EFFECT OF K₂O AND MgO ON THE FORMATION AND HYDRATION ACTIVITY OF Ba-BEARING CALCIUM SULFOALUMINATE

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Submitted April 9, 2016; accepted September 17, 2016

Keywords: Ba-bearing calcium sulfoaluminate, MgO, K₂O, Formation, Hydration

Ba-bearing calcium sulfoaluminate (C₂.₇₅B₁.₂₅A₃$) is characterized by rapid hydration rate and volume stability, as a constituent of the low-CO₂ alternative clinker. In this paper, the effect of K₂O and MgO on the formation and hydration activity of Ba-bearing calcium sulfoaluminate was studied. Results show that according to DSC–TA curves 0.5 - 0.8 wt. % K₂O can reduce the decomposition temperature of CaCO₃ about 10 - 23°C and the decomposition temperature of C₂.₇₅B₁.₂₅A₃$ about 10 - 16°C. And 4.0 ~ 5.0 wt. % MgO can reduce the decomposition temperature of CaCO₃ about 10 - 23°C and the decomposition temperature of C₂.₇₅B₁.₂₅A₃$ about 10 - 16°C. The effect of MgO on hydration activity of C₂.₇₅B₁.₂₅A₃$ is a little better than that of K₂O. This may be due to the reason that MgO, especially at the optimum dosage of 3.0 - 4.0 wt. %, favors the formation of C₂.₇₅B₁.₂₅A₃$ mineral with little impurities such as BaAlO₄ which is obtained from the analysis of XRD. From the released hydration heat rate and cumulative heat release results it is found that 0.5 - 1.1 wt. % K₂O and 2.0 - 4.0 wt. % MgO promote the hydration of C₂.₇₅B₁.₂₅A₃$ because of the lattice distortion and defects. Appropriate amount of MgO (2.0 - 4.0 wt. %) and K₂O (0.8 wt. %) can improve the compressive strength and ensure it steady growth with the increase of curing ages. But 1.4 wt. % K₂O and 5.0 wt. % MgO caused BaSO₄ and BaAlO₄ to extend the hydration of C₂.₇₅B₁.₂₅A₃$ and reduce the compressive strengths at both early ages and late ages.

INTRODUCTION

Calcium sulfoaluminate (C₄A₃$) is one of the main constituents of a low-CO₂ alternative clinker [1-4], which possesses a rapid hydration rate and is the most abundant constituent of sulfoaluminate cement clinkers in marine engineering and waterproof engineering [5-9]. The substitution of Ba²⁺ for Ca²⁺ to improve the performance of C₄A₃$ has been reported [10-13]. The crystal lattice distortion and defects can be caused by the substitution of barium ions by calcium ions. Cheng Xin et al. [14-17] have synthesized the single crystal of Ba-bearing calcium sulfoaluminate, gained the structural data, and confirmed the relationship of structure and activity of Ba-bearing calcium sulfoaluminate minerals. Besides, it has been found out that Ba-bearing calcium sulfoaluminate (C₂.₇₅B₁.₂₅A₃$) develops the highest compressive strength in the series of CaO·xBaO·3Al₂O₃·CaSO₄ (C₃-xBₓA₃$) minerals [18].

Compared with C₄A₃$, C₂.₇₅B₁.₂₅A₃$ is a more promising mineral, which is characterized by high early strength, good permeability resistance, high corrosion resistance, low alkalinity and so on [19]. The hydrating induction period of C₂.₇₅B₁.₂₅A₃$ is much shorter than that of C₄A₃$ [20]: the hydration of C₂.₇₅B₁.₂₅A₃$ begins to accelerate at 4 h and most of the hydration heat is released at 4-12 h. By contrast, the hydration of C₄A₃$ mineral begins to accelerate at 23 h and its hydration heat at 42 h is equal to that of C₂.₇₅B₁.₂₅A₃$ at 12 h. It is thus clear why C₂.₇₅B₁.₂₅A₃$ mineral has the superior performances in terms of early strength and high strength.

