

Effect of MgO and Al₂O₃ on High-temperature Stability Performance of High-alumina Cement

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High-alumina cement has an important position in refractory materials with its good performance at high temperatures, but its disadvantages such as strength inversion and unstable transformation of hydration products have always limited its development. To clarify the working mechanism of high-alumina cement and improve its high temperature resistance, MgO and Al₂O₃ were added to the high-alumina cement paste. The optimal design method was used to determine the influence of each factor on the high temperature stability of the cement paste. The mix ratio of raw materials was optimized and the strength change patterns of the specimens under the optimal ratio were verified. From a microstructure perspective, the high temperature evolution of the hardened paste of high-alumina cement was explored using X-ray diffraction, scanning electron microscopy, thermogravimetry, and differential scanning calorimetry. The results show that the introduction of refractory powders, especially Al₂O₃, can significantly improve the volumetric stability of the cement paste at high temperatures. When the water-cement ratio is 0.20, the admixture of MgO is 5 % or 10 %, and Al₂O₃ is 20 %, the high temperature volume stability of the cement paste is the best. However, its corresponding mechanical strength is weakened to some extent with an increase in calcinating temperature. Moreover, the structure-property evolution process of cementite under high temperature calcinating conditions was verified by microstructural characterization, especially the influence of the powder on the volume and strength of the cement block at high temperatures. The results of this study can serve as a guide for the development of high-alumina cement and its cementing materials, as well as for the improvement of their properties.

Keywords: aluminate cement, high temperature, orthogonal design, compressive strength, meso-structure.

1. INTRODUCTION

Refractory materials are non-metallic materials and products that are chemically and physically stable and can be used normally in high-temperature environments, with certain high-temperature mechanical properties and volume stability. High-alumina cement has the advantages of fast hardening, high strength, and heat and corrosion resistance. It is mainly used to formulate expansion cement, self-stressing cement, and heat-resistant concrete, which are widely used as the “lining” of high-temperature kilns in the cement, metallurgy, petrochemical, and electric power industries [1, 2]. However, the hydration products of high-alumina cement undergo crystalline transformation with time and changes in ambient temperature, resulting in the reduction of strength at a later stage.

The high-temperature performance of concrete is essential for assessing the fire performance of various concrete structural systems [3]. High-alumina cement has been widely used to prepare refractory concrete because of its better resistance to high temperatures. The main factors affecting the performance of high-alumina cement concrete are the amount of high-alumina cement content, powder mix, and temperature. Shen et al. [4] found that when the temperature was 800 °C, the mechanical properties of specimens with alumina cement as the main cementing material increased greatly compared with ordinary fine-grained concrete specimens. Alumina cement concrete

specimens with reactive powder mixed had higher relative residual compressive and flexural strength than those without reactive powder at 800 °C. Tchekwagep et al. [5] established the relationship between pore structure changes and compressive strength after exposure to elevated temperatures of sulphoaluminate cement concrete. The results showed that with increased temperature, the porosity of the sulphoaluminate cement concrete specimens also increased, and the pore structure was gradually destroyed. Sun et al. [6] simulated changes in the strength and chloride ion permeability of fired high-alumina cement concrete at high temperatures. They found that the compressive strength decreased faster at temperatures up to 300 °C; however, at 400–1000 °C, the concrete strength remained almost constant with increasing temperature. To better guide the composition design of the low-cement high-alumina refractory castable in specific working conditions, Xu et al. [7] reported an accurate correlation between their high temperature performance and cement content. The results suggested that the critical value of cement addition in this refractory is 2 wt.%.

Hydrated high-aluminous cement proves having sufficient resistance to chemical corrosion compared with Portland cement, because of the absence of portlandite. The progress of the hydration process of high-aluminous cement is closely affected by temperature [8, 9]. Unfortunately, increased curing temperatures lead to high-alumina cement concrete undergoing significant physical and chemical transformations at high temperatures and may break the bond between the aggregates and cement

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paste, which in turn leads to disintegration and deterioration of the concrete [10–12]. Khaliq et al. [13] and Zoldners et al. [14] investigated the properties of aluminate cement in the temperature range of 23–1100 °C. By using different types of refractory aggregates, such as limestone, they found that the sudden decrease in strength of aluminate cement at 400 °C was related to the transformation reaction of the internal microstructure. The hydration products of high-alumina cement, both CAH_{10} and C_2AH_8 are medium-stabilized products, which will transform into stable C_3AH_6 at temperatures above 350 °C, with 47 % and 75 % of the original volume after transformation, respectively, and will lead to a significant increase in the porosity of the hardened body after the phase transformation [15, 16]. The same conclusion was reached by Corinaldesi et al. [17] and Shang et al. [18]. Wu et al. [19] studied the application of high-alumina cement in low-cement refractory concrete and concluded that Fe_2O_3 in high-alumina cement forms C_2F and CF with very weak cementitious properties, which reduces the strength and refractoriness of the refractory concrete. Ukrainczyk et al. [20] found that Al_2O_3 can provide more nucleation sites for the hydration of high-alumina cement and promote their hydration. However, the relationship between the rate and degree of the conversion of sub-stable hydration products CAH_{10} and C_2AH_8 to steady-state hydration products C_3AH_6 and AH_3 , and the amount of Al_2O_3 added was not clear. Zhang et al. [21] suggested that the transformation between the hydration products of high-alumina cement was caused by a “dissolution-precipitation” mechanism.

