

Alkali Activation of “Pozzolan – Calcium Aluminate Cement” Mixtures

L.Fernández-Carrasco¹, A. Fernández-Jiménez², A. Palomo²

¹*Universitat Politècnica de Catalunya, Barcelona;*

²*Eduardo Torroja Institute (CSIC), Madrid. [Spain]*

Abstract

The products of the alkali activation of aluminosilicate materials, for want of reactive aluminium, may not develop mechanical strength comparable to the MPa values typical of OPC. The present study explored the effect of calcium aluminate cement (CAC) as a source of reactive aluminium on the strength of a natural pozzolan activated with 8M NaOH. Mixed with the sodium solution and stored at 85 °C, the pozzolan failed to harden after 24 hours. It did harden, however, when 30% CAC was added to the system, reaching a compressive strength of 22 MPa under identical experimental conditions. The CAC alone developed strength of 10 MPa under these conditions. Microstructural characterization of the reaction products appeared to indicate that the CAC in fact yielded part of its aluminium to the system, prompting the conversion of the pozzolan into a cementitious alkaline aluminosilicate gel.

Key Words: alkali activation, reactive aluminium, calcium aluminate cement

1. Introducción

Alkali activation is a chemical process in which a powdery aluminosilicate material such as metakaolin or fly ash is mixed with an alkaline activator to produce a quick-setting and hardening paste [1-5]. Once hardened, these materials (termed alkaline cements, geopolymers, or hydroceramics) combine cementitious properties with the characteristics of traditional ceramics and zeolites.

Much of the research on this process reported in the literature is based on the study of metakaolin [6-8], and more recently F-type fly ash [9-11], activation. Although the main reaction product of the alkaline activation of both metakaolin and fly ash is an alkaline aluminosilicate gel (N-A-S-H gel) (in which the cementitious material, according to ²⁹Si MAS NMR analysis, comprises three dimensional networks containing Si in a variety of Q⁴(nAl) environments [9,10]), differences in the composition and microstructure of the initial material affect the microstructure of the final product. Whereas metakaolin yields a very homogeneous matrix consisting in a highly zeolitized gel with a low Si/Al ratio [3,4,12] (a zeoceramic), fly ash matrices are more heterogeneous (higher percentage of unreacted ash particles), the resulting gel having a larger Si/Al ratio and a smaller percentage of zeolites (a zeocement) [4,5,10]. In other words, the main properties of the resulting materials (material strength,

shrinkage, acid and fire resistance and so on) depend not only on process variables (per cent of soluble silica in the activating solution, curing conditions and so on) but also on the nature of the raw materials used.

Recent surveys on the mechanical strength, degree of reaction, and microstructural characteristics of a number of alkali-activated fly ash pastes have shown that the highest performing alkali-activated materials are made from fly ash with: (i) high “*reactive*” SiO_2 and Al_2O_3 contents [13] and (ii) “ $(\text{Si}/\text{Al})_{\text{Reactive}}$ ” ratios of under 2 [10].

Fly ash or other materials with the optimum proportions of reactive silica and alumina able to generate good cementitious products in the alkali activation process are not always easily found. This, in addition to the limited availability of fly ash (geographic and production limitations), led to a decision to study the alkali activation of other materials – found in abundance on the earth crust – with high reactive silica (i.e., with pozzolanic properties) but low reactive alumina contents. Similarly, the solution proposed for the shortage of reactive alumina in the working materials was to add certain amounts of calcium aluminate cement (CAC) to the mix. In prior research, the authors of the present study found that part of the aluminium provided by the CAC can be incorporated into the zeolite precursor (sodium aluminosilicate gel) that precipitates during the alkali activation of aluminosilicate materials [14].

2. Experimental

The raw materials used in this study were a natural pozzolan from Mexico (PZ5) and a commercial CAC supplied by the Ciments Molins Industrial SA plant at Barcelona, Spain. A PHILIPS PW 2400 X-ray fluorescence spectrometer with a PW 2540 VTC sample changer was used to determine the chemical composition of the two materials (see Table 1).

Initially, two working mixes were prepared by blending the solid state raw materials: **Mix 1** comprising 85% PZ5 and 15% CAC; and **Mix 2** with 70% PZ5 and 30% CAC. Alkali activation was performed by adding an 8M solution of NaOH to working mixes 1 and 2; the “caustic solution/mix 1 or mix 2” ratio was kept constant throughout at 0.4, by weight. The pastes produced were subjected to two sets of curing conditions: A (20 hours at ambient temperature and relative humidity) and B (20 hours at 85 °C and 98% relative humidity).

