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EFFECT OF MgO ON CALCINATION AND PROPERTIES OF BELITE-BARIUM CALCIUM SULPHOALUMINATE CEMENT CLINKER WITH Na₂O AND K₂O

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The High-quality limestone resources decreased sharply worldwide, and MgO-rich limestone, as an important part of low-quality limestone, is widely used in the cement production because of its low cost. The purpose of this study was to explore the effect of MgO (1-9 wt. %) on the composition and properties of belite-barium calcium sulphoaluminate cement with Na₂O and K₂O. The experimental results showed that $1 \sim 3$ wt. % of MgO in the mineral composition was in favor of calcining and stabilizing the crystal structure of M_3 – C_3 S, R– C_3 S and β - C_2 S in the cement clinker. Furthermore, the addition of MgO evidently increased the content of R– C_3 S and β - C_2 S and goes up to the highest value of 14.47 % and 22.4 % when the addition of MgO reaches 7 wt. %, and the increment of R– C_3 S and β - C_2 S was beneficial to improve the mechanical strength of the clinker. The 3d, 7d and 28d compressive strength of the cement with 7 wt. % MgO increased by about 26 %, 7.3 % and 36.2 % than that without MgO. Meanwhile, since the addition of MgO also can promote the formation of C4AF, but has little effect on the formation of C_2 , C_3 and C_3 A, the C_3 A/ C_4 AF ratio present significantly reduction, which indicate that MgO can reduce the viscosity of the liquid phase in the process of calcination. So, the utilization of MgO in low-quality limestone has a great potential to develop low-carbon and sustainable society in producing the belite-barium calcium sulphoaluminate cement.

INTRODUCTION

With the progress and development of society, green, low-carbon and sustainable development were increasingly focused. Manufacturing of Portland cement not only consume a large quantity of raw materials and energy, but also has a considerable negative environmental impact, so cement industry had always been criticized [1, 2]. For example, the manufacture of Portland cement as the most widely used building materials took about 1.7 tons of raw materials (limestone, clay, etc.) and 8.5 ×10⁵ kcal of energy to produce 1 ton of cement clinker. Meanwhile, 0.97 tons of CO₂ on average were emitted with per ton of cement produced [3-7]. It was the development direction of cement industry to reduce energy consumption, environmental pollution and improve performances of cement [4-6]. Under these circumstances belite-barium calcium sulphoaluminate cement (C_{2.75}B_{1.25}A₃\$) was prepared. It had low synthesis temperature, low limestone consumption, low CO2 emissions (less than 10 % of Portland cement), low hydration heat and good durability [4, 8-10].

In recent years, sustainable development and natural resources preservation have become global concerns. High-quality limestone resources are becoming increasingly rare, and it is deduced that 29 billion tons will

be consumed in the next 20 years [11, 12]. Thus, the utilization of low-grade limestone has gained more and more attention, and MgO-rich limestone is one of them. It is well known to us that MgO-rich limestone is abundant in China, but this kind of limestone' usage in Portland cement production is rare [13]. In the process of manufacture of belite-barium calcium sulphoaluminate cement, low-grade raw material was used which inevitably introduced impurity ions to affect the production and performance of cement. However it had been reported that for Portland cement MgO could lower the melting temperature, increase the quantity of the liquid phase, change the mineral phases' crystal structure and activate the reactivity of C₃S [14,16]. The study of S.S. Rehsi observed that doping MgO in cement could extend the hydration of cement and Ángeles G.De la Torre et al. found the addition of MgO changes the crystal structure of minerals in the clinker [17, 18].

Besides, Na_2O and K_2O (alkali) were the most frequently existing minor components in the natural raw materials and had been reported to stabilize $\alpha'H-C_2S$ and $\alpha-C_2S$ in belite clinkers [5, 19]. Considering the advantages of MgO, Na_2O and K_2O to manufacture of Portland cement, they were expected to affect belite-barium calcium sulphoaluminate cement with the same method and mechanism. However, to the current authors' knowledge no such work has been reported.

