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# Studies on effects of activators on properties and mechanism of hydration of sulphoaluminate cement

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## Abstract

The effects of activators on the properties of sulphoaluminate cement were investigated by experiments. The results of experiments show that reduction compressive strength of sulphoaluminate cement in later ages was controlled by using burnt plaster and alunite, and setting time is also prolonged by organic admixtures. The properties of sulphoaluminate cement, such as increase of expansion ratios, resistance to drying contraction and the chemical corrosion, are all increased. The hydrates and mechanism of hydration of sulphoaluminate cement are analyzed and studied by means of XRD, SEM and DTA.

*Keywords:* Hydration; Physical properties; Sulphoaluminate; Activator mechanism

## 1. Introduction

In recent years, the investigation and production of specific cements based on mineral of $C_4A_3\bar{S}$ have been making great progress [1,2]. One kind of sulphoaluminate cement is mainly composed of $C_4A_3\bar{S}$ and $\beta$-$C_2S$ [3–5]. It is widely applied in architecture engineering, cement manufactures (cement ships, telephone poles, concrete railway sleepers, etc.), emergency repairs, framework node point, permeability resistance engineering, etc., due to its properties such as high early strength, shot setting time, high strength [11], lower alkalinity, etc. Besides, the application in constructions at subzero temperature engineering attributes to the higher enhancement rate of strength for sulphoaluminate cement in subzero temperature [6] (such as its environmental temperature is $-10$, $-20$ or $-35$ °C). However, rapid setting and short interval between initial and final setting are inappropriate for some constructions of engineering. The setting time must be regulated to satisfy the demand of building engineering. The expansibility of sulphoaluminate cement comes from the solid volume increase, caused by the formation of AFt crystalline [7,8] from $C_4A_3\bar{S}$ and gypsum, but as the hydration occurs, the volume of cement minerals–water–gypsum system will be decreased, which effects many properties of the cement seriously. Therefore, the effects of multiple activators, burn plaster and alunite on the setting time, expansibility, drying shrinkage and resistance to chemical corrosion of sulphoaluminate cement, were studied and the hydrates and mechanism of hydration were also analyzed.

## 2. Experimental methods

### 2.1. Raw materials

Raw materials were sulphoaluminate cement clinker (SCC) from Yuchun Cement Plant, burnt plaster (G) from the Laboratory, gypsum (G2) and alunite (A) from Zhucheng City, Shandong Province, calcium lignosulfonate (CL), calcium molasses (CM), melamine for maldehyde resin (MMR) and $Na_2SO_4$ used as activators. The chemical compositions of main raw materials are listed in Table 1.

### 2.2. Methods

The mortar strength of the cement was tested according to GB177-85. (The water/cement ratio by 0.44, cement/

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Table 1
Chemical composition of main raw materials (wt.%)

| Raw materials | Chemical composition | | | | | | |
|---|---|---|---|---|---|---|---|
| | Loss | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $SO_3$ |
| SCC | 0.40 | 8.73 | 3.86 | 28.83 | 45.71 | 0.82 | 9.44 |
| A | 0.56 | 9.2 | 3.09 | 29.99 | 45.38 | 0.98 | 8.35 |
| $G_2$ | | | | | | | 42.1 |
| G | | | | | | | 52.0 |

standard sand by 0.4, the prisms size made with 40 × 40 × 160 mm was stipulated by the State Standards of People's Republic of China GB177-85 for Test Method of Strength of Hydraulic Cement Mortar, but compressive strengths determined by this standard was 7 MPa above the standard for ISO679:1998.) The fineness of the cement was determined by Blaine specific surface area equipment. The standard consistency water requirement and setting time were examined by the method of GB1346-89 (the State Standards of People's Republic of China for Standard Test Method for Water Requirement of Normal Consistency, Setting Time of Portland Cement). The drying contraction of cement mortar was determined by the method of GB751-81 (the State Standards of People's Republic of China for Standard Test Method for Drying Contraction of Cement Mortar). In this standard, the water/cement ratio, cement/standard sand, the curing temperature and percentage relative humidity are 0.44, 0.4, 20 ± 3 °C and 60 ± 5%, respectively, the prisms size is made with 25 × 25 × 250 mm. The expansion ratio for cement paste was examined on 25 × 25 × 250 mm prisms, which was cured in fresh water at temperature 20 ± 2 °C after being cured in curing cubicle at temperature 20 ± 2 °C and percentage relative humidity 90% for 1 day.

The specimens of sulphoaluminate cement paste (the ratio of water to cement at normal consistency was 0.28–0.30) were cured to 1, 3, 7 and 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 Kα, made by Japan, S-2500 SEM, magnification × 200K, made by HITACHI, Japan and DTA instrument, type STA 409EP, sensibility $S = 0.4078$ μm/mW, atmosphere air, by NETZSCH, Germany. The grain size distribution for fine particles that passed through the sieve with 0.077 mm square mesh size was tested by using FAM type laser hondrometer made in Shanghai, and the pore size distribution of cements pastes was determined by Auto pore III 9420 mercury porosimeter.