In summary, high-alumina cement has an important position in refractory materials with its good performance at high temperatures, but its disadvantages such as strength inversion and unstable transformation of hydration products have always limited its development. Therefore, the refractory properties can be further improved by adding aluminum-containing compounds. In this study, high-alumina cement was considered as the research object, and we found that the high temperature resistance of high-alumina cement was improved by incorporating MgO and Al_2O_3 . The effect of their amount and the water-cement ratio of the paste on the high temperature volume stability and residual strength of high-alumina cement were investigated. Moreover, the microstructure of the cement block and the high temperature transformation of its hydration products were studied to investigate the inner mechanism of strength change and the transformation of hydration products of high-alumina cement block under high temperature.

2. EXPERIMENTAL PROGRAM

2.1. Materials

The raw materials included cement, MgO powder, Al_2O_3 powder, polycarboxylic acid water-reducing agent, and mixing water. The cement was a commercially available Jia'nai CA50-A700 aluminate cement, in which the Al_2O_3 content was 50–55 %. The initial and final setting times were 160 min and 185 min, respectively. The flexural strengths at 1 day and 3 days were 7.34 MPa and

8.24 MPa, respectively, and the compressive strengths at 1 day and 3 days were 53.32 MPa and 64.68 MPa, respectively. The chemical composition of the cement is listed in Table 1. The MgO used was heavy burnt magnesium powder from Dashiqiao City, Liaoning Province, Tianyi Refractories Co., Ltd., and its chemical composition is shown in Table 2. Al_2O_3 powder with a fineness of 48 μm and 99 % α - Al_2O_3 content was produced by Zhejiang Gongyi Jin'ao Resistance Material Co. Ltd. The water-reducing agent was a liquid polycarboxylic acid water-reducing agent with a solid content of 40 % and water reduction rate of more than 30 %, which was produced by Shenyang Yilida Building Admixture Co., Ltd.

2.2. Mixture proportions

The text should be typed in A three-factor, a three-level orthogonal experiment that was performed according to $L_9(3^4)$. The factors and design levels of the orthogonal tests are listed in Table 3.

The orthogonal tests to determine the range of the water-cement ratio were conducted first. The water-cement ratio was set to 0.1–0.5 while keeping other factors constant, and the range of water-cement ratio was finally determined to be 0.15–0.25, considering the slump flow of the paste and the strength of the cement stone. The design doping of MgO was 0–30 %, and the final determination was 0–10 %. The design doping of Al_2O_3 was 0–30 %, and the final determination was 0–20 %. The influence of three factors and three levels of key factors on the structure and properties of high-alumina cement block at high temperatures was investigated using orthogonal tests.

2.3. Specimen preparation

According to the “Test Method for Cementitious Sand Strength (ISO method)” (GB/T 17671-2021), mortar test blocks were prepared according to the ratios presented in Table 3 (dosage of polycarboxylic acid water reducing agent was 0.4 %) at room temperature (20 ± 2) °C. After the high-alumina cement and the admixture were mixed well, the polycarboxylic acid water reducing agent was added to the water and mixed well. Subsequently, the mixture was poured into the well-mixed cement and admixtures, standard sand was added, and quickly mixed using a mortar mixer. The homogeneously mixed mortar was loaded into 20 mm \times 20 mm \times 20 mm molds with 12 samples per group and immediately vibrated on a vibrating table for 30 s; the excess cement paste was wiped off with a flat trowel, and the surface was smoothed. The prepared samples were placed in a standard maintenance room at an ambient temperature of (25 ± 3) °C, and after 6 h, they were demolded and placed in water for conditioning. The samples were kept in water for 28 days and then taken out and dried in an oven at 50 °C for 24 h before the next test.

2.4. Test method

2.4.1. High-temperature test

Four temperature levels were set for this test: room temperature (20 ± 2) °C, 600 °C, 900 °C and 1200 °C, respectively.