Consequently, this study covered four cementitious matrices: Mixes 1A and 2A (cured under the A conditions) and Mix 1B and 2B (cured under the B conditions). Mortar prisms measuring 4x4x16 cm were made from the four matrices and tested for compressive strength upon finalization of the curing

period. Mineralogical and microstructural characteristics were studied on formless samples.

The following techniques and instruments were used to determine the mineralogy and microstructure of the hardened materials: X-ray diffraction (XRD) with a Siemens D500 instrument; infrared analysis with an FTIR-8300 Fourier transform infrared spectrophotometer with a frequency range of 4000 to 400 cm^{-1} .

Table 1.- Chemical analysis of raw materials

| | %SiO ₂ | %Al ₂ O ₃ | %Fe ₂ O ₃ | %CaO | %MgO | %Na ₂ O | %K ₂ O | L.O.I. | I.R. | %SiO ₂ r |
|------------|-------------------|---------------------------------|---------------------------------|-------|------|--------------------|-------------------|--------|------|---------------------|
| PZ5 | 65.56 | 12.60 | 0.75 | 4.50 | 1.33 | 0.51 | 1.06 | 12.45 | 1.24 | 64.05 |
| CAC | 2.94 | 40.52 | 12.91 | 34.89 | 0.5 | 0.14 | 0.06 | 0.36 | 2.82 | --- |

(%SiO₂ r : reactive silica); L.O.I. : loss on ignition; I.R. : insoluble residue

3. Results

3.1.- Mechanical strength:

Table 2 gives the results of the compressive strength tests conducted on the mortar specimens 24 hours after mixing the raw materials. The two most relevant facts to be deduced from the table are: 1) only the specimens cured at 85 °C (curing condition B) hardened quickly enough to generate compressive strength values comparable to the results recorded for commercial cements; 2) the CAC content in the initial system had a significant effect on mechanical strength development . Initially, the higher the CAC content, the better the mechanical performance.

Table 2.- Compressive strength

| System | Compressive strength (MPa) |
|---------------|-----------------------------------|
| Mix 1A | 0.5 |
| Mix 2A | 0.7 |
| Mix 1B | 9.3 |
| Mix 2B | 22.3 |

3.2.-XRD:

Figure 1 shows the diffractograms for the four working mixes prepared as specified above. Table 2 summarize the mineralogical findings for the working mixes, respectively.

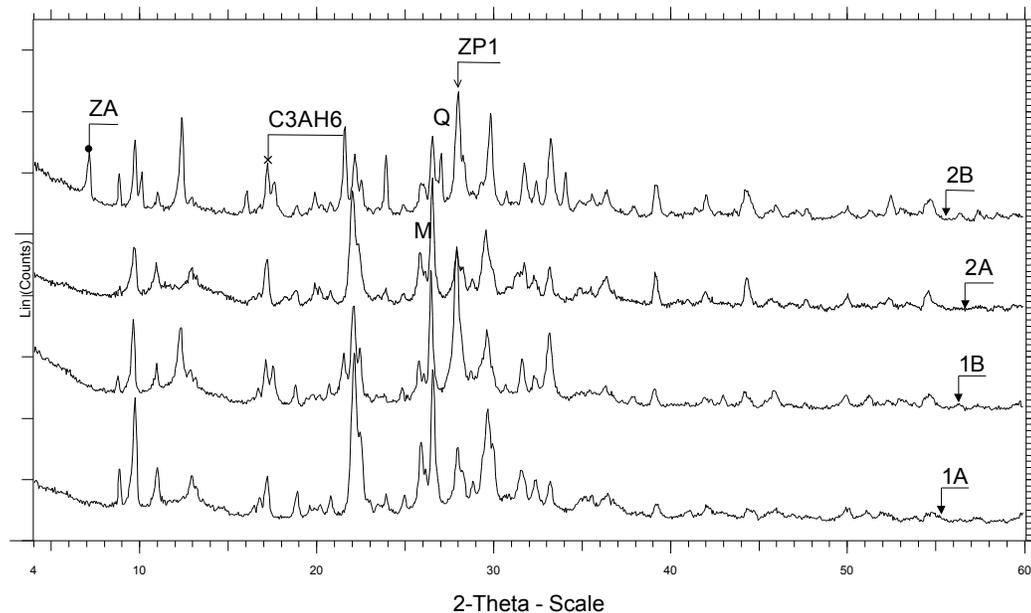


Figure 1.-: X-ray diffractograms of working mixes (ZA = zeolite A, ZP1 = zeolite P1 and Q = quartz).