In this paper the effect of MgO was investigated in the mineral formation of belite-barium calcium sulphoaluminate cement clinker in the presence of Na₂O and -K₂O. Meanwhile hydration and hardening properties, such as compressive strength development, hydration rate, hydration heat release and microstructures of hydration products, were characterized. It was hoped that this paper could offer available data for further industrial production of belite-barium calcium sulphoaluminate cement and effective utilization of magnesia-rich limestone in this type of cement clinker.

EXPERIMENTAL

Sample preparation

The cement clinker was synthesized using analytical reagent grades of CaCO₃, SiO₂ (99.0 % from Damao Chemical Reagent Factory, China), Fe₂O₃, Al₂O₃, BaSO₄, BaCO₃, CaF₂, MgO, Na₂CO₃ and K₂CO₃ (99.0 % from Sinopharm Chemical Reagent Co., Ltd, China), to eliminate the influences of other impurities on cement clinker production as much as possible. The designed mineral composition and chemical composition of belite-barium calcium sulphoaluminate cement clinker were listed in Table 1(the blank clinker without dopants), and 0.6 % CaF₂ was added as the mineralizing agent.

In the reference sample, the content of Na_2O and K_2O was 0.5 wt. % and 1.2 wt. % ($Na_2O \cdot eq = 1.29$; percentage in relation to the blank clinker, the same rule applies as follows) respectively, which were added into the raw materials of the blank clinker. Then six samples are prepared by adding 0, 1, 3, 5, 7 and 9 wt. % MgO into the reference sample, and they are named as C0, C1, C3, C5, C7 and C9, respectively.

Raw materials (with particle sizes finer than 74 μ m) were mixed and wet ground in a planetary mill for 40 minutes to ensure a homogenous mixture resulted in. Mixtures were then dried to a water content of about 10 % by weight and compressed to form Φ 60 mm ×10 mm cylindrical specimens. The cylinders were oven-dried at 105° C for 1-2 h before being calcined at a heating rate of 5° C·min⁻¹ to 1380° C and held for 90 min and then cooled down quickly. The calcined samples were ground to the residue weight of a 74 μ m sieve less than 5 % by a planetary mill prior to property measurements.

The ground clinkers were mixed with 10.0 wt. % $CaSO_4 \cdot 2H_2O$ (99.0 % from Sinopharm Chemical Reagent Co., Ltd, China). Then, cement pastes were prepared at a water/cement ratio of 0.30, cast in $20 \, \text{mm} \times 20 \, \text{mm} \times 20 \, \text{mm}$ molds, vibrated to remove air bubbles, and then wiped

to achieve surface flat with a scraper. The molded pastes were kept at $20 \pm 2^{\circ}\text{C}$ and relative humidity exceeding 95 % for 24 h, and then removed from the molds. The demolded pastes were then cured in a water tank at $20 \pm 2^{\circ}\text{C}$ for 3, 7 and 28 days.

Test method

f-CaO tests

The content of f-CaO in cement clinkers was measured by ethanediol-alcohol method according to GB/T 176-2008 Methods for Chemical Analysis of Cement.

X-ray diffraction (XRD)

XRD data were collected on D8 ADVANCE X-ray diffractometer with strictly monochromatic Cu K α radiation ($\lambda=0.154$ nm) produced by Bruker in Germany. The overall measurements for clinkers 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. Besides, the measurements for hydration products were carried out in the range of 5° to 60° (2θ) with a step size of 0.02° (2θ), a step time of 0.2 s per pattern.

To quantitatively evaluate the amount of crystalline phases in the samples, Quantitative XRD (Q-XRD) technique was used during this work. Q-XRD results were obtained through the Rietveld method [20, 21]. For this purpose, all samples were characterized by Laboratory X-ray powder diffraction (LXPRD). LXPRD plots were analyzed using the Rietveld method with Topas 4.2 software package from Bruker AXS GmbH [22, 23].

Petrographic description

Microscopic images of clinkers were captured by using a Motic 310A microscope (Motic Instruments Inc., Canada) equipped with a Moticam Pro 285A camera. The samples were embedded in the sublimed sulfur before polishing. The polishing process was performed on the glass by hand with three kinds of fineness of aluminium oxide, and the polished samples were cleaned in absolute ethyl alcohol with an ultrasonic cleaner for 10 minutes. The polished surface was etched in 1 % ammonium chloride aqueous solution for 6 seconds.

