

Alkali Activation of Calcium Silicate Clinker: Hydration and Microstructure Properties

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Abstract

Synthesized CSC (Calcium Silicate Clinker: C₃S 70% and C₂S 30%) was hydrated in water as a control, and alkaline solutions: NaOH or KOH (5 M). The hydration kinetics was characterized by isothermal calorimetry. Hydrated samples after 28 days of curing were characterized by XRD (X-ray diffraction), FTIR (Fourier transform infrared spectroscopy) and SEM (Scanning electron microscopy). The results showed that the contact of synthesized phases with the liquid phase during hydration is affected by the presence of alkalis. The hydration of CSC in presence of alkalis leads to the acceleration of hydration and penetration of Na⁺ and K⁺ into the C-S-H structure, leading to the stimulation and generation of C-(N)-S-H and C-(K)-S-H. SEM observations revealed a significant difference in the morphology and composition of C-S-H in the presence of NaOH or KOH. The chemical activation of calcium silicate phases can be a promising solution to increase the hydraulic and mechanical properties of the resulting cementitious products.

Keywords

Calcium silicate clinker, Silicate phases, Alkali activation, Hydration kinetics, Ion inclusions

Introduction

The main ingredients of clinker are calcium silicates. Tricalcium silicates (C₃S, alite) and dicalcium silicates (C₂S, belite) make up about 75% of ordinary Portland clinker. These phases react with water under dissolution-precipitation process, resulting in the development of C-S-H and Portlandite [1]. C₃S is well known for its high hydraulic reactivity, while C₂S has slow hydration reaction kinetics which gives it specific properties [2, 3].

Some works have been done on hydration process of alite and belite in the presence of alkali activators and showed intense early hydration kinetics of C₃S and C₂S by increasing the dissolution and precipitation rates and leading to the precipitation of portlandite and C-S-H gel [4-6].

The chemical activation of Portland clinker phases can increase the hydraulic and mechanical properties of the resulting products; hence the need to understand the behavior of calcium silicates, a major part of clinker, with respect to the alkali activators can be promising in terms of mechanical performances and durability aspect. This paper aims to investigate the effects of Na⁺ or K⁺ ions on the chemical composition, mineralogy and morphology of C-S-H obtained from hydrated phases of synthesized calcium silicate clinker formed using a solid-state process.

Alkaline solutions of NaOH or KOH are used during the hydration step of the CSC samples, acting as alkaline activators. Hydration kinetics are monitored

by microcalorimetry, and the hydrated samples are followed by XRD and SEM-EDS (Energy dispersive X-ray spectroscopy) after 28 days of curing.

Materials and Method

Calcium carbonate (99.9% wt.) and silicon oxide (99.9% wt.) were used as starting materials to synthesis CSC by solid-state reaction. They are mixed as follows: 77 and 23 wt.% respectively, and heated at 600 °C for 24 h, then ground with ethanol to make a homogeneous mixture after quenching in the open air. After that, obtained powder was sintered at 1350 °C for 1h in which CSC sample is obtained. XRD analysis of CSC powder (< 45 μm) was performed using RIGAKU X-ray diffractometer equipped with CuKα radiation source and wavelength of 1.54056 Å. The analyses were performed with a scan speed of 5°/min and a diffraction angle 2θ of 5° to 85°.

In order to make an approach between the main hydrated products identified by XRD and their structures, the Diamond 2.1d [7] software from the Crystallographic Information Files published in the literature is used to establish the retention mechanism of Na and K through the C-S-H structure.

Hydration of the samples was then performed by adding distilled water, NaOH or KOH solution of 5 M. The hydration kinetics was followed by Tian-Calvet microcalorimeter in which 1 g of the solid is used and liquid/solid of 0.4 during first 70 h. The clinker hydration process takes place on a nanometric scale.

The mineralogical characterization after 28 days of curing was also done on hydrated CSC with w/s of 0.4 stored at room temperature. The present phases were explored by the same X-ray diffractometer described above. FTIR analysis of hydrated samples was determined in the wavenumber range of 4000 - 400 cm⁻¹ using JASCO FTIR-4600 spectrometer.

