Mechanistic Study of the Effects of Magnesia Reactivity on Setting and Hardening of Basic Magnesium Sulfate Cement

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Abstract

Basic magnesium sulfate (BMS) cement was prepared by magnesia with different reactivities derived from calcination of basic magnesium carbonate at 600 to 1000°C. The effects of reactivity of magnesia on the setting time and compressive strength of BMS cement was investigated. Furthermore, XRD, SEM, MIP, hydration heat evolution and the pore solution composition were used to analyze the action mechanism of magnesia reactivity. The results show that the main strength phase of 5Mg(OH)₂·MgSO₄·7H₂O (5·1·7 phase) was formed in BMS cement prepared by magnesia with calcination temperature higher than 600°C. The magnesia with a high BET surface area and low crystallite dimension showed a high adsorption capacity for citrate ions in magnesium sulfate solution, decreasing their concentration in the pore solution. By acting as a soft template for 5·1·7 phase formation, the decrease in citrate ions resulted in a low amount of 5·1·7 phase, forming Mg(OH)₂ instead, leading to a low-strength BMS cement.

1. Introduction

Basic magnesium sulfate (BMS) cement is a type of magnesium-based cement developed after magnesium oxychloride (MOC) cement (Walling et al. 2016). BMS cement can be considered as a modified MgO-MgSO₄·H₂O ternary system with appropriate additives such as citric acid and citrates (Qin et al. 2018; Wang et al. 2018; Wu et al. 2014), tartaric acid (Wu et al. 2017), phosphoric acid and phosphates (Wu et al. 2016), and organic phosphates (Wu et al. 2016), in which the main hydrate strengthening phase is 5Mg(OH)₂·MgSO₄·7H₂O (5·1·7 phase) (Wu et al. 2014; Runčevski et al. 2013; Guo et al. 2017). Owing to the higher early strength, lower weight, better salt corrosion resistance, better processing and decoration performance, and good steel protection properties compared to those of the MOC cement, BMS cement has been widely used in the production of various composite wall plates, low-weight thermal insulation products, and precast reinforced concrete (Walling et al. 2016; Kahle et al. 1972; Zhou et al. 2012).

The raw materials for BMS cement mainly include magnesium and magnesium sulfate, and the production cost of magnesia has a significant impact on the large-scale production and application of BMS cement-based materials. For example, in China, magnesia for the production of BMS cement is mainly obtained from calcined magnesite (light burnt magnesia, LBM), 90% of which is concentrated in the Liaoning Province (Wu et al. 2014, 2017, 2015). Large scale production of the BMS cement products in the western region is limited because of the high transportation cost of LBM. Therefore, a cheap raw material to produce magnesium oxide for BMS cement is urgently required (Wu et al. 2014; Li et al. 2017). The western region of China has abundant magnesium by-product resources such as the salt lake, approximately 8 to 10 tons of by product magnesium chloride is obtained after the extraction of potassium chloride, and magnesia can be prepared from magnesium chloride by brine-lime milk method (Liu et al. 2019), brine-ammonium carbonate method (Hu et al. 2007), and direct thermal decomposition method (Luong et al. 2018). The above methods for producing MgO include the calcination of precursors such as Mg(OH)₂ and basic magnesium carbonate, and the reactivity of MgO varies with the calcination conditions (Tan et al. 2014; Wu et al. 2018; Chen et al. 2017). Some reports show that the reactivity of MgO has a noticeable effect on the performance of BMS cement. Li et al. (2017) compared the strengths of BMS cement prepared using LBM with three active magnesia contents of 43.2%, 60% and 70%, measured by the hydration method of Dong et al. (2010). The relative content of the 5·1·7 phase in the cement prepared using 60% active magnesia was the highest, affording the highest strength. Li et al. (2020) compared the BMS cement prepared by MgO derived from the calcination of brine precipitation products and LBM, and the former showed a higher early strength. Chen et al. (2018) investigated the BMS cement prepared using light...
burnt dolomite and found that the BMS cement prepared using magnesia at a calcination temperature of 850°C had the highest strength. In our previous report (Wu et al. 2018), the magnesium-rich by products obtained in the production of lithium carbonate from salt lake were used to prepare BMS cement. Low calcination temperature (such as 500°C) resulted in quick setting but afforded poor volume stability and low later strength, whereas a high temperature (such as 800°C) afforded a high later strength but low early strength. However, the mechanism of the effect of MgO reactivity on the setting and hardening of BMS cement has not been completely clarified.

