Basic magnesium sulfate cement (BMSC) is a new type of gas-hardening magnesium cementitious material. In this study, basic magnesium carbonate was used as the raw material to obtain different active magnesium oxides by calcination at different temperatures to prepare BMSC with MgO:MgSO_4:2H_2O = 5:1:20. The effect of different active magnesium oxides and different mineral admixtures and their content on the compressive strength of BMSC before and after soaking was analyzed, and the influence of MgO activity on the water resistance of BMSC was explored. The experimental results show that the activity of MgO has a significant impact on the water resistance of BMSC, and the water soaking was analyzed, and the influence of MgO activity on the water resistance of BMSC was explored. The experimental results show that the activity of MgO has a significant impact on the water resistance of BMSC, and the water resistance of BMSC prepared from low-activity MgO is better, mainly because the hydration products of BMSC prepared by low-activity MgO are 5·1·7 phases. The MgSO_4 in the 5·1·7 phase is insoluble in water; consequently, the free MgSO_4 in BMSC is scarce; thus, the phase remains unchanged. After selecting low-activity MgO (T1000) and adding mineral admixtures to study its water resistance, it was found that the BMSC softening coefficient increases with an increase in the mineral admixture content. Both fly ash and silica fume were found to improve the water resistance of BMSC and increase its water resistance.

**1. Introduction**

Basic magnesium sulfate cement (BMSC) is a new type of gas-hardening magnesium cementitious material developed similarly to the earlier developed magnesium oxychloride and magnesium oxysulfide cement (Wu 2014). Compared with magnesium oxychloride cement, BMSC shows a series of advantages such as lightweight, high strength, resistance to carbonization, excellent reinforcement performance, and good water resistance. Wu et al. (2016) pointed out that 5Mg(OH)_2·MgSO_4·7H_2O (5·1·7 phase) was formed by adding other substances such as phosphoric acid and citric acid as additives to magnesium oxysulfide cement and then undergoing various complex reactions. The 5·1·7 phase is the main strength phase of BMSC (Guo et al. 2017). This type of cement has a wide range of uses in the field of civil engineering, mainly for the production of various composite panels and lightweight insulation products (Wu et al. 2016; Zeng et al. 2020). In addition, it can also be used for the production of reinforced concrete components (Zhou et al. 2012). At present, the active magnesium oxide used in the production of BMSC is mainly light burned magnesite, and 90% of magnesite production is concentrated in Liaoning, Shan-dong, and other regions (Wu et al. 2001). However, due to its high transportation costs, it has restricted the use of magnesite to produce BMSC-based products on a large scale in western regions of China.

In the salt lake area of western China, a large number of magnesium by-products can be produced. For example, if 1 ton of potash fertilizer is produced, 8 to 10 tons of magnesium chloride are produced as a by-product (Wu et al. 2001). When the magnesium-lithium in the salt lake brine is relatively high, a large amount of magnesium slag can be obtained by calcining lithium carbonate (Zhu et al. 2008). In addition, high-quality activated magnesium oxide can be obtained using the dolomite-brine method (Zhang et al. 2011), the limestone-brine method (Xu et al. 2007), the magnesium chloride-ammonium bicarbonate method (Zhang et al. 2011), and the pyrolysis method (Wu et al. 2001). No matter which method is used, the magnesium oxide must undergo a calcination process. The specific surface area and degree of crystallization of magnesia produced by different calcination processes are different, which leads to different activities. Birchal et al. (2000) studied the influence of the magnesite calcination process on the activity of magnesium oxide and the rate of hydration reaction. They found that the temperature is the main factor affecting the specific surface area and activity of magnesium oxide. Wu (2014) used high-activity analytically pure MgO, light burned MgO powder, and light burned dolomite powder as raw materials to prepare magnesium oxysulfide cement and studied the influence of magnesia raw materials on the performance of magnesium oxysulfide cement. The results showed that the source of the raw material magnesium oxide significantly affected the setting and hardening time as well as...
the mechanical properties of magnesium oxysulfide cement. However, other studies have shown that the water stability of basic magnesium sulfate cement-based materials is weak. When BMSC encounters water, its hardened body strength loss is significant and its water resistance is poor; thus, it loses its use value (Wang et al. 2018). Li et al. (2016) have shown that adding water glass to BMSC can improve its water resistance. An et al. (2017a, 2017b) found that adding potassium chloride to BMSC reduces its pressure resistance and affects its water resistance. Xu et al. (2018) found that adding potassium chloride to BMSC reduces its pressure resistance and affects its water resistance. Xu et al. (2020) found that adding 40% fly ash to BMSC significantly reduces the strength of BMSC, and BMSC containing 20% fly ash has the highest strength. However, there is a lack of systematic research on the mechanisms whereby different active magnesium obtained at different calcination temperatures influence the water resistance of BMSC and the measures necessary to improve the water resistance of BMSC.