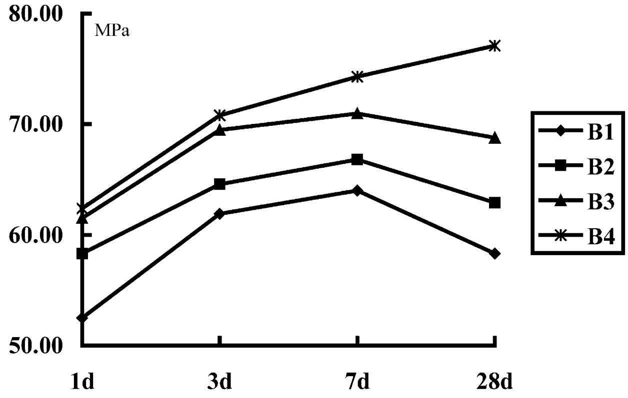

Fig. 1. Effects of fineness compressive strength.

## 3. Results and discussion

### 3.1. Effect of fineness on setting time and strength of the mortar

In order to investigate the effect of fineness on strength and setting time of sulphoaluminate cement, the cements with the composition as in Table 2 were ground for different durations to achieve different fineness. The experimental results of these cements are shown in Table 2, Figs. 1 and 2.

The experimental results in Table 2 show that, with the increase of specific surface area, the weight percentage of particles, which is smaller than 60.0 μm, especially smaller than 30.0 μm, increase, the average size in diameter is getting smaller and the setting time shortens gradually. Figs. 1 and 2 also illustrate that the compressive and flexural strengths increase by different degrees at every age with the increase of specific surface area, but strength values of $B_1$, $B_2$ and $B_3$ specimen are lower at Day 28 than that at Day 7, except the compressive strength of the mortars made with $B_4$, which implies that the burnt plaster could retard the regression of the compressive strength of sulphoaluminate cement.

Table 2
Specific surface area ($m^2/kg$), particles sizes distribution and setting time

| No. | Dosages (wt.%) | | | Surface area | Scope of diameters size (μm) and weight distribution (%) | | | | | Average sizes (μm) | Setting time (min) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SCC | $G_2$ | G | | >90 | 90–60 | 60–30 | 30–10 | < 10 | | Initial | Final |
| $B_1$ | 95 | 5 | – | 396.5 | 14.9 | 22.8 | 27 | 22.6 | 12.5 | 41.3 | 22 | 44 |
| $B_2$ | 95 | 5 | – | 437.2 | 8.1 | 19.7 | 29.3 | 27.3 | 15.6 | 33.5 | 20 | 40 |
| $B_3$ | 95 | 5 | – | 514.3 | 3.1 | 14.6 | 30.7 | 32.7 | 18.9 | 27.1 | 14 | 32 |
| $B_4$ | 95 | – | 5 | 521.0 | 2.6 | 13.2 | 30.1 | 33.8 | 20.3 | 25.7 | 8 | 21 |

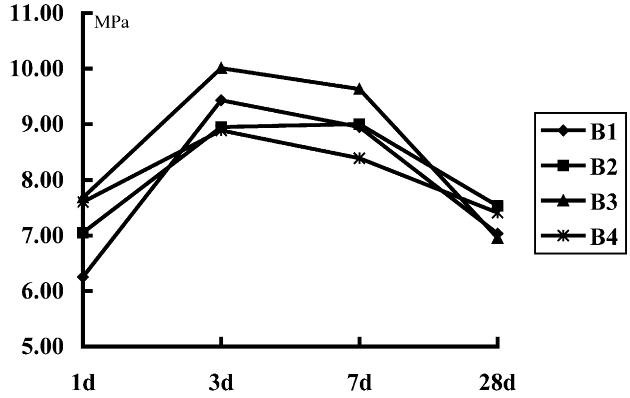

Fig. 2. Effects of fineness on flexural strength.

### 3.2. Effect of activators on setting time and strength

In order to avoid the short setting time of sulphoaluminate cement, the CL and CM have been used as activators to regulate the hydration speed of cement and the specific surface areas of specimens are controlled in 320–340 m$^2$/kg. The dosages came from the specimen $B_4$, where the activators are added in, and the experimental results are shown in Table 3.

Table 3 shows that the initial and final setting time of cement are prolonged as the activators are introduced in the experiment. With the increase of the amount of CL, the setting time is prolonged gradually in Group C, but shortened at the CL amount of 0.7%; thus, the best amount of admixed of CL is within the scope of 0.3–0.5%. Similarly, the setting time is also prolonged by CM by different degrees; the best amount of CM is 0.3–0.5%, too. The same experimental principle has also been shown by the results of Groups D and E, but the setting time lengthening tendency is suppressed by the alunite. In the results of Groups C, D and E, the setting time are shortened with the growing amount of alunite from 0% to 5%, which indicates that the setting speed could be accelerated by alunite.