Table 2.- XRD identification of crystalline phases in matrices

| Samples | C ₃ AH ₆ | Quartz | g | Zeolite A | Zeolite P1 |
|---------|--------------------------------|--------|-----|-----------|------------|
| Mix 1 A | +↓ | ++++ | +++ | --- | --- |
| Mix 2 A | + | +++↑ | ++↑ | --- | --- |
| Mix 1 B | +↓ | +++↑ | ++↑ | --- | ++ |
| Mix 2 B | + | ++↑ | +↑ | ++ | ++ |

g = mullite; + present; - absent

A very high crystalline content (primarily monocalcium aluminate) was found for the CAC, while the crystalline phases (quartz and a natural zeolite of the heulandite family whose empirical formula is $\text{Ca}_{1.23}(\text{Al}_2\text{Si}_7)\text{O}_{18} \cdot 6\text{H}_2\text{O}$) accounted, naturally, for a smaller proportion of pozzolan PZ5.

The most abundant product of CAC hydration, formed during alkali activation of the materials studied, was C₃AH₆. No diffraction lines were observed for any of the aluminium hydroxide polymorphs; nonetheless, there is every indication that regardless of the amount of CAC blended with the pozzolan in the initial system (15 or 30%) and regardless of the curing conditions (A or B), 100% of the CAC reacted in these systems, since no remains of anhydrous calcium aluminates were found.

Moreover, X-ray diffraction detected the presence of certain zeolites in the systems cured at 85 °C. Specifically, zeolite P1 was always formed in these systems, regardless of whether the initial mix contained 15 or 30% CAC. Zeolite A, on the contrary, was only found in systems containing 30% CAC.

3.3.- FTIR spectroscopy

The most relevant signals on the FTIR spectrum for CAC (Figure 2) were the absorption bands in the region between 850 and 650 cm^{-1} – the bands at around 840, 805 and 780 cm^{-1} – attributed to AlO_4 groups; the bands between 750 and 400 cm^{-1} – with bands at about 720, 685, 640 and 570 cm^{-1} , ascribed to AlO_6 groups; and the bands at under 400 cm^{-1} owing to Ca-O bonds [15,16].

The absorption bands attributed to crystalline and amorphous SiO_2 on the IR spectrum for pozzolan PZ5 clearly overlapped (Figure 2b). Signals due to the Al-O bond also appeared. All in all, the traces appeared to indicate that the material denominated PZ5 was a zeolite mineral, in all likelihood of the heulandite family (confirming the XRD findings) with clearly visible bands at 1638 cm^{-1} (H-O-H), 1190 cm^{-1} (“shoulder”), 1060 cm^{-1} (very intense), 730 cm^{-1} and 670 cm^{-1} (weak), 605 cm^{-1} (medium) and 465 cm^{-1} (intense).

The band due to Si-O and Al-O vibrations, which in the natural PZ5 pozzolan appeared at around 1060 cm^{-1} , shifted to lower frequencies after alkali activation (Figure 3): appearing at around 1000 cm^{-1} in the Mix 2B spectrum, 1010 cm^{-1} in the Mix 1B pattern and 1030 cm^{-1} in the Mix 2A and 1A spectra (materials cured at ambient temperature). The two latter spectra – for samples 2A and 1A – showed a shoulder at around 1200 cm^{-1} similar to the one observed on the PZ5 pattern, which was barely visible in the spectra for the mixes cured at 85 °C. It may be deduced from the foregoing that the materials cured at 85 °C showed a higher degree of reaction than the mixes cured at ambient temperature, a development logically related to the higher mechanical strength observed in the former.