Table 1. Chemical composition of CA50-A700 cement

Chemical compositions	Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	MgO	SO ₃	TiO ₂
Contents, %	53.66	33.26	8.35	2.01	0.34	0.33	0.32

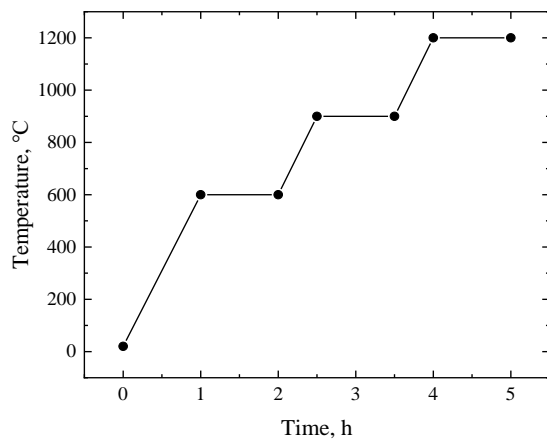
Table 2. Chemical composition of MgO

Chemical compositions	MgO	Fe ₂ O ₃	SiO ₂
Contents, %	95	1.77	3.03

Table 3. Orthogonal test factors and design levels

Specimen ID	Orthogonal design	Factor A: Water-cement ratio	Factor B: MgO, %	Factor C: Al ₂ O ₃ , %
S1	A1B1C1	0.15 (level 1)	0 (level 1)	0 (level 1)
S2	A1B2C2	0.15	5 (level 2)	10 (level 2)
S3	A1B3C3	0.15	10 (level 3)	20 (level 3)
S4	A2B1C2	0.20 (level 2)	0	10
S5	A2B2C3	0.20	5	20
S6	A2B3C1	0.20	10	0
S7	A3B1C3	0.25 (level 3)	0	20
S8	A3B2C1	0.25	5	0
S9	A3B3C2	0.25	10	10

The heating process was completed in the chamber electric furnace, and the same heating rate was used at the four temperatures (see Fig. 1 b). In the room temperature test (20 ± 2) °C, the high-alumina cement products were cured for 28 days and then put into a drying oven at 50 °C. After drying and natural cooling to room temperature, they were tested. The specimens were calcined at 600 °C, 900 °C, and 1200 °C using the same heating rate. Subsequently, they were annealed for 1 h and cooled to room temperature before being tested.

**Fig. 1.** Specific heating intervals

2.4.2. Volume stability test

The test blocks before and after high-temperature calcination were subjected to volumetric testing using the drainage method (kerosene instead of water) because of the presence of voids and cracks on the surface of the test samples after calcination. Using water as a medium would affect the accuracy of the results since water plays a very important role in the chemical reaction of the high-alumina cement. In contrast, kerosene does not participate in the hydration reaction of high-alumina cement and evaporates easily.

The tests were performed as follows, according to the GB/T 17671-2021. (1) The specimen was put into a drying

oven at 100 ± 2 for 2 h and then placed into a measuring cylinder with an outer diameter of 32 mm and a measuring range of 200 mm. Kerosene was added to the 50 mm mark and then the measuring cylinder was covered with a cling film and left for 24 h. The initial volume V_1 of the test block was noted; (2) After drying, the specimens were placed in a high temperature furnace for calcination under different calcination regimes; (3) Step (1) was repeated for the calcined specimen, and the sample volume V_2 was obtained after the high temperature treatment.

2.4.3. Compressive strength test

The compressive strength of high-alumina cement specimens after calcination at (20 ± 2) °C, 600 °C, 900 °C, and 1200 °C was measured using a Gorell SVC-4500VA press in accordance with the “Test Method for Cementitious Sand Strength (ISO Method)” GB/T 17671-2021. Three parallel tests were conducted for each specimen, and the average value was taken as the volume stability index of the specimen.

2.4.4. Microscopic test

Specimens of high-alumina cement blocks with different components at different temperatures were removed separately and crushed. Test blocks with fresh sections were selected and placed in reagent bottles, soaked in anhydrous ethanol to terminate the hydration of the cement, and placed in a sealed container for testing.

The changes in the mineral composition of cementite were analyzed using a Shimadzu XRD-7000S type X-ray diffractometer (XRD). Powder specimens were used for XRD analysis. After drying the block specimens, they were ground with a ceramic mortar, sieved out with a 200-mesh fine sieve, and then put into an X-ray diffractometer for analysis.

The microstructural features of the specimen sections were observed with a Japanese Hitachi S-4800 Field Emission Scanning Electron Microscope (SEM). The SEM test is performed by selecting a thin sheet specimen with a flat surface and drying it at a temperature of 50 °C for 1 hour. When observing, because of the poor electrical

conductivity of cement paste, the specimen should be sprayed with gold on the surface of the specimen first, thus making the specimen conductive.

Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis were performed using a synchronous thermal analyzer (STA) model STA449F5, NETZSCH, Germany.

