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Influence of Aluminum Sulfate on Hydration and Properties of Cement Pastes

Chao Chen¹ and Zhenping Sun²*

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Abstract

This study evaluates the influence of aluminum sulfate (AS) on hydration and properties of cement pastes. The hydration behavior of cement paste contributed by AS was identified via isothermal calorimetry, X-ray diffraction (XRD), scanning electron microscope (SEM) and helium pycnometry. Setting time, compressive strength and pore structure of accelerated cement paste were also evaluated. Results indicate that the addition of AS can reduce setting time significantly and increase compressive strength of cement paste. Moreover, hydration process of accelerated cement paste can be divided into four stages according to absolute volume change measured by helium pycnometry, which are dissolution-crystallization stage, induction stage, rapid shrinkage stage and structure compacting stage. More nano-scale pores (pore diameter smaller than 10 nm) are generated in structure compacting stage, resulting in the “fake” absolute volume expansion. The rebound rate of shotcrete can be reduced with the increase of AS.

1. Introduction

Sprayed concrete is a kind of construction material which can form integral structure with proper thickness, with both sufficient rigidity and strength in a short time. Therefore, it has been widely used in engineering cases which require fast setting and rapid hardening, such as shotcrete preparation for underground mining, tunnel construction, as well as emergency repairing works and so on (Galobardes 2013; Galobardes et al. 2016; Aggoun et al. 2008; Maltese et al. 2007a, 2007b)

The advantages of sprayed concrete can be mainly attributed to the corporation of set accelerators, which can decrease setting time and increase early strength. Accelerators can be divided into alkaline accelerators and alkali-free accelerators. Although alkaline accelerators have the advantage of more general range of application and smaller cost (Salvador et al. 2016), it can impair later age compressive strength (Han et al. 2014). Moreover, it could pose a threat to workers’ health. Therefore, it was forbidden in most western countries. Alkali-free accelerators, of which the most effective accelerating component is aluminum sulfate (AS, to be abbreviated as AS in this paper) has been widely used in engineering cases in recent years due to its good performance.

Substantial work has been conducted in the field of accelerated cement paste, which revealed AS can alter hydration mechanism and microstructure development of cement paste, thus resulting in changes in setting behavior, strength development and concrete properties (Wang et al. 2015). Salvador et al. (2016) discovered that the AFt is the main hydrate formed when aluminum sulfate based accelerator is used. Recently, Salvador et al. (2016) and Maltese et al. (2007b) studied mechanical properties of sprayed cementitious matrices containing accelerators. In spite of some research have done, the results were almost qualitative and in-depth study of AS modified cement system is still limited. In addition, few work has addressed the influence of AS on the rebound rate of shotcrete.

In this study, hydration behavior, heat evolution, setting behavior, compressive strength and absolute volume change of AS modified cement paste were investigated. Moreover, the influence of AS on rebound rate of shotcrete was also studied. Helium pycnometry, a new method to study hydration behavior from a quantitative standpoint (Sant et al. 2006) was performed in this study. The results obtained would be an important reference to accelerator manufactures for the development of alkali-free accelerators without numerous and extensive field spray trials.

2. Materials and methods

In this section, materials, specimen production process and test are described. All the test were conducted in Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education of Tongji University.

2.1 Raw materials

(1) Cement

According to Chinese Standard GB8076-2008, reference cement must be used for test of cement paste with
chemical admixture (such as setting accelerators). Therefore, reference cement was used in this study. Table 1 shows the mineralogical composition determined by XRD-Rietveld refinement as well as chemical composition determined by XRF spectrometry, respectively. Physical properties of reference cement are shown in Table 2.

