Development of fly ash-based geopolymers using powder sodium silicate activator

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Abstract

Geopolymer manufacturing by means a ready-mix procedure using powder sodium silicate as activator is described in this paper. Its characteristics are compared with conventional geopolymers using aqueous sodium silicate. Degree of reaction, mercury intrusion porosity and compressive strength were measured at different curing times. Three durability tests were carried out. The geopolymer obtained using powder activator showed slightly lower mechanical properties and better durability results than those found for geopolymers based on aqueous activators. In addition, the manufacture of geopolymers based on powder silicate was easy and simpler than the more common procedure using sodium silicate solutions, so the ready-mix manufacturing could be an alternative to produce geopolymers.

Keywords: Geopolymers, fly ash, degree of reaction, mercury porosimetry, compressive strength, durability tests

1. Introduction

Geopolymers present an enormous potential as a source of products with mechanical and durability properties which can provide an added value for several applications, mainly in the construction field, where geopolymers are competitive with cementitious products [1].

Geopolymer manufacture shows relatively high costs due to the soluble silicate price. The use of alternative silicate sources such as solid silicate, which is cheaper than aqueous solutions, could have a great interest [2]. Some research have carried out to study the use of solid sodium silicate for geopolymer manufacture, most of them related to the concept of one-part geopolymers [3, 4]. One-part geopolymers search for a simplification in manufacture, in a similar way to the Portland cement-based procedure, mixing precursors and activators in solid form and adding just water. Powder sodium silicate was preferred over solutions because it is easy to handle and the powder dissolves easily.

The main objective of this paper is to develop solid silicates-based geopolymers, searching for an easier manufacturing, which could enhance the commercial viability and large-scale applications in the construction industry. Other objective is to study the durability of them in different environments in order to define their specifications.

2. Experimental

2.1. Materials

Low calcium fly ash from the coal combustion (Los Barrios, Spain) was used as precursor. Major elements were determined after chemical-attack-dissolution at 750 ºC and using atomic absorption spectroscopy. Values (w/w%) are: SiO_2-63.9; Al_2O_3-21.5; CaO-3.94; Fe_2O_3-5.86%; MgO-1.84: Na_2O-0.68; K_2O-1.67; LOI-3.32. Amorphous phase, measured after XRD and using DIFFRAC-EVA software, was 85 w/w%. Mineral phases are quartz and mullite. A commercial sodium silicate solution (AS) was used as aqueous activator (SiO_2(w/w%)=27; Na_2O(w/w%)=8). A powder sodium silicate (PS) (particle size less than 200 µm) (SiO_2(w/w%)=75.6; Na_2O(w/w%)=22.6) was used for comparison reasons. Analytic reagent-grade NaOH was used to change the Na_2O/SiO_2 ratio.

2.2. Preparation of geopolymers

Two geopolymers were manufactured: "Aqueous Silicate" (AS) and "Powder Silicate" (PS). The AS-geopolymers were manufactured by mixing the fly ash with a solution prepared adding NaOH to the AS in order to increase the Na_2O/SiO_2 weight ratio up to 0.494. The PS-geopolymer was manufactured by mixing the fly ash with the PS and latter adding a solution prepared dissolving NaOH in water (final Na_2O/SiO_2 weight ratio is also 0.494). Both geopolymers used the same amount of fly ash. All reactives were mixed during 4 minutes in a planetary mixer, until a thixotropic paste was obtained. All geopolymer were cured at 60 ºC.

2.3. Methods

After 2, 7, 28 and 60 days, degree of reaction (DoR) (Fernández-Jiménez [5]), porosities and pore size distribution (mercury intrusion porosimetry (MIP)), and compressive strength (CS), were analyzed (three samples of each composition were analyzed). After 28 days, three durability tests were carried out: an

acid attack resistance test [6] and two thermal cycling tests, a freezing test (Freezing-16ºC-Water 20ºC) and a drying test (Drying 60ºC-Water 20ºC) in cycles of 24 hours (20 cycles) (two samples of each composition were analyzed).

3. Results and discussion

3.1. Degree of reaction

PS-geopolymer showed lower DoR than AS-geopolymer in every time (see Figure 1B). This could be attributed to an incomplete dissolution of sodium silicate from the powder silicate, resulting in a lower amount of reactive silicate liberated into the medium. Besides, it is well known that solid-solid reactions are slower than solid-liquid reactions since the contact type is more difficult. DoR also increased along the time, obtaining a practically constant value at 28 days.

