



# Microstructural evolution of aluminum hydroxide gel during the hydration of calcium sulfoaluminate under different alkali concentrations

Yangyang Zhang, Jun Chang\*

School of Civil Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

## HIGHLIGHTS

- Crystallinity of AH<sub>3</sub> phase improved with an increase of alkali concentration.
- AH<sub>3</sub> phase had a nanocrystalline structure in low alkaline conditions.
- AH<sub>3</sub> phase presented a well-crystalline nature in high alkaline conditions.
- AH<sub>3</sub> phase can react with OH<sup>-</sup> ion and even disappear in high alkaline conditions.

## ARTICLE INFO

### Article history:

Received 19 February 2018

Received in revised form 31 May 2018

Accepted 1 June 2018

### Keywords:

Aluminum hydroxide

Calcium sulfoaluminate cement

Alkali

Microstructure

## ABSTRACT

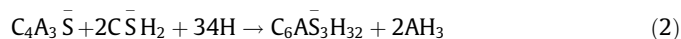
The present paper discusses the microstructural evolution of aluminum hydroxide (AH<sub>3</sub>) formed during the hydration of calcium sulfoaluminate in neutral and alkaline solutions (0-M NaOH, 0.01-M NaOH, 0.1-M NaOH, 1-M NaOH, 5-M NaOH and 8-M NaOH). Rietveld method and field emission scanning electron microscopy measurements were used to observe the evolution of crystallite size and particle size distribution, respectively. Furthermore, various characterization methods were used to complement the microstructure of AH<sub>3</sub> phase. The result of <sup>27</sup>Al MAS-NMR spectroscopy indicated the absence of the amorphous AH<sub>3</sub> phase in all hydrated pastes. The degree of crystallinity, with respect to the AH<sub>3</sub> phase, improved with increasing alkali concentration. However, AH<sub>3</sub> phase can also react with OH<sup>-</sup> ion and even disappear in high alkaline conditions. In low alkaline conditions (i.e., 0-M NaOH, 0.01-M NaOH, 0.1-M NaOH), the AH<sub>3</sub> phase had a nanocrystalline structure with an average crystallite size of about 8–9 nm and particle size distribution ranging from 110 nm to 210 nm. In high alkaline conditions (i.e., 5-M NaOH and 8-M NaOH), the AH<sub>3</sub> phase presented a well-crystalline nature. The average crystallite size increased up to about 30–40 nm and the particle size distribution was mostly 800–1400 nm (5-M NaOH) or 1000–1500 nm (8-M NaOH).

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

During the hydration of calcium sulfoaluminate (CSA) cements, aluminum hydroxide (AH<sub>3</sub>) is an important hydration product and coexists with other crystalline phases, e.g., monosulfate phase (also known as AFm), ettringite phase (also known as AFt) and so on [1–3]. For instance, ye'elimite (C<sub>4</sub>A<sub>3</sub>S, calcium sulfoaluminate or Klein's salt), typically accounting for over 50 wt%, is a main mineral in CSA cements [3–5], and its hydration mechanism has been studied over the last several decades [2,6,7]. Cement chemical shorthand notation is used: C: CaO; A: Al<sub>2</sub>O<sub>3</sub>; S: SO<sub>3</sub>; and H: H<sub>2</sub>O. The

hydration mechanism of C<sub>4</sub>A<sub>3</sub>S strongly depends on the amount and the type of calcium sulfate, as different crystalline phases are formed with the amount of calcium sulfate [8]. Without calcium sulfate supply, C<sub>4</sub>A<sub>3</sub>S reacts with water to form AFm phase and AH<sub>3</sub> phase according to reaction (1). With sufficient calcium sulfate supply, the reaction instead leads to the formation of AFt phase and AH<sub>3</sub> phase per reaction (2). Additionally, in the case of sufficient belite (C<sub>2</sub>S) supply, such as in belite-calcium sulfoaluminate cement, the AH<sub>3</sub> phase would be consumed and strätlingite (C<sub>2</sub>ASH<sub>8</sub>) formed, as seen in reaction (3).



\* Corresponding author.

E-mail address: [mlchang@dlut.edu.cn](mailto:mlchang@dlut.edu.cn) (J. Chang).



