HYDRATION HARDENING PROCESS CONTROL TECHNOLOGY OF LOW ALKALINITY SULPHOALUMINATE CEMENT

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Abstract
The influence of borax (Na₂B₄O₇·10H₂O) and lithium compounds (LiOH·H₂O) on setting time, hydration process, mechanical properties and microstructure of low alkalinity sulphoaluminate cement was studied. The quick hardening and ultra early strong model with borax as retarder was established, and the hydration hardening process control measures of low alkalinity sulphoaluminate cement were discussed. Results showed that, borax has a good retarding effect of low alkalinity sulphoaluminate cement, lithium compounds can effectively solve the problem of long retarding time and slow strength development based on borax retarding mechanism, borax and lithium compound only have an impact on the formation rate, not on the type of hydration products, the addition of borax and lithium compound can optimize the microstructure of hardened slurry, by reducing the total porosity and average aperture of low alkalinity sulphoaluminate cement. Therefore, the hydration exothermic chemical process and the condensation hardening process of low alkalinity sulphoaluminate cement can be controlled by appropriate amounts of borax and lithium compound.

1. INTRODUCTION
The manufacture of Portland cement and Blended cement consumes not only consumes a vast amount of energy but it also generates undesirable CO₂ emissions. low alkalinity sulphoaluminate cement is an attractive class of low-energy cements from the viewpoint of saving energy and releasing less CO₂ into the atmosphere during their production[^1-2]. However, their hydraulic activity, does not match that of the ordinary Portland cement and needs improvement before they can be used on their own. The special cement contains calcium sulfoaluminate instead of high-temperature and hence high-energy tricalcium silicate and tricalcium aluminate, mainly containing C₄A₃S, β-C₂S and CS. Low alkalinity sulphoaluminate cement was widely applied in architecture engineering, cement manufactures (cement ships, telephone poles, concrete railway
sleepers, etc.\(^3\)-\(^5\), emergency repairs, framework node point, permeability resistance engineering, etc., due to its properties such as high early strength, shot setting time, high strength, lower alkalinity, etc. However, rapid setting and short interval between initial and final setting are inappropriate for some constructions of engineering. The flowing property and setting time must be regulated to satisfy the demand of building engineering, otherwise it will seriously hindered the popularization and application of low alkalinity sulfoaluminate cement.

To control the hydration exothermic chemical process and the condensation hardening process of low alkalinity sulfoaluminate cement, it is necessary to know the hydration hardening process and the microstructure of cement as characterized by the functional admixtures. For the low alkalinity sulfoaluminate cement and hardened cement paste, characterization parameters are setting time, the hydration rate, mechanical properties and pore structure characteristics, etc.

In this paper, the influence of borax\((\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O})\) and lithium compounds\((\text{LiOH} \cdot \text{H}_2\text{O})\) on setting time, hydration process, mechanical properties and microstructure of low alkalinity sulfoaluminate cement was studied, the quick hardening and ultra early strong model on borax as retarder was established, and the hydration hardening process control measures of low alkalinity sulfoaluminate cement was discussed. The purpose of the investigation is to provide theoretical guidance for low alkalinity sulfoaluminate cement application and develop its special function.

2. HYDRATION HARDENING PROCESS CONTROL THEORY MODEL DESIGN

Anhydrous sulfoaluminate\((\text{Ca}_4\text{Al}_3\text{S})\) is a porous skeleton structure formed by aluminum-oxygen tetrahedron in low alkalinity sulfoaluminate cement clinker, as shown in Fig.1. There are many lattice defects on the surface of anhydrous sulfoaluminate\(^[6]\). The lattice defect site is hydration activation point, anhydrous sulfoaluminate occur hydration reaction rapidly and generate Ettringite when it contacts water as shown in Eq. (1).

\[
3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 + 2\text{Ca}^{2+} + 2\text{SO}_4^{2-} + 38\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + 2(\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})\text{(gel)}
\]

low alkalinity sulfoaluminate cement have rapid setting and short interval between initial and final setting due to the anhydrous sulfoaluminate mineral hydration characteristics. Therefore, delaying ettringite formation is an effective way to extend the setting time of low alkalinity sulfoaluminate cement, that is parcel cement clinker particles in the early hydration by adding functional admixture.