More intention is thus being paid to C₂.₇₅B₁.₂₅A₃$-C₃$ cement. In earlier researches, C₂.₇₅B₁.₂₅A₃$ was introduced into belite-rich cement to produce belite-C₂.₇₅B₁.₂₅A₃$ cement, which is a new type of energy-efficient and environmentally friendly cement [21]. It was reported that C₂.₇₅B₁.₂₅A₃$ enhanced the early age property of this cement compared with belite cement [22-24]. It was known that there exist various minor components in the natural materials (limestone, clay, etc.) for cement production, such as MgO, K₂O and so on. Therefore, it is essential to figure out the influence of MgO and K₂O on the formation and hydration activity of C₂.₇₅B₁.₂₅A₃$, and currently no such work has been reported.
This study mainly investigates the separate role of K$_2$O and MgO in the C$_{2.75}$B$_{1.25}$A$_3$S formation and the hydrating and hardening properties, such as hydration rate, hydration heat release, compressive strength development and microstructures of hydration products. It is hoped that this paper could offer available data for scientific system and further industrial production of belite-barium calcium sulfoaluminate cement.

**EXPERIMENTAL**

**Sample preparation**

The samples were synthesized by using analytical chemical reagent grades of CaCO$_3$, Al$_2$O$_3$, BaSO$_4$ and BaCO$_3$ (99.0% from Sinopharm Chemical Reagent Co., Ltd, China) to eliminate the influences of other impurities as much as possible. K$_2$O and MgO were separately added into the raw materials of C$_{2.75}$B$_{1.25}$A$_3$S (2.75CaO·1.25BaO·3Al$_2$O$_3$·CaSO$_4$), whereas the K$_2$O and MgO were respectively derived from K$_2$CO$_3$ and MgO (99.0% from Sinopharm Chemical Reagent Co., Ltd, China). Table 1 shows the specific dosages of dopants (percentage in relation to the pure C$_{2.75}$B$_{1.25}$A$_3$S). The pure C$_{2.75}$B$_{1.25}$A$_3$S without dopants is taken as the blank. The raw materials (finer than 74 μm) were mixed and wetly ground in the planetary mill for 40 minutes to ensure homogenous. Mixtures were then dried and formed 40 mm × 40 mm × 3 mm cubes. After that, the cubes were oven-dried at 105°C for 1-2 h before calcined to 1380°C at a heating rate of 5°C·min$^{-1}$, held for 2 h and then cooled immediately. The calcined samples were ground to the residue weight of less than 5.0% for a 74 μm sieve.

Table 1. Dosages of added K$_2$O and MgO (wt.%).

<table>
<thead>
<tr>
<th>Dopants</th>
<th>Specific dosages</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$O</td>
<td>0 0.5 0.8 1.1 1.4</td>
</tr>
<tr>
<td>MgO</td>
<td>0 2.0 3.0 4.0 5.0</td>
</tr>
</tbody>
</table>

The ground samples were mixed with 8.0 wt. % CaSO$_4$·2H$_2$O (99.0% from Sinopharm Chemical Reagent Co., Ltd, China). Pastes were prepared at a water/cement ratio of 0.35, cast in 20 mm × 20 mm × 20 mm molds and vibrated to remove air bubbles. The molded pastes were kept at 20 ± 2°C and relative humidity exceeding 95.0% for 12 h, and then removed from the molds. The demolded samples were cured in a water tank at 20 ± 2°C for 1, 3, 7 and 28 days.

**Sample testing**

**Free-CaO tests**

The content of free-CaO in cement clinkers was measured according to ethanediol-alcohol method by the fast f-CaO measurement apparatus.

**Thermal analysis**

Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) test were performed to monitor the reaction process of C$_{2.75}$B$_{1.25}$A$_3$S mineral formation. The equipment used was a simultaneous thermal analyzer (TGA/DSC) from Mettler Toledo. The dynamic heating ramp varied between 30°C and 1500°C at a heating rate of 10°C·min$^{-1}$ with α-alumina (α-Al$_2$O$_3$) as the reference material. Measurements were carried out in alumina crucibles under Argon atmosphere.

