

Effect of curing time on microstructure and mechanical strength development of alkali activated binders based on vitreous calcium aluminosilicate (VCAS)

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Abstract. The aim of this paper is to study the influence of curing time on the microstructure and mechanical strength development of alkali activated binders based on vitreous calcium aluminosilicate (VCAS). Mechanical strength of alkali activated mortars cured at 65 °C was assessed for different curing times (4–168 h) using 10 molal NaOH solution as alkaline activator. Compressive strength values around 77 MPa after three days of curing at 65 °C were obtained. 1.68 MPa/h compressive strength gain rate was observed in the first 12 h, decreasing to 0.95 MPa/h for the period of 12–72 h. The progress of geopolymeric reaction was monitored by means of TGA and, electrical conductivity and pH measurements in an aqueous suspension. Significant decrease in pH and electrical conductivity were observed in the 4–72 h period, demonstrating the geopolymerization process. Furthermore, SEM images showed an important amount of (N, C)ASH gel and low porosity of the developed matrix.

Keywords. Compressive strength; alkali activation; vitreous calcium aluminosilicate; geopolymerization.

1. Introduction

The alkali activation process is a chemical reaction based on the polymerization of an alumino-silicate source material with a high alkaline solution to form stable binding material commonly called “alkali activated binder” or “geopolymer” (Duxson *et al* 2007; Davidovits 2008). This process involves the agglutination of small species (molecules and ions) in order to form larger ones that precipitate as a gel. This gel has generally been accepted as a zeolitic precursor (NASH gel), and it contains tetrahedral SiO₄ and AlO₄ randomly distributed along the polymeric chains which are cross-linked by oxygen bridges. The negative charge on the AlO₄⁻ group is charge-balanced by alkali cations (typically Na⁺ and/or K⁺) available in the alkaline solution (Fernández-Jiménez *et al* 2005; Duxson *et al* 2007; Yao *et al* 2009). As can be observed in the literature (Komnitsas and Zaharaki 2007; Pacheco-Torgal *et al* 2008a), the geopolymerization process depends essentially on three factors: alkaline solution, alumino-silicate source material and curing conditions. The most common alumino-silicate source materials used in the geopolymerization process are slags (Puertas *et al* 2000; Bernal *et al* 2011), metakaolin (Lin *et al* 2009; Marín-López *et al* 2009; Zivica *et al* 2011) and fly ashes (Fernández-Jiménez *et al* 2005; Lloyd *et al* 2009). However, in the last years, the use of different alumino-silicate materials have been performed: natural pozzolans (Xu and van Deventer

2000; Najafi Kani *et al* 2012), tungsten mine waste (Pacheco-Torgal *et al* 2008b, c), ceramic waste (Puertas *et al* 2006; Reig *et al* 2010), FCC catalyst residue (Tashima *et al* 2012) construction and demolition waste (Lampris *et al* 2009; Payá *et al* 2012).

The alkaline solutions frequently used to produce geopolymers are sodium and/or potassium silicate solution due to the improvements in mechanical properties provided by the addition of extra soluble silica. Nevertheless, it is important to state that silicate solutions are expensive and its high cost may make unavailable the use of this component in alkaline activator. Some studies have been performed to substitute sodium silicate solution by silica fume (Zivica 2004) or nanosilica (Rodríguez *et al* 2012) dissolved in sodium hydroxide solution.

The other important factor that controls the geopolymerization process is the curing process. In this case, one must take into account of the following parameters: temperature, humidity and curing time. Most of the researches stated the importance of high relative humidity during the geopolymeric reaction due to the shrinkage problems that can be generated in dry curing conditions (Criado *et al* 2011). Concerning to the time and temperature of curing, it is important to point out that these variables are directly related between them: it means that for higher temperatures, less curing time is necessary to achieve the geopolymerization process.

In this paper, vitreous calcium aluminosilicate (VCAS) is used as alumino-silicate source material in the production of alkali activated binders. VCAS is a high reactive pozzolan which has been successfully used in blended Portland cement

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(Hossain *et al* 2008; Neithalath *et al* 2009). The first study related to the application of VCAS in alkali-activated systems was performed by Tashima *et al* (2009). The authors studied the influence of NaOH concentration for alkali activated mortars cured at 65 °C for three days: the obtained mortars showed important enhancement in compressive strength, especially for alkaline solutions with 10 molal in NaOH.