The composition of the hydration products is one of the fundamental factors affecting the performance such as setting and hardening of cement. In recent years, numerous literature reports (Wu et al. 2014, 2017, 2015; Runčevski et al. 2013; Guo et al. 2017) have described that the formation of 5·1·7 phase instead of Mg(OH)2 in BMS cement leads to high strength, good volume stability, and good water resistance, after the addition of appropriate additives. According to the previous studies on the hydration mechanism of BMS cement, the formation of a large amount of 5·1·7 phase and a small amount of low-gelling Mg(OH)2 is related to the complexation or adsorption of the additives (such as tartaric acid) and the hydration layer of MgO (Wang et al. 2018; Wu et al. 2015, 2017). However, complexation and adsorption are related to the reactivity of MgO, which is further correlated with the crystallinity or specific surface area obtained by different calcination conditions of the precursor.

Therefore, in this study, BMS cement was prepared using magnesia with different reactivities, obtained via the calcination of pure basic magnesium carbonate at different temperatures. The setting time and compressive strength of BMS cement prepared using these different magnesia were investigated. In addition, hydration phase composition, pore distribution, pore solution composition, and hydration heat evolution were analyzed to determine the mechanism of the effect of magnesia reactivity on the setting and hardening of BMS cement.

2. Materials and methods

2.1 Raw materials
Magnesia used in this study was obtained by the calcination of basic magnesium carbonate (4MgCO3·Mg(OH)2·5H2O) at 600 to 1000°C. Analytically pure basic magnesium carbonate was purchased from Tianjin Damao Chemical Reagent Co., Ltd. (Tianjin, China). The specific surface area of basic magnesium carbonate was determined as 16.03 m²/g using the Brunauer-Emmett-Teller (BET) method employing a surface analyzer (Gemini VII 2390, Micromeritics, Norcross, Georgia, USA). The D50 and D90 values (17.86 μm and 38.25 μm, respectively) of the basic magnesium carbonate powder were analyzed by laser diffraction using Mastersizer 2000 particle analyzer (Malvern Panalytical Ltd., Malvern, United Kingdom) method with ethanol as the dispersant. Pure magnesium sulfate (MgSO4·7H2O) and sodium citrate (Na3C6H5O7·2H2O, SC) were purchased from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China) and used as raw materials and additives for preparing BMS cement.

2.2 Preparation of magnesia with different reactivities
Figure 1 shows the thermogravimetry/differential scanning calorimetry data of basic magnesium carbonate analyzed by a synchronous thermal analyzer (STA449F3). Thermal decomposition of basic magnesium carbonate is divided into two steps and two endothermic peaks are observed at approximately 243.7°C and 450.9°C. The first endothermic peak at 243.7°C corresponds to the loss of all crystal water molecules [Eq. (1)]. The second endothermic peak at 450.9°C is due to the complete decomposition of basic magnesium carbonate into MgO as shown in Eq. (2) (Morozov et al. 2003). Therefore, to obtain different crystallinity of magnesia, magnesium carbonate was calcined in a muffle furnace (GWL-1200°C) at temperatures ranging from 600°C to 1000°C for 2 hours with a heating rate of 5°C/min. According to the law of thermal decomposition and considering that the content of pure basic magnesium carbonate is > 99%, the content of powdered magnesia obtained by calcination can be expressed by Eq. (3).

\[
\text{4MgCO}_3\cdot\text{Mg(OH)}_2\cdot5\text{H}_2\text{O(s)} \xrightarrow{243.7°C} \text{4MgCO}_3\cdot\text{Mg(OH)}_2(s) + 5\text{H}_2\text{O(g)} \tag{1}
\]

\[
\text{4MgCO}_3\cdot\text{Mg(OH)}_2(s) \xrightarrow{-450.9°C} 5\text{MgO(s)} + \text{H}_2\text{O(g)} + 4\text{CO}_2(g) \tag{2}
\]

\[
W_i = \frac{5M_i(W_i - W_f)}{4M_c + M_H(100 - W_f)} \times 100\% \tag{3}
\]

where \(W_i\) is the total weight loss percentage, \(W_f\) is the weight loss in the first step [Eq. (1)], \(M_i\) is the relative molecular mass of CO₂, and \(M_H\) is the relative molecular mass of H₂O.