Specimens $B_5$, $B_6$ and $B_7$ are derived from $B_3$, when activators were added in it, respectively; $B_8$, $B_9$, $B_{10}$, $B_{11}$ and $B_{12}$ were from $B_4$, according to the amount listed in Table 4. These experimental results indicate that the hydration rate of sulphoaluminate cement is reduced by the MMR and CM greatly, while the $Na_2SO_4$ accelerates the hydration rate of the cement.

The strength of the mortars made with samples $B_4$ to $B_{12}$ was increased by different degrees at every age compared with that of $B_3$. The compressive strength for $B_5$ increased by 8 MPa at Day 28 compared to $B_3$, especially the regression of the compressive strength for $B_4$, $B_5$, $B_8$ and $B_{10}$ did not occur simultaneously at Day 28. But the regressions in $B_4$, $B_6$, $B_9$, $B_{11}$ and $B_{12}$ contented $Na_2SO_4$ by 1% appeared, although they were of higher strength at Day 1, 3 or 7; the decline in compressive strengths made with sulphoaluminate cement follows at 28 days, not at 1 year [12]. Thus, the effect of MMR, CM and burnt plaster on the retardation to regression of the compressive strength was higher than that of $Na_2SO_4$ at Day 28.

### 3.3. Effect of burnt plaster and alunite on the expansibility of cement paste

The solid volume increases gradually as the minerals of cement clinker turn into hydration products, but in this hydration process the total volume of cement minerals–water–gypsum system decreases. For example:

$$C_3A + 3C\overline{S}H_2 + nH \rightarrow C_3A \cdot 3C\overline{S} \cdot H_{32}(AFt) \qquad (1)$$

In Eq. (1), the solid volume increases by 129.55%, while the total volume of system decreases by 6.15%, which is called chemical shrinkage, leading to the internal flaw in cement stone. Therefore, many properties of cement, such as physical strength, resistance to permeability, frost and chemical erosion, are affected by the internal flaw. The chemical shrinkage ratio can be controlled by the amount of burnt plaster and alunite added in sulphoaluminate cement, and the expansion also takes place in hydration process. The experimental results are shown in Table 5 ("–" means shrinkage, "+" signs expansion and the specific surface areas of specimens are 320–340 m$^2$/kg).

Experimental results of Groups I, J and K in Table 5 show that the expansibility of sulphoaluminate cement is improved with the increase of the amount of burnt plaster added in the cement. The expansion ratio is negative as the burn plaster is 5%, while the expansion ratio achieves positive values as the amount of burnt plaster is much more than 7%, as shown by experimental data of Groups J and K. The reason is that the increase of expansion ratio appears with the growing amount of ettringite (AFt) produced from

Table 3
Effect of activators on setting time (min)

| No. | Dosages (wt.%) | | | | | Setting time | |
|---|---|---|---|---|---|---|---|
| | SCC | G | A | CL | CM | Initial | Final |
| $C_0$ | 95 | 5 | – | – | – | 15 | 28 |
| $C_1$ | 95 | 5 | – | 0.3 | – | 32 | 51 |
| $C_2$ | 95 | 5 | – | 0.5 | – | 31 | 48 |
| $C_3$ | 95 | 5 | – | 0.7 | – | 25 | 40 |
| $C_4$ | 95 | 5 | – | – | 0.1 | 12 | 37 |
| $C_5$ | 95 | 5 | – | – | 0.3 | 19 | 33 |
| $C_6$ | 95 | 5 | – | – | 0.5 | 21 | 32 |
| $D_1$ | 92 | 5 | 3 | 0.3 | – | 26 | 45 |
| $D_2$ | 92 | 5 | 3 | 0.5 | – | 22 | 52 |
| $D_3$ | 92 | 5 | 3 | 0.7 | – | 21 | 45 |
| $D_4$ | 92 | 5 | 3 | – | 0.1 | 10 | 27 |
| $D_5$ | 92 | 5 | 3 | – | 0.3 | 13 | 23 |
| $D_6$ | 92 | 5 | 3 | – | 0.5 | 12 | 24 |
| $E_1$ | 90 | 5 | 5 | 0.3 | – | 26 | 41 |
| $E_2$ | 90 | 5 | 5 | 0.5 | – | 25 | 39 |
| $E_3$ | 90 | 5 | 5 | 0.7 | – | 25 | 40 |
| $E_4$ | 90 | 5 | 5 | – | 0.1 | 15 | 31 |
| $E_5$ | 90 | 5 | 5 | – | 0.3 | 20 | 29 |
| $E_6$ | 90 | 5 | 5 | – | 0.5 | 15 | 23 |