In this paper, a specific study is carried out on the influence of curing time on the development of mechanical strength of alkali activated VCAS (AA-VCAS) mortars activated by 10 molal NaOH solution.

2. Experimental

The vitreous calcium aluminosilicate (VCAS), supplied by Vitrominerals, was used as alumino-silicate source material in the production of alkali-activated binders. Its chemical composition, determined by XRF, is shown in table 1. This material presents a mean particle size of about 12 μm and irregular shape morphology with a dense-compact structure (see figure 1). In figure 2, the XRD pattern for VCAS sample is presented. The XRD pattern indicates that VCAS is an amorphous material which was identified by the baseline deviation in the range of 15–35°. The presence of quartz crystals as impurities is detected by its characteristic pattern: quartz (PDFCARD-461045).

A 10 molal alkaline solution was prepared using sodium hydroxide (98% purity) supplied by Panreac SA. The mortar

Table 1. Chemical composition of VCAS (wt%).

SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	Others
57.9	12.92	23.51	2.88	0.74	0.13	0.47	1.45

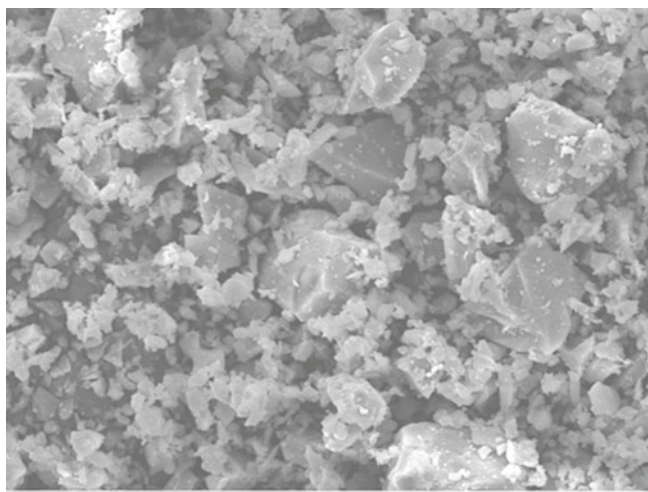


Figure 1. SEM image of VCAS sample.

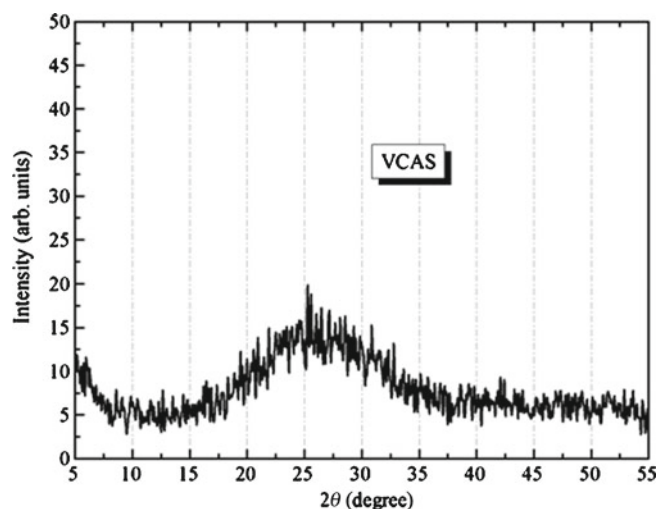


Figure 2. XRD pattern for VCAS sample.

samples (AA-VCAS mortars) were prepared using siliceous sand (UNE-EN 196-1 standard). The sand/VCAS ratio was fixed to 3 and the water/VCAS ratio was 0.45. The mortar specimens (40 × 40 × 160 mm³) were cured at 65 °C in high relative humidity (RH ~ 100%) for different curing times: 4, 8, 12, 24, 48, 72 and 168 h. Mechanical strength tests were performed in an universal test machine following the procedures described on UNE-EN 196-1 standard. Flexural strength is an average calculated from three samples and the compressive strength is an average calculated from six samples (standard deviation values were also calculated).