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

Table 1. Designed mineral composition (wt. %) and chemical composition of raw materials (expressed as oxides, wt. %).

C_3S	C_2S	C_3A	C_4AF	$C_{2.75}B_{1.25}A_3\overline{S}$	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	BaO
37.5	37.5	4.6	11.5	9.0	22.4	7.7	3.7	60.6	1.4	4.1

feature was examined by using a Field Emission Scanning Electron Microscope (GUANTA 250-FEG,USA) with a Link Energy Disperse Spectroscopy (LinkISIS300 type, UK) system. The distribution of elements in minerals was analyzed by Energy Spectrum analysis (EDS).

Compressive strength

Compressive strength of the samples at 1, 3, 7 and 28 days was evaluated by a universal compression machine (MTS CMT5504, USA). Each representative value was an average determined from six specimens with same formulation and curing condition.

Hydration heat-evolution test

An isothermal heat-conduction calorimetry (TAM air C80, Thermometric, Sweden) was used to measure the hydration heat evolution of cements with 10.0 wt. % $CaSO_4 \cdot 2H_2O$. The water/cement ratio was 0.45 and experimental temperature was $30.0 \pm 0.1^{\circ}C$. Cements and water were tempered for several hours before mixing, then 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 very beginning when water was added. Data acquisition was performed for about 6 days.

RESULTS AND DISCUSSION

f-CaO content

The variations of f-CaO content in clinker samples with the addition of MgO are given in Figure 1. It can be seen from Figure 1, the content of f-CaO in all cement clinker samples was less than 0.80 %. This is a good indicator of the burnability of raw materials. In reference sample, the content of f-CaO was 0.46 %. With the rises of MgO dosage, the f-CaO content in cement clinkers decreased firstly and then increased, but the volatility was not obvious. When MgO dosage was $1.0 \sim 3.0$ wt. %, the content of f-CaO decreased obviously and when

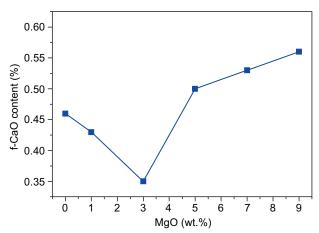


Figure 1. f-CaO content of clinker samples.

MgO dosage was 3.0 wt. %, f-CaO content reached the lowest, only 0.35 %. This is attributed to good fluxing effect of MgO, because a suitable amount of MgO can reduce the viscosity of the liquid phase and increase the content of liquid phase to promote the formation of C_3S , during which f-CaO was consumed [24, 25]. However, when MgO dosage was over 3.0 wt. %, the f-CaO content increased remarkably and MgO dosage reach to 9.0 wt. %, the content of f-CaO is 0.56. So it was concluded that a high MgO content (> 3.0 wt. %) is not helpful for the burnability.

XRD analysis of hydration products

XRD patterns of all studied clinkers are showed in Figure 2. The quantitative phase analysis of clinker minerals in different polymorphs will be discussed below. It can be seen from Figure 2 that characteristic mineral C_{2.75}B_{1.25}A₃\$ and the main minerals of Portland cement are seen in this new type of cement clinker. The characteristic diffraction peaks of C_{2.75}B_{1.25}A₃\$ had slightly enhanced in C3~C7 samples, indicating $3.0 \sim 7.0$ wt. % content of MgO contributed to the formation of C_{2.75}B_{1.25}A₃\$. In addition, with the increase of MgO, C₃S diffraction peak at 29.2° (2θ) were significantly enhanced in C3, C7 and C9 samples, and the other diffraction peak about C₃S and C₂S changed not obvious. What's more, after doping MgO, diffraction peaks of C_4AF ($2\theta = 12.1^\circ$) significantly enhanced, while the diffraction peaks of C₃A had little changed. This variation suggests that MgO promotes the formation of C₄AF, which is consistent with Li's findings, but affects little on the formation of C₃A[13, 26]. Besides, when MgO content was 5.0 wt. %, the diffraction peak of f-MgO appeared and its intensity increased with the MgO content increasing, which indicated that excessed MgO in the clinker will result in f-MgO.

