



# AH<sub>3</sub> phase in the hydration product system of AFt-AFm-AH<sub>3</sub> in calcium sulfoaluminate cements: A microstructural study

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## HIGHLIGHTS

- Microstructure of AH<sub>3</sub> phase in both of the AFm-AH<sub>3</sub> and AFt-AH<sub>3</sub> systems was thoroughly characterized.
- AH<sub>3</sub>-H phase in both of the AFm-AH<sub>3</sub> and AFt-AH<sub>3</sub> systems has a microcrystalline or nanocrystalline structure.
- Average crystal size of the AH<sub>3</sub>-H phase in AFt-AH<sub>3</sub> system is close to 20 nm.
- Ion activity product of the AH<sub>3</sub>-H phase in the AFm-AH<sub>3</sub> system is smaller than that in AFt-AH<sub>3</sub> system.

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## ABSTRACT

In calcium sulfoaluminate cements, two hydration product systems, namely the monosulfate (AFm) – aluminum hydroxide (AH<sub>3</sub>) system and the ettringite (AFt) – AH<sub>3</sub> system, were created based on the reactions of ye'elimite with and without gypsum. From chemically synthesized samples, the composition and microstructure of the AH<sub>3</sub> phase in the hydration product system AFt-AFm-AH<sub>3</sub> were characterized using X-ray diffraction, Rietveld method, thermogravimetric analysis, <sup>27</sup>Al magic angle spinning nuclear magnetic resonance spectroscopy, field emission scanning electron microscopy, and inductively coupled plasma optical emission spectroscopy. It was seen that AH<sub>3</sub> phase in both AFm-AH<sub>3</sub> system and AFt-AH<sub>3</sub> system had a gibbsite-like structure presented in a microcrystalline or nanocrystalline structure, while the AH<sub>3</sub> phase in the AFt-AH<sub>3</sub> system had an average crystallite size close to 20 nm.

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## 1. Introduction

Calcium sulfoaluminate (CSA) cements, a low CO<sub>2</sub> potential alternative to ordinary Portland cements, are obtaining increasing interest from both researchers and industry [1]. A wide range of CSA cements, known as the “third cement series”, were developed in the Chinese market in the 1970 s [2]. CSA cements have found wide application in China as a binder because of their unique advantages, e.g., in leakage and seepage prevention projects, pre-fabricated concrete, reinforced concrete, concrete in bridges and pipes, concrete in seawater, etc. [2–6]. CSA cements require less limestone and a lower maximum clinkering temperature (about 1250 °C) to manufacture, and the CSA clinkers are more friable than ordinary Portland cement clinkers. Thus, CSA cements have

significant manufacturing cost reduction relative to ordinary Portland cements [7–9]. In addition to these advantages, CSA cements have other valuable properties, including rapid hardening and strength development, high early strength, and good chloride corrosion resistance [10,11].

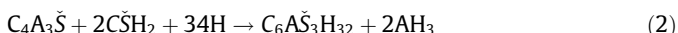
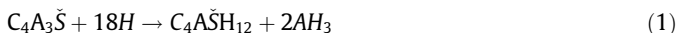
The valuable properties of CSA cements have a close relation with its major phase, ye'elimite (C<sub>4</sub>A<sub>3</sub>Š, calcium sulfoaluminate or Klein's salt), which typically accounts for over 50 wt%. Cement chemistry notation will be used hereafter: C: CaO; A: Al<sub>2</sub>O<sub>3</sub>; F: Fe<sub>2</sub>O<sub>3</sub>; Š: SO<sub>3</sub>; and H: H<sub>2</sub>O. In the crystallographic studies of Cuesta et al. and Glasser et al., it was shown that stoichiometric C<sub>4</sub>A<sub>3</sub>Š is orthorhombic at room temperature and that cubic C<sub>4</sub>A<sub>3</sub>Š can be preserved by incorporation of iron and sodium [12–14]. The hydration of C<sub>4</sub>A<sub>3</sub>Š is mainly affected by the amount and the reactivity of calcium sulfate [10,15–17]. Previous studies have also shown that the contents of the calcium sulfate supply have an influence on the hydration rate and the properties of hardened CSA cements. Low contents of calcium sulfate exert an accelerating effect on the

Abbreviations: AH<sub>3</sub>-C, AH<sub>3</sub> phase synthesized by chemical method; AH<sub>3</sub>-H, AH<sub>3</sub> phase during the hydration of C<sub>4</sub>A<sub>3</sub>Š; C, CaO; A, Al<sub>2</sub>O<sub>3</sub>; F, Fe<sub>2</sub>O<sub>3</sub>; Š, SO<sub>3</sub>; H, H<sub>2</sub>O.