3. RESULTS AND DISCUSSION

3.1. Analysis of the effect of temperature on the bulk stability of high-alumina cement

Volume stability is the most important property of the gelling materials used under high-temperature conditions. The volume changes of the high-alumina cement specimens after calcination at 600 °C, 900 °C, and 1200 °C are shown in Fig. 2 a. A positive difference analysis of the high-alumina cement specimens after high-temperature calcination is shown in Fig. 2 b, c and d. k_i is the mean value of each influencing factor at the same level, and the extreme difference R is the magnitude of the change in the test index within the range of values for that factor. A larger R value indicates that the change in the level of the influencing factor (A: water-cement ratio, B: amount of MgO powder, C: amount of Al_2O_3 powder) has a greater effect on the volume change of the high-alumina cement after high temperature calcination, which indicates that the influencing factor is more important.

From Fig. 2 a and Fig. 2 b, it can be seen that the volume stability of the test blocks is not significantly affected by calcination at 600 °C. And the volume of the test blocks varied within a small range for each group of samples at 600 °C and 1 h constant temperature, especially when the refractory powder was added. With an increase in the MgO and Al_2O_3 , the volume of the specimen decreased. In comparison, the volume change of the Al_2O_3 -doped high-alumina cement specimens was smaller than that of the MgO, while the volume change of the specimens tended to decrease with an increase in the water-cement ratio. The factor that had the greatest effect on the volume of the specimen at 900 °C was the water-cement ratio (see Fig. 2 a and c), followed by the amount of Al_2O_3 , while the amount of MgO had the least significant effect on the volume change of the specimen.

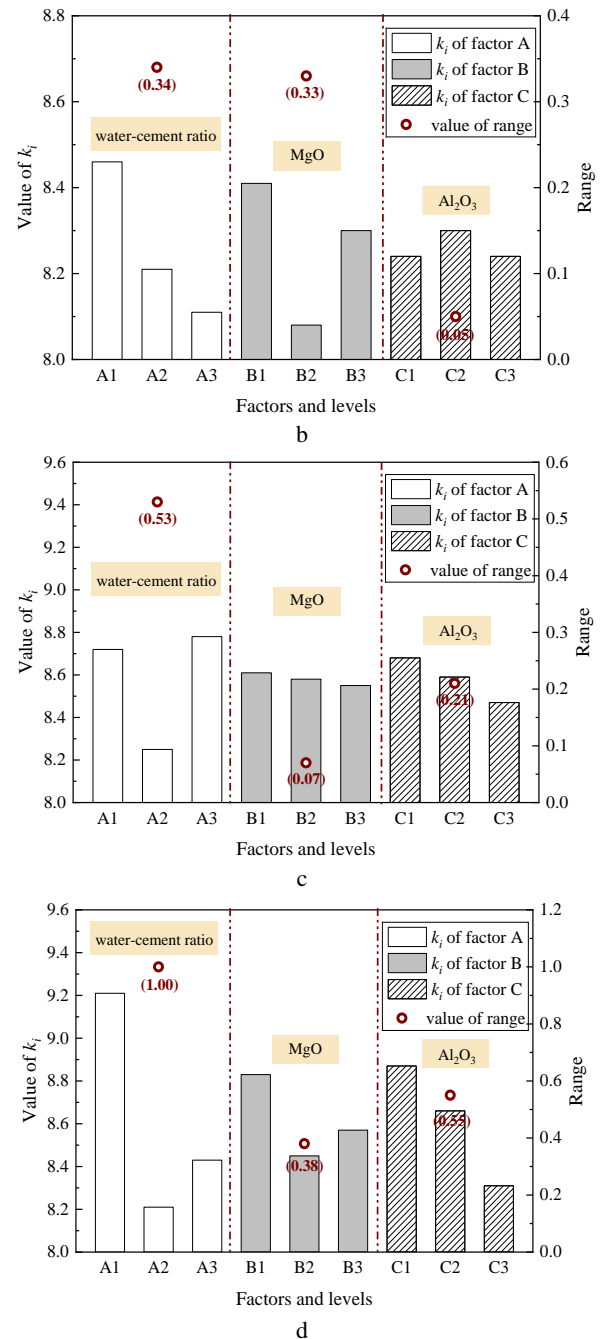
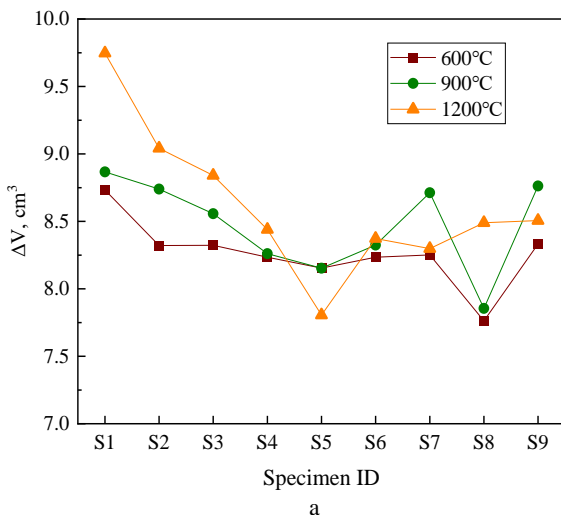