Borax is a white powder crystal, whose scientific name is sodium borate 10 hydrs. It is a solid structure with flat sides and are symmetrical in shape because of the unique arrangements of the molecules with repeated patterns. It can be solubled in water and the solution have highly alkaline. Calcium borate film formed by the borax is similar to gel, which have the characteristics of semi-permeable membrane and water molecules and small ions can penetrate through the calcium borate film. Low alkalinity sulfoaluminate cement mainly containing \(\text{Ca}_4\text{Al}_3\text{S}, \beta\text{-C}_2\text{S}\) and \(\text{CS}\), Which can provide \(\text{Ca}^{2+}\) for borax , the calcium borate film can package the cement clinker and prevent the cement hydration, so borax can be used as a low alkalinity sulfoaluminate cement retarder\(^[7-8]\).
Fig. 2 show the hydration of low alkalinity sulphoaluminate cement mixed with borax after 30 minutes of X-ray diffraction diagram and electron micrograph. The results show that hydration after 30 minutes no diffraction peaks of ettringite, but there is the peak calcium borate (3.425 Å, 7.75 Å), and electron micrograph shows the cement particles are coated by many small particles, so the calcium borate wrapped retardation model is feasible.

In the cement paste of low alkalinity sulphoaluminate cement, based on the retarding mechanism of calcium borate film formed by borax, the hydration of low alkalinity sulphoaluminate cement can be accelerated when the cement clinker slow hydration internal calcium borate film produce crystallization pressure can forced the parcel layer fracture, or water molecules and smaller ion slow permeating through calcium borate wrapped layer [9-11].

In the research process, with the small cation radius of lithium compounds, quickly permeating through the calcium borate film and occurs hydration reaction occurs with unhydrated cement, and damage the calcium borate formed wrapped layer, so that all of the mineral composition of low alkalinity sulphoaluminate cement hydration and hardening in a very short time, and the model of retardation and then early strength was established (as shown in Fig. 3).

3. MATERIALS AND EXPERIMENTAL WORK

3.1 Raw materials

One type of commercial low alkalinity sulphoaluminate cement has been used in this study, with the compressive strength of 35 MPa after 1 day and 47 MPa after 7 days tested according to JC659-2003. The mineralogical composition of clinkers is shown in Table 1. By mineral composition calculation formula, the theoretical content of each mineral was calculated: 2CaO·SiO₂ content is 17.08% and 3CaO·3SiO₂·CaSO₄ content is 45.05%.

| Table 1 Mineralogical composition of low alkalinity sulphoaluminate cement |
|-------------------|------------|----------|--------|---------|---------|--------|--------|
| CaO          | Al₂O₃      | SiO₂     | SO₃     | MgO     | Fe₂O₃   | TiO₂   |
| 48.7         | 22.6       | 5.96     | 18.2    | 1.85    | 1.40    | 0.51   |
Pure analytical reagents borax (Na₂B₄O₇·10H₂O) and lithium compounds (LiOH·H₂O) were used as raw materials. The chemical compositions of main raw material were listed in Table 2 and Table 3.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>borax (Na₂B₄O₇·10H₂O)%</td>
<td>≥ 99.5%</td>
</tr>
<tr>
<td>Sodium carbonate (Na₂CO₃) %</td>
<td>≤ 0.1%</td>
</tr>
<tr>
<td>Insoluble matter in water %</td>
<td>≤ 0.04%</td>
</tr>
<tr>
<td>sodium sulphate (Na₂SO₄) %</td>
<td>≤ 0.1%</td>
</tr>
<tr>
<td>Sodium Chloride (NaCl) %</td>
<td>≤ 0.03%</td>
</tr>
<tr>
<td>Iron (Fe) %</td>
<td>≤ 0.002%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium compounds(LiOH·H₂O)%</td>
<td>≥ 95.0%</td>
</tr>
<tr>
<td>Lithium carbonate (Li₂CO₃) %</td>
<td>≤ 2.0%</td>
</tr>
<tr>
<td>Insoluble matter in water %</td>
<td>≤ 0.005%</td>
</tr>
<tr>
<td>sodium sulphate (Na₂SO₄) %</td>
<td>≤ 0.01%</td>
</tr>
<tr>
<td>Sodium chloride (NaCl) %</td>
<td>≤ 0.005%</td>
</tr>
<tr>
<td>Iron (Fe) %</td>
<td>≤ 0.002%</td>
</tr>
</tbody>
</table>

