al_2O_3 + Fe_2O_3) for our SLS glass being above of 50%, it is similar to pozzolanic class C fly ash, but not to pozzolanic class F fly ash (this requires that $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$). This pozzolanic potential means that the formation of C-S-H is possible when our glass is used as a Supplementary Cement Material (SCM) in Portland concretes. However, in this contribution, SLS glass is alkali-activated by NaOH water solutions, at significantly higher pH than in Portland cements, so that specific formation mechanisms are expected [21].

2.2 Mortars and pastes

Standard mortars (according to EN196-1) are made using several NaOH concentrations in the mixing water, of 2, 4, 5 and 8 M and a (W/C) ranging between 0.39 and 0.49. For (W/C) = 0.39, molar ratios (Na/Si) = 0.62, 0.66 or 0.79 for 4, 5 or 8 M, (Ca/Si) = 0.21 and (Al/Si) = 0.02. Pure silica sand (from Leucate, France) is used with a standard grain size distribution. In order to avoid shadowing effects due to quartz presence, cement pastes of the same formulations are also made for XRD and MAS NMR measurements. All mortars and pastes are cured for 24 h at 20 °C or 65 °C, and then cured at 20 °C in ambient air, or under water, until being tested for mechanical strength. All paste samples analyzed by XRD, SEM and MAS NMR are cured in ambient air.

An optimal mortar formulation is obtained at 4 M NaOH and W/C = 0.39, cured for 24 h at 65 °C. In this case, mortar compressive strength is of 43.4 MPa (air curing, 7 days) and 33.9 MPa (water curing, 7 days), i.e. a difference of 22%. It evolves to 51.4 MPa (air curing, 28 days) and 31.5 MPa (water curing, 28 days), i.e. a difference of 39%. This means a decrease by only 7% between 7 and 28 days for water cured mortar, and an increase by 18% with air curing.

2.3 XRD measurements

The diffraction data are collected at room temperature with a Bragg-Brentano diffractometer in the θ/θ geometry (Brucker Advance D8 type), equipped with a lynx-eye detector, using the CuKα1 and Kα2 radiations (λ = 1.54060 and 1.54440 Å, at 40.0 kV and 40.0 mA), from 5 to 70° 2θ range, with 0.02° steps and 0.5 s acquisition time per step.

2.4 ^{29}Si MAS NMR measurements and decomposition

^{29}Si MAS NMR spectra are recorded at a Larmor frequency of 79.5 MHz using a Bruker Avance 400 MHz (9.4 T) spectrometer. The spectra are obtained with 736 to 2048 scans, with a pulse length of 5 μs (corresponding to a π/2 flip angle) and a relaxation delay of 120 to 600 s. The samples are spun at the magic angle of 54.71° and at spin rates of 5 kHz in 7 mm outer diameter zirconia rotors, with TMS (TetraMethylSilane) used as reference. Spectral deconvolution is performed with Dmfit software [22] in order to identify and quantify the silicate units Q^n, where n is the number of bridging oxygen atoms of the silicate under investigation.

3. Results and discussion

3.1 SEM observations

The paste microstructure in SLS glass AAC mortar is observed on a fracture surface (Fig. 1). The expected structure of a geopolymer cement is observed, with so-called geopolymeric micelles or particulates [15] (Fig. 1 top). Moreover, the AAC paste displays a number of individual needles, sprouting out of the particulates (Fig. 1 bottom left). These are visually similar to C-S-H, generally observed on the fracture surface of hydrated Portland cement, and displaying "urchin"-like arrangements at the micrometric scale. These arrangements are well documented, e.g. as observed by M. Moranville in [23]. The question arises as to whether the needles present in AAC paste are actually C-S-H. As their density is very low, it has not been possible to analyze them in the SEM (by Energy Dispersive X Ray spectroscopy).

3.2 XRD analysis

Further, the presence of C-S-H has been investigated on cement paste by XRD (Fig. 2). As expected, the paste, like the initial glass powder, is mainly made of amorphous matter, so that no identification is possible on the diffractograms, whatever the NaOH concentration. Even the small peaks visible for the 8 M NaOH could not be attributed to a particular phase, containing Ca, Na, Si, Al or K.

3.3 ^{29}Si MAS NMR experiments

^{29}Si MAS NMR experiments probe the environment of individual ^{29}Si atoms, so that amorphous media can be investigated. In this contribution, glass powder is compared to AAC paste with 4, 5 and 8 M NaOH concentration (Fig. 3). The degree of reticulation and structuration of the glass powder and of the pastes is