Effect of Aluminum Sulfate on the Hydration of Tricalcium Aluminate

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Abstract: Aluminum sulfate (AS), as the main composition of alkali-free accelerator, was widely used to accelerate the setting and promote the early strength in the sprayed concrete. In this study, effect of AS on the hydration reaction of C3A was investigated, which is one of the most important cement clinker minerals in the early age of cement hydration. The hydration reaction and products of C3A-AS system were characterized with hydration heat test, X-ray diffraction, thermogravimetric analysis, scanning electron microscope, and thermodynamic modeling. Results indicate that AS could hinder the hydration reaction in the very early age but then accelerate C3A hydration by producing SO4-AFm, OH-AFm, and gibbsite. The findings are expected to provide theoretical guidance for the product research and engineering application of alkali-free accelerator.

Keywords: Aluminum sulfate, C3A, Portland cement, alkali-free accelerator.

1. Introduction

Sprayed concrete is a common construction material used in the construction process of mines and tunnels to ensure the construction safety by strengthening the surface structure. Accelerator is a chemical admixture added into sprayed concrete to obtain rapid setting and high early strength [1-3]. Among the various types of accelerators, the advantage of alkali-free accelerator is increasingly prominent, due to its excellent workability and strength performance and good environmental friendliness [4-6]. Aluminum sulfate (AS) is one of the main functional components in alkali-free accelerator. The released Al3+ and SO42- ions from AS can influence the cement hydration reaction process by facilitating the formation of ettringite (AFt) to reduce the setting time accelerate the hydration reaction [7]. However, the studies found that the effect of AS was dependent on the cement composition, indicating that the mechanism of AS affecting cement hydration was not completely revealed [8].

Tricalcium aluminate (C3A) is one of the most important minerals among the Portland cement clinker minerals. Due to the high reactivity and the rapid reaction rate in the early age, C3A largely determined the early performance of cement, which is important for the efficacy of accelerator. Accordingly, the hydration reaction of C3A-AS system greatly affected the early hydration of Portland cement-AS system [9]. It has been found that the addition of AS could significantly promote the C3A hydration [10]. The research of Paglia et al. on the alkali-free accelerator revealed that AS increased the amount of AFt in the early age to promote the C3A reaction.

This study researched the effect of AS on C3A hydration. The hydration heat test was conducted to reveal the early hydration reaction process. And microscopic measurements results, including XRD,
TGA, and SEM, examined the hydrates assemblage. The equilibrium phase assemblage was analyzed by the thermodynamic modelling.

2. Experimental

2.1. Materials

The AS (reagent-grade Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·18H\textsubscript{2}O) dosage referred to the solid content after deducting the content of crystal water.

C\textsubscript{3}A mineral used in this experiment was prepared by sintering process. The mixture of raw materials, including Ca(OH)\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, was pressed into plate. With the constant heat rate of 5 °C/min, 450 °C was kept for 2 h, then continued heating, and then kept 1320 °C for 3 h. The sintered C\textsubscript{3}A was ground, and then calcined twice to improve the purity. The XRD pattern of the prepared C\textsubscript{3}A is presented in figure 1.

![Figure 1. XRD patterns of C\textsubscript{3}A.](image)

2.2. Sample Preparation

After AS was dissolved, with the water/C\textsubscript{3}A particle ratio of 0.4, the fresh C\textsubscript{3}A paste was prepared. The dosages of AS were 0%, 3%, and 6%, respectively named as CA0AS, CA3AS, and CA6AS. The C\textsubscript{3}A-AS pastes were cured in the chamber with 20±2 °C and > 90% R.H. After cured for different ages, the broken samples were immersed in ethanol for 3 d. The sample pieces were dried in the oven and ground into powders for measurements.

2.3. Measurement

2.3.1. Hydration Heat. The isothermal calorimetry (TAM AIR, made by SETARAM company in France) was used with the air atmosphere. In this test, the mass of sample was 2 g with water/C\textsubscript{3}A ratio of 1:1.

2.3.2. XRD. X-ray diffractometer (XRD, D8 DISCOVER) was used in the experiment. The parameter was set to current of 40 kV and 40 mA and rate of 6°/min.

2.3.3. TGA. The comprehensive thermal analyzer (STA449F3, provided by NETZSCH in Germany) was used, with 10 °C/min heating rate from 50 °C to 1000 °C in the nitrogen atmosphere.

2.3.4. Thermodynamic Modeling. According to the composition of C\textsubscript{3}A-AS paste, thermodynamic modeling was established with the Gibbs free energy minimization software (GEMS).