Table 4
Effects on setting time (min) and strength (MPa)

| No. | Activators (wt.%) | | | Setting time | | Flexural | | | | Compressive | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | MMR | $Na_2SO_4$ | CM | Initial | Final | 1 day | 3 days | 7 days | 28 days | 1 day | 3 days | 7 days | 28 days |
| $B_3$ | – | – | – | 14 | 32 | 7.68 | 10.0 | 9.63 | 6.95 | 61.5 | 69.5 | 71.0 | 68.8 |
| $B_5$ | 1.3 | – | – | 18 | 36 | 7.46 | 10.2 | 10.9 | 8.53 | 70.5 | 78.2 | 83.3 | 86.2 |
| $B_6$ | – | 1 | 0.5 | 15 | 33 | 7.87 | 11.44 | 12.9 | 7.53 | 71.2 | 76.8 | 81.4 | 77.3 |
| $B_7$ | 1.3 | – | 0.5 | 22 | 40 | 7.07 | 9.35 | 9.10 | 7.69 | 61.3 | 77.9 | 80.2 | 80.0 |
| $B_4$ | – | – | – | 8 | 21 | 7.61 | 8.89 | 8.38 | 7.41 | 62.4 | 70.8 | 74.3 | 77.1 |
| $B_8$ | 1.3 | – | – | 19 | 27 | 7.45 | 11.28 | 10.96 | 8.0 | 67.1 | 74.7 | 75.7 | 82.4 |
| $B_9$ | – | 1 | 0.5 | 12 | 23 | 7.04 | 11.16 | 11.82 | 7.74 | 69.9 | 81.2 | 80.7 | 79.8 |
| $B_{10}$ | 1.3 | – | 0.5 | 23 | 32 | 7.05 | 10.14 | 11.4 | 8.44 | 65.8 | 77.8 | 82.5 | 83.4 |
| $B_{11}$ | 1.3 | 1 | – | 9 | 17 | 7.3 | 11.6 | 12.3 | 9.41 | 68.4 | 73.6 | 82.2 | 80.2 |
| $B_{12}$ | 1.3 | 1 | 0.5 | 11 | 23 | 6.42 | 10.8 | 12.2 | 8.91 | 68.0 | 76.5 | 83.0 | 80.2 |

the $SO_4^{2-}$, $Al^{3+}$ and $Ca^{2+}$ ions. So, a suitable amount of burnt plaster is very important. The best amount of burnt plaster 7–9% is recorded in order to keep sufficient $SO_4^{2-}$ supply for much more ettrigite formation.

The expansibility of sulphoaluminate cement also improves with the increase of alunite from 0% to 11%. The alunite dissolves to release $SO_4^{2-}$ and $Al^{3+}$, which reacts with $Ca(OH)_2$ to form AFt. Therefore, the more the amount of alunite, the more the amount of AFt and the greater the expansibility of cement. The best amount of alunite is 7–9%.

### 3.4. Effect of fineness and activators on the drying contraction of cement mortar

The drying contraction resulting in appearance of internal cracks may occur when the water in the cement stone loses in dry surroundings. The drying contraction ratio has been tested in order to investigate the effect of fineness and activators. The data are listed in Table 6.

With the increase of specific surface area, the contraction ratios of specimens $B_1$, $B_2$ and $B_3$ at same age are reduced and turned to the expansion ratios. It illustrates that the densification of cement stone structure increases with high specific surface area, and the ability to protect water against evaporation is also high. The expansion ratio of samples $B_4$, $B_{12}$ is similar to that of $B_3$, but it is stabilized by burnt plaster after 3 months. The results indicate that, according to the requirements of building engineering, the drying contraction ratio or expansion ratio can be controlled by the burnt plaster and other activators.

Table 5
Effect of burnt plaster and alunite on expansion ratio ($10^{-4}$)

| No. | Dosages (wt.%) | | | Expansion ratio | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | SCC | G | A | 1 day | 3 days | 7 days | 14 days | 28 days | Half year |
| $I_0$ | 95 | 5 | – | −15.7 | −16.2 | −17.0 | −16.5 | −17.8 | −15.9 |
| $I_1$ | 92 | 5 | 3 | −13.6 | −13.9 | −15.8 | −15.7 | −14.0 | −15.0 |
| $I_2$ | 90 | 5 | 5 | −11.9 | −12.8 | −13.0 | −12.0 | −12.7 | −11.5 |
| $I_3$ | 88 | 5 | 7 | −8.7 | −9.2 | −9.8 | −9.7 | −8.53 | −8.9 |
| $I_4$ | 86 | 5 | 9 | −7.0 | −8.3 | −8.8 | −9.1 | −8.2 | −8.9 |
| $I_5$ | 84 | 5 | 11 | −4.7 | −7.3 | −7.8 | −6.8 | −5.8 | −5.4 |
| $J_0$ | 93 | 7 | – | 0.1 | 0.2 | 0.1 | 0.3 | 0.2 | 0.3 |
| $J_1$ | 90 | 7 | 3 | 2.1 | 0.9 | 0.9 | 5.4 | 2.6 | 2.9 |
| $J_2$ | 88 | 7 | 5 | 3.5 | 5.1 | 1.4 | 1.9 | 2.6 | 3.8 |
| $J_3$ | 86 | 7 | 7 | 2.6 | 1.8 | 1.4 | 2.4 | 3.1 | 2.7 |
| $J_4$ | 84 | 7 | 9 | 2.4 | 1.6 | 2.1 | 2.4 | 2.9 | 2.6 |
| $J_5$ | 82 | 7 | 11 | 2.7 | 2.3 | 3.0 | 3.6 | 5.4 | 4.3 |
| $K_0$ | 91 | 9 | – | 0.2 | 0.3 | 0.2 | 0.4 | 0.3 | 0.4 |
| $K_1$ | 88 | 9 | 3 | 2.0 | 0.7 | 1.1 | 1.8 | 3.5 | 2.4 |
| $K_2$ | 86 | 9 | 5 | 2.0 | 0.9 | 1.1 | 1.8 | 2.9 | 2.7 |
| $K_3$ | 84 | 9 | 7 | 2.4 | 1.6 | 1.9 | 2.4 | 3.3 | 2.5 |
| $K_4$ | 82 | 9 | 9 | 2.6 | 2.0 | 2.3 | 2.9 | 3.5 | 3.0 |
| $K_5$ | 80 | 9 | 11 | 2.9 | 2.7 | 3.1 | 3.6 | 4.0 | 3.3 |