**X-ray diffraction (XRD)**

XRD data were collected on D8 ADVANCE X-ray diffractometer with strictly monochromatic Cu Kα radiation ($\lambda = 0.154$ nm) produced by Bruker in Germany. The overall measurements for samples were carried out in the range of 10° to 60° (2θ) with a step size of 0.02° (2θ), a step time of 4 s per pattern, an accelerating voltage of 40 kV and a current of 40 mA.

**Scanning electron microscopy (SEM)**

Pieces of hydrated samples at different ages were coated with carbon to provide a conductive surface for SEM imaging. Observation of mineral morphological feature was examined by using a Field Emission Scanning Electron Microscope (GUANTA 250-FEG, USA) with a Link Energy Disperse Spectroscopy (LinkISIS300 type, USA) system. The distribution of elements in minerals was analyzed by Energy Spectrum analysis (EDS).

**Hydration heat-evolution test**

An isothermal heat-conduction calorimetry (TAM air C80, Thermometric, Sweden) was used to measure the hydration heat evolution of samples mixed with 8.0 wt. % CaSO$_4$·2H$_2$O. The water/cement ratio was 0.35 and experimental temperature was 25.0 ± 0.1°C. Samples and water were tempered for several hours before mixing. Then the water was injected into the reaction vessel and the samples were stirred in the calorimeter for several minutes. This procedure allowed monitoring the heat evolution from the beginning when water was added to samples. Data acquisition was performed for about 6 days.

**Compressive strength test**

Compressive strength tests were carried out according to Chinese standard titled Common Portland Cement (GB 175-2007). The determination of compressive strength was performed after 0.5, 1, 3, 7 and 28 days of hydration, and subsequently the hydration reactions of the pastes were stopped by absolute ethyl alcohol. Each resultant value of compressive strength was an average value calculated from six determinations.
RESULTS AND DISCUSSIONS

The formation of C_{2.75}B_{1.25}A_{3}$

Thermal analysis

Figure 1 shows the DSC and TG curves of raw mixtures with K$_2$O. The DSC curves display a number of thermal effects, and TG curves show the associated decarbonation as the main weight loss. Table 2 gives the temperature of peaks labeled in Figure 1. The two small endothermic peaks at about 300°C and 500°C, corresponding to small weight losses, result from the dehydration and dehydroxylation caused by moisture absorption of raw material Al$_2$O$_3$ (Wang S. D., 2013). The sharp endothermic peaks between 800°C and 900°C (3# position), with substantial weight losses associated, correspond to the decomposition of CaCO$_3$. It can be seen that the addition of K$_2$O (0.5 ~ 1.1 wt. %) leads to a lower decomposition temperature of CaCO$_3$, and especially at 0.8 wt. % K$_2$O, the temperature is decreased by 23°C (Table 2). In contrast, 1.4 wt. % K$_2$O has little effect on decomposition temperature of CaCO$_3$. This indicates that a certain content of K$_2$O contributes to the decomposition of CaCO$_3$, which favors the formation of C$_{2.75}$B$_{1.25}$A$_{3}$ mineral. Finally, the small peak at about 1400°C in each sample is observed (4# position). This peak is within a large downward trend, due to partial decomposition of C$_{2.75}$B$_{1.25}$A$_{3}$. The 5# peak means the massive decomposition of C$_{2.75}$B$_{1.25}$A$_{3}$. It is found from Figure 1 and Table 2 that K$_2$O accelerates the decomposition of C$_{2.75}$B$_{1.25}$A$_{3}$, and the decomposition temperature reduces gradually with increasing K$_2$O dosage. While K$_2$O reaches the maximum dosage as designed 1.4 wt. %, the temperature is still over 1360°C which is the synthesized temperature of belite-C$_{2.75}$B$_{1.25}$A$_{3}$ cement.