At present, domestic research on BMSC mainly focuses on cement hydration mechanisms and macro-mechanical properties. There are few studies on BMSC water resistance, and there is a lack of relevant literature. The MgO activity used in the preparation of BMSC cement greatly impacts the type and quantity of BMSC hydration products. Therefore, it is necessary to study the water resistance of BMSC prepared with different active magnesium oxides and propose specific improvement measures for its water resistance. In this study, BMSC was prepared by calcining basic magnesium carbonate at different temperatures to obtain magnesia with different activities. BMSC was soaked in water for 30 days and 120 days to test its macroscopic and microscopic properties, and minerals were added to the magnesia calcined at 1000°C. To prepare BMSC from the mixture, we explored whether the addition of a mineral admixture could effectively improve the water resistance of BMSC.

### 2. Experimental

#### 2.1 Raw materials

The raw materials used for specimen preparations were,

1. **Basic magnesium carbonate**:
   
   
   \[ 4 \text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot \text{H}_2\text{O} \] (analytical reagent; Tianjin Damao Chemical Reagent Co., Ltd.)

2. **Magnesium sulfate**: magnesium sulfate heptahydrate
   
   \[ \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \] (Aladdin Chemical Reagent Co., Ltd.)

3. **Additives**: analytical pure sodium citrate
   
   \[ \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O} \] (Macleans Chemical Reagent Co., Ltd.)

4. **Mineral admixtures**: The mineral admixtures used in this study were fly ash and silica fume. Fly ash was obtained from a large power plant in Liaoning Province, China. The silica fume was obtained from the dense silica fume produced in Qinghai Province. The chemical composition is shown in **Table 1**.

#### 2.2 Specimen preparation

To prepare control in the ratio of \( \text{MgO} : \text{MgSO}_4 \cdot \text{H}_2\text{O} = 5:1:20, \), add 0.5% citric acid, mix different active MgO raw materials with 25.0% MgSO4 solution, stir evenly to obtain BMSC pure slurry; pour it into a stainless steel mold measuring 20 mm × 20 mm; cure for 1 day at a temperature of 20 ± 3°C and relative humidity of 50 ± 5%; then disassemble the mold and cure it at a certain temperature room temperature for 28 days before soaking the BMSC test block in ionized water in the mold. The raw material ratio content of the BMSC sample is shown in **Table 2**. The samples are denoted as T\( \text{m} \)\( \text{P} \)\( \text{n} \), T\( \text{m} \)\( \text{F} \)\( \text{A} \)\( \text{P} \)\( \text{n} \), T\( \text{m} \)\( \text{F} \)\( \text{A} \)\( \text{P} \)\( \text{n} \), T\( \text{m} \)\( \text{S} \)\( \text{F} \)\( \text{P} \)\( \text{n} \), and T\( \text{m} \)\( \text{S} \)\( \text{F} \)\( \text{P} \)\( \text{A} \)\( \text{P} \)\( \text{n} \), where \( \text{T} \) is the calcination temperature, \( \text{d} \) is the BMSC curing time, \( \text{P} \) is the BMSC soaking time, FA is fly ash, and SF is silica fume. For example, T600d28 represents BMSC prepared from MgO calcined at 600°C and cured at room temperature for 28 days. Similarly, T600P120 represents MgO calcined at 600°C and soaked in water for 120 days, and T1000-10%FAP30 refers to the

### Table 1 Chemical composition of fly ash and silica fume.

| Chemical composition/ % | SiO2 | SO3  | CaO | Na2O | Fe2O3 | H2O | C   | K2O | MgO | Al2O3 | LL | Total |
|-------------------------|------|------|-----|------|-------|-----|-----|-----|-----|-------|----|-------|
| Fly ash                 | 36.15| 2.18 | 12.80| 0.46 | 3.79  | /   | /   | 0.74| 2.75| 32.46  | 4.52| 95.85 |
| Silica Fume             | 88.70| /    | 0.80 | 0.30 | 0.55  | 0.75| 4.70| /   | 0.90| 0.30   | /  | 97.0  |

### Table 2 The raw material ratio content of BMSC samples.

| Sample          | Molar ratio | MgO/g | 25 wt% MgSO4/g | SC/g | FA/g | SF/g |
|-----------------|-------------|-------|----------------|------|------|------|
| T600            | 5           | 1000  | 1946.1         | 5    | /    | /    |
| T700            | 5           | 1000  | 2249.8         | 5    | /    | /    |
| T800            | 5           | 1000  | 2368.1         | 5    | /    | /    |
| T900            | 5           | 1000  | 2388.1         | 5    | /    | /    |
| T1000           | 5           | 1000  | 2399.9         | 5    | /    | /    |
| T1000-10%FA     | 5           | 1000  | 2399.9         | 5    | 100  | /    |
| T1000-20%FA     | 5           | 1000  | 2399.9         | 5    | 200  | /    |
| T1000-10%SF     | 5           | 1000  | 2399.9         | 5    | /    | 100  |
| T1000-20%SF     | 5           | 1000  | 2399.9         | 5    | /    | 200  |
BMSC prepared by calcination at 1000°C with 10% fly ash and soaking in water for 30 days.