### 3.5. Chemical resistance

The main erosion ions, $SO_4^{2-}$, $Mg^{2+}$ and $Cl^-$, diffuse through the capillary pores into the inner concrete first and then react with the hydration products of the cement, such as the hydrated aluminate, C–S–H gel, to form the expanding products AFt or products without gelating property. The structure of the cement stone is destroyed and the building is broken down. Although the sulfoaluminate cement has been shown to exhibit high resistance to sulfates [12], the erosion is examined in "accelerated test" conditions for three kinds of solutions with high concentration erosion ions as listed in Table 7. According to the proportion of Table 4, the mortar samples have been made with 40 × 40 × 160 mm size. They have been cured in fresh water for 14 days first and then immersed respectively in three kinds of corrosive solutions for another 465 days and subjected to strength test. The

Table 6
Drying contraction ratio of cement mortar ($10^{-4}$)

| No. | 7 days | 14 days | 21 days | 28 days | 3 months | 6 months | 1 year |
|---|---|---|---|---|---|---|---|
| $B_1$ | −3.41 | −7.55 | −7.60 | −7.28 | −7.51 | −7.36 | −8.17 |
| $B_2$ | −1.40 | −1.43 | −2.16 | −1.70 | −1.21 | −1.60 | −1.8 |
| $B_3$ | +0.70 | +0.48 | +0.24 | +0.60 | +1.44 | +0.86 | +0.91 |
| $B_4$ | +0.53 | +0.15 | +0.25 | +0.13 | +0.32 | +0.52 | +0.47 |
| $B_{12}$ | +1.10 | +0.73 | +1.17 | +0.85 | +0.87 | +0.80 | +0.78 |

Table 7
Ions concentrations of erosion solution (mg/l)

| Solution | $SO_4^{2-}$ | $Mg^{2+}$ | $Cl^-$ |
|---|---|---|---|
| L | 5000 | 8100 | 20 000 |
| M | 10 000 | 12 800 | 30 000 |
| N | 20 000 | 18 700 | 40 000 |

results are shown in Table 8. Taking the strength of specimens cured for the same duration in fresh water as a control, we can determine the chemical resistance ability of the cement by the strength reduction ratio. In Table 8, the numerator is strength (MPa) and the denominator is strength ratio (%).

The experimental results in Table 8 show that the flexural strength of samples $B_4$ and $B_{12}$ and the compressive strength of $B_4$ increase by different degrees in three kinds of solutions with high concentration erosion ions for 465 days, for example, flexural strength of specimen $B_4$ increases by 40% in solution M and the compressive strength increases by 9% in solution N. The high ability of resistance to chemical erosion is associated with the presence of large crystals of ettringite and lower volume porosities (see Table 9). While the strength loss of sample $B_1$ and $B_2$ is heavy, the compressive strength of $B_2$ decreases by 35% in solution L and decreases by 41% in solution M. Thus, activators promote the hydration degree of sulphoaluminate cement and density of the structure, and improve the ability of chemical resistance of the cement.

## 4. Hydration product and mechanism analysis

### 4.1. Hydration product analysis

#### 4.1.1. XRD analysis

Figs. 3 and 4 give the XRD patterns of specimens hydrated at Days 1, 3, 7 and 28, respectively. The main hydration products are ettringite (*d*: 9.67, 5.67 and 3.88 Å), the diffraction peaks of calcium sulphoaluminate hydrate, $C_3A{\cdot}CaSO_4{\cdot}12H_2O$ (AFm) (*d*: 4.71, 2.86 and 2.47 Å) for $B_3$ specimen also appeared at all ages. Otherwise, the peak values of ettringite in specimens $B_{11}$ and $B_{12}$ are higher than that in $B_3$, implying that the more AFt are produced by the promotion of activators, yet AFm hydration products are lower than that of $B_3$. Existence of $C_4A_3\bar{S}$ (*d*: 3.75, 2.65 and 2.17 Å) and β-$C_2S$ (*d*: 2.78, 2.73 and 2.60 Å) is confirmed by the detection of above diffraction peaks; the intensity was reduced gradually with the prolonging hydration ages in every XRD patterns.