Similarly, the thermal analysis of raw mixtures doped with MgO is discussed and the results are shown in Figure 2 and Table 3. Five main endothermic peaks in the samples with MgO are also observed as discussed above. When MgO dosage are respectively 2 wt. % and 3 wt. %, the decomposition of CaCO$_3$ characterized in 800 - 900°C is slightly delayed and the delay is more evident as MgO rises. The decomposition temperature decreases by 10°C at 5.0 wt. % MgO. Meanwhile, the 4# and 5# peaks shift to a lower temperature position with MgO content increasing, which indicates that the presence of MgO plays a positive role in C$_{2.75}$B$_{1.25}$A$_{3}$ decomposition. This is in line with the effect of K$_2$O on its decomposition obtained from Figure 1, but less decline in the decomposition temperature of C$_{2.75}$B$_{1.25}$A$_{3}$ appears under the influence of MgO as given in Table 3.

Table 2. Temperature of the endothermic peaks labeled in Figure 1.

<table>
<thead>
<tr>
<th>K$_2$O Dosages (wt. %)</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
<th>5#</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>279.3</td>
<td>–</td>
<td>831.3</td>
<td>1373.2</td>
<td>1458.5</td>
</tr>
<tr>
<td>0.5</td>
<td>277.4</td>
<td>529.2</td>
<td>822.8</td>
<td>1324.6</td>
<td>1448.4</td>
</tr>
<tr>
<td>0.8</td>
<td>275.6</td>
<td>523.9</td>
<td>808.6</td>
<td>1308.2</td>
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<tr>
<td>1.1</td>
<td>273.0</td>
<td>527.2</td>
<td>825.0</td>
<td>1281.9</td>
<td>1377.1</td>
</tr>
<tr>
<td>1.4</td>
<td>276.8</td>
<td>523.9</td>
<td>835.6</td>
<td>1274.5</td>
<td>1360.6</td>
</tr>
</tbody>
</table>

Table 3. Temperature of the endothermic peaks labeled in Figure 2.

<table>
<thead>
<tr>
<th>MgO Dosages (wt. %)</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
<th>5#</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>279.3</td>
<td>–</td>
<td>831.3</td>
<td>1373.2</td>
<td>1458.5</td>
</tr>
<tr>
<td>2.0</td>
<td>218.1</td>
<td>538.8</td>
<td>835.4</td>
<td>1325.9</td>
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<tr>
<td>3.0</td>
<td>227.5</td>
<td>539.3</td>
<td>842.2</td>
<td>1302.3</td>
<td>1423.6</td>
</tr>
<tr>
<td>4.0</td>
<td>219.5</td>
<td>532.6</td>
<td>825.5</td>
<td>1288.4</td>
<td>1417.1</td>
</tr>
<tr>
<td>5.0</td>
<td>219.9</td>
<td>526.3</td>
<td>819.4</td>
<td>1274.5</td>
<td>1401.2</td>
</tr>
</tbody>
</table>

Figure 1. DSC/TG results of raw mixtures doped with K$_2$O.

Figure 2. DSC/TG results of raw mixtures doped with MgO.
XRD analysis

XRD patterns of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ doped with K$_2$O are shown in Figure 3. It can be seen that compared to the blank though the characteristic diffraction peaks ($d_1 = 0.3787$ nm, $d_2 = 0.2681$ nm) of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ at about 23.5°and 33.4°($2\theta$) vary little with doping K$_2$O, those ($2\theta = 41.2°$) are more evident and sharper. It is indicated that added K$_2$O promotes the formation of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral. The peaks ($2\theta = 41.2°$) of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ with 0.5 wt. % and 0.8 wt. % K$_2$O become higher than those with 1.1 wt. % and 1.4 wt. % K$_2$O. It means that too much K$_2$O limits the formation of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$. Besides $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$, small amounts of BaSO$_4$ and BaAlO$_4$ as the impurities are present in the samples.

It is noted that the peak intensity ($2\theta = 19.7°$) of BaSO$_4$ remarkably decreases with K$_2$O dosage of 0.5 wt. % and 0.8 wt. % while itheightens as K$_2$O content rises. Similarly, the BaAlO$_4$ peak at about 28.4° ($2\theta$) shows the same trend. These variations suggest that synthesized $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral has fewer impurities when K$_2$O dosages are 0.5 wt. % and 0.8 wt. %. Thus, it can be conclude that 0.5 ~ 0.8 wt. % K$_2$O is favorable for the formation of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral.