SEM-EDS analysis for hydrated samples were obtained by JEOL JSM-IT100 (Japan), in which the beam accelerating voltage and the working distance were 10 kV and 10 mm respectively, equipped with the gold sputter coating (JEOL Smart Coater, Japan).

Results and Discussion

XRD of CSC powder

Figure 1 shows XRD pattern of synthesized CSC. The corresponding peaks were indexed using ICDD database: #96-901-6126 assigned to alite, and #96-153-5812 assigned to belite. The indexing of the spectrum shows that the mixture consists of 70% of C₃S and 30% of C₂S.

Characterization of hydrated CSC

Isothermal calorimetry

Larger and intense peak associated with the dissolution of anhydrous CSC was noted for CSC-KOH during the first heat flux indicating additional heat release due to the ongoing ionic activity (Figure 2). Low reactivity and heat release around 2.5 mW/g is noted for CSC-W paste, while CSC-

NaOH and CSC-KOH pastes showed significant evolution: 6.0 mW/g and 7.3 mW/g, respectively. During the second peak, CSC-KOH released a heat flux greater than 1.2 mW/g after 90 min. For CSC-NaOH, a low heat release is observed. CSC-KOH displayed a significant change in reactivity compared to CSC-NaOH which can be assigned to the saturation of the interstitial solution with alkali ions. The prepared CSC contains a mixture of C₃S and C₂S phases with different proportions. These phases are known to react in different kinetics which makes it difficult to understand the influence of alkalis during 70 h.

XRD analysis

In figure 1, CSC powder hydrated with water showed the appearance of crystalline phases included clinotobermorite Ca₅(Si₆O₁₇).4(H₂O) (#96-900-2245) structurally linked to tobermorite 11 Å [8], calcite (#96-901-6706) and nekoite Ca₃(Si₆O₁₅).7H₂O (#96-900-0790). XRD pattern of CSC-NaOH shows the growth of hydrated products and the appearance of phase containing sodium called pectolite-1A NaCa₂Si₃O₈(OH) (#96-900-8135), also identified by [9-11], which is a stable crystalline phase C-(N)-S-H. Portlandite (#96-100-1788) was also noted. In the case of CSC-KOH, the appearance of new phase containing potassium, so-called

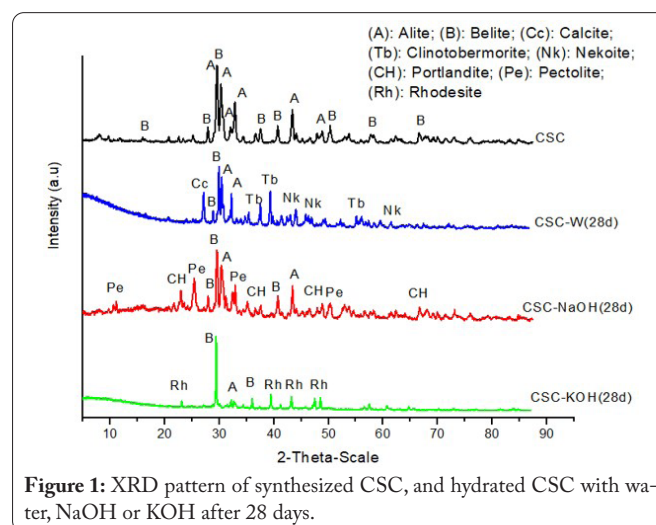


Figure 1: XRD pattern of synthesized CSC, and hydrated CSC with water, NaOH or KOH after 28 days.