Fig. 2. Volume change and range analysis of cement paste exposed to different temperatures: a – volume change index; b – range analysis of ΔV after calcination at 600°C; c – range analysis of ΔV after calcination at 900°C; d – range analysis of ΔV after calcination at 1200°C

With an increase in the water-cement ratio, the volume of the test block first decreased and then increased. By comparing with the condition obtained at 600 °C, it can be seen that the effect of water-cement ratio on high-alumina cement specimens increases significantly when the temperature increases to 900 °C.

The addition of Al_2O_3 at 600–900°C is beneficial to increase the volumetric stability of high-alumina cement test blocks. Similarly, as can be seen in Fig. 2 a and d, the factor that had the greatest effect on the volume of the specimen at 1200 °C was the water-cement ratio, followed by the amount of Al_2O_3 , and the amount of MgO had the

least significant effect on the volume change of the specimen. With an increase in the water-cement ratio and the amount of MgO, the volume of the specimen first decreased and then increased. With an increase in Al₂O₃, the volume of the specimen tended to decrease gradually.

Extreme difference analysis cannot estimate the test error, which makes it difficult to distinguish whether the test results are caused by the error or due to different levels of multiple factors, while repeated trials of analysis of variance (ANOVA) can effectively remedy this deficiency. In this study, ANOVA was performed using SPSS statistical software. The variance analysis of the volume changes after calcination at different temperatures is listed in Table 4. There was no significant change in the volume of the specimen at 600 °C and the effect of each factor was not obvious. The most significant effect on the volume of the test blocks at 900 °C and 1200 °C was the water-cement ratio, followed by the amount of Al₂O₃. The ANOVA results for the three temperatures were consistent with the results of the extreme difference analysis.

Table 4. Variance analysis of volume change after calcination at different temperatures

Temp.	Factor	SS	df	MS	F	Significance
600°C	A	0.190	2	0.095	1.409	O
	B	0.166	2	0.083	1.228	O
	C	0.006	2	0.003	0.041	O
900°C	A	0.511	2	0.255	202.495	**
	B	0.007	2	0.003	2.577	O
	C	0.065	2	0.032	25.728	*
1200°C	A	1.663	2	0.831	72.368	*
	B	0.227	2	0.114	9.898	O
	C	0.472	2	0.236	20.538	*

Notes: O non-significant; * significant; ** highly significant

In accordance with the above-mentioned T1 and T2 matching ratios, the volume changes after calcination at different temperatures were assessed according to the results of the extreme difference and ANOVA. The high-alumina cement ratios with better volumetric stability are T1 (A2B2C3) and T2 (A2B3C3), and the mix ratio of T1 and T2 are listed in Table 5. The volume changes of T1 and T2 groups are shown in Fig. 3. As can be seen from Fig. 3, the volume of pure high-alumina cement paste (A1B1C1) as the reference group increased significantly under the warming condition, and the volume of the test block expanded more than 20 % under the condition of 1200 °C, which is extremely unfavorable for utilization under high temperature conditions. In comparison, volumetric stability was significantly improved after mixing with an appropriate amount of refractory powder. Compared with that of the room temperature, the volume change in the test temperature range of the two groups of test blocks was not significant, and even a slight shrinkage was observed (T1: A2B2C3, 1200 °C), which may be related to the transformation of the hydration products inside the test blocks. The volume change of specimens in T1 remained stable from 600 °C to 900 °C, while at 1200 °C shrank slightly by 5.39 %. The T2 shrank slightly in the range of 600–1200 °C, with the largest shrinkage value of 6.18 % at 600 °C. The volume change values of T1 and T2 were significantly lower than those of the

control group (S1: A1B1C1), indicating that the addition of MgO and Al₂O₃ could effectively alleviate the problem of volume change in high-alumina cement owing to the transformation of phase composition.