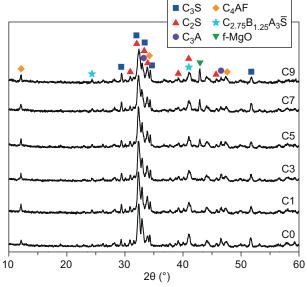


Figure 2. XRD patterns of cement clinkers doped with MgO.

Rietveld quantitative phase analysis

There are various crystalline phases in belitebarium calcium sulphoaluminate cement clinker, and some crystalline phase displayed polymorphism. In the Q-XRD analysis, the $C_{2,75}B_{1,25}A_3$ \$ mineral was not taken into account, because the crystal structure data for Rietveld quantitative analysis had not been established, and the doping elements had little effect on its formation. Table 2 showed the quantitative phase analysis results for all clinkers, as well as the Rietveld agreement factor for the refinements. It was observed that, parameters Rwp were lower than 15, it means the high credibility of refinement [21, 27]. The content of C₃S was 37.57 % in C0 sample and it was lower than that of in C3, C7 and C9 samples. With the increase of MgO dosage, C₂S contents on a corresponding reduction. This indicated that high doped MgO facilitated the formation of C₃S. This may be because in belite-barium calcium sulphoaluminate cement, when MgO dosage exceeded 5.0 wt. %, the quantity of Mg²⁺ sufficient to formed [MgO₆]¹⁰⁻.It had a big different with [SiO₄]⁴ in structure, shape and size, thus causing the phase interfacial energy increased, and providing favorable conditions for the formation of C₃S minerals. From Figure 3, we also observed that f-MgO generated when MgO dosage exceeded 5 wt. %, corresponding to the results shown in Figure 2.

Table 2. Rietveld quantitative phase analysis results of mineral composition of the resultant clinkers (wt. %).

Code	C0	C1	C3	C5	C7	C9
M_3 - C_3 S	33.39	21.66	21.4	27.71	21.18	24.61
T_3 - C_3S	4.18	6.02	3.97	1.67	3.14	2.75
$R-C_3S$	0	10.02	13.23	7.72	14.47	10.81
Total-C ₃ S	37.57	37.7	38.6	37.1	38.79	38.17
α' L- C_2 S	34.31	26.77	20.62	21.75	16.06	18.38
β - C_2S	8.85	15.46	20.93	21.75	22.03	20.02
Total-C ₂ S	43.16	42.23	41.55	42.45	38.09	38.40
C_3A	8.18	8.44	8.28	7.78	8.08	7.33
C_4AF	10.65	11.22	11.24	10.34	10.8	10.01
f-CaO	0.44	0.41	0.33	0.49	0.55	0.58
f-MgO	0	0	0	1.84	3.69	5.51
Rwp*	14.37	12.59	10.71	11.87	11.45	9.70

^{*} Rwp is the agreement factor of the Rietveld refinement

Silicate phases

Figure 3 showed the relative content of high temperature polymorphs (M₃ T₃and R) of C₃S, which was calculated from quantitative phase analysis. It was reported that M₃-C₃S and R-C₃S have better hydration activity than T₃-C₃S [28]. From Figure 3, we can see that none MgO-doped sample was primarily M₃-C₃S, indicating that the incorporation of Na₂O and K₂O can stabilize the high temperature crystalline M₃-C₃S at

room temperature. When doped MgO, R-C₃S appeared in clinker, meanwhile T₃-C₃S had decreased, which may contribute to the increase of the compressive strength and it can indicate that a certain amount of alkali-doped, MgO can stabilize a portion of R-C₃S. In the samples of 3.0 wt. % MgO and 7.0 wt. % MgO content, R-C₃S content was relatively high, respectively 13.23 % and 14.47 %. When MgO dosage was 5.0 wt. %, R-C₃S content decreased, but M₃-C₃S content increased. So it can be concluded that MgO favors the formation of C₃S and the stabilization of M₃-C₃S and R-C₃S, in which the effect was more obvious in 3.0 wt. % MgO and 7.0 wt. % MgO content.

