



# Effect of sulfur on the ion concentration of pore solution and the hydration of calcium aluminate cement



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## ABSTRACT

The ion concentration, PH value of pore solution and the hydration of two low iron calcium aluminate cements based on bauxite (BCACs) with different sulfur content were investigated by XRD, ICP-OES, PH meter and SEM. The results indicate that the sulfur in the bauxite and coal results in the formation of ye'elimite ( $C_4A_3\bar{S}$ ) in BCAC. The more the sulfur content in BCAC the more the  $C_4A_3\bar{S}$  formed. The hydration of  $C_4A_3\bar{S}$  decreases the ion concentrations of Ca, Al and the PH values but increases the concentration of S. Hydration and hydrates of CA are influenced by the hydration of  $C_4A_3\bar{S}$  in BCAC.  $CAH_{10}$  is found in the hydration of both BCAC samples, but  $C_2AH_8$  is only found in the hydrates of the BCAC with lower  $SO_3$  content.

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## 1. Introduction

Calcium aluminate cement (CAC) has been widely used in the industries for several distinct advantages over Portland cement, including higher refractoriness, rapid strength gain upon setting, enhanced resistance to abrasion, sulfate attack and alkali-silica reaction [1–3]. Setting and hardening of CAC is primarily due to the hydration of monocalcium aluminate (CA, cement notation:  $C[CaO]$ ,  $A[Al_2O_3]$ ,  $H[H_2O]$ ,  $\bar{S}[SO_3]$ ), but other compounds also participate in the hardening process, especially in long term strength development [4,5]. The hydration of CAC is dependent on curing temperature and time. It was found that  $CAH_{10}$  was the only product at 5 °C after curing for 3 days, but  $CAH_{10}$  and  $C_2AH_8$  were formed at the curing temperature of 20 °C,  $C_3AH_6$  and  $AH_3$  were formed at the curing temperature of 40 °C [6]. Both  $C_4AH_{13}$  and  $C_3AH_6$  were present after curing at 20 °C for 28 days while  $C_3AH_6$  and  $AH_3$  appeared after curing at 5 °C for 120 days [7]. The hydration of CAC can also be significantly affected by the additives, such as, citric acid,  $Li_2CO_3$  and  $Na_2CO_3$ . The formation of  $LiAl(OH)_4$  and  $NaAl(OH)_4$  withdrew  $Al(OH)_4^-$  ion from the ion solution, resulting in the increase of  $Ca^{2+}$  concentration which induced the formation of less soluble hydrate and accelerated the precipitation stage [8,9].

Calcium aluminate cement based on bauxite (BCAC) containing 50%  $Al_2O_3$  is produced using bauxite as raw material and coal as fuel. It has higher production and lower cost than CAC containing about 70%  $Al_2O_3$ , using alumina as raw material. However, some impurities are brought into BCAC from bauxite and coal, especially the sulfur, which leads to the formation of ye'elimite in the clinkers of BCAC. Ye'elimite is the key-component of sulfoaluminate cement (CSA), and much attention has been paid to the hydration of ye'elimite. It was reported that the hydrates of ye'elimite were a mixture of monosulphate (AFm) and ettringite (Aft) when it was cured at 20 °C for 2 and 7 days with W/C of 0.58 and 1.16 [10]. Only AFm was found in the hydrates when ye'elimite was cured at 21 °C and 95% Relative Humidity (R.H.) with W/C = 0.4 for 2 days [11]. Aft was also found when it was cured at same temperature and 100% R.H. with W/C = 0.5 in  $CO_2$ -free atmosphere for 2 days [12]. Hydrates of a 100% CSA clinker were AFm and  $AH_3$  when it was placed in polyethylene bags inside a thermostatic bath at 20 °C for 1–7 days in the absence of both lime and calcium sulfate [13]. Aft was formed in hydration of a commercial CSA cement (the main mineral was ye'elimite, the minor phases were belite, anhydrite, calcium aluminate, gypsum and calcite) at 20 °C with W/C = 0.4–0.5 for 24 h, and then part of Aft transformed to AFm due to lack of gypsum [14]. Portland cement with high  $SO_3$  and fineness had a potential to produce Aft when the mortar was heat cured in long term [15]. When Portland cement mortars were exposed to  $SO_2$ , under dry condition, more soluble salts ( $SO_3$  and  $K_2SO_4$ ) were formed on the surface of it. On the other hand, under

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wet conditions, less soluble salts (syngenite and gypsum) were noted on analysis [16].

A lot of studies of hydration of ye'elimite have been done. However, the effect of the hydration of ye'elimite on the hydration of CA is not studied enough. Although the sulfur content of BCAC is much less than that of commercial CSA, the influence of sulfur on hydration of BCAC is considerable because the hydration of ye'elimite changes the ion concentrations of pore solution. It is interesting to study the effect of the sulfur on the ion concentration of pore solution and the hydration of BCAC.

## 2. Experimental procedures

### 2.1. Materials

Two samples of calcium aluminate cement with different  $\text{SO}_3$  content were taken from Kerneos, China (Jianai A600). One containing 0.27%  $\text{SO}_3$  is denoted as BCAC H; the other containing 0.01%  $\text{SO}_3$  is denoted as BCAC L. Their chemical compositions obtained by X-ray fluorescence analysis (XRF, Spectrometer S4-Pioneer, Rh radiation, Bruker AXS, Germany) are listed in Table 1. The finenesses of the two BCAC samples are given in Table 2. They were obtained by a negative pressure sieve analyzer (FSY-150D, Shaoxing Xinxingsheng Apparatus Co., Ltd., China), a specific surface area analyzer (SZB-9, Hebei Kexi Instrument Co., Ltd., China) with blaine method and a laser particle analyzer (LS608, Zhuhai OMEC Instrument Co., Ltd., China). It is indicated that the compositions and finenesses of the two BCAC samples are closed except the content of  $\text{SO}_3$ .