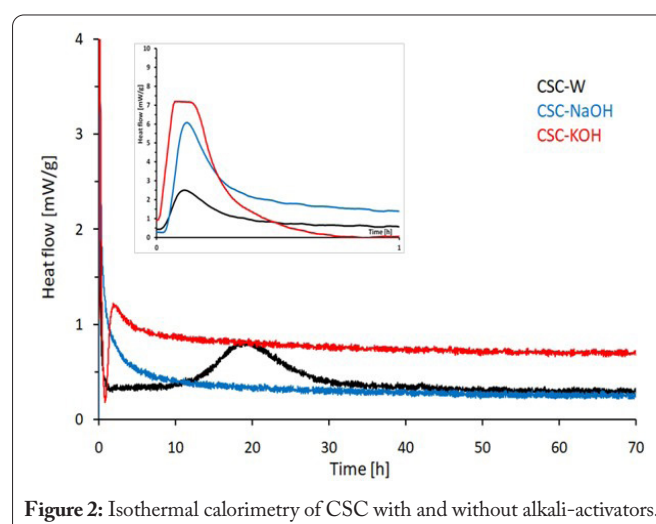


Figure 2: Isothermal calorimetry of CSC with and without alkali-activators.

Table 1: Representation of Bragg angle values as a function of identified phases.

| Bragg Angle (θ)t | 23°, 40° | 29° | 32° | 33° | 41° | 37° | 28° |
|---------------------------|-----------|--------|-------|-----------|---------|-------------|---------|
| Identified Phases | Rhodesite | Bélite | Alite | Pectolite | Nekoite | Portlandite | Calcite |

rhodesite $\text{KCa}_2(\text{Si}_8\text{O}_{18}(\text{OH}))\cdot 6\text{H}_2\text{O}$ (#96-900-8409) was detected, confirming the penetration of K^+ into C-S-H structure; C-(K)-S-H. It can be seen that the amount of alite and belite decreases, while the new phases appear. This is explained by the reaction established between the alkalis and CSC phases. Table 1 shows Bragg angle values as a function of identified phases.

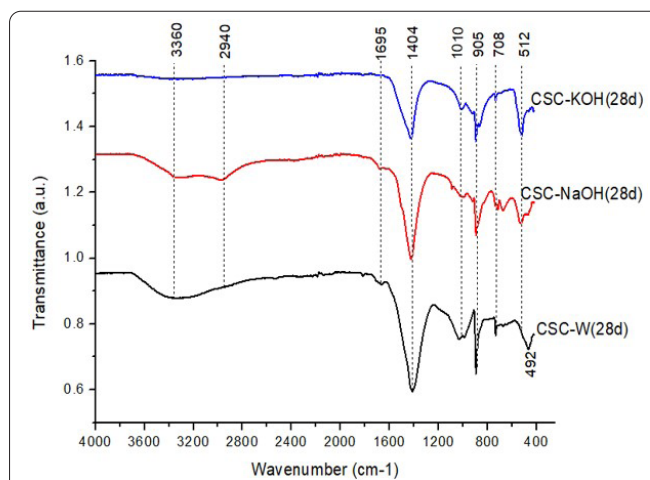
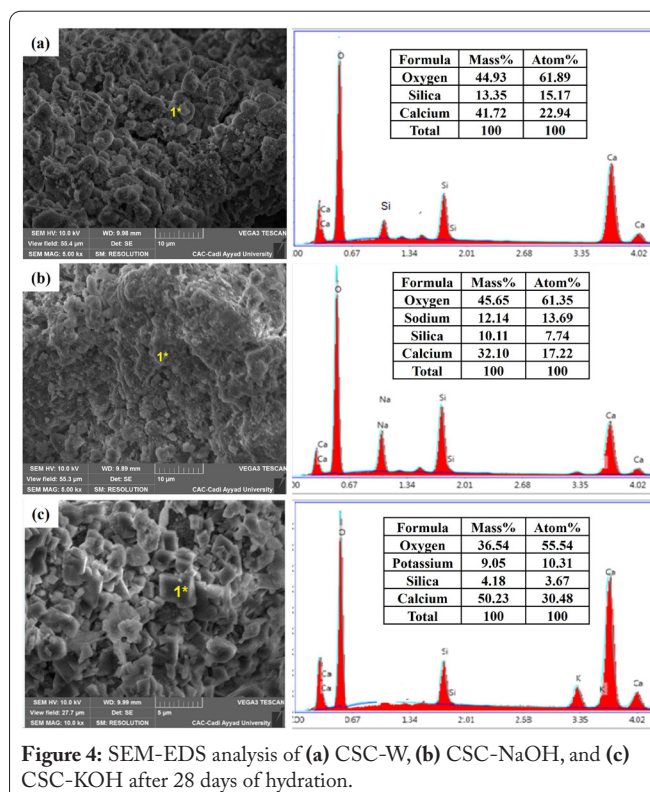
FTIR analysis

