

The Synthesis and Mechanical Performances of Barium-Calcium Sulfoaluminate Mineral

Lu L., Ye Z., Yu L., Chang J., Cheng X.
Jinan University, Jinan, China

ABSTRACT

Barium-calcium sulfoaluminate mineral, $2.75\text{CaO}\cdot 1.25\text{BaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$ ($\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{S}$), has the excellent cementing properties. The present work was to investigate the formation process, mechanical performances of $\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{S}$ and the effect of CaF_2 on the synthesis and compressive strength of the mineral. Results derived by XRD, SEM-EDS and showed that small amounts of CaF_2 could accelerate the decomposition of CaCO_3 , decrease the sintering temperature and promote the formation of $\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{S}$ at a low temperature of 1300°C . Meanwhile, $11\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot \text{CaF}_2$ was found in the formation process of $\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{S}$ when CaF_2 was added. In addition, the compounds, such as $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, $\text{BaO}\cdot \text{Al}_2\text{O}_3$ and $\text{CaO}\cdot \text{Al}_2\text{O}_3$ were formed in the sintering process of the mineral. Under the experimental conditions, a large quantity of barium-calcium sulfoaluminate mineral was found at about $1300\text{-}1350^\circ\text{C}$. When temperature was higher than 1400°C , it began to decompose slowly. The synthesized barium-calcium sulfoaluminate mineral has the properties of high early strength and the compressive strength at 1350°C that is the highest than the samples sintered at other temperatures. The small amount of CaF_2 can increase the early mechanical performance of the mineral and the optimal content of CaF_2 is 1.5wt%.

KEY WORDS: Barium-calcium sulfoaluminate; Synthesis; Mechanical performance; CaF_2

1 Introduction

In recent years, a new kind of cementing mineral, barium-calcium sulfoaluminate $(3-x)\text{CaO}\cdot x\text{BaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$ (abbr. as $\text{C}_{(4-x)}\text{B}_x\text{A}_3\bar{S}$, $x=1\sim 3$), has been found. It has been proved that have higher compressive strength than $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$ (abbr. as $\text{C}_4\text{A}_3\bar{S}$). The new series minerals were obtained by partly replacing Ca^{2+} with Ba^{2+} in $\text{C}_4\text{A}_3\bar{S}$ [1~4]. Further studies on series of the minerals $\text{C}_{(4-x)}\text{B}_x\text{A}_3\bar{S}$ ($x=1\sim 3$) showed that the mineral $1.75\text{CaO}\cdot 1.25\text{BaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$ (abbr. $\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{S}$) has optimal properties, which compressive strengths are 35.1, 59.3 and 72.1MPa at 1, 3 and 7 days age respectively [5]. CaF_2 is a good mineralizer in the production of Portland cement and Ba-bearing sulfoaluminate cement

First author: LU Lingchao (1963 -) male, Prof., Ph.D. Jinan, Shandong, China.

The National Natural Science Foundation of China (50672033) .

Tel.: +86-531-276-7977; fax: 86-531-797-4453 Email address: lulingchao@ujn.edu.cn (l. lu)

[6,7]. The effect of CaF_2 on the sintering clinker and cement properties is very important although its content is low. In this paper, the effect of CaF_2 on the synthesis and performances $\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{\text{S}}$ was analyzed, which will further give guidance for the production of alite-barium calcium sulfoaluminate cement[8].

2 Experimental

2.1 Raw Materials

Analytical grade reagents CaCO_3 , BaSO_4 , BaCO_3 and Al_2O_3 were used as raw materials. They were ground to pass 80 μm sieves.

2.2 Methods

According to the stoichiometric molar ratio of $\text{C}_{2.75}\text{B}_{1.25}\text{A}_3\bar{\text{S}}$, each reagent was weighted accurately. The code of samples and the content of CaF_2 were listed in Table 1. The raw materials were homogenized and pressed to cylinders of $\phi 50\text{mm} \times 10\text{mm}$, and then the cylinders were fired from room temperature to 1400 $^\circ\text{C}$ with a heating rate of 5 $^\circ\text{C}/\text{min}$. The holding time at different sintering temperatures was as follows: 5min at 800 $^\circ\text{C}$ and 1000 $^\circ\text{C}$, 90min at 1200 $^\circ\text{C}$, 1250 $^\circ\text{C}$, 1300 $^\circ\text{C}$, 1350 $^\circ\text{C}$ and 1400 $^\circ\text{C}$, respectively. After sintering, the samples were fast cooled in air.