The content of belite phase crystallized in different polymorphs present in clinkers co-doped with MgO calculated from quantitative phase analysis is illustrated in Figure 4. It has been reported that the order of hydration degree for different types of C_2S was $\alpha\text{-}C_2S$ > $\alpha'_H\text{-}C_2S$ > $\beta\text{-}C_2S$ > $\alpha'_L\text{-}C_2S$ > $\gamma\text{-}C_2S$ during the same curing period and condition, and $\gamma\text{-}C_2S$ scarcely reacted with water at ambient temperature [29-31], so $\gamma\text{-}C_2S$ was not the desirable polymorph. In the present study, it can

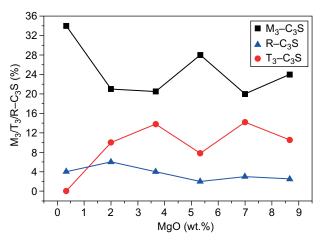


Figure 3. Relative content of M_3 - C_3S T_3 - C_3S and R- C_3S in samples.

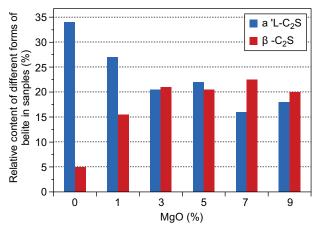


Figure 4. Content of different polyforms of belite in cement clinkers.

be seen from Figure 4 that different amount of β - C_2S and α'_L - C_2S exist and no γ - C_2S was found. In addition, Figure 4 also showed that with the dosage of MgO changed, different polymorphs of C_2S will also change in cement clinker and mainly had $\alpha'L$ - C_2S , reached to 34.31 %. After doping MgO, β - C_2S increased significantly in samples, indicating that MgO can stabilize β - C_2S . When MgO dosage was 7.0 wt. %, β - C_2S content was relatively high in samples. Due to the hydration performance of β - C_2S better than $\alpha'L$ - C_2S , therefore, more β - C_2S content promoted cement hydration.

Interstitial phases

In belite-barium calcium sulphoaluminate cement clinker, C₃A, and C₄AF all belong to the interstitial phases [20]. According to the results of Figure 2, C₃A and C₄AF are further studied here. It has been reported that MgO dominates the C₃A formation and the increase of MgO can decrease the amount of C₃A in Portland cement [24], however this rule was not observed in this study and the formation of C₃A is not regular with different doping amounts of MgO (Table 2). It has to be highlighted that the liquid viscosity is significantly influenced by the dopants. The liquid viscosity was characterized by the C₃A/C₄AF ratio of the clinkers. The results were illustrated in Figure 5. C₃A/C₄AF ratio showed a tendency of decrease and then increase in the clinker samples along with MgO dosage increasing. It also had been said, MgO was possible to reduce the viscosity of the liquid. In addition, it can be seen that when doped with 3.0 wt. % MgO, C₃A/C₄AF significantly reduced, and then with MgO content was higher than 3.0 wt. %, the C₃A/C₄AF was increased firstly then decreased, but overall a very small fluctuation range. C₃A/C₄AF maximum ratio (5.0 wt. % MgO) and C₃A/C₄AF minimum ratio (9.0 wt. % MgO) only a difference of 0.018, it was little difference on C₃A/C₄AF in 3.0 wt. $\% \sim 9.0$ wt. % MgO samples. Overall, high-

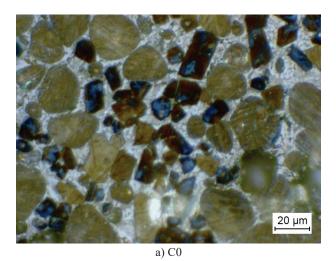
0.77 - 0.76 - 0.75 - 0.74 - 0.73 - 0.73 - 0.73 - 0.73 - 0.73 - 0.79 - 0.