The XRD patterns of the two BCAC samples obtained by X'Pert Pro, Philips, Netherland with Cu K $\alpha$  Radiation ( $\lambda = 1.5425 \text{ \AA}$ , 40 mA, 40 mV and scanning step = 0.03) are shown in Fig. 1. Phase compositions obtained by semi-quantity calculation based on crystallographic parameter (RIR) of XRD patterns are given in Table 3. It is found that the sulfur from bauxite and coal results in the formation of ye'elimite ( $\text{C}_4\text{A}_3\text{S}$ ) in the two BCAC samples. The ye'elimite ( $\text{C}_4\text{A}_3\text{S}$ ) content in BCAC H is considerably more than that in BCAC L. At the same time, the content of (CA +  $\text{CA}_2$ ) in the BCAC H is a little less than that of BCAC L.

### 2.2. Preparation of samples for investigation

In order to investigate the influence of the sulfur on the hydrates, two paste samples were prepared by mixing the two BCAC samples with distilled water in a W/C ratio of 0.6. The obtained pastes were casted into the molds (diameter = 15 mm, height = 10 mm) with vibration (amplitude = 0.75 mm, frequency = 47–50 Hz) in a room with R.H. about 90% at  $20 \pm 1^\circ\text{C}$ . After curing for 24 h, the samples were de-molded and cured in air at the same condition (R.H. = 90%,  $20^\circ\text{C}$ ) for 1 and 3 days. The samples were denoted as Paste H and Paste L, respectively.

In order to study the influence of the sulfur on the crystallization of hydrates from the pore solutions, two paste samples were also prepared by mixing the two BCAC samples with distilled water in a W/C ratio of 0.6 for 5 min. The samples of the pore solutions were prepared by centrifugation and filter. The paste samples were centrifugated to remove bigger particles, and then were filtered to obtain clean pore solutions for crystallization investigation. The

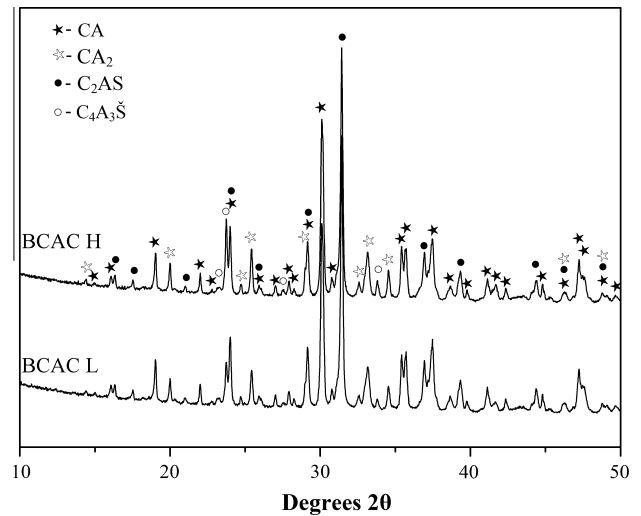
**Table 2**

Finenesses of the two BCAC samples.

	>45 $\mu\text{m}$ (%) <sup>a</sup>	Blaine ( $\text{cm}^2/\text{g}$ )	D10 ( $\mu\text{m}$ ) <sup>b</sup>	D50 ( $\mu\text{m}$ ) <sup>b</sup>	D90 ( $\mu\text{m}$ ) <sup>b</sup>
BCAC L	9.3	3750	2.64	17.1	44.63
BCAC H	8.5	3290	3.09	19.08	45.00

<sup>a</sup> With negative pressure sieving method.

<sup>b</sup> With a laser particle analyzer.



**Fig. 1.** XRD patterns of the two BCAC samples.

**Table 3**

Phase Compositions of the two BCAC samples (wt%).

	CA	$\text{CA}_2$	$\text{C}_2\text{AS}$	$\text{C}_4\text{A}_3\text{S}$
BCAC L	72	11	8	8
BCAC H	67	12	8	12

crystallization of the two pore solutions were cured in a room (air, R.H. = 90%,  $20^\circ\text{C}$ ) for 3 and 5 days respectively. After crystallization for 3 days, some compounds crystallized from the pore solutions. After 5 days, crystals existed but liquid disappeared. The water may be consumed by hydration and evaporation. These crystalline substances from the two pore solutions are denoted as Crys H and Crys L, respectively. The particles obtained by centrifugation from the two paste samples were also cured in the same condition for 3 days, and denoted as Particle H and Particle L, respectively.

The paste samples, the crystalline samples and particle samples separated from the pore solutions by centrifugation were immersed in acetone (Chemical Pure) for 6 h to withdraw free water in order to stop hydration [9,12,17] of these after cured. A fraction of the pastes and particles was milled in an agate mortar and then dried at  $25^\circ\text{C}$  for 24 h for XRD analyzing. All solid samples were stored in a closed desiccator (without vacuum application) to avoid further hydration and/or carbonation.

In order to measure conveniently the ion concentration and the PH value, two suspensions of BCAC with a higher W/C ratio of 10

**Table 1**

Chemical compositions of the two BCAC samples (wt%).

	LOI	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{TiO}_2$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{SO}_3$
BCAC L	0.23	7.68	50.87	2.07	34.94	0.70	2.54	0.42	0.07	0.01
BCAC H	0.32	7.18	50.71	2.27	34.16	0.99	2.50	0.47	0.07	0.27

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