3. Results and Discussion

3.1. Effect of AS on C\textsubscript{3}A Hydration

The addition of AS into C\textsubscript{3}A paste would influence the hydration reaction process and the hydration products. The hydration reaction would result in the release of the hydration heat, and the produced hydrates were mainly characterized by XRD, TGA, and SEM.
3.1.1. Hydration Heat. The hydration heat results can reflect the reaction extent, due to the fact that the hydration reaction was accompanied by the heat release during the hydration of C₃A. In the presence of AS, the early hydration heat of the C₃A paste (i.e., CA0AS, CA3AS, and CA6AS samples) was characterized, and the hydration exothermic peaks are shown in figure 2.

![Figure 2](image-url)

**Figure 2.** The hydration exothermic rates and hydration heats of AS-modified C₃A pastes (a): hydration exothermic rate, (b): hydration heat.

As revealed in figure 2(a), the exothermic peak appeared at 0.5 h in CA0AS sample, related to the rapid hydration rate of C₃A mineral. With 3% AS added, the exothermic peak came at about 1 h, later than the control sample. When the dosage of AS increased to 6%, the appearance of exothermic peak was postponed to 2 h. Accordingly, AS would obviously reduce the early hydration rate of the C₃A paste, and the effect would increase with the rise of AS dosage.

The released hydration heat was presented in figure 2(b). Compared to the control sample, the hydration heat of CA3AS sample was lower before about 1.5 h but higher after 1.5 h. Similarly, the same hydration heat released by the control sample and CA6AS sample came at near 3 h. Thereby, AS hindered the early reaction of C₃A, but then facilitated hydration reaction instead.

The hydration heat released in the three samples was listed in table 1. At 0.5 h age, the released hydration heat was 64.63 J/g in CA0AS, 12.44 J/g in CA3AS, and 1.52 J/g in CA6AS, implying the hindering effect of AS on C₃A reaction in the early age. But at 4 h, the released heat was 191.99 J/g in CA3AS sample, and 204.45 J/g in CA6AS sample, higher than 177.14 J/g in CA0AS sample, which revealed the acceleration effect of AS on C₃A reaction in the late age.

| Time (h) | CA0AS | CA3AS | CA6AS |
|----------|-------|-------|-------|
| 0.5      | 64.63 | 12.44 | 1.52  |
| 2        | 137.71| 137.01| 107.23|
| 4        | 177.14| 191.99| 204.45|
| 8        | 217.10| 244.56| 269.66|
| 16       | 257.09| 297.34| 311.89|

The hydration heat test results indicate that AS could promote C₃A reaction after the early hinderance on the hydration reaction, and the effects could be strengthened with the increase of AS dosage.

3.1.2. Phase Assemblage. According to the hydration heat result, the addition of AS could evidently influence the hydration reaction process, which could be attributed to the new reaction process and
produced hydrates in C₃A-AS system. In this part, the phase assemblages of CA0AS, CA3AS, and CA6AS samples, were characterized by XRD, TGA, and SEM.

The XRD patterns of samples added with different AS dosages are shown in figure 3.

![Figure 3](image.png)

**Figure 3.** XRD patterns of samples added with different AS dosages (CA0AS, CA3AS, and CA6AS samples) at different ages: (a) 5 min, (b) 0.5 h, (c) 2 h, (d) 4 h, (e) 24 h, (f) 28 d.

As revealed in figure 3(a), at the age of 5 min, the diffraction peak intensity of C₃A was higher in CA3AS and CA6AS sample in comparison with the control sample, attributed to the low hydration extent in the sample added with AS. On the contrary, the lower peak of C₃A in CA0AS could be observed, related to the formation of C₃AH₆ generated from the hydration process of C₃A. Thus AS hindered the hydration reaction of C₃A in the very early age.

At the age of 0.5 h in figure 3(b), SO₄-AFm and OH-AFm could be observed in CA3AS and CA6AS samples. It reveals that AS can affect and participate the hydration reaction of C₃A by generating new hydrates.

At the ages of 2 h and 4 h in figure 3(c) and figure 3(d), the reduction of peak intensity of C₃A was observed in the three samples, indicating the hydration degree increased with the curing age.

At the age of 24 h in figure 3(e), C₃AH₆ phase appeared in CA3AS sample. And the peak intensity of phases in CA0AS sample at 24 h had little change in comparison with that at 4 h, revealing that the hydration of C₃A in the control sample might be complete.

At 28 d age in figure 3(f), compared with the control sample, 3% AS could promote the hydration of C₃A and the formation of C₃AH₆. The peak intensity of C₃A sample added with 6% AS was reduced from 24 h to 28 d, ascribed to the continuous hydration.