Figure 5. The variation curve of C3A/C4AF ratio of the resultant clinkers.

doped MgO can reduce C₃A/C₄AF ratio and reduce the viscosity of the liquid phase, which will be benefit to f-CaO absorb and promote the formation of C₃S clinker. The results were in accordance with the results of Figure 1.

Microscopic observation

The microscopic images of clinkers captured by metallurgical microscope were presented in Figure 6. It was known that in cement clinker alite occurred as angular subhedral to euhedral crystals in blue color, whereas belite occurred as round and lamellar crystals in tan-to-brown color [26, 32]. In C0 sample, the size of alite was $5 \sim 40~\mu m$ which was hexagonal plate-like and columnar, and the size of belite was $7 \sim 40~\mu m$ which was round granular. Alite and belite distribution was uniform, and the boundary of crystal was clear, which indicating high doped alkali was beneficial to mineral development. Comparing with C3 and C0 petrographic photos, the size of alite slightly reduced and the number increased in C3, while the size of belite changed little. Comparing with



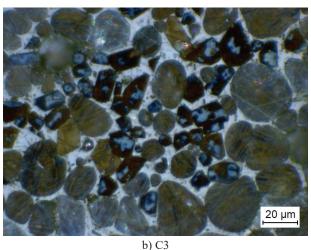
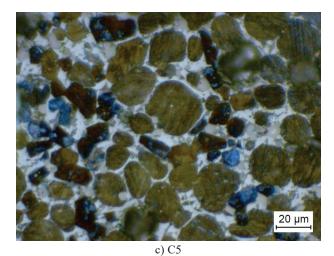


Figure 6. Microscopic view of clinker samples. (Continue on next page)



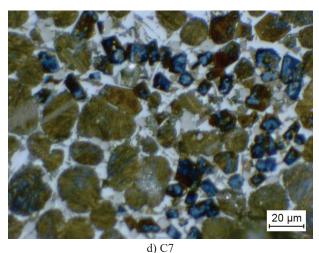


Figure 6. Microscopic view of clinker samples.

C5 and C0 the size of alite reduced significantly, and appeared small MgO grains in C5. Comparing with C7 and C0 petrographic photos, the size of alite and belite were significantly reduced and the size range of alite was $5 \sim 18~\mu m$, but the number of alite significantly increased in C7. In addition, the boundary of two minerals crystal became roughly, which may be due to dope MgO made the crystal deteriorated, and therefore reduced the crystal size. All in all, MgO made the size of alite and belite in cement clinker smaller, which was beneficial to cement hydration.

Compressive strength

Compressive strength of samples doped with MgO, Na₂O and K₂O were showed in Figure 7. Table 3 gave the strength increase rate of samples doped with MgO. From the table it showed that when hydration 1d, the compressive strength of cement with MgO had decreased. At the time of hydration 3d, MgO-doped samples compressive strength of cement had increased, except 5.0 wt. % MgO content, and MgO contented with 3.0 wt. %, 7.0 wt. % and 9.0 wt. % intensity growth

was relatively high, respectively 25 %, 26 % and 27 %. With the extension of hydration age, the intensity of the reference sample increased slowly and its 28d strength only 75.8 MPa. Meanwhile, when MgO content was 3.0 wt. % and 7.0 wt. %, the late strength of the sample was relatively high, and the 28d intensity of 9.0 wt. % MgO cement was slightly lower than that of 3.0 wt. % and 7.0 wt. % MgO. It thus can conclude that MgO to promote the development of cement strength of the best dope were 3.0 wt. % and 7.0 wt. %.

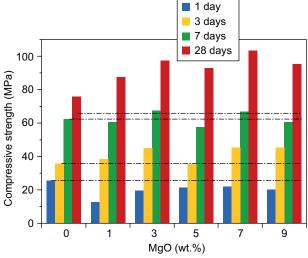


Figure 7. Compressive strengths of cement pastes.

Table 3. Strength increase rate of MgO-doped samples relative to the reference sample (C0).