Table 8
Resistance to chemical corrosion (MPa/%)

| No. | | Fresh water | L | M | N |
|---|---|---|---|---|---|
| $B_1$ | Flexural | 8.9/100 | 9.23/104 | 7.58/85 | 9.23/104 |
| | Compressive | 74.7/100 | 68.7/92 | 44.2/59 | 43.3/58 |
| $B_2$ | Flexural | 9.92/100 | 6.28/62 | 7.04/71 | 5.84/59 |
| | Compressive | 80.4/100 | 52.5/65 | 47.2/59 | 56.3/70 |
| $B_4$ | Flexural | 6.45/100 | 8.1/126 | 9.03/140 | 8.73/135 |
| | Compressive | 72.3/100 | 78.2/108 | 77.6/107 | 78.5/109 |
| $B_{12}$ | Flexural | 9.0/100 | 10.15/113 | 10.41/116 | 10.85/121 |
| | Compressive | 100.9/100 | 97.8/97 | 98.2/97 | 90.5/90 |

Table 9
Porosity and pore size distribution (%) of cement paste for 28 days

| No. | Porosity (%) | MPD (Å) | APD (Å) | >10 (μm) | 10–1 (μm) | 1–0.1 (μm) | 0.1–0.05 (μm) | 0.05–0.01 (μm) | <0.01 (μm) |
|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | 20.28 | 135 | 230 | 4.00 | 1.85 | 2.00 | 6.15 | 75.95 | 10.05 |
| $B_2$ | 21.45 | 154 | 286 | 2.00 | 1.10 | 1.00 | 1.15 | 76.50 | 18.25 |
| $B_4$ | 17.22 | 55 | 105 | 1.95 | 1.20 | 0.14 | 0.61 | 70.10 | 26.00 |
| $B_{12}$ | 18.34 | 68 | 146 | 2.10 | 1.90 | 0.75 | 0.50 | 67.85 | 26.90 |

MPD: median pore diameter, APD: average pore diameter.

#### 4.1.2. DTA analysis

Figs. 5 and 6 are the thermograms of specimens $B_3$, $B_{11}$ and $B_{12}$ hydrated at different ages. The dehydration peaks of C–S–H gel (at 110 °C), AFt (at 110 °C) and $Al(OH)_3$ gel (at 110 and 270 °C) in the pastes of $B_{11}$ and $B_{12}$ are higher, and the endothermic peaks of calcium carbonate (at 670 °C) and AFm (at 160 °C) are absent, or are lower than in $B_3$ at Days 1, 3, 7 and 28, implying higher contents of C–S–H gel, AFt and $Al(OH)_3$ gel and lower AFm for $B_{11}$ and $B_{12}$ than that for $B_3$. The calcium carbonate is formed by the reaction between the $Ca(OH)_2$ released from the hydration of β-$C_2S$ in the cement stone at Day 28 and $CO_2$ in atmosphere, leading to the endothermic peaks.

#### 4.1.3. SEM analysis

The large amount of $Al(OH)_3$ gel exists in harden pastes of sample $B_{12}$ at Day 1 (see Fig. 7) and short rod-like

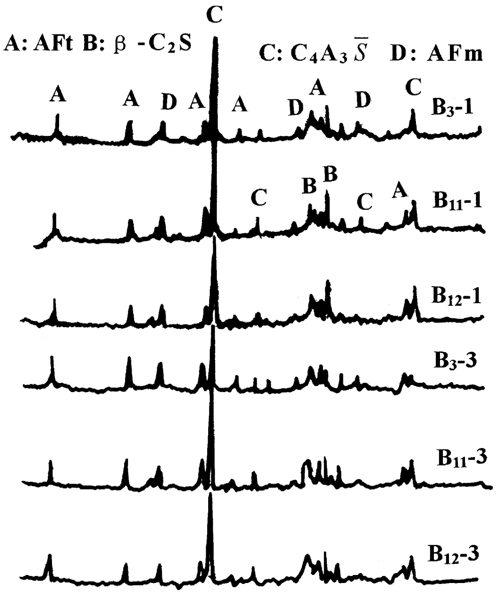

Fig. 3. XRD patterns of paste at 1 and 3 days.

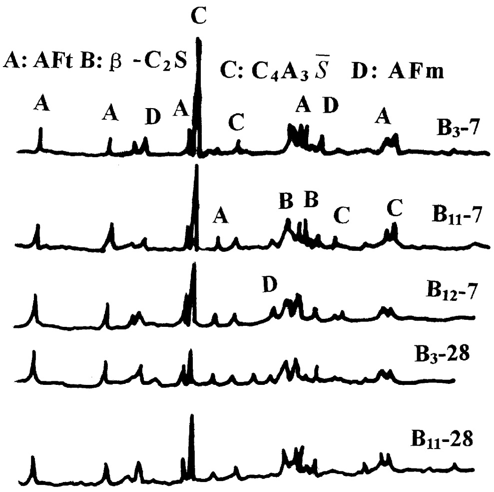

Fig. 4. XRD patterns of paste at 7 and 28 days.

crystals of ettringite exist in $B_{11}$ hydrated at Day 3 (see Fig. 8). The tabular or lamellar crystals of calcium sulphoaluminate hydrate $C_3A{\cdot}CaSO_4{\cdot}12H_2O$, which came from the inversion of ettringite, exist in the hardened paste of sample $B_3$ hydrated at Day 28 (see Fig. 9), leading to the strength reduction of cement stone, for example, in Table 4, the compressive strength of $B_3$ decreases to 68.8 MPa at 28 days from 71.0 MPa at 7 days.