TGA was conducted to verify the phase assemblage of C₃A-AS system, and the results are illustrated in figure 4. The weight loss peaks at about 300 °C and 430 °C were ascribed to the decomposition of C₃AH₆, and the peaks at the range of 30-220 °C resulted from the dehydroxylation of SO₄-AFm and OH-AFm [6].
TG curves at the age of 5 min in figure 4(a) indicate that the combined water mass in the control sample was the larger than samples added with AS. And the DTG curve shows that the hydrate in CA0AS sample was C₃AH₆. These findings confirm that the addition of AS into C₃A paste could hinder the early hydration reaction of C₃A mineral.

At the age from 0.5 h to 24 h, as revealed in figure 4(a)-(e), the main phase in CA0AS sample was C₃AH₆, while the weight loss peaks of C₃AH₆, SO₄-AFm, and OH-AFm, were found in CA6AS sample. Thereby AS participated in the C₃A reaction and generated new phases.

At 28 d in figure 4(f), it was found according to the weight loss in TG curves that the mass of the combined water in samples added with AS was larger than that in the control sample. The result demonstrates the promotion of AS on the C₃A reaction in the late age.

3.1.3. Microscopic Morphology. Figure 5 reveals the microscopic morphology of hydrates produced by the hydration reaction of C₃A in CA0AS and CA6AS samples at the age of 0.5 h, 24 h and 28 d.

At the age of 0.5 h, cubic crystals were formed in the control sample without AS in figure 5(a), which was C₃AH₆ according to the XRD and TGA results. However, the hydration products of C₃A in CA6AS sample added with 6% AS in figure 5(b) was mainly flake crystal, which was inferred as SO₄-AFm and OH-AFm phases according to XRD and TGA.

At the age of 24 h, the hydration products in the control sample in figure 5(c) were still cubic C₃AH₆ crystals, while the flake crystals connected by amorphous gel in CA6AS sample in figure 5(d).

At 28 d age, there were a large number of pores in the microstructure of the control sample in figure 5(e). However, the formation of flake crystals, cubic crystals and gels made the microstructure compact in CA6AS sample in figure 5(f).
Figure 5. The microscopic morphology of CA0AS and CA6AS samples hydrated for different ages: (a) CA0AS sample at 0.5 h, (b) CA6AS sample at 0.5 h, (c) CA0AS sample at 24 h, (d) CA6AS sample at 24 h, (e) CA0AS sample at 28 d, (f) CA6AS sample at 28 d.

3.2. Mechanism

The thermodynamic modelling was conducted for the hydration reaction of C₃A-AS system, and the results are plotted in figure 6. The predicted results indicate that C₃AH₆ was the only stable product in the hardened pure C₃A paste. When the AS dosage increased from 0% to 6%, SO₄-AFm, OH-AFm and gibbsite were produced but C₃AH₆ was reduced. The reaction of C₃A-AS system can be ascribed to equations (1-2).

The effect of AS on C₃A reaction could be divided into two parts: a) AS accelerated C₃A reaction after the hinderance in the very early age; b) AS promoted the generation of SO₄-AFm, OH-AFm and gibbsite but decreased C₃AH₆.
The hinderance effect of AS on the early hydration was dependent on the reaction in equation (2), which might be attributed to the reason that the surface of C₃A particles were covered by generated flake hydrates which reduced reaction rate by hindering the water transport and the ions dissolution process.

\[
2(3\text{CaO} \cdot \text{Al}_2\text{O}_3) + 12\text{H}_2\text{O} \rightarrow 2\text{C}_3\text{AH}_6 \quad (1)
\]

\[
8(3\text{CaO} \cdot \text{Al}_2\text{O}_3) + \text{Al}_2\text{SO}_4 + 46\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca(OH)}_2 \cdot 12\text{H}_2\text{O} + 14 \text{Al} \cdot (\text{OH})_3 \quad (2)
\]

**Figure 6.** Thermodynamic modeling of C₃A-AS system (Gibbsite: Al(OH)₃, OH-AFm: C₄AH₁₃, SO₄-AFm: calcium monosulfoaluminate (3CaO·Al₂O₃·CaSO₄·12H₂O)).

4. Conclusion
The hydration reaction of C₃A could be influenced by the addition of AS, due to the participation of AS in the hydration process. And the effect could be strengthened with the increase of AS dosage. AS could accelerate C₃A reaction after the early hinderance. The C₃A-AS system mainly generated hydrates including SO₄-AFm, OH-AFm, and gibbsite.

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