CSA cements are receiving an increase in attention as a low- $\text{CO}_2$  alternative to Portland cements. CSA cements, also known as the “third cement series”, exhibit a number of advantages, e.g., a smaller limestone requirement, lower sintering temperature requirement, easier grinding, rapid hardening, high early strength, good sulfate and chloride corrosion resistance, etc [9–12]. CSA cements have been widely used in Europe, the U.S. and China in many aspects, including hazardous waste encapsulation, leakage and seepage prevention projects, prefabricated concrete, waterproof layers, concrete in bridges and pipes, concrete in seawater, low temperature construction, etc [9,13,14]. However, the relation between macro-properties and microstructure of the hydrated products is still not fully understood. The chemical nature of the  $\text{AH}_3$  gel needs to be further studied.

The  $\text{AH}_3$  phase formed during the hydration of CSA cements exhibits the broad, multiple but weak XRD peaks although it was located at the same position as the reflections of gibbsite crystal structure [11,15,16]. Similar results have also been found for the hydration of calcium aluminate cements or other minerals [17–20]. However, previous research on CSA-cement based materials mainly studied the  $\text{AH}_3$  phase as an accessory and crystallography studies of the  $\text{AH}_3$  phase are still limited. Many studies have focused on the influence of pH on the type and microstructure of aluminum hydroxide polymorph. Du et al. [21], for instance, have found that amorphous aluminum hydroxide, boehmite ( $\text{AlOOH}$ ), and bayerite were present at pH = 5–6, 7, 8–11, respectively. However, other findings observed the formation of boehmite at pH = 8–10 [22,23]. Although there are some differences in their studies, it is now generally accepted that with increasing the pH of the liquid phase, aluminum hydroxide exhibits various types of polymorph, i.e., from amorphous structure to crystalline structure, and from  $\text{AlOOH}$  crystal to  $\text{Al}(\text{OH})_3$  crystal [21–23]. And all the existing evidences indicate the formation of  $\text{Al}(\text{OH})_3$  crystal prepared by chemical precipitation as the pH value is >11 [21,22]. However, broadening seen in the XRD patterns of  $\text{AH}_3$  phase is found although the pore solution in CSA cement pastes exhibits a higher pH, about 12–13 [24,25]. Thus, it is interesting to study the microstructure evolution of  $\text{AH}_3$  phase under different alkali concentrations within CSA cements, and the different pH is common when CSA cements are mixed with ordinary Portland cements [26–28].

Previous researches have focused on the influence of alkaline media on the hydration of CSA cements and calcium aluminate cements. Ogawa et al. [29], for instance, have observed that the hydration of  $\text{C}_4\text{A}_3\text{S}-\text{CSH}_2-\text{H}_2\text{O}$  system was accelerated in the 0.05-M and 0.2-M NaOH solution. Similar results are also observed in Winnefeld et al.'s calorimetric study of synthetic  $\text{C}_4\text{A}_3\text{S}$  hydration in the 0.01-M and 0.1-M KOH solution [30]. In a recent paper, Sánchez-Herrero et al. investigated the hydration of  $\text{C}_4\text{A}_3\text{S}$  in the 8-M NaOH solution. They found that high pH favors the conversion processes of hydration productions, forming hydrogarnet, thenardite and nordstrandite precipitation in the hydrated pastes. However, Chatterji et al. observed that the addition of NaOH would retard the hydration of  $\text{C}_3\text{A}$  somewhat, especially at early age [31]. Fernández-Jiménez et al. likewise observed that the presence of alkaline media can retard the initial strength development [32]. More generally, data regarding the influence of alkaline media on the microstructure of  $\text{AH}_3$  formed during the hydration of CSA cements are very limited.