Table 1 Experiment scheme

| Samples No. | 1 | 2 | 3 | 4 |
|---------------------------|---|-----|-----|-----|
| $\text{CaF}_2/\text{w}\%$ | 0 | 1.0 | 1.5 | 2.0 |

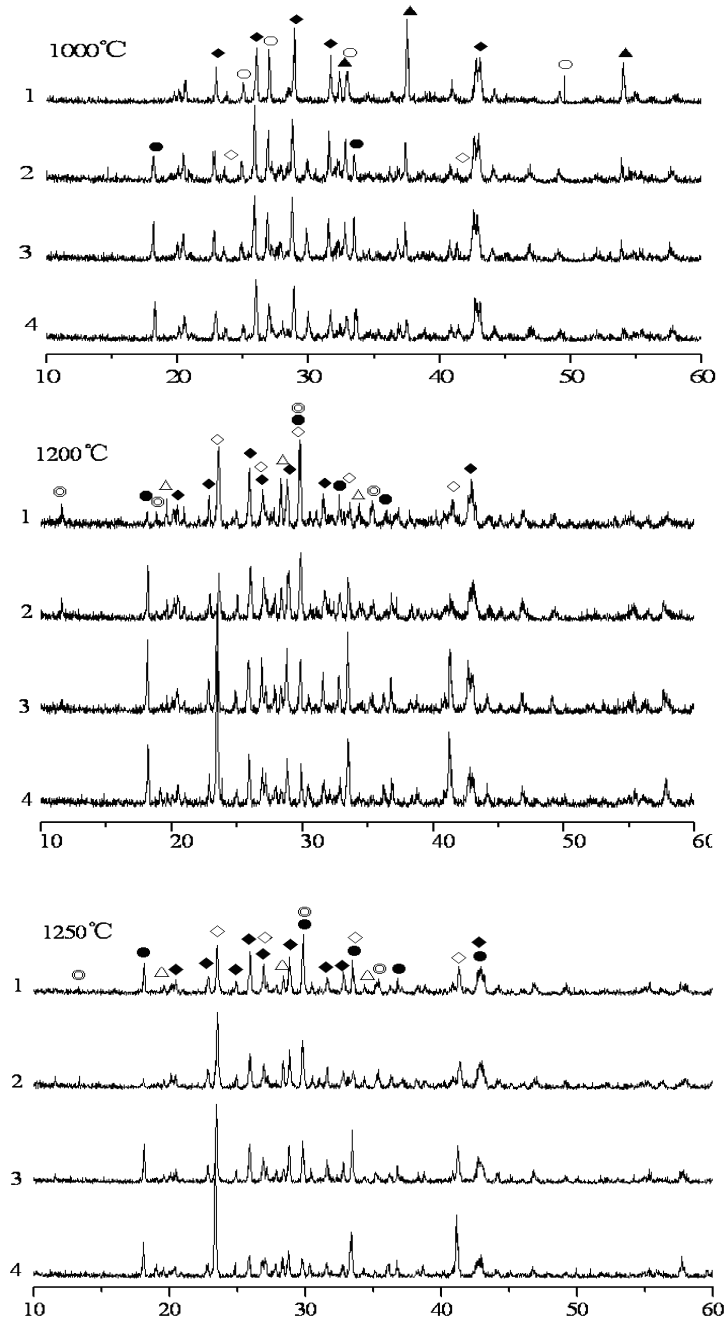
After adding 5 wt% gypsum, the clinker was ground to fine powders whose fineness is indicated by the residue of the 80 μm sieve. The minerals were mixed with water to a cement paste with a W/C ratio of 0.3. The paste was put into a 2 \times 2 \times 2cm³ mould by vibration. These paste specimens were demoulded after being cured in moist air at 20 $^\circ\text{C}$ for 24 hrs, then were cured in water at 20 $^\circ\text{C}$ to each age for measuring the compressive strength which was average value of the four specimens. The X-ray diffraction (XRD) analysis was performed on a D/max-rA diffractometer to identify the mineral phases. S-2500 scanning electronic microscope (SEM) equipped with a link ISIS-30 energy dispersive X-ray spectrometer (EDS) was used to investigate the mineral microstructure and feature.