Sample	Strengt	Strength improvement rate (versus C0, %)					
label	1d	3d	7d	28d			
C1	-50	8	-3	16			
C3	-23	25	8	28			
C5	-15	-0.7	-7	22			
C7	-14	26	7	36			
C9	-20	27	-3	26			

XRD patterns of hydration products

The unhydrated silicates and hydration products of CH and ettringite were examined by X-ray diffraction showed in Figure 8. Although the intensity of the diffraction peak was not linearly proportional to the content of crystalline phase, some important information can be obtained from the comparisons of the relative intensity and changes of the intensity with the prolongation of hydration ages. As showed in Figure 8, at 3 days diffraction peaks of C_{2.75}B_{1.25}A₃\$ disappeared, indicating C_{2.75}B_{1.25}A₃\$ been fully hydrated. What's more, Ca(OH)₂ and ettringite diffraction peaks appeared more obvious, but C-S-H diffraction peak was relatively weak.

The intensity of unhydrated C_3S and C_2S diffraction peak were still high. In addition, it can be seen that in C7 and C9 samples, $Ca(OH)_2$ diffraction peak $(2\theta = 18.0^\circ)$ was significantly enhanced, at the same time, the variation in peak of ettringite at 9.0° reflected the same results, indicating that C7 and C9 in the 3d hydration degree was higher, which was consistent with the results of compressive strength.

At 28 days, the hydration products ettringite, Ca(OH)₂ and C–S–H diffraction peaks significantly enhanced, while unhydrated silicates (C₃S and C₂S) diffraction peaks decreased significantly and C₃S diffraction peak declined more obvious. From this phenomenon it can be conclude that the hydration of 28d was significantly higher than 3d, and therefore the mechanical properties improved.

To reflect the effect of MgO on the hydration of cement in detail, the heat liberation of hydration of C0, C1 and C7 during 140 h were further measured as shown in Figure 9. Figure 9a and Figure 9b respectively displayed the rate of hydration heat release and the cumulative heat release. It can be seen from the Figure 9, within a few hours, there was a strong exothermic peak. The reason why was that C₃A and C_{2.75}B_{1.25}A₃ hydrate to produce ettringite and barium-containing ettringite in pre-induced period (ettringite formation period). With the hydration reaction, the hydration product gradually increased, and form a coating in clinker mineral surface, so that the hydration rate slow down, that means the beginning of the induction period. From Figure 9 we knew that induction period C1 and C0 samples were

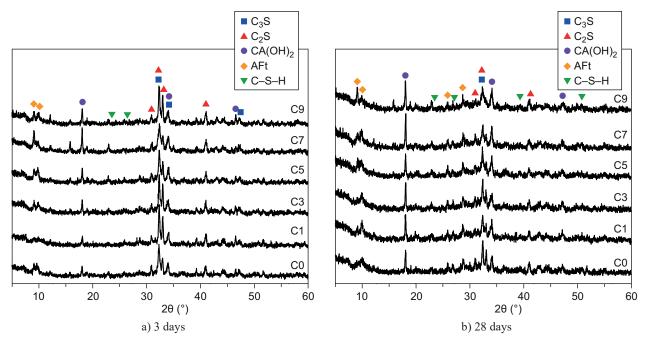


Figure 8. XRD patterns of studied pastes hydrated at the curing ages.

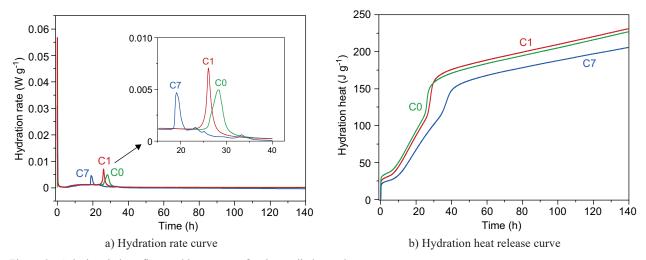


Figure 9. Calorimetic heat flow and heat curves for the studied samples.

similar, while the maximum rate of hydration C1 was larger than C0, and the induction period of C7 sample was minimal. This showed that under alkaline conditions, MgO can promote the hydration of cement and when MgO content was high, the hydration effect was obvious. This result was consistent with the compressive strength results.