3.2 Experimental methods

Measurements of hydration heat have been carried out in a differential micro-calorimeter for all samples under the following conditions: mass sample = 4 g, T = 20°C, W/C = 0.45. The paste setting time and mortar strength of the cement was tested according to JC/T659-2003 low alkalinity aluminate cement industry standards of People’s Republic of China. The specimens of sulphaoluminate cement paste (the ratio of water to cement at normal consistency was 0.29) were cured for 28 days, respectively, then they were taken out from fresh water and washed by the anhydrous ethanol and acetone to stop their hydration and dried at the temperature of 60-70°C. Matter phase analysis of these specimen hydrates were conducted on X-ray diffractometer, type D/max-RA, 12 kW, Radiation Source, Cu Ka, made by Japan, S-2500 SEM, magnification×200K, made by HITACHI, Japan and DTA instrument, type STA 409EP, sensibility S=0.4078μm/mW, atmosphere air, by NETZSCH, Germany. The grain size distribution for fine particles which passed through the sieve with 0.077 mm square mesh size was tested by using FAM type laser sizer made in Shanghai, and the pore size distribution of cements pastes was determined by Auto pore III 9420 mercury porosimeter.

4. RESULTS AND DISCUSSION

4.1 Thermodynamical properties analysis

The hydration process of low alkalinity sulphaoluminate cement is exothermic, i.e. heat is released as the reaction progressing. This property is used in laboratories to monitor the hydration process by using a special micro-calorimeter to record the rate of heat conduction needed to keep the temperature constant. The results are often presented as the calorimetric curve, the hydration heat and hydration rate curves of low alkalinity sulphaoluminate cement mixed with borax or lithium compounds were shown in Fig.4 and Fig.5. The dosages used for the borax was 0.0wt.%，0.2wt.%，0.5wt.% and 1.0wt.% of low alkalinity sulphaoluminate cement. The dosages used for the lithium hydroxide was range from 0 to 6g per 10kg low alkalinity sulphaoluminate cement.

Fig.4 showed that borax can reduce the early hydration heat and the heat release rate, and effectively delay the early hydration process of low alkalinity sulphaoluminate cement. The best amount of borax is 0.2–0.5wt.%. Fig.5 showed that lithium hydroxide can increase the early hydration heat and the heat release rate, can effectively accelerate the early hydration process, and the best amount of lithium hydroxide is 0.03–0.05%,. Therefore, the early hydration exothermic
process of low alkalinity sulphoaluminate cement can be controled by using borax and lithium hydroxide, especially compound using the borax and lithium hydroxide.

![Graph showing hydration heat and hydration exothermic rate vs. hydration time and borax dosage.]

**Fig. 4. Influence of borax on the hydration of low alkalinity sulphoaluminate cement**

**4.2 Initial and final setting times**

The extent of setting time caused by admixture depends on the cement characteristics, the admixture dosage, and the admixture type. For example, overdosage borax may produce excessive retardation, while its ultimate strength may be reduced. The influence of borax and lithium hydroxide on setting time was show in Fig.6.

![Graph showing initial and final setting time vs. lithium hydroxide dosage for different borax dosages.]

**Fig. 6. Influence of borax and Lithium hydroxide on the setting time of low alkalinity sulphoaluminate cement**

The experimental results show that the setting time of low alkalinity sulphoaluminate cement from 90min to 96min When the dosage of borax is 0.4wt.%. By adding lithium hydroxide, the setting time can realize the regulation, and the regulation range of initial setting time was from
96min to 60min when the dosage of lithium hydroxide was from 0.00wt.% to 0.06wt.%. At the same time, the initial setting time of low alkalinity sulphoaluminate cement from 25min to 30min with the dosage of borax is 0.2wt.%, and the regulation range of initial setting time is from 25min to 16min by adding lithium hydroxide.

4.3 Compressive strength

The effect of borax and lithium hydroxide on strength of low alkalinity sulphoaluminate cement was investigated. The dosages of borax are 0.2wt.% and 0.4wt.%, and the activator of lithium hydroxide was from 0.00wt.% to 0.06wt.% , the experimental results of these cements were shown in Fig.7.