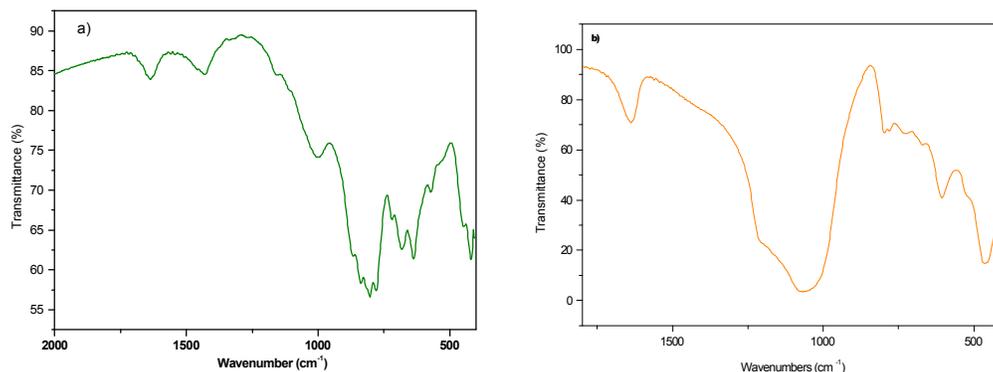


Figure 2.- IR spectra for: a) CAC and b) pozzolan PZ5.

Moreover, the absorption band at around 800 cm^{-1} due to AlO_4 -type vibrations, present in both the pozzolan PZ5 and CAC spectra (although with different intensities), was observed to practically disappear from the samples cured at $85\text{ }^\circ\text{C}$ (but not from the patterns for the matrices cured at ambient temperature). A new band was observed in the $85\text{ }^\circ\text{C}$ mix spectra at around 750 cm^{-1} (particularly in Mix 1B), characteristic of TO_4 bonds ($\text{T} = \text{Si}, \text{Al}$).

Finally, the band characteristic of the absorption generated by the OH groups in compound C_3AH_6 (at approximately 3360 cm^{-1}) was not observed in any of the spectra. There was, however, a wide absorption band in the $3700\text{-}3200\text{ cm}^{-1}$ region on all the spectra which could be explained, in principle, by the presence of amorphous aluminium hydroxide, although the presence of amorphous hydrated calcium aluminates cannot be ruled out altogether.

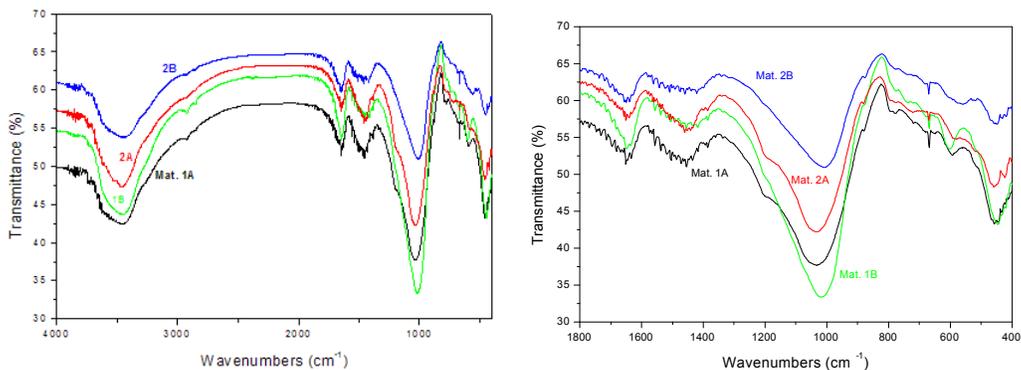


Figure 3.- IR spectra of the alkali activated systems

4. Discussion

The two stages generally described in zeolite synthesis mediated by an alkaline attack on aluminosilicate materials are: A) a first nucleation stage in which the initial aluminosilicates are dissolved in the alkaline medium, favouring the formation of zeolite precursors and B) a second stage in which the various nuclei reach a critical size and begin to crystallize [17,18].

Zeolite crystal size depends on the nucleation rate – crystal growth rate ratio [17,18]. As a general rule, a high nucleation rate in the presence of low crystal growth yields small crystals. These are the conditions under which N-A-S-H gel usually forms. The extremely high alkalinity of “alkali-activated cementitious” systems favours the rapid dissolution of the amorphous/vitreous phases of raw materials, while the normally moderate working temperatures (60-80° C) and short duration of thermal treatment (20-24 hours) determine low crystal growth rates.

Consequently, the following hypothesis is advanced as an explanation for the setting and hardening of alkali-activated pastes and the nature of the main reaction product: N-A-S-H gel (see Figure 4) [19].