Table 1 Mineralogical and chemical compositions of the cement.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Content (%)</th>
<th>Material composition</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃S</td>
<td>57.26</td>
<td>C₃O</td>
<td>71.90</td>
</tr>
<tr>
<td>C₂S</td>
<td>13.87</td>
<td>SiO₂</td>
<td>19.60</td>
</tr>
<tr>
<td>C₃A</td>
<td>1.94</td>
<td>Al₂O₃</td>
<td>3.92</td>
</tr>
<tr>
<td>C₄AF</td>
<td>16.23</td>
<td>Fe₂O₃</td>
<td>5.21</td>
</tr>
<tr>
<td>Others</td>
<td>10.70</td>
<td>MgO</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO₃</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na₂O</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₂O</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LOI</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Minor phases</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total sum</td>
<td>100.00</td>
</tr>
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</table>

Table 2 Cement properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Result</th>
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<tr>
<td>Total heat of hydration(J/g)*</td>
<td>415.97</td>
</tr>
<tr>
<td>Molar ration C₃A/SO₃</td>
<td>0.87</td>
</tr>
<tr>
<td>Special surface BET(m²/kg)</td>
<td>570</td>
</tr>
<tr>
<td>Blaine specific surface(cm²/g)</td>
<td>3800</td>
</tr>
<tr>
<td>Initial/finial setting time(min)</td>
<td>130/165</td>
</tr>
</tbody>
</table>

* The total heat of hydration was estimated from the mineralogical composition of the cement, determined by XRD, as the relative sum of the heats of hydration of the individual phases (C₃S:510J/g; C₂S:260J/g; C₃A:1100J/g; C₄AF:410J/g) (Yang et al. 2017).

Table 3 Mix proportion of cement paste.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cement (g)</th>
<th>Deionized water (g)</th>
<th>Superplasticizer (g)</th>
<th>AS (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>AS-2%</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>AS-3%</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>AS-4%</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>AS-5%</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>AS-6%</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>AS-7%</td>
<td>100</td>
<td>39.54</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 4 Mix proportions of shotcrete specimen.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Mix proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement (kg/m³)</td>
</tr>
<tr>
<td></td>
<td>Fine aggregate (kg/m³)</td>
</tr>
<tr>
<td></td>
<td>Coarse aggregate (kg/m³)</td>
</tr>
<tr>
<td></td>
<td>Water (kg/m³)</td>
</tr>
<tr>
<td></td>
<td>Superplasticizer (kg/m³)</td>
</tr>
</tbody>
</table>

(2) Aggregate
The fine aggregate used in this study was natural river sand with a fineness modulus of 3.4, an apparent density of 2.724 g/cm³, and a water absorption of 1.1%. The coarse aggregate used was gravel with continuous grading from 5 to 10 mm. The density and absorption were 2600 kg/m³ and 0.71%, respectively.

(3) Water
In order to avoid either seasonal composition variation or possible existence of contaminations dissolved in tap water, distilled water was used in this study.

(4) Aluminum sulfate
Aluminum sulfate octadecahydrate (AS) was a reagent of chemical purity. The dosages (weight percent of cement) of AS investigated were from 2% to 7%.

(5) Superplasticizer
In order to provide fluidity and mouldability, a superplasticizer based on polycarboxylate solution (46% of solid content) was used.

2.2 Cement paste compositions
Water to cement ration (w/c) of 0.4 (by weight) was used for all cement pastes. Water contents present in the superplasticizer were deducted from the water added to the mix in order to keep the w/c ration constant. The mix proportion of cement paste is given in Table 3, which were used for all the test methods. Moreover, 4% (by weight of cement) of AS was used to conduct the BET absorption and SEM test to clarify the hydration behavior.

The mix proportions of shotcrete specimen are shown
in Table 4. The dosages (weight percent of cement) of AS investigated were from 2% to 7%.

2.3 Test methods
(1) Setting time
Setting time of cement pastes with different dosages of AS were measured according to Chinese standard GB/T 1346-2011.

(2) Compressive strength
Mortar prisms of the size 160 × 40 × 40 mm were casted according to Chinese standard JC477-2005 for the determination of compressive strength.

(3) Rebound rate
In order to measure the rebound rate of shotcrete with different AS dosage, 1m³ shotcrete was sprayed using a small-scale equipment. Then the rebound concrete was collected and the rebound rate of shotcrete was calculated according to the following equation:

\[
[C] = \left( \frac{M_r}{M} \right) \times 100\%
\]

where [C] Rebound rate (%), \([M_r]\) Mass of the rebound concrete (kg), \([M]\) Mass of 1m³ shotcrete (kg).