3 Results and discussion

3.1 Synthesis of the mineral

With the increase of sintering temperature, the barium-calcium sulfoaluminate formed through solid-phase reaction. Meanwhile, some substance or intermediate compounds could also form. In order to investigate the type of the minerals and their formation conditions,

especially the formation temperature, samples sintered at different temperatures were analyzed by means of XRD. The results are showed in Fig. 1.



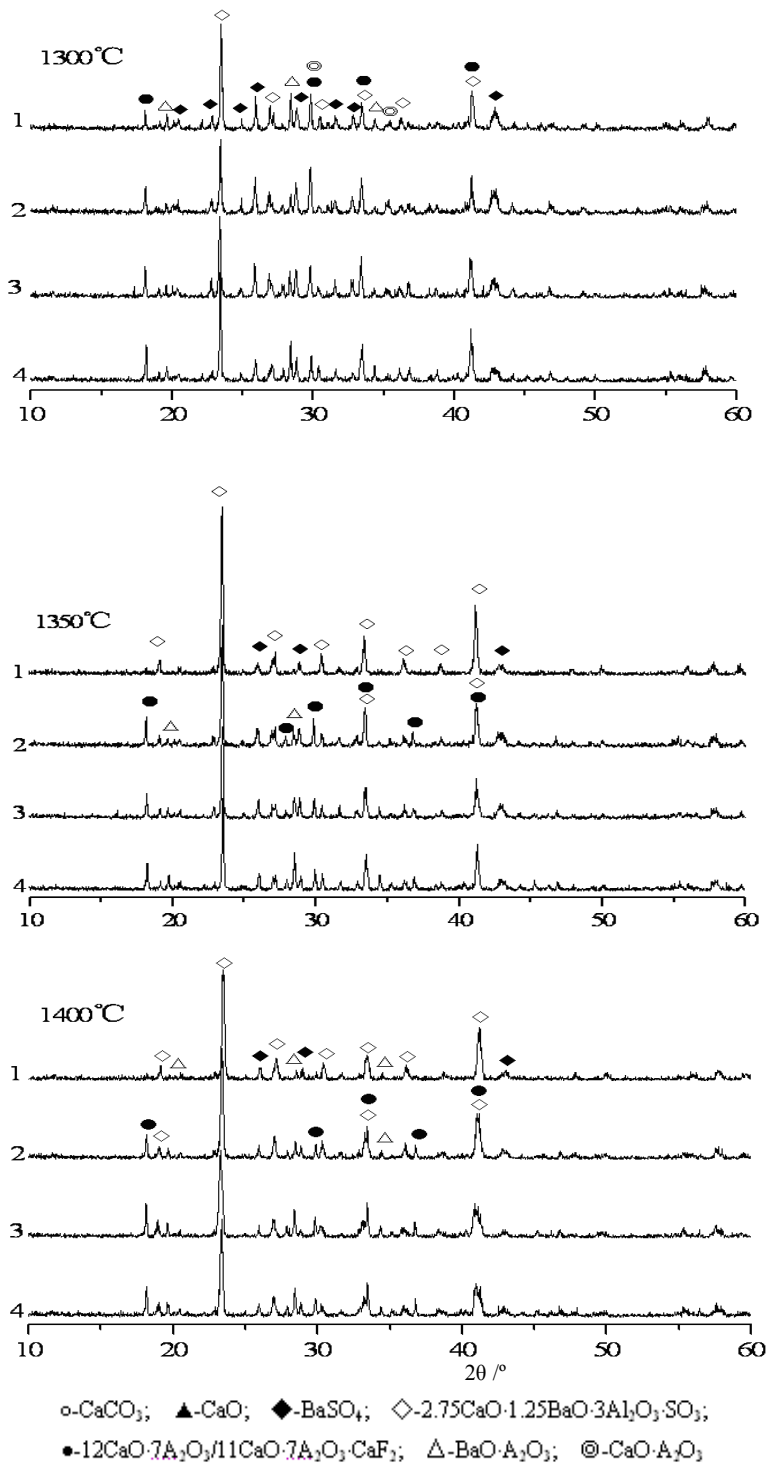


Figure 1 X-ray diffraction (XRD) patterns of samples at different sintering temperature