The dissolution of the amorphous/vitreous component in the initial contact between the aluminosilicate materials and the alkali solution leads to the immediate precipitation of a mechanically weak, Al-rich gel (intermediate reaction product). The formation of this intermediate reaction product would be explained by the high Al^{3+} ion content in the alkaline medium in the very early stages of the process (from a few minutes into the reaction through the first 4-5 hours), since reactive aluminium dissolves very quickly (faster than silicon because Al-O bonds are weaker than Si-O bonds and therefore more easily severed).

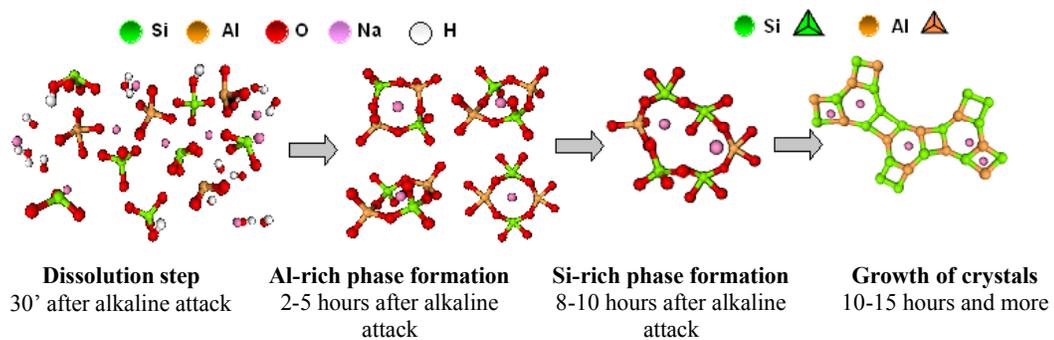


Figure 4.- Nanostructural stages of the alkali activation reaction [19].

As the reaction progresses, more Si-O groups in the raw materials separate out, raising the Si concentration in the medium and driving the formation of the zeolite precursor (the N-A-S-H gel). The precursor, in turn, grows gradually richer in Si, a development that is detected in infrared spectroscopy as a shift in the T-O asymmetric stretching vibration band at around 1000 cm^{-1} to higher frequencies.

Finally, the authors believe (concurring with Van Deventer et al. [11]), that N-A-S-H gel is a product consisting essentially of aggregated, ultra-small nanocrystals. The observation in many alkali-activated systems of the existence of small quantities of perfectly crystallized zeolites such as herschelite, zeolite Y, zeolite P, analcime, linde type A, and so forth [17,18] provides support for this hypothesis.

CAC is a very common cementitious material presently used for special applications only. Normal CAC hydration at ambient temperature generates CAH_{10} and sometimes C_2AH_8 . Both aluminates are hexagonal and metastable, inevitably evolving with time toward the only thermodynamically stable form at ambient temperature: C_3AH_6 (hydrated calcium aluminate crystallizing in the cubic system). This process takes place more or less rapidly depending on a number of factors intervening in CAC hydration, primarily temperature and the water/cement ratio [20, 21].

Nonetheless, under certain conditions CAC hydration may follow different paths. For instance, the presence of a high proportion of CO_2 , a high water/cement ratio, high porosity or a moderately alkaline medium may trigger a series of reactions known as alkaline hydrolysis [22-24]:



Alkaline hydrolysis may lead to the irreversible deterioration of calcium aluminate cement concrete. In this chemical process, contrary to developments during the alkali activation of aluminosilicates, the alkalis act as a catalyst but do not form a part of the final reaction products.

One of the primary aims of the present study was to explore an intermediate situation between these two extremes; in other words, alkali activation (with very high OH^- concentrations) of aluminosilicate material / CAC mixes. The initial idea was to observe whether (at least part of) the aluminium in the CAC could be taken up in the natural pozzolan activation reaction, stimulating the formation of N-A-S-H gel as the primary reaction product.

The detection with X-ray diffraction of the formation of zeolite A- or P1-type species (with very different Si/Al ratios) in some of the systems studied may suggest that the aluminosilicic pozzolan material present in the initial mixes was activated as a result of contact with the alkaline solution, generating N-A-S-H (at least partially). Moreover, the failure to detect hexagonal hydrate (CAH_{10} , C_2AH_8) or any of the aluminium hydroxide polymorphs in any of the working systems is evidence of "anomalous" hydration of the CAC present in the materials studied; such anomalous hydration led here to the formation of isometric hydrated calcium aluminates rather than to the precipitation of crystalline bayerite – more commonly found in the presence of alkalis. In other

words, the CAC may be contributing with its alumina to the alkali activation of pozzolan PZ5, as anticipated.