Similar mixtures without sand (pastes) were prepared for the microstructural analysis. The geopolymerization process of AA-VCAS pastes was monitored by means of electrical conductivity and pH measurements in an aqueous suspension. In this case, a Crison microCM2201 conductimeter and a Crison micropH2001 pH-meter (Alkali resistant pH-electrode Crison 5204) were used. This analysis was performed using 1 g of milled alkali-activated VCAS paste and 10 ml of deionized water. The mixture was magnetically stirred for 10 min before the conductivity and pH measurements. Thermogravimetric analysis (TGA) characterization of AA-VCAS pastes were carried out in a TGA 850 Mettler Toledo thermobalance, using sealed and pin-holed 100 μL -aluminum crucibles in a nitrogen atmosphere in the 35–600 °C range at 10 °C/min heating rate. Pastes studied by TGA were previously ground with acetone and filtered under vacuum, and then dried at 60 °C for 30 min. Scanning electron microscopy (SEM) JEOL JSM-6300 was used to analyse the microstructure development of fractured surface pastes.

3. Results and discussion

3.1 Mechanical strength studies

Table 2 summarizes the mechanical strength values of AA-VCAS mortars cured at 65 °C for different times in

4–168 h range. A continuous increase in the mechanical properties (flexural R_f and compressive R_c strengths) of AA–VCAS mortars are observed with the curing time. Flexural strength values higher than 7 MPa were obtained after 48 h of thermal treatment. After this curing age, the flexural strength was maintained in similar values. The maximum flexural strength obtained for AA–VCAS mortars was similar to those obtained for standard mortars using ordinary Portland cement. No evidence of flexural decay were identified, confirming the stability of the binding matrix in these curing conditions.

The increase in compressive strength was also observed with the curing time. In figure 3, the effect of curing time on the compressive strength development of alkali-activated VCAS mortars activated with 10.0 molal of NaOH is shown. Mortars cured for few hours present an acceptable compressive strength, achieving 5.6 MPa in 4 h. As can be observed, an interesting compressive strength development is observed for this system in the first 72 h: a compressive strength gain rate around 1.68 MPa/h was observed for AA–VCAS mortars in the first 12 h, decreasing to 0.95 MPa/h for a period of

12–72 h. After 72 h of curing, the increase in the compressive strength is negligible (see table 2).

The compressive strength results suggest that AA–VCAS mortars activated with 10.0 molal NaOH solution and cured with ~100% RH at 65 °C temperature should be cured for 3 days (72 h) to achieve very good compressive strength. An increase in the curing time for 168 h does not present a significant increment on the mechanical properties of AA–VCAS mortars. The curve of compressive strength (R_c) vs curing time (t , h, range 4–72 h) for AA–VCAS mortar can be fitted ($R^2 = 0.99$) using the following mathematical model:

$$R_c = a * (1 - b^t), \quad (1)$$

where R_c is the compressive strength (MPa); t the curing time (h); a and b are 120.45 and 0.9863 (MPa), respectively.

3.2 Microstructural studies

Thermogravimetric analyses (TGA) of AA–VCAS pastes for different curing times are summarized in table 3. The results showed an increase in the total weight loss (%) with the curing time. After 72 h of curing, the total weight loss achieves a maximum value of 19.17%. The increase in weight loss is related to the progress of geopolymerization process. The dissolution process in alkaline medium implies that Si–O–Si, Al–O–Al and Si–O–Al bonds are broken, yielding Al–OH and Si–OH groups. In the geopolymerization process, part of these new groups are arranged (condensation reaction) to form new Si–O–Al bonds. However, some of the Si–OH and Al–OH groups remain unreacted. The weight loss observed in TGA for geopolymerized paste is attributed to the decomposition (water loss) of these Si–OH groups and Al–OH groups, and also to the water molecules bonded to ions (sodium and calcium).

Another instrumental technique used to assess the geopolymerization reaction is the analysis of pH and electrical conductivity measurements of geopolymeric pastes in an aqueous suspension. For this purpose, water suspensions (1 g of milled geopolymerized paste and 10 g of deionized water) were prepared for each curing time: in these conditions, free OH^- and Na^+ ions were released from the pores of the powdered paste to the solution. The results showed a decrease in the pH and the electrical conductivity values, indicating the geopolymerization reaction progress by the consumption of OH^- and Na^+ ions. Figure 4 shows the pH and electrical conductivity changes for different curing times. In the first 48 h of the reaction, a decrease in the pH values is detected, from 13.35 to 12.59. Similar results are presented by electrical

Table 2. Influence of curing time on the mechanical properties of AA–VCAS mortars.