### 2.3 Specimen analysis and characterization

The specific surface areas of the different active magnesium oxides were measured via the isothermal N\textsubscript{2} adsorption method. The instrument used was Gemini VII 2390 surface area meter; the compressive strength was measured according to GB175-2007 standard using a testing machine with a maximum force of 300 KN, and the loading rate was 0.3 KN/s. An X-ray diffractometer (D/max-2500PC) was used to analyze the samples under CuK\textalpha\textsubscript{α} radiation (\(\lambda = 0.15419\) nm) at 30 kV accelerating voltage (2\(\theta\) = 5 to 70 degrees) to obtain XRD patterns using scanning electron microscopy (SEM, JSM-6610LV). Microstructure characterization of gold-plated alkaline magnesium sulfate cement samples was also performed; the instrument required to determine the pore distribution of BMSC was an automatic mercury porosimeter (Auto Pore IV 9500). The water resistance test is performed by curing the test block in the air for 28 days and then soaking it in water. After soaking the sample for the requisite time, the cement test block is taken out and dried in a natural indoor environment. The compressive strength is tested after 24 hours. \(R_f\) is calculated by Eq. (1).

\[
R_f = \frac{R(x,n)}{R(A,28)} \quad (1)
\]

\(R(x,n)\) represents the compressive strength (MPa) of the specimen immersed in water for \(n\) days, and \(R(A,28)\) represents the compressive strength (MPa) of the sample cured in air for 28 days.

### 2.4 Preparation and characterization of activated magnesium oxide

In this experiment, MgO with different activities was obtained by calcining basic magnesium carbonate at different temperatures. Figure 1 shows the X-ray diffraction (XRD) patterns of the different active magnesium oxides. It can be seen that the main product of basic magnesium carbonate calcined at different temperatures is MgO, and as the calcination temperature increases, the intensity of the MgO diffraction peak increases. Figure 2 shows the BET-specific surface area of different active magnesium oxides. Table 3 shows the properties of activated magnesia obtained at different calcination temperatures. It can be seen from the table that with the increase in calcination temperature, the specific surface area of magnesium oxide gradually decreases, the crystal grain size increases, and the discoloration time of citric acid is prolonged. For example, when the calcination temperature increases from 700°C to 1000°C, the specific surface area decreases from 99.6 m\textsuperscript{2} to 32.7 m\textsuperscript{2}, the grain size increases from 12.8 nm to 29.5 nm, and the citric acid discoloration time extends from 23.5 s to 121.2 s. The main reason is that with the increase of the calcination temperature, the magnesium oxide continues to sinter, increasing the degree of crystallinity, and decreasing the internal defects of the magnesium oxide, making the interior of the magnesium oxide more compact and reducing the occurrence of OH\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} in the magnesium sulfate solution. The number of active sites for reaction, and thus the activity of magnesium oxide, decrease.

### Table 3 Properties of MgO obtained at different calcination temperatures.

| Calcining temperature/°C | Specific surface area/m\textsuperscript{2}/g | Grain size/nm | Citric acid discoloration time/s |
|--------------------------|---------------------------------------------|---------------|---------------------------------|
| 600                      | 143.5                                       | 11.2          | 21.1                            |
| 700                      | 96.8                                        | 12.3          | 23.5                            |
| 800                      | 78.4                                        | 18.9          | 38.6                            |
| 900                      | 53.1                                        | 21.6          | 75.3                            |
| 1000                     | 33.9                                        | 28.6          | 121.2                           |
3. Effect of different active magnesium oxides on BMSC after soaking in water

3.1 Compressive strength
BMSC samples prepared with different active magnesium oxides in the ratio MgO:MgSO₄·H₂O = 5:1:20 were cured in air for 28 days and then soaked in water. As T600 and T700 were cured in air for 3 days and 7 days, respectively, they shrank and cracked, and then became slag-like after being soaked in water; hence, their strength was not tested.