Many researchers have observed that the crystallinity, morphology or crystallite size have an important effect on the cement properties such as compression strength. Generally, the interlocking of fibrillar, needle-like or prismatic crystals probably could make an important contribution to the strength of CSA cement

pastes [33]. Hargis et al., for instance, have observed that the assembly of stellate ettringite crystals would contribute to the mechanical strength of hydrated  $\text{C}_4\text{A}_3\text{S}$  pastes due to the interlocking of adjacent stellate clusters [34]. However, previous studies confirmed that the cement pastes that contain more aluminum hydroxide would have higher indentation modulus, hardness and compression strength than that contain more ettringite [35,36]. Additionally, poorly crystalline or microcrystalline  $\text{AH}_3$  phase, which like C–S–H gel, may make an important contribution to the strength of CSA systems, but  $\text{AH}_3$  phase with larger crystallite size could form a bigger fraction of porosity leading to a lower mechanical performance. As mentioned before, the pH has an important influence on the microstructure of aluminum hydroxide, thus it would be interesting to study the influence of alkaline media on the microstructure of  $\text{AH}_3$  formed during the hydration of CSA cements, which is a favorable step to better evaluate and explain the mechanical performances of CSA cements.

The present study aims primarily to explore microstructural evolution of  $\text{AH}_3$  formed during the hydration of  $\text{C}_4\text{A}_3\text{S}$  under different alkali concentrations. The microstructure of the  $\text{AH}_3$  phase was fully characterized by X-ray diffraction (XRD) utilising the Rietveld method,  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance ( $^{27}\text{Al}$  MAS-NMR), inductively coupled plasma optical emission spectroscopy (ICP-OES), thermogravimetry and derivative thermogravimetry (TG-DTG), and field emission scanning electron microscopy (FE-SEM) analyses.

## 2. Materials and methods

### 2.1. Preparation of hydrated samples

To evaluate the effect of alkali on the microstructure of  $\text{AH}_3$ ,  $\text{C}_4\text{A}_3\text{S}$  was synthesized by homogenizing suitable amounts of dried analytically pure reagents: 40.43 wt%  $\text{CaCO}_3$ , 18.33 wt%  $\text{CaSO}_4$  and 41.24 wt%  $\text{Al}_2\text{O}_3$  (99.0% from Sinopharm Chemical Reagent Co., Ltd, China). The mixture was ground in a planetary mill during 10 min with reverse rotation. The resulting powder was heated at 1300 °C for 4 h, hereafter ground to pass a sieve with an 80- $\mu\text{m}$  mesh. The values of  $d_{10}$  (i.e., 10% of the particles has a diameter below this criterion, similarly hereinafter),  $d_{50}$  and  $d_{90}$ , i.e., the particle size distribution, were 4.9  $\mu\text{m}$ , 14.8  $\mu\text{m}$  and 35.3  $\mu\text{m}$ , respectively, measuring by a laser diffraction particle size analyzer. Rietveld refinement of the XRD patterns for the clinkers, performed using TOPAS 4.2 software, showed that the synthetic  $\text{C}_4\text{A}_3\text{S}$  was 96.9 wt% pure, and other phases, i.e.,  $\text{C}_{12}\text{A}_7$  and  $\text{CaO}$ , were 2.0 wt% and 1.1 wt%, respectively.

Hydrated pastes were prepared using a liquid-to-solid (L/S) ratio of 1.0.  $\text{C}_4\text{A}_3\text{S}$  powder hydrated under different alkali solutions (0-M NaOH (i.e., deionized water, hereafter H) solution, 0.01-M NaOH (N0.01) solution, 0.1-M NaOH (N0.1) solution, 1-M NaOH (N1) solution, 5-M NaOH (N5) solution and 8-M NaOH (N8) solution). Solutions 0.01 and 0.1 M could be used to simulate basic condition of an ordinary Portland cement with which CSA cements are often mixed [26–28]. Solutions 5 and 8 M are also necessary to use for this study. Firstly, such higher pH not only has the ability to significantly modify the hydration of  $\text{C}_4\text{A}_3\text{S}$ , but also approach to the alkalinity that is appropriate to activate the hydration of hybrid cements [25]. Additionally, the  $\text{AH}_3$  phase was activated and presented a well-crystalline nature when such higher pH (i.e., solutions 5 and 8 M) was used in this work. The pastes were mixed for 2 min using a laboratory mixer and stored in sealed polythene bags at  $20 \pm 1$  °C and then one paste specimen was ground to pass an 80  $\mu\text{m}$ -mesh sieve at different curing ages (1 d, 28 d). The obtained powders were stirred with a larger volume of absolute

Download English Version:

<https://daneshyari.com/en/article/6712692>

Download Persian Version:

<https://daneshyari.com/article/6712692>

[Daneshyari.com](https://daneshyari.com)