![Fig. 1 Thermogravimetry/differential scanning calorimetry data for basic magnesium carbonate.](image)
2.3 Preparation of the specimen

To prepare BMS cement specimens, the MgO : MgSO₄ : H₂O molar ratio was fixed at 5 : 1 : 20. First, MgSO₄·7H₂O was added to deionized water and stirred at room temperature to prepare 25 wt.% magnesium sulfate solution. Second, 1.0% (by weight of MgO) of sodium citrate (SC) was mixed with the magnesium sulfate solution to form a clear and uniform solution. Then, a predetermined amount of MgO calcined at different temperatures was mechanically stirred with the magnesium sulfate solution to form the BMS cement paste. The BMS slurries were cast in 20 × 20 × 20 mm³ steel molds and cured at 20 ± 3°C and 50 ± 5% relative humidity (standard curing). After 24 hours, the specimens were demolded and cured until their required ages were attained. The BMS cement samples prepared with different temperatures were labeled as T600, T700, T800, T900, and T1000, where the numerals correspond to the temperatures. The raw material contents of the specimens are included in Table 1.

XRD tests show that the composition of the hydration phase of BMS cement prepared according to MgO : MgSO₄ : H₂O = 5 : 1 : 80 and MgO : MgSO₄ : H₂O = 5 : 1 : 20 are the same. The pore solution cannot be obtained after the cement is hardened. Therefore, in order to obtain the pore solution during the hydration conveniently, BMS cement paste was prepared by the calcination of magnesia at 700°C and 1000°C with a molar ratio of MgO : MgSO₄ : H₂O = 5 : 1 : 20 and 1% (by weight of MgO) of added SC, subsequently denoted as PT700 and PT1000, respectively. To prevent uneven hydration due to the sedimentation of magnesia and solid particles, the cement paste was placed in an oscillator at a constant temperature of 20°C. The pore solutions corresponding to different hydration times were obtained by high pressure extrusion-centrifugation filtration method (Fig. 2).

2.4 Specimen analysis

The setting time of the BMS cement curing system was measured according to the Chinese national standard protocol GB/T1346-2011 using Vicar instruments at 20 ± 3°C.

The compressive strength was determined according to the GB175-2007 testing standard. The BMS cement specimens after curing for 1, 3, 7, and 28 days were analyzed using a machine with a maximum force of 300 kN at a loading rate of 2.4 kN/s.

To determine the crystal phase composition of the BMS cement samples cured for different durations, the cement sample after termination of hydration was freeze dried, and then ground into powder (D90 < 35 μm) with an agate mortar before XRD test. An X-ray diffractometer (D/max-2500PC, Rigaku Corporation, Tokyo, Japan) was used to analyze the sample with CuKα radiation (λ = 0.15419 nm) and an acceleration voltage of 30 kV in the 2θ range of 5 to 70° to obtain X-ray diffraction (XRD) patterns.

The microstructures of the BMS cement samples were characterized by scanning electron microscopy (SEM, JSM-6610LV, JEOL, Ltd., Tokyo, Japan) of the fractured surfaces after gold coating. Gold spray thickness was 20 nm, and the SEM test voltage was 15 kV.

The hydration heat release rate of the BMS cement paste was measured at a constant temperature of 20°C using a four-channel isothermal calorimeter (Calmetrix-4000HPC, Calmetrix Inc., Boston, Massachusetts, USA).

The porosity and pore distribution of BMS cement cured in air for 28 days were measured employing the mercury intrusion porosimetry (MIP) method using an automatic mercury porosimeter (AutoPore IV 9500, Micromeritics, Norcross, Georgia, USA).