In figure 3, bands at 492 and 512 cm^{-1} are characteristics of the bending region of SiO_2 indicating presence of C_2S phase [12-15]. Signals corresponding to the band 708 cm^{-1} are characteristics of C-O stretching vibrations. The main vibrations of C_3S are attributed to the symmetrical stretching of silicate tetrahedra SiO_4^{4-} at 905 cm^{-1} [16]. Two bands around 1010 and 1404 cm^{-1} correspond to the vibration of Si-O-Si elongation. The 1695 cm^{-1} band appears for CSC-W and CSC-NaOH is characteristic of the stretching vibration C-O that can be attributed to portlandite and carbonates [17]. The bands 2940 and 3360 cm^{-1} appear in the case of CSC-W and CSC-NaOH are characteristics of the stretching vibrations generated by O-H bonds associated with water molecules adsorbed in the C-S-H gel [18].

SEM-EDS analysis

Figure 4 shows that CSC-W has a less compact microstructure with an open structure of C-S-H that appears as gel with a homogeneous phase of composition of calcium, silicon, and oxygen (Figure 4a). CSC-NaOH microstructure appears to be dense and homogeneous, while CSC-KOH showed more compact and uniform morphology. EDS analysis illustrates the presence of sodium and potassium with calcium, silicon, and oxygen, confirming their inclusions in the modified C-(N)-S-H (Figure 4b) and C-(K)-S-H (Figure 4c) phases in coexistence with C-S-H in CSC-NaOH and CSC-KOH samples, respectively.

In the case of CSC-W, the microstructure is described as having a less compact and open structure of C-S-H, appearing as a gel with a homogeneous phase of calcium, silicon, and oxygen (Figure 4a). For CSC-NaOH, the microstructure is characterized as dense and homogeneous; the accompanying EDS analysis confirms the presence of sodium and calcium, silicon, and oxygen, indicating the inclusion of these elements in the modified C-(N)-S-H phases (Figure 4b). Similarly, CSC-KOH is described as having a more compact and uniform morphology, consistent with the expected characteristics of this sample. The EDS analysis in this case confirms the presence of potassium, calcium, silicon, and oxygen, indicating their inclusion in the modified C-(K)-S-H phase (Figure 4c) alongside the presence of C-S-H. Overall, the statement suggests that the observations made in figure 4 align with the anticipated morphology and composition of the different phases and compounds being analyzed.

**Figure 3:** FTIR spectra of hydrated samples after 28 days.**Figure 4:** SEM-EDS analysis of (a) CSC-W, (b) CSC-NaOH, and (c) CSC-KOH after 28 days of hydration.

Conclusion

CSC was successfully synthesized by solid-state reaction. The mineralogical composition showed the presence of alite (70%) and belite (30%) in CSC. The hydration kinetics of CSC with NaOH or KOH (5 M), in comparison with water, demonstrated higher hydraulic reactivity of KOH solution due to the saturation of the interstitial solution with alkali ions. After 28 days of curing, XRD and FTIR illustrated the presence of portlandite and calcite in CSC-W and CSC-NaOH. On the other hand, hydration in the presence of NaOH with CSC

stimulates the precipitation of C-(N)-S-H phase, in which Na^+ replaces Ca^+ in the structure. Hydration in the presence of KOH stimulates the precipitation of C-(K)-S-H phase. These findings were confirmed by SEM-EDS analysis; hence it showed the presence of sodium or potassium with calcium, silicon, and oxygen, confirming their inclusions in the modified C-(N)-S-H and C-(K)-S-H in coexistence with C-S-H gel. These results aimed at clarifying a suitable contribution for the chemical activation of CSC phases to form additional phases with adequate hydraulic and mechanical performances.

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Conflict of Interest

None.

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