(4) Absolute volume change
Helium pycnometer is specifically designed to measure the absolute volume of solid or liquid materials by employing Achimedes’ principle of fluid (gas) displacement and Boyle’s law of gas expansion. It has been widely used in many research fields such as food (Mateus et al. 2007), phytology (Hill and Ormondroyd 2004), materials (Ayral et al. 1992; Ramírez-Arreola et al. 2015) and so on. Moreover, the testing process is in-situ, continuously and non-destructive. In our previous study (Yang et al. 2017a; 2017b), helium pycnometry was proved to be suitable for monitoring the absolute volume change of cement paste in early-age hydration process. Therefore, it is suitable for studying the hydration behavior of cement. Helium pycnometer (Ultrapyc 1200e, Quantachrome, The U.S.) was used in this study to measure absolute volume change of accelerated cement paste at early hydration age. The operating principle of helium pycnometer is shown in Fig. 1. The specific testing steps have been introduced in our former work (Yang et al. 2017a; 2017b).

(5) Isothermal calorimetry
In order to clarify the influence of AS on the hydration mechanism of cement paste, isothermal calorimetry was conducted using a commercial I-cal 4000 isothermal calorimeter at 20℃ during 24 h with accelerated cement paste based on a Chinese standard GB 12959-2008.

(6) X-ray diffraction analysis
XRD analysis was performed by using the X-ray diffractometer of D/max 2550 VB 3+PC at a scanning step of 0.02° and with a scanning range of 5° - 75°.

(7) Pore structure analysis
Brunauer-Emmett-Teller (BET) absorption method was conducted to evaluate the pore structure of cement paste. The hydration of cement paste was stopped at certain age by successively immersing the crushed pastes into ethyl alcohol and drying them under 40℃ for 3 days. N₂ was used as an adsorbate. Pore volume and pore size of tested sample were calculated based on adsorbed N₂ amount.

(8) Scanning electron microscope
For microstructural investigations, hardened cement paste specimens with fresh fractured surface without any polishing treatment were prepared and observed with a FEI Nova Nano SEM 450.

3. Results and discussion
3.1 Setting time
The setting time of cement pastes with different AS dosage are presented in Fig. 2. The figure indicates that both initial and final setting time of accelerated cement pasted were reduced significantly when the AS dosage increased from AS dosage increased from 0% to 7%. The setting time became stable when the AS dosage was higher than 6%. This suggests that 6% might be the optimal dosage of AS to be used in the mix-design of shotcrete.
3.2 Isothermal calorimetry

Figure 3 demonstrates the heat evolution curves of cement pastes with different AS dosage measured by isothermal calorimetry. Two hydration exothermic peaks can be found in the heat flow curves. The first exothermic peak reaches 43.90 mW/g in the blank cement paste, while 62.75 mW/g for the accelerated cement paste with 2% AS. Moreover, it can be seen from Fig. 3 that with the increase of AS, the hydration heat release rate increased, demonstrating the early accelerating effect of AS. The first heat flow peak of mainly results from the formation of ettringite (AFT), seen from Eq.(1). For the second exothermic peak, which results from the hydration of calcium silicate phases (mainly C₃S), the higher the AS dosage is, the earlier the onset of the second exothermic peak will be.

\[
2[\text{Al(OH)}_4]^- + 6\text{Ca}^{2+} + 4\text{OH}^- + 3\text{SO}_4^{2-} + 26\text{H}_2\text{O} \rightarrow C_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}
\]  
(Salvador et al. 2016)  
\[(\Delta rG_{298}^0 = -15207.02\text{kJ/mol})\]

By the integration of the heat flow curves, the energy released by accelerated cement hydration during the first 24 h was calculated and depicted in Fig. 4. The degree of hydration was determined from the calorimetric curve as the ratio of the heat released at a certain time to the total theoretical heat of cement hydration presented in Table 2. It shows that total hydration heat and hydration degree of accelerated cement pastes was increased compared with the blank cement paste. However, it also shows that the total hydration heat and hydration degree increased at the beginning of the hydration process and decreased in the later age as the dosage of AS enhanced. This depressed hydration ability may due to the increased quantity of AFT, which acts as a barrier on the surface of cement particles during the hydration of calcium silicate (Han et al. 2014).