Fig.7 indicate that the compressive strength of low alkalinity sulphoaluminate cement was reduced when adding borax, the higher the dosage was, the more obvious it would be. The compressive strength for adding 0.2wt.% borax reduced by 2 MPa at 2 hours compared to pure low alkalinity sulphoaluminate cement system, and reduced 5 Mpa with the dosage reaching 0.4wt.%. The decline in compressive strengths due to borax follows at 28 days. Nevertheless, the lithium hydroxide can accelerated early-age and later-age strength development , which can make up for the negative impact of borax and significantly increase the compressive strength. Thus, borax and lithium hydroxide not only can be used to regulate the hydration process, but also to control the setting time and promote the development of strength.

4.4 Phase compositions

Fig. 8 give the XRD patterns of pure low alkalinity sulphoaluminate cement specimen hydrated Days 28, and Fig.9 to 11 give the XRD patterns of specimens mixed with borax or lithium hydroxide. The main hydration products are ettringite (d: 9.67, 5.67 and 3.88 Å ), the diffraction peaks of C₄A₃S (d: 3.75, 2.65 and2.17 Å ) and β-C₂S (d: 2.78, 2.73 and 2.60 Å ) is confirmed by the detection of above diffraction peaks, these results show that borax and lithium compound only have an impact on the formation rate, not on the type of hydration products.
4.5 pore structure

The effect of borax and lithium hydroxide on pore size distribution of low alkalinity sulphaolunate cement was investigated. The dosages of borax is 0.4wt.% and the activator of lithium hydroxide is 0.03wt.%. The experimental data of the pore size distribution of experimental specimens at the age of 28 days was given in Table 4.

<table>
<thead>
<tr>
<th>Experimental specimens</th>
<th>Total porosity (%)</th>
<th>Average pore size (nm)</th>
<th>Pores portion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Over 200nm</td>
<td>100-200nm</td>
<td>20-100nm</td>
</tr>
<tr>
<td>Pure cement</td>
<td>13.42</td>
<td>14.8</td>
<td>2.17</td>
</tr>
<tr>
<td>Adding borax</td>
<td>12.15</td>
<td>13.7</td>
<td>1.30</td>
</tr>
<tr>
<td>Adding lithium hydroxide</td>
<td>15.02</td>
<td>18.2</td>
<td>4.09</td>
</tr>
<tr>
<td>Adding borax and lithium hydroxide</td>
<td>12.65</td>
<td>13.2</td>
<td>2.61</td>
</tr>
</tbody>
</table>

The results showed that using borax as retarder can qualitatively improve the pore structure and pore size distribution of low alkalinity sulphaolunate cement paste. The experimental data in Table 4 undoubtedly confirmed the phenomenon of pore structure “coarsening” due to lithium hydroxide use in low alkalinity sulphaolunate cement, the increase in porosity is due to a higher proportion of micropores with a radius of 200–500nm. For low-alkali sulphaolunate cement, the early hydration and hardening rate is very fast, addition of the lithium hydroxide can further accelerate the hydration reaction process, making the hydration reaction product can’t be ordered distribution and accumulation, leading to the increase of porosity and average pore size. Compared with Single-doped lithium hydroxide the total porosity and average pore size with double-doped borax and lithium hydroxide reduced obviously, lower than that of the pure cement system. Therefore, double-doped borax and lithium hydroxide in low alkali sulpha-alunate cement system is feasible, which can give full play to their special properties, components of each other.

5. CONCLUSIONS

- The retardation model of low alkalinity sulphaolunate cement by using borax as retarder to wrap the cement particle was established, and designed the model of retardation and then early strength base on the retarding mechanism of calcium borate film formed by borax.
- Borax has a good retarding effect on low alkalinity sulphaolunate cement, and the best amount of admixed of borax is within the scope of 0.2–0.5wt.%. 

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Lithium compounds can effectively solve the problems of long retarding time and slow strength development based on borax retarding mechanism. The best amount of lithium hydroxide is 0.03–0.5 wt. %.

Borax and lithium compound only have an impact on the formation rate, not on the type of hydration products. Double-doped borax and lithium hydroxide in low alkali sulpho-aluminate cement system is feasible, which can give full play to their special properties, components of each other.

The hydration exothermic chemical process and the condensation hardening process of low alkalinity sulphoaluminate cement can be controlled by appropriate amounts of borax and lithium compound.

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