Table 5. Mix ratio of volumetric stability group in orthogonal test

Specimen ID	Water-cement ratio	MgO, %	Al ₂ O ₃ , %
T1(A2B2C3)	0.2	5	20
T2(A2B3C3)	0.2	10	20

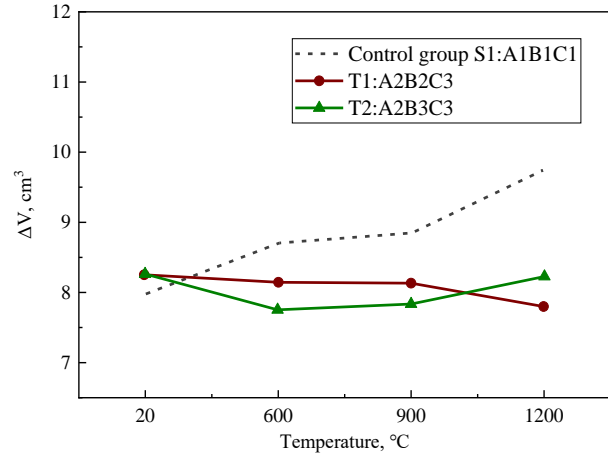


Fig. 3. Relationship between temperature and volume change

3.2. Effect of temperature on the compressive strength of high-alumina cement

In addition to volume stability, mechanical properties are also important indicators of high temperature-resistant cementitious materials. The proper mechanical strength must be maintained under high-temperature conditions to ensure that the high-temperature resistant cement can support the self-weight, external forces, and the influence of temperature stresses during use. To determine the change in strength at different temperatures, specimens were prepared in two groups with better high-temperature volumetric stability, specifically T1 and T2, and the compressive strength was tested at different temperatures. The results are shown in Fig. 4. As can be seen from Fig. 4, the room temperature strength of pure high-alumina cement paste (S1:A1B1C1) reached 100.95 MPa, and the strength slightly increased under the condition of heating up to 600 °C, but significantly decreased at 900 °C, to only 81.85 MPa, a decrease of 18.92 %. Continuing the temperature increase to 1200 °C, the compressive strength slightly decreased to 79.93 MPa. In comparison, the mechanical strength of the high-alumina cement samples with the addition of refractory powder showed a trend of increasing and then decreasing with increasing temperature, with the highest compressive strength at 600 °C, followed by a significant decrease in strength at 900 °C and 1200 °C. The higher the temperature, the smaller the residual strength, and the same conclusion was obtained in the reference [4, 6, 8]. At 1200 °C, the residual compressive strength of these two groups was only 42–43 MPa, which may be related to the transformation of hydration products inside the specimens. MgO and Al₂O₃ are typical refractory powders. They are stable in physical and chemical properties at high temperatures when used

alone; however, when used together, they undergo a chemical reaction at 1200–1300 °C, resulting in the generation of active magnesium spinel (containing MgO or Al₂O₃). In addition, the hydration products of high-alumina cement can form high-temperature stable phases such as CA₆ with refractory fillers containing Al₂O₃, which is beneficial for improving the high-temperature resistance of high-alumina cement. The experimental results shown in Fig. 4 indicate that the mechanical strength of the high-alumina cement paste mixed with refractory powder is affected by high temperatures and needs to be improved in future work.

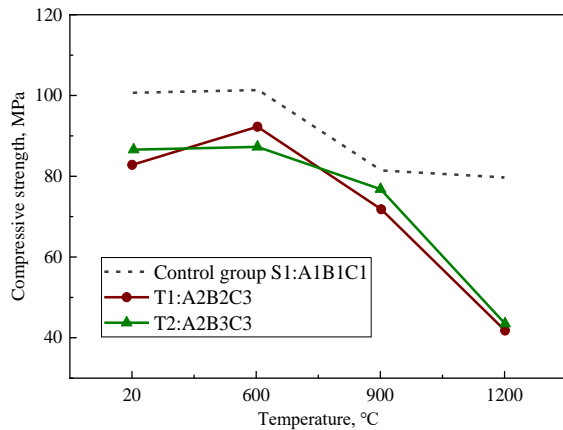


Fig. 4. Relationship between temperature and compressive strength

3.3. Effect of temperature on the hydration products of high-alumina cementite

Fig. 5 shows the XRD patterns of T2 (see Table 5) at room temperature (20 ± 2) °C, 600 °C, 900 °C and 1200 °C. As shown in Fig. 5, melilite (C₂AS) is a more stable component, which can exist stably after calcination at different temperatures, and the diffraction peaks have high and sharp peaks. The components of high-alumina cement are CA, CA₂, CA₆ and C₁₂A₇. Among them, CA is the most dominant hydrate phase in high-alumina cement, with content as high as 40 % – 70 %.