	R_f (MPa)	R_c (MPa)
4 h	0.87 ± 0.20	5.60 ± 0.44
8 h	2.19 ± 0.16	13.63 ± 0.61
12 h	2.52 ± 0.03	20.21 ± 1.11
24 h	3.99 ± 0.46	34.73 ± 1.69
48 h	7.68 ± 0.87	55.23 ± 1.90
72 h	7.61 ± 0.46	77.18 ± 2.25
168 h	7.94 ± 0.32	79.83 ± 2.05

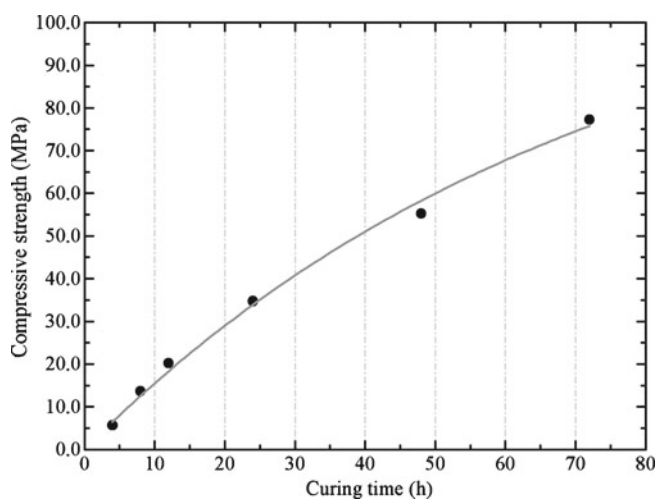


Figure 3. Compressive strength development of AA–VCAS mortars. Solid circles are experimental data and solid line is fitting curve according to (1).

Table 3. Total weight loss (%) for AA–VCAS pastes at different curing times.

Curing time (h)	3	12	24	48	72	168
AA–VCAS	7.71	11.09	13.42	15.79	19.17	18.06

conductivity measurements: a decrease from 42800 $\mu\text{S}/\text{cm}$ to 9430 $\mu\text{S}/\text{cm}$.

After 48 h of curing, no changes are observed in pH and electrical conductivity values. Nevertheless, comparing

these results with mechanical properties of mortars, it can be assumed that the improvement on compressive strength is related to the reorganization in the microstructure of AA-VCAS system. The microstructure development of

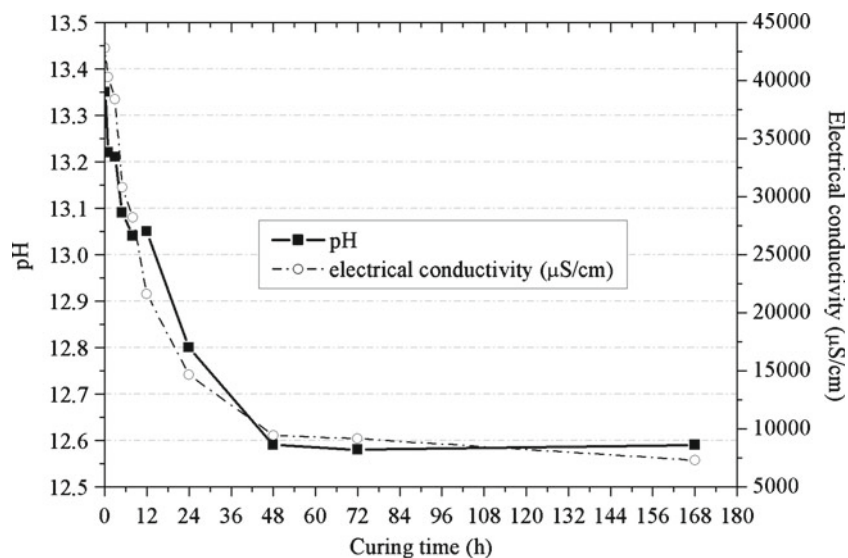


Figure 4. pH and electrical conductivity values for AA-VCAS pastes for different curing times.