At 1000°C for 5 min, minerals including CaO, BaSO₄ and CaCO₃ are observed in sample1 without CaF₂, indicating that CaCO₃ did not decompose completely and BaSO₄ did not react fully with other oxides at this temperature. In the samples added with a small quantity of CaF₂, the

XRD peaks of CaCO_3 weaken slowly along with increasing CaF_2 . Meanwhile, CaO content was lower than that in the sample without CaF_2 . It proves that CaF_2 accelerates the decarbonation reaction. In addition, the characteristic peaks of $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$ appear in the XRD patterns and the diffractive intensity is the highest in the sample with 1.5% CaF_2 . Barium-calcium sulfoaluminate is found in sample 2 and sample 3. It indicates that small amount of CaF_2 could promote the reaction of CaO with other substances and lead to the formation of $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$ and barium-calcium sulfoaluminate at a lower temperature.

When the samples were burned at 1200°C , peaks of C_{12}A_7 were observed in sample 1 and peaks of barium-calcium sulfoaluminate were also noted in all samples. Peaks of BaSO_4 weaken obviously. It proves that barium-calcium sulfoaluminate could be synthesized at about 1200°C . The intensities of diffractive peaks of barium-calcium sulfoaluminate in the samples containing 1-1.5% CaF_2 are higher than that in other samples. Therefore, the suitable amount of CaF_2 benefits to the formation of the mineral. Moreover, other minerals such as $\text{BaO}\cdot\text{Al}_2\text{O}_3$ (BA), $\text{CaO}\cdot\text{Al}_2\text{O}_3$ (CA) also formed, but their peaks are weak.

When the samples were sintered at 1300°C for 120min, the peaks intensity of barium-calcium sulfoaluminate increase continually. It can also be seen that the d-values (3.7858, 3.7953, 3.8049, 3.7953nm) of the mineral increase with the addition of CaF_2 . It implies that more amounts of Ca^{2+} ions were replaced by Ba^{2+} iron along with temperature increasing and CaF_2 benefit to this reaction.

When the samples were roasted at 1350°C for 120min, the diffractive peaks of barium-calcium sulfoaluminate in sample1 reveal the sharpest intensity than that in other samples containing CaF_2 . The reason is that small amounts of $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$ still exist because of the addition of CaF_2 , which consumes part of Al_2O_3 , leading to a decrease of barium-calcium sulfoaluminate.

When sintering temperature was at 1400°C , peaks of barium-calcium sulfoaluminate in all samples were weaker than that in the samples sintered at 1350°C , suggesting that the mineral began to decomposition slowly above 1360°C .

Some samples were examined by SEM-EDS in order to analyze the effect of CaF_2 on the composition and microstructure of minerals (Fig2-Fig5).

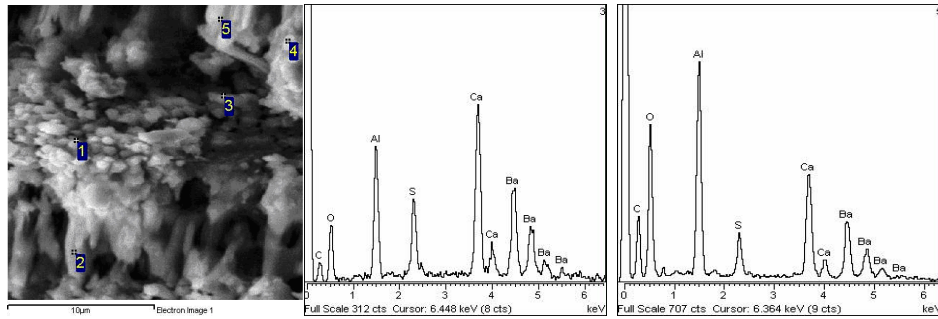


Figure 2 SEM photographs of sample1 (1200°C)

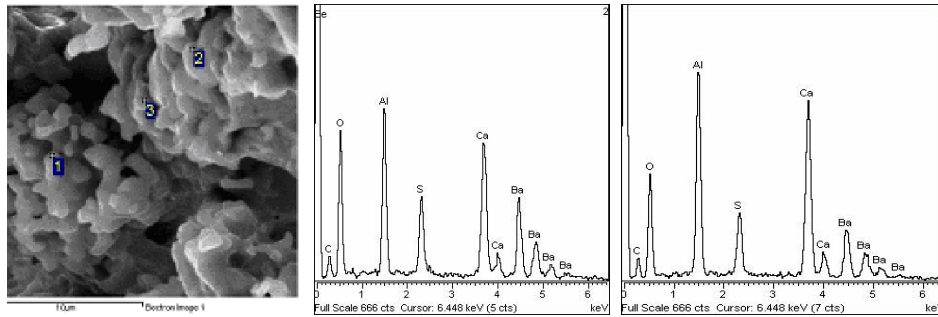


Figure 3 SEM photographs of sample 3 (1200°C)