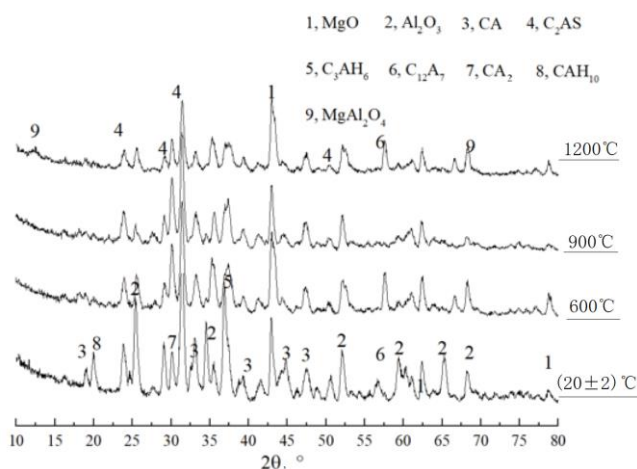


Fig. 5. XRD pattern of T2 after calcination at different temperatures

The CA is able to undergo hydration reaction in a relatively short period of time and provide early bond strength. In addition, the initial hydration products are CAH₁₀ and C₂AH₈, which accelerate their transformation into C₃AH₆ when the temperature increases [17, 18]. The diffraction peaks of CAH₁₀ and C₃AH₆ became weaker in the XRD pattern after the temperature rises from (20 ± 2) °C, whereas the diffraction peak of C₁₂A₇ was enhanced, indicating that CAH₁₀ and C₃AH₆ changed to C₁₂A₇ after dehydration. Compared with the XRD pattern after calcination at 600 °C, the diffraction peak position of the XRD pattern after calcination at 900 °C did not change much, but the diffraction intensity decreased, indicating that the hydration products have been completely decomposed, but no obvious solid-phase reaction has occurred and no phases such as CA₂ and CA₆ have been formed yet. The structure of each hydration product suffered a certain degree of damage with an increase in temperature.

3.4. Microstructural characteristics

To further investigate the microscopic influence of MgO and Al₂O₃ on the hydration products and transformation of high-alumina cement, SEM tests were conducted on the optimized T2, and the results are shown in Fig. 6. From Fig. 6, it can be observed that the internal components of this group of cementite were densely cemented, and needle-column CAH₁₀ was produced, but not in large quantities. The hydration products were cemented together, and the microstructure was denser with a closely connected network. This indicates that at room temperature, the addition of MgO and Al₂O₃ can make the microstructure of high-alumina cementite denser, and the density of cementite increases. When the temperature was increased to 600 °C, we can see lamellar C₂AS crystals and plate-like CA and CA₂ intertwined among them, which were well developed, uniform in size, with large crystalline particles, as well as many visible small-sized pores. The microstructure was denser, and the components were in a good state of cementation at 900 °C; we can see the plate-like CA and CA₂ crystals interwoven into sheets, the degree of crystallization was more uniform, and the size of crystalline particles was larger, but the pore size was smaller. After calcination to 1200 °C, we can easily see hexagonal lamellar crystals, and plate-like CA and CA₂ crystals intertwined together to form a denser structure. From the XRD pattern analysis, we determined that the crystal was MgAl₂O₄, namely magnesium aluminum spinel, which is a crystal with high-temperature resistance [22] and an intrinsic factor in maintaining the volume stability and strength of the specimen.

3.5. TG-DSC

Fig. 7 shows the TG-DSC curves of the specimens in T2. There was a first heat absorption peak at approximately 100 °C, which was caused by the heat absorption and evaporation of crystalline water inside the specimen. A second heat absorption peak was observed at 300 °C, which was caused by the dehydration of C₃AH₆ into C₁₂A₇ and Ca(OH)₂. At 550 °C, the third heat absorption peak that appears was caused by the

decomposition of $\text{Ca}(\text{OH})_2$, and the heat absorption peak at approximately 700°C was caused by the heat absorption decomposition of CaCO_3 .