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development of strength and also tend to cause high mechanical strengths at later ages [18]. High contents of calcium sulfate cause an increase in the hydration rate at early ages, which is useful in the manufacturing of rapid-hardening materials [19,20]. Changes in the macro-properties are related to the microstructure of cement pastes and the distribution of the hydrated products in the system of  $C_4A_3\tilde{S}$ - $C\tilde{S}H_2$ - $H_2O$ . Without calcium sulfate,  $C_4A_3\tilde{S}$  can react rapidly with water to generate monosulfate phase (AFm) and aluminum hydroxide phase ( $AH_3$ ), as seen below in reaction (1) [17]. With sufficient calcium sulfate supply, the reaction instead forms the ettringite phase (Aft) and the  $AH_3$  phase per reaction (2) [17,21].



Consequently, the contents of AFm and Aft are sensitive to the amount of calcium sulfate supplied. In previous studies, the possible reaction range of  $C_4A_3\tilde{S}$  with  $C\tilde{S}H_2$  and  $H_2O$  was also established depending on theoretical calculations of several specific hydration equations, and it was also confirmed that the three hydration products, namely the AFm, Aft and  $AH_3$  phases, were the significant components in the system of  $C_4A_3\tilde{S}$ - $C\tilde{S}H_2$ - $H_2O$  [22]. The system  $C_4A_3\tilde{S}$ - $C\tilde{S}H_2$ - $H_2O$  thus corresponds to the hydration product system Aft-AFm- $AH_3$ . However, there have been few studies that explain strength development and microstructure of CSA cement pastes associated with the composition and structure of the hydrated products. Investigating the microstructure of the hydration products is a first step in understanding the strength development. In the hydration product system Aft-AFm- $AH_3$ , the microstructure of two main hydration products, namely Aft and AFm, have been reported in previous studies as follows.

$C_4A\tilde{S}H_{12}$ , also known as AFm-12 (12  $H_2O$  hydration state of monosulfate) or monosulfate, is the most common hydration state of AFm-type phases. Other hydration states, such as monocarboaluminate, hemicarboaluminate, hydroxy-AFm, strätlingite, and monosulfate (AFm-14 and AFm-10.5), are also found in AFm-type phases [23,24]. AFm-type phases are considered as a hydrated tetracalcium aluminate-ferrite compound having the general formula  $C_4(A,F)X_2 \cdot YH_2O$  where X is a singly charged anion (i.e.,  $OH^-$ ,  $Cl^-$ , or  $[AlSi(OH)_8]^-$ ) or half doubly charged anion (i.e.,  $SO_4^{2-}$  or  $CO_3^{2-}$ ), and is a member of the lamellar double hydroxide family [23,25]. Monosulfate is known to have a good  $Cl^-$  corrosion resistance due to the ionic exchange between  $SO_4^{2-}$  and  $Cl^-$  [26]. For this work, AFm-type phases refer only to the monosulfate AFm-12 and AFm-10.5 hydration states.

Similarly, Aft-type phases is a member of the hydrated calcium aluminate family and has the general formula  $[Ca_3(Al,Fe)(OH)_{6-12}H_2O]_2 \cdot X_3 \cdot yH_2O$  [23], where X is a doubly charged anion ( $SO_4^{2-}$  or  $CO_3^{2-}$ ).  $C_6A\tilde{S}_3H_{32}$ , known as Aft or ettringite, is the most common form of the Aft-type phases. Ettringite has a hexagonal crystal structure based on the observation of its columns and channels [23]. In the CSA cement matrix, the bonding and interlocking of adjacent ettringite crystals can contribute to the strength of paste at early ages [8]. Expansion is also connected to the formation of ettringite [27–29].