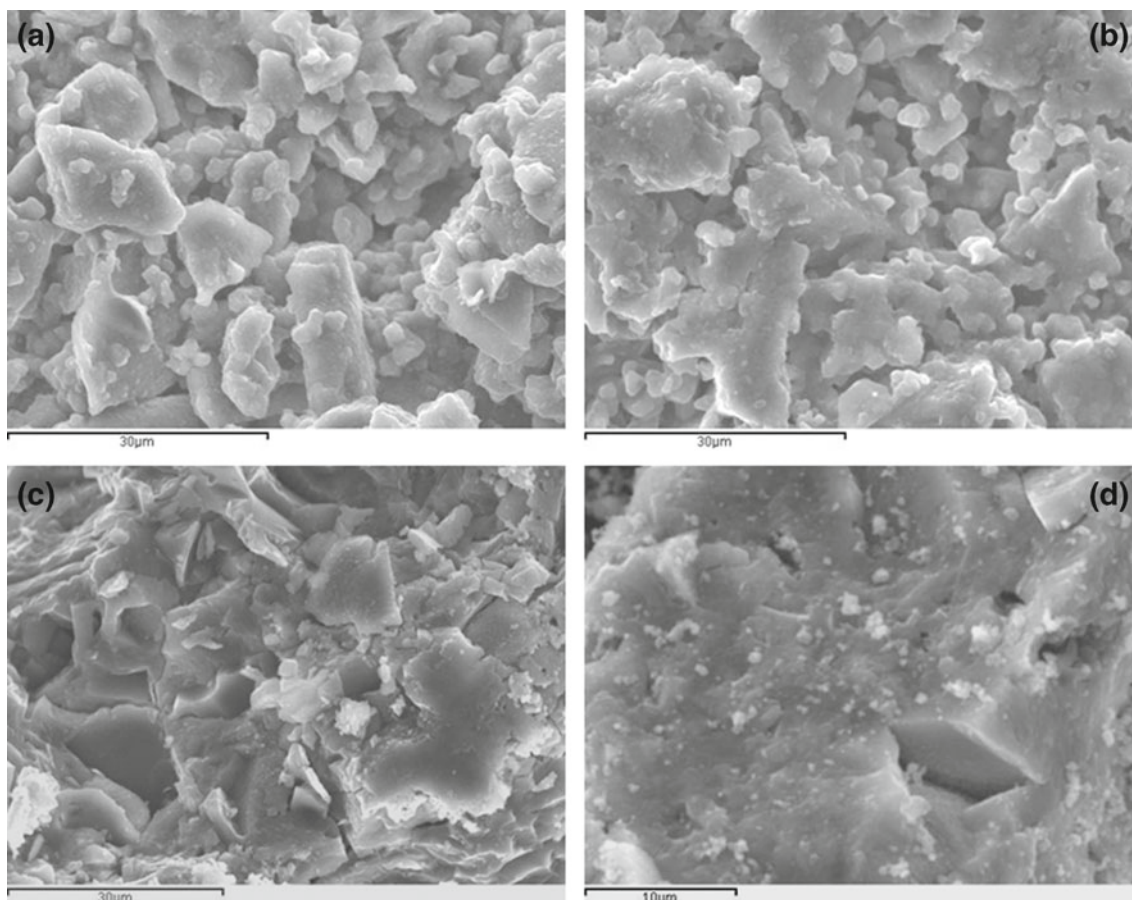


Figure 5. SEM images of AA-VCAS paste for different curing times: (a) 1 h; (b) 4 h; (c) and (d) 72 h.

AA–VCAS pastes were also analysed by means of SEM images for different curing times. In the first hour, the dissolution–coagulation process of aluminosilicate source material can be identified. In figure 5(a), a SEM image of AA–VCAS paste cured for 1 h at 65 °C is shown. It can be noticed that some VCAS particles have been dissolved and small amount of gel was formed. When the curing time was increased to 4 h, the formation of an amorphous gel (characterized by EDX as (N,C)ASH gel) can be identified (see figure 5(b)). For this curing time, the AA–VCAS paste also presents a very porous microstructure.

Pastes cured for 3 days at 65 °C (figures 5c and d), a compact-dense microstructure is observed. In this case, the presence of partially reacted VCAS particles can also be noted (see figure 5(d), up-right corner), and the amount of amorphous gel is very high, occupying an important part of the volume in the sample.

4. Conclusions

The effect of curing time on the microstructure and mechanical strength development of alkali activated VCAS have been investigated. High compressive strength mortars are obtained, yielding an important increase to 77 MPa for 3 days of curing at 65 °C. A mathematical model of compressive strength development of AA–VCAS mortars was proposed in the range 4–72 h. Electrical conductivity and pH measurements suggested that 48 h curing at 65 °C led to an increase in the geopolymerization process. A decrease of free OH⁻ and Na⁺ ions in the pore solution was related to the reaction progress. AA–VCAS pastes activated with 10 molal of NaOH after 72 h of reaction presented large amount of amorphous (N,C)ASH gel.

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