



Structural and nano-mechanical properties of Calcium Silicate Hydrate (C-S-H) formed from alite hydration in the presence of sodium and potassium hydroxide



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ABSTRACT

This research evaluates the effect of sodium and potassium hydroxide on the structure and nano-mechanical properties of Calcium Silicate Hydrate (C-S-H) formed from the hydration of pure alite. Monoclinic (MIII) alite was synthesized and hydrated, using water-to-alite ratios of 0.5 and 0.6 and additions of 10% NaOH and KOH by weight of alite. Based on results of X-ray diffraction, isothermal calorimetry, thermogravimetric analysis, Nuclear Magnetic Resonance and nanoindentation, two different effects of the alkaline hydroxides on the hydration reaction of alite, both at early and later ages, can be identified: (i) a differentiated hydration process, attributed to an enhancement in calcium hydroxide (CH) precipitation and a stimulation of the C-S-H nuclei; and (ii) an increase in the elastic modulus of the C-S-H aggregations, attributed to an electrostatic attraction between positive charges from the alkaline cations and negative charges from the C-S-H structure.

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1. Introduction

The hydration products of alite are Calcium Silicate Hydrate (C-S-H) and calcium hydroxide (CH). Of these, C-S-H is the most important, since it is responsible for most of the mechanical properties of cementing matrices [1]. It has previously been found that sodium hydroxide (NaOH) and potassium hydroxide (KOH) accelerate the early hydration process of alite [2] by enhancing the dissolution [3] and precipitation [4] rates of the hydration products. The structure of C-S-H has been widely studied, but is still not fully understood. Various models, such as the tobermorite model [5], the tobermorite/jennite model [6], and the tobermorite/calcium hydroxide solid solution model [7], have been proposed in this regard; all models agree on the presence of SiO₄ tetrahedra, which form dreierkette chains [8]. Dreierkette chains are formed by paired and bridging SiO₄ tetrahedra, coordinated to each other or to a central layer of Ca–O by oxygen atoms [9]. Shortening of the silicate chains by elimination of the bridging tetrahedra has been associated with a more advanced hydration process [10] and higher Ca/Si ratios [11].

According to several authors, the blending of alkaline activated aluminosilicates and ordinary Portland cement (OPC), called hybrid

cement [12], is a viable option to replace a percentage of OPC, and thus reducing the CO₂ emissions associated with its fabrication [13]. NaOH and KOH are the typical alkaline activators for silica and alumina [14]; therefore, it is worthwhile to study the hydration process of OPC in their presence. Since the clinker consists of up to 70% alite [15], the hydration of pure alite samples in the presence of NaOH and KOH serves as a good indicator of OPC performance during its hydration in hybrid matrices.

Nanoindentation studies of C-S-H samples have identified different elastic behaviors for the same hydrated phase, which are associated with different packing densities [16]. Ultra High Density C-S-H (UHD C-S-H) [17], High Density C-S-H (HD C-S-H), and Low Density C-S-H (LD C-S-H) have been clearly differentiated according to their elastic modulus [18]. Improved mechanical performance of cementing matrices has been linked to a higher presence of HD C-S-H [19]. This work studies the influence of alkaline hydroxides on the hydration process, structure and nano-mechanical properties of C-S-H formed from pure alite.

2. Materials and methods

The materials used in this study were CaO, SiO₂, MgO, Al₂O₃, NaOH and KOH; all of these were reagent grade and were produced by Merck. Alite of the monoclinic MIII polymorph was synthesized following a procedure detailed in previous literature on the subject [20].

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2.1. Alite production

The alite produced for this research was characterized via XRD analysis; the resulting diffraction pattern obtained is presented in Fig. 1. Diffraction peaks typical of alite were found; the inset in the figure shows the features of the pattern (between 32.0° – 34.0° and 51.0° – 53.0° 2θ), which identify the alite as monoclinic MIII [1]. Two small peaks, characteristic of belite, were also found. Rietveld refinement was used to assess the purity of the phases produced; PANalytical X'Pert HighScore Plus software was used for the refinement. The intensity of the belite peaks was not high enough to clearly identify the polymorph; therefore, the β polymorph was assumed for the refinements. The results showed that 97.2% of the sample was MIII alite and 2.8% was β -belite (χ^2 : 2.79; wRp: 0.0384).

2.2. Sample preparation

The alite was divided into two portions in order to study its hydration in the presence of alkalis; the first portion was used to measure heat release during the first 40 h of the reaction, and the second portion was left to hydrate for 28 days in order to determine its mineralogical and nano-mechanical properties. Control samples were produced by hand-mixing alite with deionized water for 2 min, using water-to-alite ratios (w/a) of 0.5 and 0.6. Samples blended with NaOH and KOH (addition of 10% hydroxide by weight of alite) were produced by dissolving the hydroxides in deionized water (maintaining the same w/a ratios) and then hand-mixing these with the alite for 2 min. Proportions and nomenclature are presented in Table 1.