Although many reserachers have focused on AFm phase and Aft phase, a microstructural investigation of the  $AH_3$  phase in the hydration product system Aft-AFm- $AH_3$  is missing in literature. It is necessary to study the microstructure of the  $AH_3$  phase in this hydration product system since the  $AH_3$  phase is always present. In the hydration product system Aft-AFm- $AH_3$  there are two special hydration product systems, namely when  $AH_3$  phase forms in the presence of only AFm or Aft (i.e., AFm- $AH_3$  and Aft- $AH_3$  systems).

This work investigates the microstructure of the  $AH_3$  phase when it forms in both the special hydration product systems.

The  $AH_3$  phase, known widely as  $Al(OH)_3$ , has been applied in a variety of fields, such as antacid in medicine, inorganic additive for antflaming, flocculating agent for purifying water, etc. Amorphous aluminum hydroxide, aluminum monohydroxide (boehmite), and aluminum trihydroxides are the main forms of aluminum hydroxides with their formation being governed by the pH and temperature of the hydrolyzing powder suspension [30–32]. Gibbsite, nordstrandite, and bayerite are the three common polymorphs of aluminum trihydroxides. In the CSA cements, there are a limited number of studies on the microstructure of the  $AH_3$  phase, which is an important gel and similar to the calcium-silicate-hydrate (C-S-H) gel in some respects. The use of C-S-H gel contributes significantly to the strength of Portland cement. It has been reported that C-S-H gel has a solid density of around 2.6 g/cm<sup>3</sup> with average Ca/Si ratio of about 1.6–1.75, and is nanocrystalline with a length scale of more than 3 nm [33–37]. However, many previous studies mainly reported the  $AH_3$  phase as an accessory, especially in the CSA-cement based materials. Winnefeld et al., observing  $AH_3$  by backscattered electron images, reported that  $AH_3$  has a dark gray background in the backscattered electron images [5,16]. Song et al. used scanning electron microscopy (SEM) at relatively low magnifications and found that the structure of  $AH_3$  phase in belite-calcium sulfoaluminate cement contains small amounts of Ca due to trapped hydrogarnet within  $AH_3$  particles, and that the  $AH_3$  phase has a villous morphology and covers the surface of other particles forming a thin coating [38], which has also been found in  $C_4A_3\tilde{S}$ - $C\tilde{S}H_2$ - $CH$ - $H_2O$  system [39]. In belite-calcium sulfoaluminate cement, the  $AH_3$  phase would be consumed and reacted with belite to form strätlingite ( $C_2ASH_8$ ) when the initial content of  $C_4A_3\tilde{S}$  is higher than twice that of belite, as seen in reaction (3) [19].



Considering the complexity of CSA-cement based materials, it is advisable to simplify the investigation to a relatively small numbers of hydration products. Since AFm, Aft and  $AH_3$  phase are the three most important hydration products in CSA cements, it would be useful to perform the microstructural characterization of the  $AH_3$  phase in the presence of only AFm or Aft.

This work is focused on the microstructure of  $AH_3$  phase in two different hydration product systems, the AFm- $AH_3$  system and the Aft- $AH_3$  system, which are created according to reactions (1) and (2) by hydrating  $C_4A_3\tilde{S}$  with and without gypsum. The resulting AFm- $AH_3$  and Aft- $AH_3$  systems were examined by X-ray diffraction (XRD) and thermogravimetry and derivative thermogravimetry (TG-DTG) measurements. To better characterize the  $AH_3$ -H phase, specifically the  $AH_3$  phase during the hydration of  $C_4A_3\tilde{S}$ , various aluminum hydroxides were chemically synthesized to compare with the  $AH_3$ -H phase of both the AFm- $AH_3$  and Aft- $AH_3$  systems. XRD qualitative analysis, the Rietveld method, and the internal standard method were employed for determining phase compositions. In addition to these techniques, TG-DTG, nuclear magnetic resonance (NMR), field emission scanning electron microscopy (FE-SEM), and inductively coupled plasma optical emission spectroscopy (ICP-OES) techniques have also been performed to provide a microstructural observation of the  $AH_3$  phase in the AFm- $AH_3$  and Aft- $AH_3$  systems.

## 2. Materials and methods

### 2.1. Preparation of aluminum hydroxides

Samples of the  $AH_3$ -C phase ( $AH_3$  phase synthesized by chemical method) with different pH levels were synthesized by

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