The porosity of MIP is defined as the volume fraction of pores in the sample, calculated as (V_p - V_s)/V_s, where V_p is the volume of mercury displaced by the sample and V_s is the volume of the sample.

The pH value of the pore solution was determined using a pH meter (PHS-3C), and another portion was used to determine the concentrations of Mg²⁺ and SO₄²⁻ ions in the liquid phase. For determining Mg²⁺ and SO₄²⁻ concentrations, ethylenediaminetetraacetic acid (EDTA) titration and EDTA back titration barium methods were used, while potassium dichromate oxidation-spectrophotometry method was used to measure citrate (Qu 2010).

| Specimens | Magnesia powder (g) | 25 wt.% magnesium sulfate solution (g) | SC (g) |
|-----------|---------------------|--------------------------------------|--------|
| T600      | 1000                | 1945.8                               | 10     |
| T700      | 1000                | 2250.2                               | 10     |
| T800      | 1000                | 2367.6                               | 10     |
| T900      | 1000                | 2388.0                               | 10     |
| T1000     | 1000                | 2400.0                               | 10     |

Table 1 Raw material contents of the specimens.
3 Results and discussion

3.1 Characterization of magnesia with different reactivities

Figure 3 shows the XRD data of MgO obtained by calcining basic magnesium carbonate at different temperatures. The intensities of the diffraction peaks of magnesia increase with an increase in the calcination temperature. Among them, the diffraction peak intensity of MgO obtained by calcining basic magnesium carbonate at 1000°C is the highest. This is consistent with the law that MgO content increases with the increase of temperature. Although magnesium carbonate is not completely decomposed at a low temperature such as 600°C, the diffraction peaks of other substances are not observed in the XRD data because of the presence of a small amount of non-decomposed content. The crystallite dimensions of magnesia calcined at different temperatures were calculated using the half peak width of the crystal face (1 0 0) of magnesia according to the Scherrer equation shown below:

\[ D = \frac{K \gamma}{B \cos \theta} \]  

where \( K \) is Scherrer’s constant, \( D \) is the average thickness of the grain perpendicular to the crystal surface, \( B \) is the half height width of the measured sample diffraction peak, \( \theta \) is the diffraction angle, and \( \gamma \) is the X-ray wavelength, which is 0.154056 nm.

The properties of magnesia obtained from magnesium carbonate calcined at different temperatures were calculated using the half peak width of the crystal face (1 0 0) of magnesia according to the Scherrer equation shown below:

| Temperature (°C) | Magnesia content (%) | Crystallite dimension (nm) | BET surface area (m²/g) | Citric acid color change time (s) |
|------------------|----------------------|---------------------------|-------------------------|-------------------------------|
| 600 °C           | 81.45                | 10.1                      | 142.28                  | 20.9                          |
| 700 °C           | 93.76                | 12.8                      | 99.54                   | 23.3                          |
| 800 °C           | 98.65                | 19.1                      | 76.31                   | 38.8                          |
| 900 °C           | 99.50                | 23.3                      | 52.59                   | 74.2                          |
| 1000 °C          | 100                  | 29.5                      | 32.72                   | 120.6                         |

Table 2 Properties of magnesia obtained by calcined at different temperatures.

3.2 Setting time

Figure 4 shows the setting times of BMS cement prepared with MgO calcined at different temperatures. The setting time of BMS cement increases with an increase in the calcination temperature. When the calcination temperature is increased from 600°C to 1000°C, the initial setting time of BMS cement increases from 0.12 to 7 hours, and the final setting time increases from 0.3 to 19.75 hours. This implies that with an increase in the calcination temperature, the crystallite dimension of magnesia continues to increase and BET surface area continues to decrease, resulting in an increase in the setting time of BMS cement.