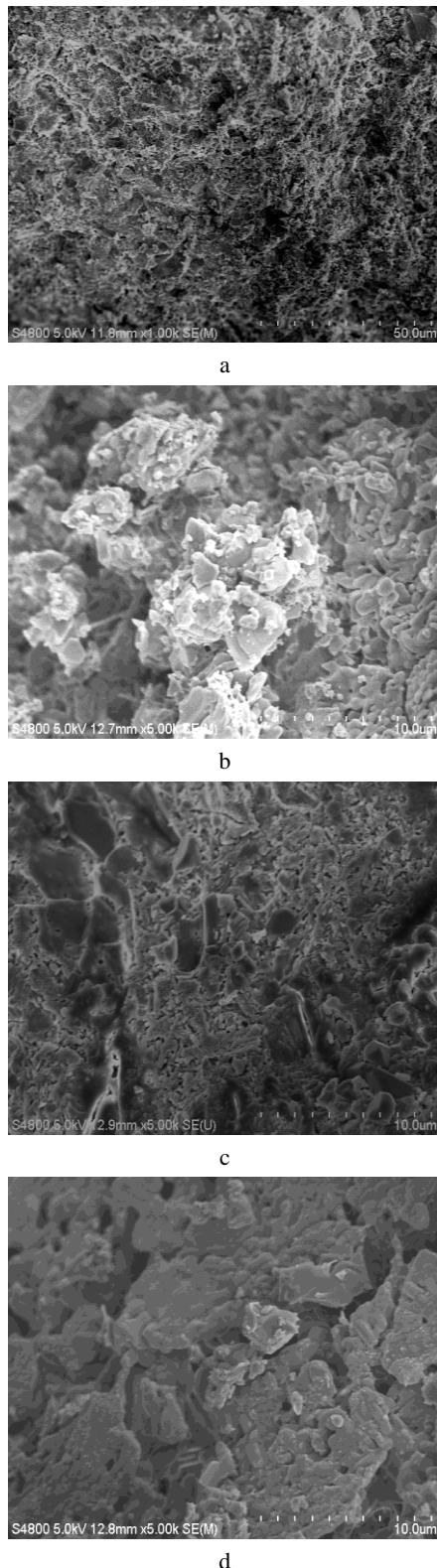


Fig. 6. Micromorphology of T2: a— $(20 \pm 2)^\circ\text{C}$; b— 600°C ; c— 900°C ; d— 1200°C

It can also be seen that as the temperature increased, there was a larger loss of mass caused by C_3AH_6 dehydration as the temperature increased to approximately 300°C .

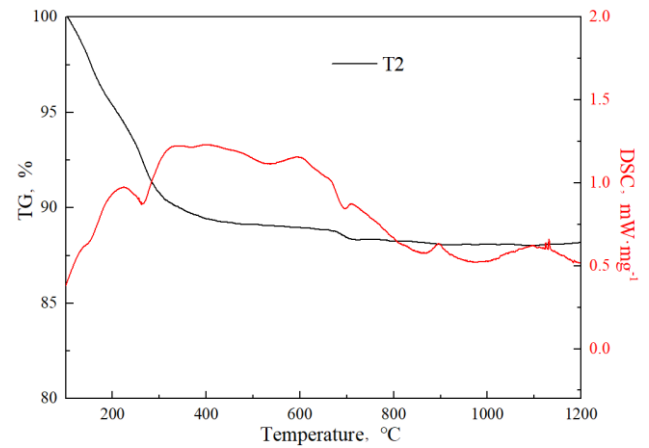


Fig. 7. TG-DSC spectra of T2

4. CONCLUSIONS

To improve the high temperature stability of high-alumina cement, MgO and Al_2O_3 were added into high-alumina cement pastes with different water-cement ratios. The effect of MgO and Al_2O_3 on the volume change pattern of high-alumina cement at $600\text{--}1200^\circ\text{C}$ was revealed by the optimal experimental design combined with the analysis of variance method. The high temperature structural evolution of the hardened cement paste was also characterized and analyzed from XRD, SEM, and TG-DSC. The following conclusions were drawn from the results of this study:

1. The introduction of MgO and especially Al_2O_3 , can significantly improve the volumetric stability of high-alumina cement at $600\text{--}1200^\circ\text{C}$. At $600\text{--}1200^\circ\text{C}$, as the water-cement ratio changed from 0.15 to 0.25, the volume of high-alumina cement became smaller and then increased as the water-cement ratio increased. As the amount of MgO increased from 0 to 10 %, the volume at 600°C first became smaller and then increased, and the volume at the higher temperature decreased with an increase in MgO . Moreover, as the amount of Al_2O_3 increased from 0 to 20 %, the volume of cementite decreased slightly. Spinel formation compensates for shrinkage caused by the sintering of the material at 1200°C .
2. ANOVA showed that the volumetric stability of high-alumina cement was best when the water-cement ratio was 0.2, the admixture of MgO was 10 %, and the admixture of Al_2O_3 was 20 %. Under this ratio, the volume of high-alumina cement will remain stable or even shrink slightly during the process of temperature increase from room temperature to 1200°C . The volumetric stability was good at temperatures below 900°C . The volume shrinks slightly at 1200°C , by 5.39 % compared to the volume at room temperature.
3. The best volumetric stability at high temperature (water-cement ratio of 0.2, 10 % of MgO , and 20 % of Al_2O_3), the strength of high-alumina cement test block increased first with the increase in temperature and then decreased, and the strength was maximum at 600°C . However, a significant decrease occurred in the temperature range of $900\text{--}1200^\circ\text{C}$; the mechanical strength at 1200°C could still reach more than 42 MPa.

4. The compositions of the calcined high-alumina cement with different ratios after calcination included C_2AS and CA. When the amount of MgO was 10% and Al_2O_3 was 20 %, $MgAl_2O_4$ was produced after calcination at 1200 °C. From the microstructure, it was observed that there were more pores inside the specimen after calcination at 600–900 °C due to the loss of crystalline water, and a more compact structure was obtained at 1200 °C. Al_2O_3 can promote the production of CA, CA_2 , and spinel, thus compensating for the pores caused by the loss of crystalline water. This study investigates the performance characteristics of high-alumina cement at high temperatures from hydration products. Future research should consider the extent of chemical reactions and molecular structure changes.

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