Samples used to measure mineralogical and nano-mechanical properties were stored in air tight containers for 28 days. After reaching testing age, their hydration process was stopped using acetone. A piece of each sample was embedded in epoxy resin and the remainder was ground in a grinding mill and passed through a No. 200 sieve. Acetone was also used as a refrigerant during the grinding process. These samples were used for X-ray diffraction (XRD) analysis, Thermogravimetric Analysis (TGA) and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (^{29}Si MAS NMR). Small pieces of the hydrated samples were mounted in epoxy resin, sanded using 100, 220, 320, 600 and 1200 grit silicon carbide paper, and polished using $1\ \mu\text{m}$ diamond paste; throughout the sanding and polishing procedures, isopropyl alcohol was used as a lubricant and a refrigerant. These samples were used for the nanoindentation tests.

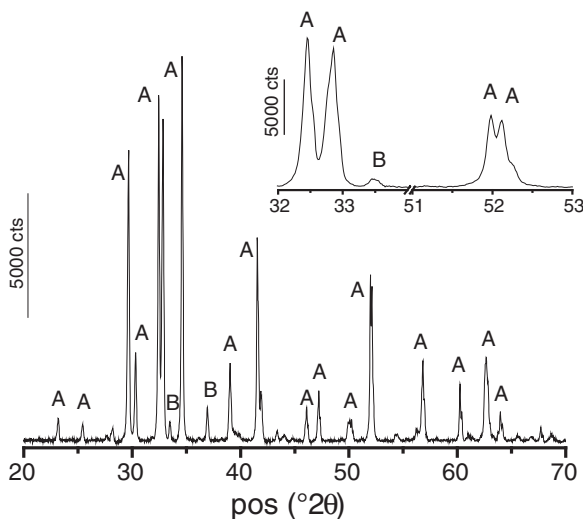


Fig. 1. XRD pattern of alite produced (A: alite, B: belite).

Table 1

Proportions and nomenclature of the samples analyzed.

| w/a | Addition of alkalis by mass of alite | Concentration of alkalis | Nomenclature |
|-----|--------------------------------------|--------------------------|-------------------------------------|
| 0.5 | – | – | A(0.5) |
| | 10% NaOH 10% KOH | NaOH 5.0 M KOH 3.6 M | A(0.5)/NaOH(10%) A(0.5)/KOH(10%) |
| 0.6 | – | – | A(0.6) |
| | 10% NaOH 10% KOH | NaOH 4.1 M KOH 3.0 M | A(0.6)/NaOH(10%) A(0.6)/KOH(10%) |

2.3. Testing procedures

XRD analyses were carried out using PANalytical X'Pert PRO equipment, with radiation from a Cu source of wavelength $\text{K}\alpha_1 = 1.5406\ \text{\AA}$, in a 2θ interval between 10° and 70° , with a step of 0.02° and an accumulation time of 30 s. A TAM Air isothermal calorimeter set to $25\ ^{\circ}\text{C}$ was used to measure heat release over the course of 40 h; admix accessories were used to inject the mixing water and mix the samples for 2 min. TGA was performed with Hi-Res TGA 2950 Netchz equipment, using an alumina crucible, N_2 atmosphere and a heating rate of $20\ ^{\circ}\text{C}/\text{min}$, up to $900\ ^{\circ}\text{C}$. ^{29}Si MAS NMR tests were performed at room temperature using a Bruker Avance 400 MHz Wide Bore spectrometer with a ^{29}Si probe, 2000 scans per sample and a 12 KHz frequency. Nanoindentation tests were carried out using a G200-MTS system nanoindenter equipped with a Berkovich tip. Two tests were performed on each sample; each test consisted of 196 indents made in a 14×14 grid ($15\ \mu\text{m}$ between adjacent grid points), for a total of 392 indentations on each sample. The maximum load used in each indent was 2 mN, applied in 10 s, held for 5 s and released in 5 s.

3. Results and discussion

3.1. Isothermal calorimetry

Variations in the kinetics of the hydration reaction induced by the alkalis were studied using isothermal calorimetry. The heat flow curves obtained were normalized to the mass of the solids; these are presented in Figs. 2 and 3. For better visualization, the curves corresponding to control samples A(0.5) and A(0.6) are presented as insets in each figure. Three well-differentiated events were found for the control samples. The first was a small peak associated with the dissolution of the

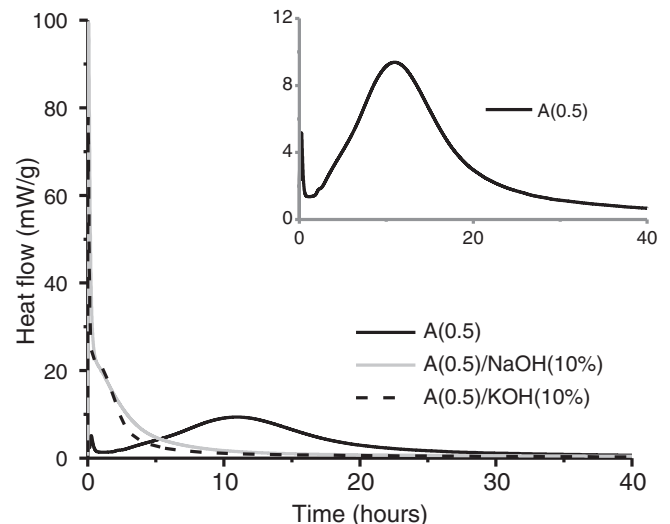


Fig. 2. Heat flow curves of alite and alite mixed with alkalis (w/a 0.5).

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