The setting time is related to the formation rate of hydration products, that is, the hydration rate of magnesia in magnesium sulfate solution. The rate of hydration can typically be expressed as the heat release of hydration. Figure 5(a) shows the hydration heat release rates
of BMS cement samples prepared with magnesia calcined at different temperatures. The hydration process can be divided into five stages – i.e., pre-induction, induction, acceleration, deceleration, and stabilization periods, which are consistent with the previous reports (Wen et al. 2014; Wu et al. 2019). The setting time is related to the time at the end of the induction period or the beginning of the acceleration period, such that longer is the end of the induction period, shorter is the setting time. The induction period increases with an increase in the calcination temperature of MgO. For T600 sample, the pre-induction and induction periods cannot be observed in Fig. 6(a) because the large BET surface area of MgO accelerates the reaction rate with magnesium sulfate solution. The induction period increases from 1.6 to 11.8 hours with an increase in the calcination temperature from 700°C to 1000°C. The hydration reaction of BMS cement is a solid-liquid interface reaction, the rate of which is related to the BET surface area of MgO. Larger the BET surface area, faster is the hydration rate, leading to the rapid formation of hydration products and a short induction period.

The BMS cement prepared using high-activity magnesia shows a higher cumulative hydration heat in the early stage of hydration, but as the hydration reaction progresses, the cumulative hydration heat of the BMS cement prepared using low-activity magnesia increases rapidly and continues increasing at 3 days of hydration, which may be related to the types of hydration products formed.

### 3.3 Compressive strength

Compressive strength is one of the important performance indicators of cementitious materials. Figure 6 shows the compressive strength development of BMS cement prepared using magnesia calcined at different temperatures. The reactivity of magnesia has noticeable effects on the compressive strength development of BMS cement. Among the BMS cement samples, T600 and T700 are severely cracked after curing for 2 and 7 days, such that their strengths after curing for 7 or 28 days cannot be tested. As shown in Fig. 7, cracks appeared in T700 after 7 days of curing, and they were broken after 28 days, while no cracks still appeared in T1000 after 28 days of curing.

Although it is observed that lower is the calcination temperature of MgO, faster is the setting speed, early strength such as 1 day strength does not follow the trend of the strength being higher as the setting speed becomes faster. For example, the 1 day strengths of T600 and T700 are 11.3 and 27.0 MPa, respectively, which are only 23.9% and 57.1% of that of T800 (47.3 MPa). The different compositions of the early hydration phases in BMS cement can be one of the important causes of this phenomenon (Section 3.4). The early strength of BMS cement decreases with an increase in the calcination temperature when the calcination temperature of magnesia is > 800°C. Due to the low hydration rate, the 1 day strength of T1000 is < 0.5 MPa, which is lower than the
detection limit of the testing machine. Therefore, to prepare BMS cement-based materials with high early strength requirements such as in low temperature environments, the calcination temperature of MgO should be appropriately decreased.

As shown in Fig. 6, the later strength of BMS cement increases with an increase in the calcination temperature of MgO, that is, BMS cement prepared using magnesia with a high calcination temperature has a high later strength, but its setting and hardening are slow. The 28 day strength of T1000 is 103.0 MPa, which is greater by 18.8% than that of T800 (86.7 MPa), which may be because of the different micro-morphology of the strengthening phase such as 5·1·7 phase in BMS cement prepared using magnesia with different reactivity.

### 3.4 Hydration phase composition and microstructure

The phase composition and microstructure during the hydration of cementitious materials are the most fundamental parameters affecting the setting and hardening characteristics of cement. Figure 8 shows the XRD pattern of BMS cement prepared with magnesia calcined at different temperatures after curing for 1 and 28 days. As shown in Fig. 8(a), no characteristic diffraction peaks of the 5·1·7 phase, but instead of Mg(OH)₂ are observed in the data for T600, indicating that a large amount of magnesium sulfate in the liquid phase does not participate during the formation of hydration strengthening phases, which is the main cause of serious cracks in T600 after curing for 2 days. With an increase in the calcination temperature of magnesia, the diffraction peaks of Mg(OH)₂ disappear and those of the 5·1·7 phase begin to gradually appear; higher the calcination temperature of magnesia, sharper are the diffraction peaks of 5·1·7 phase. According to the classical crystal growth theory, a low hydration rate leads to a low nucleation rate, which allows a facile growth of the crystal, indicating that a low reactivity of magnesia is favorable to form the strengthening phase with high crystallinity in the BMS cement. In addition, the diffraction peaks of unreacted MgO in both T900 and T1000 are sharp and intense, which confirms the low hydration rate and low early strength of BMS cement prepared with low-activity magnesia.