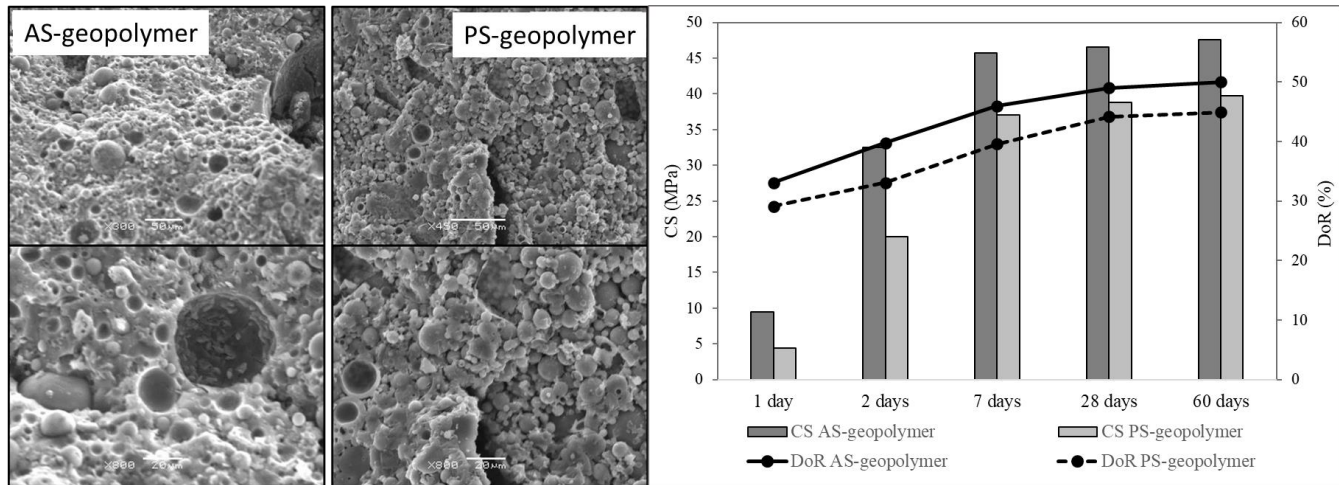Figure 1. SEM images. DoR results. CS results

| Figure 1A | Figure 1B |

SEM images at 28 days of curing were obtained. Fly ash-based geopolymers have described as a system consisting of fly ash particles, a poor differentiated and homogeneous mass surrounding-bonding particles (geopolymer gel), and intergranular-intragranular porosity [7]. Spherical-shaped fly ash particles were presented in both AS and PS-geopolymers (Figure 1A), which suggests only partial ash dissolution to produce them. Relative proportion of geopolymer gel over the other two components (ash-porosity) gives an idea of the reactivity and the geopolymerization degree. This relative proportion appeared to be higher in the AS-geopolymer, also showing a lower amount of un-reacted particles and intergranular-intragranular porosity than the PS-geopolymer, in concordance with the DoR results.

3

3.2. Porosity

For each curing time, the AS-geopolymer were less porous (total pore volume at 28 days=0.1024 mL/g) than the PS-geopolymer (total pore volume at 28 days=0.134 mL/g). As commented, PS-geopolymer showed lower DoR than AS-one, with a great amount of gel and less space between un-reactive particles, so it is reasonable that AS-geopolymers porosity was lower. Besides, porosities decrease along the time for both materials which can be displayed in the pore size distributions (PSD) (Figure 2A:AS-geopolymer; Figure 2B:PS-geopolymer).

Figure 2. PSD graphs of AS-geopolymer (2A) and PS-geopolymer (2B)