Based on the above analysis, the main hydration products are the ettringite, C–S–H gel, $Al(OH)_3$ and calcium sulphoaluminate hydrate(AFm). Besides anhydrous $C_4A_3\overline{S}$ and β-$C_2S$ remained in the cores enclosed by the hydration products. The activators improve the hydration to produce more products and density of the structure.

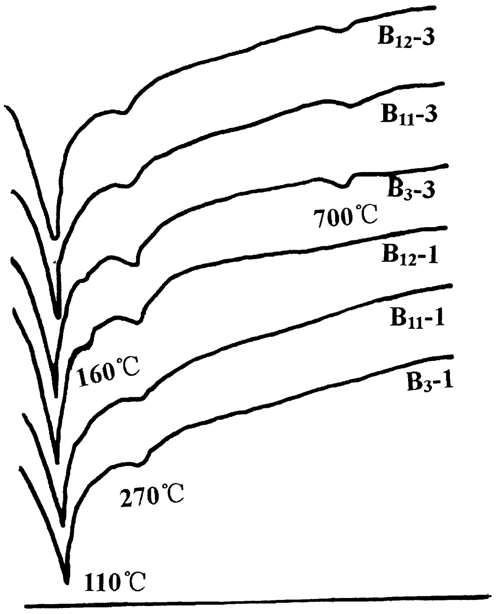

Fig. 5. Thermograms of paste at 1 and 3 days.

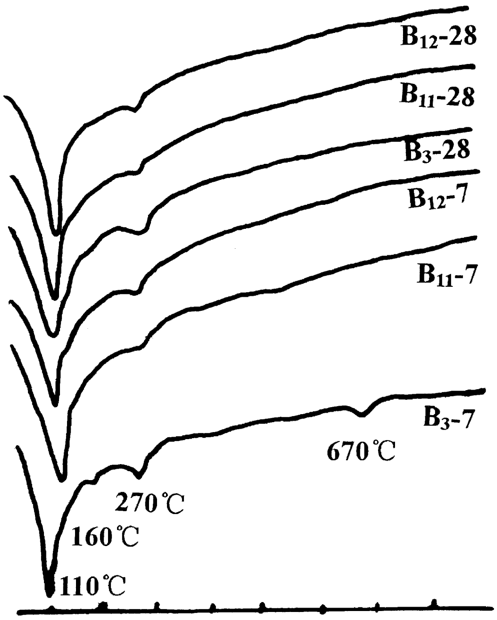

Fig. 6. Thermograms of paste at 7 and 28 days.

### 4.2. Mechanism analysis of hydration

The main minerals of sulphoaluminate cement are $C_4A_3\overline{S}$, β-$C_2S$ and $C_{12}A_7$. They react with water and gypsum to form hydration products. The reaction equations are the following.

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + nH \rightarrow 2Al(OH)_3 + C_3A \cdot 3C\overline{S} \cdot H_{32}(AFt) \quad (2)$$

$$C_{12}A_7 + 12C\overline{S}H_2 + nH \rightarrow 3Al(OH)_3 + 4C_3A \cdot 3C\overline{S} \cdot H_{32}(AFt) \quad (3)$$

$$C_{12}A_7 + nH \rightarrow 3Al(OH)_3 + 4C_3AH_6 \quad (4)$$

$$\beta\text{-}C_2S + mH \rightarrow C - S - H + Ca(OH)_2 \quad (5)$$

$$AH_3 + C_3A \cdot 3C\overline{S} \cdot H_{32} + Ca(OH)_2 \rightarrow C_3A \cdot C\overline{S}H_{12}(AFm) \quad (6)$$

The higher solubility and rapid solution of gypsum make the concentration of $SO_4^{2-}$ ions reach the saturation point immediately in water. According to Eqs. (2) and (3), the ettringite is formed and the $Al(OH)_3$ gel is released quickly covering the external surface of $C_4A_3\overline{S}$ and $C_{12}A_7$. Thus, the diffusion velocity of water through products layer is decreased and the setting time is prolonged. Because the formation speed of ettringite is high, more defects exist in the ettringite, resulting in the lower stability and transforma-

Fig. 7. SEM photo of $B_{12}$ hydrates at 1 day.

tion to calcium sulphoaluminate hydrates (AFm) after 7 days with the inadequateness of concentration of $SO_4^{2-}$ ions according to Eq. (6). Therefore, the calcium sulphoaluminate hydrate exists in the cement pastes hydrated for 28 days, and the strength of samples decreases after 7 days. In contrast, the slow dissolution of burnt plaster [9,10] makes the ettringite formation slow and the crystal structure of ettringite stabilized. Thus, the transformation is difficult and the regression of compressive strength does not occur at Day 28. When the CL and CM are absorbed on the surface of mineral grains of cement clinker, a hydrophilic thin film is formed. With the water film between two particles thickening, the coherence of cement particles and condensation of hydration products are retarded, resulting in postponed setting of the cement paste.