Compared to the data shown in Fig. 8(a), the XRD patterns of T600, T700, and T800 in Fig. 8(b) are almost unchanged after curing for 28 days, which further confirms the rapid hydration of BMS cement prepared with high-activity magnesia. Notably, the formation and growth of Mg(OH)₂ can easily lead to the collapse of the strength and afford poor volume stability as observed for T600 and T700.

The contents and grain sizes of the 5·1·7 phase in BMS cement after curing for 1 and 28 days are included in Table 3. When T700-T1000 cement specimens are cured

### Table 3 Phase composition of BMS cement after curing for 1 day and 28 days determined with Topas 4.2.

| Sample          | 5·1·7 Phase (%) | Mg(OH)₂ (%) | MgO (%) | Crystallite dimension |
|-----------------|-----------------|-------------|---------|-----------------------|
|                 |                 |             | CS-5·1·7 phase (nm) | CS-Mg(OH)₂ (nm) |
| T600-1 day      | -               | 92.29       | 7.71    | -                     | 9.8        |
| T700-1 day      | 90.91           | 9.09        | -       | 14.6                  | 8.2        |
| T800-1 day      | 99.16           | -           | 0.84    | 25.3                  | -          |
| T900-1 day      | 74.90           | -           | 17.16   | 28.3                  | -          |
| T1000-1 day     | 38.25           | -           | 61.75   | 39.6                  | -          |
| T600-28 days    | -               | 98.07       | 1.93    | -                     | 9.8        |
| T700-28 days    | 90.5            | 9.5         | -       | 16.1                  | 11.3       |
| T800-28 days    | 100             | -           | -       | 26                    | -          |
| T900-28 days    | 100             | -           | -       | 30.7                  | -          |
| T1000-28 days   | 100             | -           | -       | 41                    | -          |

Fig. 8 XRD data of BMS cement prepared using magnesia with different reactivity after curing for 1 day (a) and 28 days (b).
for 28 days, the content of the 5·1·7 phase increases from 90.5% to 100%, and the grain size of the 5·1·7 phase increases continuously, which indicates that with an increase in the calcination temperature of MgO, the low-activity MgO results in the formation of 5·1·7 phase with high crystallinity in BMS cement.

**Figure 9** shows the SEM images of BMS cement prepared with different magnesia after curing for 28 days. For the T600 sample, no needle-like 5·1·7 phase is observed but instead Mg(OH)₂ and unreacted magnesium sulfate with low crystallinity are detected, which is consistent with the results of the XRD analysis of the hydration phase. In T700, flaky Mg(OH)₂ is formed together with needle-like 5·1·7 phase. However, no Mg(OH)₂ crystals are observed in T1000, but instead interlaced growth of needle-like 5·1·7 phase is observed, and the length: diameter ratio of the 5·1·7 phase is higher than that in T700. Therefore, it can be inferred that the compressive strength of BMS cement is not only related to the amount but also the length to diameter ratio of the 5·1·7 phase, and magnesia with low crystallinity is more favorable for the formation of 5·1·7 phase with high length to diameter ratio in BMS cement.

![Fig. 9 Scanning electron microscopy images of BMS cement samples of T600 (a, b), T700 (c, d) and T1000 (e, f) after curing for 28 days.](image)
Table 4 Pore size distributions of different BMS cement samples after curing for 28 days.

| Samples | Porosity (%) | Average pore diameter (nm) | ≤ 10 nm (%) | > 10 nm (%) |
|---------|--------------|----------------------------|-------------|-------------|
| T700    | 24.75        | 34.81                      | 7.85        | 92.15       |
| T800    | 38.90        | 40.97                      | 2.15        | 97.85       |
| T900    | 39.44        | 55.40                      | 0.87        | 99.13       |
| T1000   | 38.88        | 65.73                      | 0.13        | 99.37       |