Figure 2A

Figure 2B
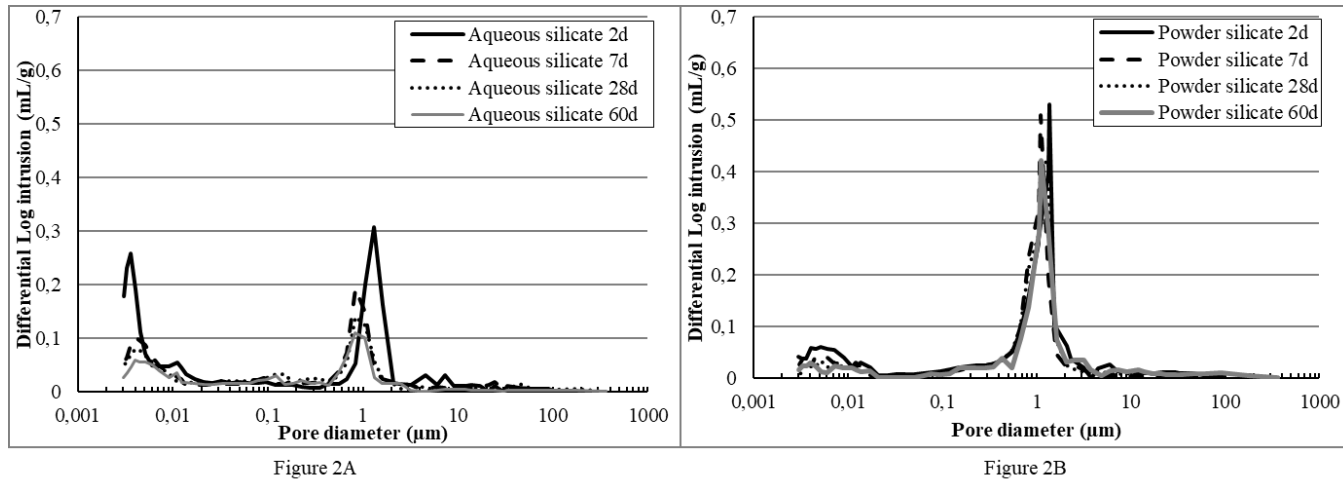
AS-geopolymer PSD showed two peaks along the time: small pores, created in the geopolymeric gel (0.003-0.015 µm) and large pores, created between un-reacted particles and geopolymeric gel (0.5-2 µm). In 2-7 days, a reduction in small and large pores volume was observed. Large pore peak shifted to lower diameter (0,6-1 µm) possibly due to the gel produced during reaction fills the pores. From 7 to 60 days, pores volume also reduced, due to the total pores closing.

PSD of PS-geopolymer was almost monomodal with large pores around 0.4-4 µm and small pores around 0.003-0.015 µm. Pore volume (peak area) in the 0.4-4 µm zone was higher here than in AS-geopolymers, but the proportion of pores in the 0.003-0.015 µm zone was lower. As PS-geopolymer had more un-reacted particles than AS-geopolymer (SEM results), the pores amount generated between un-reacted particles and geopolymeric gel (large pores) was greater. As the development of geopolymeric gel is

lower, the content of small pores was also lower. The main effect of curing time in PS-geopolymer was the pore volume reduction of the finest pores (less than 0.02 µm).

3.3. Compressive strength

AS-geopolymer presented higher CS than PS-geopolymer in all curing times (Figure 1B) in accordance with the DoR values which suggesting that AS could contribute with a major amount of silicate in the medium, favoring the gel formation and producing greater CS.

3.4. Acid attack resistance

Specimens of both geopolymers were immersed in 1M H_2SO_4 and in water for 14 days. After immersion, samples were dried and the mass loss and CS were determined. Both geopolymers showed a mass loss after water-immersion (1.3%). The CS reduction was around 10 % in both materials. Geopolymers are not affected by the hydration process as cementitious (Portland) matrixes did when are cured under water. It seems that the water immersion of geopolymers only caused a structure weakening and a slight CS reduction.

The H_2SO_4-attack had a deeper effect on the structure than the water since the mass loss after de H_2SO_4-immersion was higher than the water-immersion (1.4% (PS-geopolymer)-1.8% (AS-geopolymer)). Due to this, PS-geopolymer presented higher resistance to H_2SO_4-attack (CS reduction=21%) than AS-geopolymer (CS reduction= 40%). Although the AS-geopolymer was less porous than the PS-one, it presented a higher pore volume in the small pores zone, leading to the increment of the exposed area due to these finer pores, so the acid can reach them easily and the matrix could be highly deteriorated. Bakharev [8] states that geopolymer structure deterioration during acid attack is due to depolymerization of aluminosilicate polymers, leading to the formation of fissures in the matrix, crystallization of zeolites and formation of a fragile grainy-structure. This could be appreciated in both geopolymers by means the loss of mass commented and the increment of pore volume in the range of great pores (see Figure 3 for PS-geopolymer).