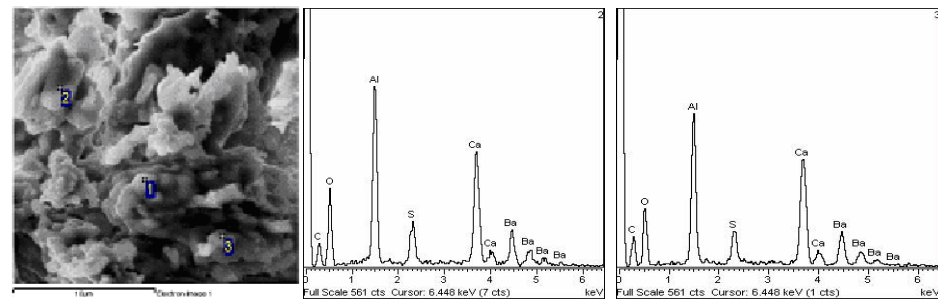


Figure 4 SEM photographs of sample 1 (1350°C)

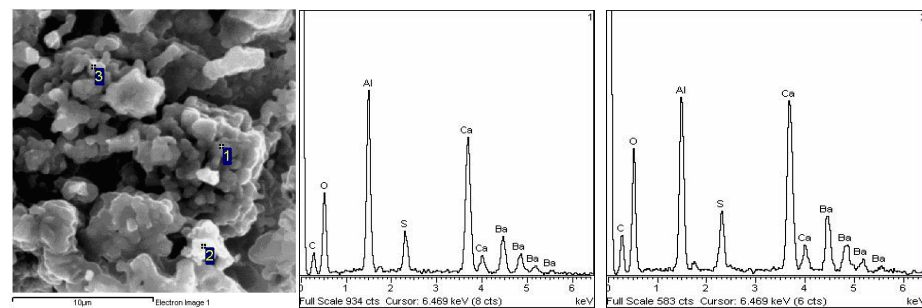


Figure 5 SEM photographs of sample 3 (1350°C)

Fig.2 gives the SEM graph of sample 1 obtained at 1200°C. The outline of the minerals is blurry and their growth is not integrative. Fig.3 illustrates that the content of barium-calcium sulfoaluminate in sample 3 with 1.5% CaF₂ was more than that in sample 1 at the same sintering temperature. The size of the mineral was about 2-4 µm and their shape was more irregular. Fig.4 and Fig.5 are SEM graphs of the sample 1 and sample 3 sintered at 1350°C. It can be found that the content of

barium-calcium sulfoaluminate increased continuously compared with the samples obtained at 1200°C. Large amounts of barium-calcium sulfoaluminate are observed in sample 3, their shape is regular rhombus and the boundary is clear correspondingly. According to the EDS analysis in Fig.4, the constituent of the mineral is $C_{2.82}B_{0.86}A_{2.75}\bar{S}$, approaching to the designed proportion.

3.2 Mechanical performances of the mineral

Table 2 gives the mechanical performances of barium-calcium sulfoaluminate mineral at 1250-1400°C sintering temperature. The mineral has high compressive strength at the early hydration, and the strength increased gradually with sintering temperature. When the temperature is 1350°C, the compressive strength reaches the maximum. If the temperature is increased continuously the strength is reduced and the loss of the early strength is more obvious. In addition, we can find that the strength increased gradually with addition CaF_2 in the mineral and reach the maximum when the content of CaF_2 is 1.5%. The compressive strength at 3, 7 and 28 days curing age are 73.1 79.6 and 102.9MPa individually, which exhibits the excellent mechanical performance at the early period of hydration. When CaF_2 is added continually in the mineral, the strength begins to decrease. This show a few CaF_2 can promote the systemization of $C_{2.75}B_{1.25}A_3\bar{S}$ and benefits the increase of the early strength of the mineral.