Microstructures of hydration samples

Figure 10 displayed the SEM and EDS photographs of the fracture surface of hardened pastes at 3 days. As showed in Figure 10, in C0 hydration sample, the main hydration products after 3 days were short rod-shaped ettringite and the cotton-shaped structure of C–S–H, but

there existed some cracks. There were also exist some of needle bar-like ettringite, but the amount of C–S–H became fewer in C5 sample. C–S–H was mainly filled in the space occupied by water before and cemented together, so that the structure was dense and the performance of the mechanical properties increased. If the gel material was decreased, the cement strength was affected. As we can see from Figure 10c, the ettringite became longer and thicker compared with C0 and C5. In addition, gel intertwined with ettringite, which improved the density of structure and provided the basis for the strength. As we can see from the EDS photograph, the trace elements Na, K and Mg were detected on the hydrated product, which indicating that alkali and MgO could be dissolved in the hydration product. Above three

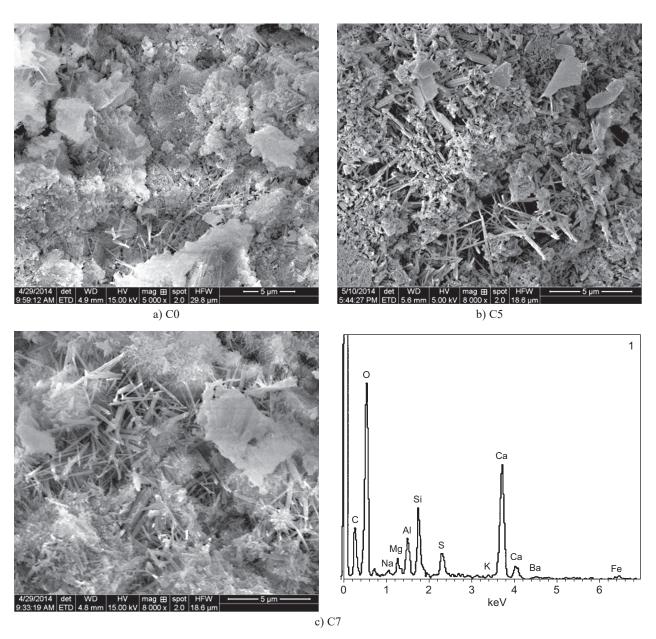


Figure 10. SEM-EDS images of hydrated cement pastes at 3 days; a) C0: the reference; b) C5: samples doped with 5 wt. % MgO; c) C7: samples doped with 7 wt. % MgO.

samples SEM, the hydration degree of C7 sample was larger, and the hydration degree of C5 is smaller, which were consistent with the XRD analysis of the previous hydration samples.

CONCLUSIONS

From the present study, the following major conclusions can be drawn:

- Appropriate amount of MgO (1 ~ 3 wt. %) can improve the burnability of raw materials, promote the formation of C₃S, and stabilize M₃-C₃S and R-C₃S. In addition, 7 wt. % MgO also favors the formation of C₃S and it makes the amount of C₃S to the maximum, reaching 38.79 %.
- MgO favors the formation of β-C₂S. Excessive MgO
 (> 7 wt. %) decreases the amount of C₂S.
- MgO favors the formation of C₄AF, but affects little on the formation of C_{2.75}B_{1.25}A₃\$ and C₃A. Doped MgO reduce C₃A/C₄AF ratio and it decreases the viscosity of the liquid.
- 1~3 wt. % MgO and 7 wt. % MgO can increase the compressive strength of the cement, but excessive MgO will lead to negative effect. The compressive strength of the sample with 7 wt. % MgO at 3, 7 and 28 days are 45.1, 66.81 and 103.2 MPa, which increases by 26 %, 7.3 %, and 36.2 % respectively compared to the cement without MgO dopant.
- MgO promotes the hydration rate and more MgO promote the hydration effect obvious. CH and AFt obviously increase according to XRD patterns.
- Sample with 7 wt. % MgO displays a dense and compact microstructure, in which more long acicular ettringite and C-S-H phases are observed.

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