The information deduced from the IR spectra described above may be somewhat more conclusive than the XRD findings for the interpretation of the processes controlling the reactions in the systems under study.

The band associated with T-O stretching vibrations in the spectrum in Figure 3 shifts perceptibly with respect to its location on the Figure 2b spectrum. The magnitude of the shift depends on the amount of CAC in the initial mix and especially on the curing conditions. Since the exact position of this band depends on the Al/Si ratio of the product, it moves downward at higher concentrations of the tetrahedrally positioned Al atom in the system. Moreover, the replacement of an Si^{+4} by an Al^{+3} entails a reduction in the T-O-T angle, with the signal shifting to a lower frequency due to the smaller bonding force and the greater length of the Al-O than the Si-O bond. The modal value of the bonding force constant is smaller for the Al-O-Si than for the Si-O-Si bond.

Figure 5 shows the frequency differential ($\Delta\lambda$) or overall shift in the T-O stretching vibration band in each of the working systems. This shift is much more intense in the systems cured at 85 °C than the ones cured at ambient temperature, which might initially be interpreted to attest to the formation in the latter of a reaction product (N-A-S-H gel) with a high Si/Al ratio and therefore high mechanical strength [5,10]. But in fact these materials develop very poor mechanical strength (see Table 1). The more reasonable explanation would be that the degree of reaction in these materials cured at ambient temperature is scant, with a high percentage of unreacted pozzolan PZ5 24 hours after alkali activation. That fraction of unreacted material, mixed with the scant reaction products, would account for the position of this band at high frequencies on the IR spectrum. Such a hypothesis would be supported by the presence of the shoulder at 1200 cm^{-1} appearing on the PZ5 spectrum and still visible on the IR spectra for mixes 1A and 2A. In mixes 1B and 2B, on the contrary, the dissolution of the chemical species in the medium (Si from pozzolan PZ5 and Al from the CAC) is considerably accelerated by the curing temperature. This generates optimal conditions for the formation of an aluminium-rich N-A-S-H gel, responsible for both the mechanical strength developed by these mixes and, naturally, the sizeable shift in the T-O band on the infrared spectrum in Figure 5.

The bands appearing between 800 and 500 cm^{-1} are associated with the tetrahedral vibrations formed by what are known as secondary building units (SBU) and fragments of the aluminosilicate system [5,25]. These bands are characteristic of double or single rings (depending on the structure of the material) and/or TO_4 (T=Si, Al) tetrahedral bonds. Hence, the changes occasioned by the formation of three-dimensional structures as a result of ring inter-connections generates variations in the number, shape and position of the

bands in this area of the spectrum, which is likewise modified by variations induced in the Si/Al ratio.

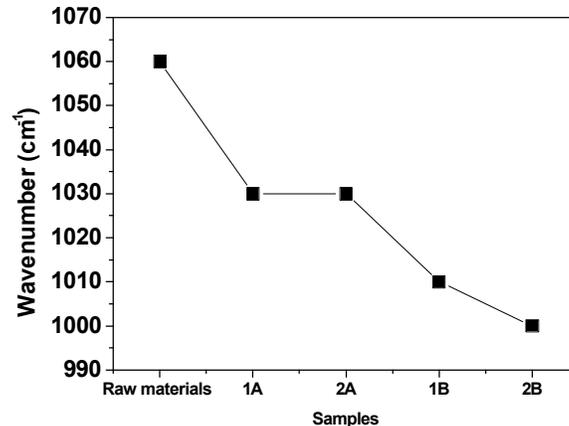


Figure 5. Shift in the T-O band associated with asymmetric stretching vibrations

Conclusions

The chief conclusions to be drawn from the present study are as follows:

- 1- In the CAC-puzzolan mixes, under conditions of high alkalinity, CAC does not undergo the normal hydration process: neither hexagonal hydrates nor $\text{Al}(\text{OH})_3$ are detected, while small proportions of cubic hydrates are observed.
- 2- CAC may be used as a source of reactive Al in the alkali activation of materials with low reactive alumina but high reactive silica contents. The results presented in this paper in fact show that CAC improves the mechanical performance of alkali activated pozzolan.

Acknowledgements

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