Figure 4 is the XRD patterns of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ doped with MgO. Different from the sample with K$_2$O, no BaAlO$_4$ peaks appear in the samples doped with MgO. Moreover, the intensities of BaSO$_4$ peaks ($d_1 = 0.3092$ nm, $d_2 = 0.2488$ nm, $d_3 = 0.2100$ nm) change little with MgO dosage increasing. This indicates that MgO makes significant sense to the synthesis of pure $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral. Besides, it is clearly observed in Figure 4 that characteristic peaks of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ ($d_1 = 0.3787$ nm, $d_2 = 0.2681$ nm) obviously strengthen when the MgO dosage is 4.0 wt. %, and the intensity of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ peaks increases to the maximum. However, the peak at about 23.5° is obviously weakened when MgO dosage reaches to 5.0 wt. %. This illustrates that MgO promotes the formation of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral at the dosage of 3.0 ~ 4.0 wt. %. Additionally, it can be seen that the characteristic diffraction peak of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral ($2\theta = 23.5°$) shifts to a lower diffraction angle position with increasing MgO content. This may be due that Mg$^{2+}$ partially substitutes Ca$^{2+}$ or Ba$^{2+}$ in the same main group elements in the periodic Table of chemical elements and this results in a rise in the interlunar spacing.

Morphology and mineralogy analysis

Monocrystal $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ has a complete crystal shape belonging to rhombic dodecahedron (Cheng X., 2013). Whereas, $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral is usually not regular rhombic dodecahedron, but close to the dodecahedron or shape of sphere (Wang S. D., 2013; Wang C. P., 2005). Regarding the results of Figure 3 and Figure 4, only SEM and EDS pictures of samples optimized by appropriate K$_2$O and MgO are illustrated in Figure 5. As shown from Figure 5a, the pure $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral in our study is nearly of small size of 0.5 ~ 2 μm with the spherical shape, and parts are wrapped in each other with unclear grain boundary. However, from Figure 5b, it is found that there is a morphology of sphere and polyhedron, and grains grow well with clear grain boundaries. Moreover, K$_2$O favors the formation of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ crystals with big size. In the sample with 0.8 wt. %, the particles are uneven distributed with the size ranging from 0.3μm to 3μm. Under the influence of MgO, the $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral generally occurs as regular smooth and round appearance but the boundaries between grains are not very clear (Figure 5c). Furthermore, small particles and homogeneous distribution are observed, compared with the blank and the samples with K$_2$O. At 4 wt. % MgO, particle size is in the range of 0.3 ~ 1 μm, which may further enhance the hydration of $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral. In general, $\text{C}_2\text{.75B}_1\text{.25A}_3\text{S}$ mineral grains form well with clear grain boundaries when dopants are added.
Figure 5. SEM-EDS images of various samples. (a) the blank, (b) sample with K₂O, (c)sample with MgO.
The hydration activity and mechanical property

Hydration heat analysis

It has been reported that the hydration of C_{2.75}B_{1.25}A_3$ includes five stages: initial hydration period, induction period, acceleration period, deceleration period and stabilization period (Chang J., 2002). To reflect the effect of K$_2$O and MgO on the early-age hydration activity of C$_{2.75}$B$_{1.25}$A$_3$ in detail, the hydration heat liberations of studied samples during 24 hours are measured as shown in Figure 6 and Figure 7, respectively.