3.3 Identification of hydration stage

According to heat flow rate of cement hydration, Taylor divided cement hydration into five stages, which were dissolution stage, induction stage, acceleration stage, deceleration stage and stable stage (Taylor 1997). While for accelerated cement pastes, Salvador et al. (2016) divided cement hydration into five general hydration stages according to the chemical processes, which were pre-induction period, acceleration reaction, induction period, acceleration period and deceleration period.

Figure 5 illustrates volume change and heat flow of accelerated cement paste with 4% AS. It can be seen from Fig. 5 that the trend of the absolute volume change and the heat flow are relative to each other. The slight difference of the turning time of the two curves may result from the difference of the two test methods.

Therefore, according to the different characteristics of each stage, the absolute volume change obtained by helium pycnometry can be divided into four stages, which are: dissolution-crystallization stage, induction stage, repaid shrinkage stage and structure compacting stage (shown in Fig. 5).

(1) Dissolution-crystallization stage

Figure 6 demonstrates the early absolute volume change of cement paste with different AS dosage. It can be seen in Fig. 6 that a great volume decrease happens in the
dissolution stage. Table 5 illustrates the absolute volume change of cement paste with different AS dosage at different hydration stages. The absolute volume of the blank cement paste decreases 0.0084 mL/g, while the absolute volume of the cement paste with 2% SA decreases 0.0081 mL/g. Moreover, the absolute volume of the cement paste decreased less when AS dosage increased from 0% to 6%. It has been reported (Taylor 1997; Ma et al. 2015) that the combination of exothermic wetting and early-stage reaction occurs at this stage, which causes the great decrease of the volume change of the accelerated cement paste.

For the accelerated cement paste, it can be seen from Eq. (1) that the heat released in the formation of early AFT is identical with the first hydration heat peak in Fig. 5.

3. Figure 7 was the XRD patterns of the accelerated cement pastes with 4% AS and reference cement paste at different hydration time. Figure 7(b) shows the presence of AFT (9.1°, 15.8° and 22.9°) can be found at an early hydration age (30 min). Figure 8 was the SEM image of accelerated cement paste at 30 min. It can be observed that the ettringite in needle shape has formed in the hardened cement specimen, which is in a good agreement with the accelerated setting behavior of the cement pastes with accelerators.

Table 6 demonstrates the classification of hydration process of accelerated cement paste. It can be seen from Table 6 that with the increase of AS, the duration of dissolution stage was shortened, which may be attributed...
to the accelerating effect of aluminium ions. The more aluminium ions in the solution, the faster and more amount the AFt will generate.

(2) Induction stage
In the induction stage, absolute volume of accelerated cement paste decreases very slowly, seen from Figs. 5 and 6. The absolute volume of the blank cement paste decreases 1.7×10⁻³ mL/g, while the absolute volume of the cement paste with 2% AS decreases only 8×10⁻⁴ mL/g. The absolute volume of the cement paste decreased less when AS dosage increased from 0% to 4%. Moreover, the duration of this stage was shortened with the addition of the AS. It can be seen from Table 6 that the duration of the induction stage was reduced significantly when AS dosage increased from 0% to 6%. Especially there seems no induction stage when the AS dosage was 6%.

As calcium and sulfate ions have constantly been consumed in the dissolution-crystallization stage, gypsum and alite dissolutions are favored in this stage, which will accelerate the onset of the main hydration peak. Moreover, AS will increase the ion concentration, which will improve the hydration of C₃S, therefore accelerating the induction stage compared with the blank cement paste.

(3) Repaid shrinkage stage
In the repaid shrinkage stage, the absolute volume of the cement pastes decreases dramatically. For the blank cement paste, the absolute volume of the cement paste decreases 2.67×10⁻² mL/g. While the absolute volume of the cement paste with 2% AS decreases 1.21×10⁻² mL/g.

Moreover, a second exothermic peak happens at the same time. It can be seen from the XRD patterns of the accelerated cement pastes at 5 h and 8 h in Fig. 7 that the intensity of C₃S and Ca(OH)₂ changed much during this stage, which implies that the great decrease of the volume change results from the continuously hydration of calcium silicate phases (mainly C₃S) (Taylor 1997).

Moreover, it can be seen from Table 6 that the duration of the repaid shrinkage stage decreases from 12.7 h to 6.4 h when the AS dosage increase from 0% to 4%. However, for the cement paste with 6% AS dosage, the duration of the repaid shrinkage stage lasts about 9.6 h.