With the prolongation of hydration ages, the dissolution of burnt plaster and alunite keeps a certain concentration of $SO_4^{2-}$, which reacts with $C_4A_3\bar{S}$ or $Al(OH)_3$ gel to form ettringite, densifying the structure of the cement stone. The $Al(OH)_3$ gel comes from two parts, one is from the hydration of $C_4A_3\bar{S}$ and $C_{12}A_7$ as Eqs. (2)–(4) illustrate and another is from the dissolution of alunite. There are two parts $Al(OH)_3$ gel supply enough to form ettringite. The $Ca(OH)_2$ saturation solution takes up when $\beta$-$C_2S$ hydrates to form C–S–H gel as expressed in Eq. (5). Then, the reaction between $Ca(OH)_2$, $Al(OH)_3$ gel and $SO_4^{2-}$ takes place as Eq. (7).

$$AH_3 + 3CH + 3C\bar{S}H_2 + nH \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32} \tag{7}$$

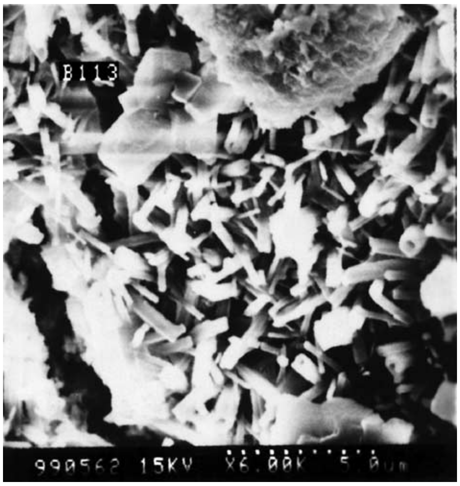

Fig. 8. SEM photo of $B_{11}$ hydrates at 3 days.

Fig. 9. SEM photo of $B_3$ hydrates at 28 days.

The ettringite fills macropores. The interline large pores are cut-off to disintegrate toward the smaller pores and the diameter of pores reduces gradually. Therefore, the density of cement stone structure is increased, the regression of compressive strength is retarded and the resistance to chemical erosion is higher. The amount of burnt plaster and alunite must be proper, because the anhydrous $C_4A_3\bar{S}$, $Al(OH)_3$ and $Ca(OH)_2$ exist in cement paste, they react with $CaSO_4$ to form ettringite, which causes a higher expansion ratio in cement stone, leading to the destruction of building structure at later ages. The $Na_2SO_4$ used as activator improves the strength of sulphoaluminate cement at Days, 1, 3 and 7, but the high forming speed of ettringite gets the crystals to have many defects, which transform easier to form calcium sulphoaluminate hydrate and reduce the strength.

Based on the above analysis, the crystal structure of ettringite is stabilized when alunite and burnt plaster substituted for gypsum admixes with cement clinker. The formation of ettringite with a certain concentration of $SO_4^{2-}$ and $Al(OH)_3$ gel after 7 days increases the density of cement paste structure and suppresses the regression of compressive strength. It has not only compensated shrinkage of the cement stone, but also made it slightly expanded. When the CL and CM are absorbed on the surface of mineral grains of the cement clinker, the coherence of hydration products are retarded and the hydration speed of mineral clinker reduces, and the setting time is prolonged.

## 5. Conclusions

(1) The proper composition of burnt plaster and alunite improved the strength of sulphoaluminate cement, and retarded the reduction of the compressive strength after 7 days, and not only compensated shrinkage, but also made the product slightly expanded. The best contents of these activators: burnt plaster and alunite were 7–9%, respectively, added in cement clinker. The $Na_2SO_4$ improved the early strength, but did not suppress the regression of compressive strength after 7 days. The setting time was prolonged by the activators of CL, CM, the best amounts were 0.3–0.5% admixed in cement, respectively, and MMR, with the optimum content 1.3%. Meanwhile, the increase of the weight percentage of particles that were smaller than 60 μm in diameter promoted the process of mineral hydration and improved the strength of cement.

(2) The hydration products of sulphoaluminate cement were ettringite, $Al(OH)_3$ gel, C–S–H gel and calcium sulphoaluminate hydrates (AFm). With the existence of appropriate amounts of burn plaster and alunite, the ettringite from the hydration between the $SO_4^{2-}$ and $C_4A_3\bar{S}$ or $Al(OH)_3$ gel increased the density of paste structure, and the transformation for ettringite to calcium sulphoaluminate (AFm) is inhibited, thus, the regression of compressive strength is suppressed after 7 days. The condensation of $Al(OH)_3$ gel, C–S–H gel and ettringite between each other increased the density of the structure of cement stone and improved the resistance to drying contraction and chemical corrosion.

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