Figure 6 respectively displays released hydration heat rate and cumulative heat release of samples doped with K$_2$O. Obviously, added K$_2$O with various dosages has different influences on the hydration reaction. Rather intense heat liberation within few minutes is due to the initial rapid hydration of C$_{2.75}$B$_{1.25}$A$_3$ in the pre-induction period. It can be seen that the first signal in sample with 1.4 wt. % K$_2$O occurs 10 minutes later in the initial hydration than that of other samples (Figure 6a). Soon thereafter, the overall rate of hydration is slowed down in the induction period. The end time of the induction period has an important effect on the hydration. As shown from Figure 6a, 1.4 wt. % K$_2$O has an adverse effect on hydration reaction of C$_{2.75}$B$_{1.25}$A$_3$, which retards the induction period nearly 6 hours compared with the blank. This delay is also observed from the accumulated hydration heats (Figure 6b). It was explained that 1.4 wt. % K$_2$O caused the formation of BaSO$_4$ and BaAlO$_4$ in Figure 3 which had no or little hydrating activity. However, the hydration process significantly accelerates with less K$_2$O added. At 0.8 wt. % MgO, the second big broad signal appears firstly, and then in one hour there also exists the singal in the sample with 0.5 wt. % K$_2$O. The accumulated hydration heats with 0.5 wt. % and 0.8 wt. % are 510 Jg$^{-1}$ and 498 Jg$^{-1}$, respectively. 0.5 - 1.1 wt. % K$_2$O could cause lattice distortion and defects during the formation of C$_{2.75}$B$_{1.25}$A$_3$, which was favorable to hydrating activity of C$_{2.75}$B$_{1.25}$A$_3$. The phenomena indicate that high amount of K$_2$O (1.4 wt. %) has noticeable retarding effects, while appropriate amount of K$_2$O (< 1.1 wt. %) plays a significant role in the hydration process.

The hydration heat flow and cumulative heat release of samples doped with MgO are illustrated in Figure 7. It can be seen that there are few differences among the studied samples in the initial hydration, which all happen in 15 minutes (Figure 7a). However, for the following stage there exists a big difference between the samples with and the blank. It is clear that MgO remarkably shortens the induction period. The acceleration period of the sample with 5.0 wt. % MgO appears over 6 hours earlier than that of the blank. The induction period of the sample with 4.0 wt. % MgO is comparable with that of the sample with 3.0 wt.% MgO while the hydration rate of 4.0 wt. % MgO sample is the largest as high as 0.072 Wg$^{-1}$. Meanwhile, the stabilization period of samples with MgO nearly arrives after 8 h. However, for the blank it occurs after 14 h. This means that MgO distinctly enhances the hydration activity of C$_{2.75}$B$_{1.25}$A$_3$. From Figure 6b. It can be discovered that how long the total heat release approaches corresponds with the rate of heat release. On the other hand, it can be seen that MgO helps the acceleration period of hydration arrive within 4 hours except for the sample with 2.0 wt. %. In contrast, the acceleration periods of samples with 0.5 ~ 1.1 wt. % K$_2$O appear within 7 h, which are 3 hours later than those of samples with 3.0 ~ 5.0 wt. % MgO. Furthermore, the maximum hydration rate of 0.5 wt. % K$_2$O-doped sample is about 0.045 Wg$^{-1}$, which is smaller than that of 4.0 wt. %-doped MgO of 0.072 Wg$^{-1}$. It is indicated that the effect of MgO on hydration activity of C$_{2.75}$B$_{1.25}$A$_3$ is a little better than that of K$_2$O. This may be due to the reason that MgO, especially at the optimum dosage of 3.0 ~ 4.0 wt. %, favors the formation of C$_{2.75}$B$_{1.25}$A$_3$ mineral with little impurities which is obtained from the analysis of Figure 3 and Figure 4. Besides, the results are also supported by the results of Figure 5.
Compressive strength

Pictorial diagrams of the compressive strengths of cementitious materials are provided in Figure 8, and Table 4 gives the strength increase rates of others doped with K$_2$O or MgO. Figure 8 shows that the compressive strengths of all cementitious materials increase with increasing curing time. It is apparent that doped K$_2$O and MgO separately have different influences on the compressive strengths. Compared with the blank, 0.8 wt. % K$_2$O is helpful to the compressive strengths, especially at the early curing time. The compressive strengths of cementitious material with 0.8 wt. % K$_2$O at 0.5 d and 1 d are 38 % and 33 % higher than the blank, respectively. But the compressive strengths of cementitious material with 1.4 wt. % K$_2$O are less than the blank at the same curing time. Appropriate amount of K$_2$O improves the compressive strength while high content of K$_2$O (1.4 wt. %) lead to an adverse effect. All results discussed here are in accordance with the previous results of Figure 6.