(4) Structure compacting stage
In the structure compacting stage, the absolute volume of accelerated cement paste increases linearly, as shown in Fig. 6. The higher amount the AS added in the cement paste, the greater the volume will increase. However, the hydration heat flow and the XRD patterns indicate that the hydration of accelerated cement paste slowed down considerably at this stage, as shown in Figs. 3 and 7. Therefore, some physical reactions rather than chemical reactions happen at this stage.

Figure 9 shows the pore size distribution and accumulated pore volume of the cement pastes with 4% AS at different hydration stages. As can be seen from Fig. 9, compared with the induction period (4 h) and the repaid shrinkage stage (12 h), the amount of the nano-scale pores (pore diameter smaller than 10 nm) in the accelerated cement pastes increases in structure compacting stage. The theory of crystallization pressure seems to be the plausible mechanism to explain this volume increasing phenomena. With the continuous formation and accumulation of hydration products (especially the AFt), the pore size will decrease. Once the pore size becomes small enough, hydration products can’t generate in these pores any more. Therefore, hydration products have to grow into the outer spaces of the pore resulting in the generation of the nano-scale pores.

As stated in (Yang et al 2017a), helium pycnometer couldn’t detect nano-scale pores by flowing a narrow entrance(indicated with the red arrows in Fig. 10), which will result in an overestimation of the absolute volume of cement paste. Therefore, with the cement hydration, when the pore becomes small enough (nano-scale) (Taber 1916), the helium molecular cannot reach the pore by penetrating its narrow entrance leading to a “fake” volume change. This “fake” volume expansion gives firm evidence to the structure compaction of accelerated cement paste in this stage.

<table>
<thead>
<tr>
<th>Table 6 Classification of hydration process of the accelerated cement paste /h.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolution -crystallization stage</td>
</tr>
<tr>
<td>Blank</td>
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<tr>
<td>AS -2%</td>
</tr>
<tr>
<td>AS -4%</td>
</tr>
<tr>
<td>AS -6%</td>
</tr>
</tbody>
</table>

Fig. 8 SEM image of accelerated cement paste at 30min.
3.4 Strength
Figure 11 shows the compressive strength of cement pastes with different AS dosage. It can be seen that AS enhanced the compressive strength. However, the 28 d compressive strength and the 90 d compressive strength decreased with the increase of the AS dosage, which may be result from the disruption of the sulfate in the cement paste.

3.5 Rebound rate
Figure 12 shows the rebound rate of shotcrete with different AS dosage. It can be seen that the rebound rate of shotcrete was greatly reduced with the increase of AS dosage from 2% to 6%. However, the rebound rate will increase when the AS dosage exceeds 6%. This may suggest that the optimal dosage of AS to be used in the shotcrete may be 6% considering the rebound rate.
4. Conclusions

This study evaluates the influence of aluminum sulfate on properties and hydration of cement pastes. Based on the analysis of the experimental results, the following conclusions can be drawn:

Adding of aluminum sulfate (AS) accelerate cement setting behavior significantly. Setting time of cement paste can be reduced from over 100 min to a few minutes, depending on the dosage of AS used. AS seems not to further reduce setting time when the dosage is more than 6%.

According to the different characteristics of each stage, the absolute volume change of the accelerated cement paste obtained by helium pycnometry can be divided into four stages, which are: dissolution-crystallization stage, induction stage, repaid shrinkage stage and structure compacting stage. In the dissolution stage, the combination of exothermic wetting and early-stage reaction results in the early rapid shrinkage of the accelerated cement pastes. In the induction stage, the volume change of the accelerated cement paste decreases slowly, and the duration of this period is shortened with the addition of AS. In the rapid shrinkage stage, the hydration of C3S dominates in this stage, therefore the volume change of the accelerated cement paste decreases dramatically. In the structure compacting stage, more nano-scaled pores are generated during this stage and the increased AS dosage will reduce the shrinkage of the accelerated cement paste.

Addition of AS can enhance compressive strength of the cement paste. However, the compressive strength decreases with the increase of AS at 28 d and 90 d.

Addition of AS can reduce the rebound rate of the shotcrete. However, when the AS dosage is more than 6%, the rebound rate will increase.

Acknowledgements

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Reference