3.5 Pore structure

Figure 10 shows the cumulative porosity of BMS cement after curing for 28 days. The cumulative porosity of T700 is lower than the porosities of the other samples. As shown in Table 4, the average pore size increases with an increase in the calcination temperature of magnesia. For instance, the pore size of T1000 is 65.73 nm, which is approximately twice as that of T700. Unlike Portland cement, the hydrate strengthening phase mainly exists in the form of crystals in BMS cement (He et al. 2019). The higher the amount of hydrate strengthening phase formed with high crystallinity, lower are the number of gel pores (< 10 nm) and higher are the number of intergranular pores (> 10 nm) in BMS cement. Therefore, to some extent, the average pore size may reflect the crystallinity of hydrate phase in BMS cement. In the BMS cement prepared using high-activity magnesia, some part of magnesium sulfate does not participate in the formation of 5·1·7 phase, and may precipitate with a low crystallinity (because no diffraction peaks of magnesium sulfate are observed in the XRD data of T600 and T700) during curing in air, which increases the gel pore number as shown in Table 4. The reason for the low porosity of T700 is that the density of the precipitating solid magnesium sulfate (the density of MgSO₄·7H₂O is 1.68 g/cm³) is lower than that of the 5·1·7 phase (1.89 g/cm³).

3.6 Pore solution composition

The liquid phase compositions of PT700 and PT1000 cement samples with different hydration times were determined. The change in pH, Mg²⁺ and SO₄²⁻ concentrations in the liquid phase and the adsorption capacity of magnesia to citrate in magnesium sulfate solution are all correlated to the activity of magnesia. The change in liquid phase composition reflects the type and rate of hydration products formed during the hydration process, which is indicative of the setting and hardening process of BMS cement.

As observed in Fig. 11, with the progress of hydration, Mg²⁺ and SO₄²⁻ concentrations in the pore solution of PT700 decrease rapidly from 0.67 mol/L to 0.55 mol/L and 0.57 mol/L, respectively, in 1.5 h. The concentrations of Mg²⁺ and SO₄²⁻ increase slightly to 0.59 mol/L and 0.61 mol/L, respectively, after 5 hours of hydration, which indicates that some SO₄²⁻ and Mg²⁺ do not participate in the formation of hydration products but are only absorbed by MgO. The ion concentration changes slightly after 5 hours of hydration and the SO₄²⁻ concentration decreases to 0.63 mol/L within 72 hours, which is approximately 6% decrease, further confirming that high-activity magnesia is not conducive to the formation of solid phase hydration products. The changes in the ionic concentration in the pore solutions of PT1000 and PT700 are different. Within 4 hours of hydration, the SO₄²⁻ and Mg²⁺ concentrations show an upward trend, and the SO₄²⁻ concentration increases from 0.67 mol/L to 0.72 mol/L, which indicates that during hydration, magnesia first combines with water to form a hydration layer and simultaneously adsorbs some water, resulting in a short term increase in the ion concentration in the liquid phase. When the hydration reaction lasts for 5 to 8 hours, Mg²⁺ and SO₄²⁻ concentrations decrease slowly. This corresponds to the induction period in the hydration process. After 8 hours of hydration, the ion concentration of the liquid phase decreases rapidly, which corresponds to the main reaction stage (reaction process after the induction period) in the hydration process of BMS cement. After 72 hours hydration of PT1000, the concentration of SO₄²⁻ in the liquid phase decreases from 0.67 mol/L to 0.14 mol/L, corresponding to approximately 79% decrease, which confirms that most of the ions in the liquid phase participate in the formation of solid phase hydration products.

Figure 12 shows the change in the liquid phase pH with the progress of the hydration reaction. The pH val-
ues of the PT700 and PT1000 liquid phases increase rapidly and then decrease within 72 hours of hydration, and the hydration times in which their pH values begin to decline are 1 hour and 3 hours, respectively, indicating that the hydration rate of PT700 magnesia in magnesium sulfate solution is higher. For 72 hours hydration, the pH of PT1000 liquid phase is higher than that of PT700, and considering the weak acidity of magnesium sulfate solution, the consumption of magnesium sulfate in PT1000 liquid phase is higher.