Figure 3. PSD of PS-geopolymer before and after durability tests
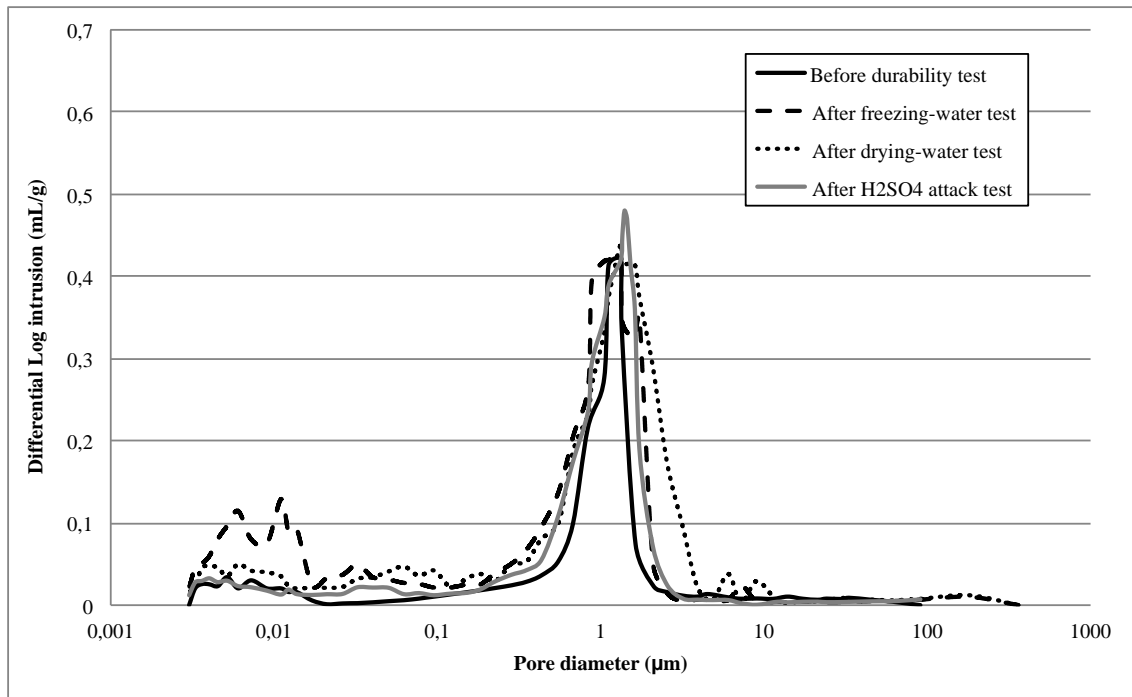
3.5. Thermal Cycling Durability

Both geopolymers deteriorated when exposed to thermal cycling. PS-geopolymer showed the lowest CS loss after 20 cycles, as occurred after the H_2SO_4-attack. CS reduction was 24%, after freezing-water test and 40%, after the drying-water test. The AS-geopolymer CS reduction was 75% in the freezing-water test and 93% after the drying-water test. Both geopolymers were less altered by the freezing-water than to the drying-water cycles. After freezing-water test, PS-geopolymer presented a total porosity increment from 0.134 to 0.303 mL/g. After the drying-water test, the increment was to 0.359 mL/g. Figure 3 shows the PSD before and after the tests.

Just as happened in the H_2SO_4-attack, as the PS-geopolymer presented a lower pore area exposed to environment, the heat or water penetrated in the structure was lower, the effect of attacks was less important and the CS fell in a lesser extent. The freezing-water test produced an increment of pores in the small pores zone (Figure 3), possibly due to the stress led by the water freezing affected in a greater extent to the geopolymeric gel [9]. However, the shrinkage produced by the drying-water test affected more to the larger pores (generated between un-reacted particles and gel).

4. Conclusions

PS-geopolymers presented slightly lower DoR than AS-geopolymers, which would explain the highest porosities and lowest CS of PS-one. Both geopolymers showed similar PSD with two peaks, one in the 0.4-4 µm-zone and other in the 0.003-0.015 µm-zone. AS-geopolymer manifested a high pore volume in the zone of fine pores due to a great gel development. PS-geopolymer showed a high pore volume in the zone of 1 µm due to a great amount of un-reacted particles. Although both geopolymers showed similar mechanical properties, the PS-geopolymer was the most resistant to the acid-attack and thermal cycling tests, with the lowest CS reduction, possibly attributed to its lower pore area (manifested as lower pore volume in the finer pores zone) exposed to the different attacks. Even so, the durability tests produced an increment of porosities, the PSD showed mainly the highest increments of pore volume in the zone of 0.4-4 µm (biggest pores).

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