Table 2 Compressive strength of the hardened paste of the mineral

| No. | Sintering temperature /°C | Compressive strength /MPa | | | |
|-----|---------------------------|---------------------------|-------|-------|-------|
| | | 1d | 3d | 7d | 28d |
| 1 | 1250 | 39.3 | 34.1 | 40.3 | 36.5 |
| 2 | | 34.0 | 40.0 | 46.1 | 48.1 |
| 3 | | 39.5 | 49.4 | 63.6 | 64.7 |
| 4 | | 56.8 | 81.9 | 91.2 | 92.5 |
| 1 | 1300 | 45.7 | 51.1 | 44.1 | 44.9 |
| 2 | | 35.6 | 43.2 | 49.1 | 50.3 |
| 3 | | 47.6 | 65.7 | 59.0 | 68.8 |
| 4 | | 52.35 | 64.93 | 66.15 | 80.25 |
| 1 | 1350 | 62.8 | 56.4 | 65.6 | 73.9 |
| 2 | | 57.2 | 46.7 | 68.7 | 70.3 |
| 3 | | 73.1 | 79.6 | 86.9 | 102.9 |
| 4 | | 53.9 | 57.7 | 69.8 | 89.5 |
| 1 | 1400 | 37.5 | 39.0 | 36.6 | 26.3 |
| 2 | | 52.1 | 64.2 | 73.4 | 93.5 |
| 3 | | 57.8 | 62.1 | 75.8 | 102.2 |
| 4 | | 29.3 | 34.7 | 40.3 | 66.4 |

4 Conclusions

(1) The barium-calcium sulfoaluminate began to form at about 1160°C,

large quantities of the mineral were found at about 1300-1350°C. When sintering temperature was higher than 1400°C, the mineral began to decompose slowly.

(2) A small amount of $C_{12}A_7$, CA and BA were formed in the sintering process of barium-calcium sulfoaluminate. When CaF_2 was added, $C_{11}A_7 \cdot CaF_2$ was found in the sintering process, then Al_2O_3 in raw materials was consumed partly, which leads to a decrease of the quantity of barium-calcium sulfoaluminate above 1300°C.

(3) CaF_2 can decrease the formation temperature of barium-calcium sulfoaluminate and promote the mineral synthesis at a low temperature of 1300°C.

(4) The optimal sintering temperature of the $C_{2.75}B_{1.25}A_3\bar{S}$ mineral is 1350°C and the suitable content of CaF_2 is 1.5%. The compressive strength of the mineral at 3, 7 and 28 days curing age are 73.1 79.6 and 102.9 MPa respectively

REFERENCES

- [1] I.Tereanu, M. Muntean, I. Dragnea, Type3($CaO \cdot Al_2O_3$) $M_x(SO_4)_y$ compounds and compatibility relations in $CaO - CaO \cdot Al_2O_3 - M_x(SO_4)_y$ systems. II Cement 83 (1) (1986) 39-45
- [2] Chang Jun, Lu lingchao, Study on ba-bearing calcium sulfoaluminate cement mineral. Journal of the Chinese Ceramic Society 27 (6) (1999) 644-650
- [3] Zhang Wensheng, Ouyang Shixi, Chen Yimin, Study on the Compound formation in system $CaO - Al_2O_3 - BaSO_4$ and the formation kinetics of $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$. Journal of the Chinese Ceramic Society 29 (4) (2001) 305-308
- [4] Zhang Wensheng, Li Beixing, Chen Yimin, Study on the stability of the mineral $3CaO \cdot 3Al_2O_3 \cdot BaSO_4$. Journal of the Chinese Ceramic Society 28 (6) (2000) 497-500
- [5] Cheng Xin, Chang Jun, Lu Lingchao, Study of Ba-bearing sulfoaluminate minerals and cement. Cement and Concrete Research 30 (1) (2000) 77-81
- [6] Chang Jun, Cheng Xin, Influence of fluorite on the Ba-bearing sulfoaluminate cement. Cement and Concrete Research 31 (1) (2001) 213-216
- [7] Zhang Wensheng, Yu Qijun, Feng Xiuji, Study on the clinkering process of the barium-containing sulfoaluminate cement clinker. Journal of Building Materials 1 (2) (1998) 182-185
- [8] Cheng Xin, Lu Lingchao, The study on the mineral system of alite-calcium barium sulphominate with good binding characteristic. Journal of the Chinese Ceramic Society 32 (3) (2004) 321-326