Based on prior literature reports (Wang et al. 2018; Wu et al. 2015, 2017), the formation of a large amount of 5·1·7 phase requires the addition of appropriate additives such as citrate in BMS cement. Therefore, a specific range of citrate ion concentration in the pore solution is necessary to form the 5·1·7 phase. The mechanism of action of citrate ion concentration in the pore solution is shown in Fig. 14. First, MgO₆ octahedral is formed after the reaction of MgO surface with H₂O, which forms a sandwich structure with a specific layer spacing that can ensure the entry of hydrous sulfate because of the strong complexation of citrate ions. When the citrate concentration in liquid phase is very low, only OH⁻ with a small radius can enter the spaces of MgO₆ octahedral, resulting in the

![Fig. 12 Change in the pH of PT700 and PT1000 with time.](image1)

![Fig. 13 Change in the Citrate concentrations of PT700 and PT1000.](image2)

![Fig. 14 Formation of 5·1·7 phase in BMS cement.](image3)
formation of Mg(OH)\(_2\). The citrate in liquid phase acts as a soft template in the formation of 5·1·7 phase in BMS cement. As shown in Fig. 13, the concentration of citrate ions decreases rapidly at an early stage (before the acceleration stage of BMS cement) of the hydration of BMS cement; when the calcination temperature of basic magnesium carbonate is 700°C, the reactivity of MgO is high, and the excessive surface defects lead to the large adsorption capacity of MgO to citrate, which leads to the sharp decrease of citrate concentration in the liquid phase. After hydration for 1 hour, the concentration of citrate ions decreases to nearly zero (< 0.05 g/L) in PT700, while that in PT1000 is still > 0.06 g/L after hydration for 72 hours, which is conducive to the continuous formation of 5·1·7 phase. In addition, the fluidity of PT700 slurry is still high after hydration for 72 hours, while PT1000 is coagulated and hardened, which shows that when magnesium sulfate participates in the formation of hydration products (5·1·7 phase) in the solid phase, this results in the combination of water with the hydration products in the form of crystal water or adsorbed water.

4. Conclusions

This study describes the effect of magnesia reactivity on the setting and hardening of BMS cement. Based on the experimental results, the following general conclusions are obtained.

(1) With an increase in the calcination temperature, the BET surface area of MgO decreases and grain size increases gradually, resulting in a gradual decrease in activity.

(2) MgO activity has a noticeable effect on the setting and hardening of BMS cement. Although the hydration rate of high-activity MgO is high, its early and late strengths are low and the volume is unstable, which can easily cause cracking. When the MgO activity is low, the hydration rate is low, but the late strength is high.

(3) The hydration products of BMS cement prepared using MgO with different reactivity are different. The main hydration product of high-activity MgO is Mg(OH)\(_2\), and that of MgO with low activity is 5·1·7 phase. Therefore, high-activity MgO should not be used in the preparation of high-performance BMS cement.

(4) The concentration of the admixture (citrate ion) in the liquid phase of BMS cement prepared using high-activity MgO decreases rapidly, with a loss of its soft template function, resulting in a failure to form the 5·1·7 phase.

Considering that the hydration rate of BMS cement prepared with high-activity MgO obtained by low calcination temperature is fast, but that the main hydration phase is Mg (OH)\(_2\) instead of 5·1·7 phase, which results in low strength of BMS cement, the addition of 5·1·7 phase crystal seeds may induce the preferred formation of 5·1·7 phase to improve the strength. Thus, the low energy consumption BMS cement prepared with high-activity MgO possessing performances of rapid hardening, early and high strength may be obtained by adding 5·1·7 phase. In addition, considering the pillaring effect of citrate in 5·1·7 phase formation and specific structure of the intermediate, advanced methods and technologies such as ion exchange of 5·1·7 phase with citrate to obtain pure intermediate and nuclear magnetic resonance spectroscopy can be employed to determine the molecule structure of precursor of 5·1·7 phase to reveal hydration mechanism of BMS cement further.

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