Compared with the blank, it is helpful for the compressive strengths to add 2.0 wt. % MgO and 4.0 wt. % MgO, especially at the early curing time. And with the increasing MgO addition, the compressive strengths increase. The compressive strengths of cementitious material with 4.0 wt. % MgO at 0.5 d, 1 d and 28 d are 47 %, 56 % and 13 % higher than the blank, respectively. Appropriate amount of MgO (2.0 - 4.0 wt. %) improves the compressive strength. All results discussed here are in accordance with the previous results of Figure 7.

Table 4. Strength increasing rate of samples with additions relative to the blank sample/%.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Strength improvement rate</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>0.5 d</td>
</tr>
<tr>
<td>0.8 wt. % K$_2$O</td>
<td>38</td>
</tr>
<tr>
<td>1.4 wt. % K$_2$O</td>
<td>-25</td>
</tr>
<tr>
<td>2.0 wt. % MgO</td>
<td>18</td>
</tr>
<tr>
<td>4.0 wt. % MgO</td>
<td>47</td>
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</table>

CONCLUSIONS

In this paper, from the basis of multiple perspectives, we studied the influence of K$_2$O and MgO on the formation and hydration activity of C$_{2.75}$B$_{1.25}$A$_3$S. Major conclusions can be drawn as follows:
- According to DSC-TA curves 0.5 - 0.8 wt. % K$_2$O can reduce the decomposition temperature of CaCO$_3$ about 10 - 23°C and the decomposition temperature of C$_{2.75}$B$_{1.25}$A$_3$S about 10 - 16°C. And 4.0 ~ 5.0 wt. % MgO can reduce the decomposition temperature of CaCO$_3$ about 10 - 23°C and the decomposition temperature of C$_{2.75}$B$_{1.25}$A$_3$S about 10 - 16°C. So 0.5 ~ 0.8 wt. % K$_2$O and 4.0 ~ 5.0 wt. % MgO can respectively promote the decomposition of CaCO$_3$ and lower the decomposition temperature of C$_{2.75}$B$_{1.25}$A$_3$S mineral.
Effect of K₂O and MgO on the formation and hydration activity of Ba-bearing calcium sulfoaluminate

- 0.5 - 0.8 wt. % K₂O is favorable for the formation of C₂.₇₅B₁.₂₅₃A₅S mineral. Too much K₂O limits the formation of C₂.₇₅B₁.₂₅₃A₅S. When K₂O content reaches up to 1.4 wt. %, small amounts of BaSO₄ and BaAlO₄ as the impurities are present. At the same time 3.0 - 4.0 wt. % MgO promotes the formation of C₂.₇₅B₁.₂₅₃A₅S mineral. Additionally, the characteristic diffraction peak (2θ = 23.5°) of C₂.₇₅B₁.₂₅₃A₅S mineral shifts to a lower diffraction angle position with increasing MgO content due to the partial replacement of Mg²⁺ to Ca²⁺ or Ba²⁺.

- From the released hydration heat rate and cumulative heat release results it is found that 0.5 - 1.1 wt. % K₂O and 2.0 - 4.0 wt. % MgO promote the hydration of C₂.₇₅B₁.₂₅₃A₅S because of the lattice distortion and defects. But 1.4 wt. % K₂O and 5.0 wt. % MgO caused BaSO₄ and BaAlO₄ to extend the hydration of C₂.₇₅B₁.₂₅₃A₅S.

- Appropriate amount of MgO (2.0-4.0 wt. %) and K₂O (0.8 wt. %) can improve the compressive strength and ensure it steady growth with the increase of curing ages. But 1.4 wt. % K₂O can reduce the compressive strengths at both early ages and late ages.

REFERENCES


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