Figure 2 shows a comparison of the compressive strength of BMSC after curing in air for 28 days and soaking in water for 30 days and 120 days. The figure also shows that the compressive strength values of T800, T900, and T1000 after 28 days of curing in air are 86.7 MPa, 101.4 MPa, and 103 MPa, respectively. After 30 days of soaking in water, the compressive strength values are 53.1 MPa, 66.9 MPa, and 82.3 MPa, which decreased by 38.4%, 34.02%, and 20.1%, respectively. After 120 days of soaking in water, the compressive strength values decreased by 48.1%, 46.8%, and 36.9%, respectively. It can be observed that the compressive strength of BMSC decreases faster after soaking in water, and the longer the soaking time, the lower is the strength. After 30 days of soaking in water, the softening coefficients are 0.61, 0.66, and 0.80, whereas after 120 days of soaking, the softening coefficients are 0.52, 0.53, and 0.63, respectively.

The test results show that the higher the calcination temperature of the magnesia precursor, the lower is the activity of magnesia. The softening coefficient of the prepared BMSC after soaking in water increases with a decrease in the activity of magnesia. Because MgO dissolves in water, the structure of BMSC becomes loose; thus, the compressive strength of BMSC decreases after soaking in water. Figure 3 shows the change in conductivity of the BMSC solution after soaking in water for 120 days. It can be seen from the figure that the conductivity of T600 is the largest, reaching 10.03 ms/cm at the beginning of soaking, followed by 9.04 ms/cm for T700, which indicates that a large amount of MgSO₄ did not participate in the reaction during the hydration reaction of T600 and T700. Therefore, it continuously dissolves immediately after soaking in water, causing the BMSC test block to become slag-like. The conductivity values of T800, T900, and T1000 in the initial stage of soaking in water are 1.59 ms/cm, 1.21 ms/cm, and 0.93 ms/cm, respectively. It can be seen that as the activity of MgO decreases, the conductivity of the solution decreases. After being soaked in water for 120 days, the conductivity values of T800, T900, and T1000 increase to 3.01 ms/cm, 2.58 ms/cm, and 2.27 ms/cm, respectively, mainly due to increasing MgSO₄ in the solution. MgSO₄ mainly comes from two sources: it is continuously dissolved out of free magnesium sulfate and magnesium sulfate in the 5·1·7 phase. It was found that the conductivity of low-activity magnesia is lower, and the conductivity of high-activity magnesia is higher, indicating that the BMSC prepared by low-activity magnesia contains less free MgSO₄ and MgSO₄ eluted in the 5·1·7 phase. Therefore, when the calcination temperature of the MgO precursor is 1000°C, the water resistance of the BMSC is the highest.

3.2 Hydration phase composition and microstructure
Figure 4 shows the XRD patterns of the BMSC prepared with different active magnesium oxides before and after soaking in water. As shown in the figure, when the BMSC prepared with different active magnesium oxides is cured for 28 days, the main hydration product of T600 is magnesium hydroxide, and the characteristic diffraction peak of the 5·1·7 phase is not observed. The hydration products of T800, T900, and T1000 are all 5·1·7 phases after curing for 28 days, and the characteristic diffraction peak of the 5·1·7 phase is relatively strong. It can be seen that when the activity of MgO is high, the degree of crystallinity decreases and the internal defects of MgO increase, which leads to cracking in the specimen curing process; when the activity of MgO is low, the degree of crystallinity gradually increases, making BMSC stronger. The intensity phase of the BMSC is mainly 5·1·7; thus, the 5·1·7 phase diffraction peak is stronger. As shown in Fig. 4(a), the main hydration products of BMSC after being soaked in water for 30 days are almost the same as those after 28 days of curing, and the main hydration products are 5·1·7 phases.

As shown in Fig. 4(b), the main phase of the BMSC after soaking in water for 120 days is 5·1·7. However, compared with 30 days of soaking in water, the diffraction peak of the 5·1·7 phase is relatively weak. After 120 days of soaking in water, the intensity of the 5·1·7 phase decreased. Therefore, the compressive strength of BMSC soaked in water for 120 days is significantly
lower than that of BMSC soaked in water for 30 days, which is in line with the aforementioned development trend of the strength of BMSC. The phase of the hydration product of BMSC after soaking in water hardly changed compared with that of curing for 28 days, and they were all 5:1:7 phases, primarily because the BMSC hydration product prepared by low-activity MgO was 5:1:7. However, MgSO₄ in the 5:1:7 phase is almost insoluble in water, and the free MgSO₄ in the BMSC is scarce; thus, the phase does not change. It was found that the water resistance of T1000 is the highest, mainly because when the calcination temperature of the magnesium oxide precursor is higher, the activity of MgO is lower, and the degree of crystallinity is higher. The dissolution rate of MgSO₄ in 5:1:7 phase is inversely proportional to the degree of crystallization. The higher the degree of crystallization, the slower the dissolution rate of MgSO₄ and the better the water resistance.

Figure 5 shows SEM images of BMSC samples before and after being soaked in water for 120 days. From Figs. 5(a), 5(b) and 5(c), it can be seen that needle-like 5:1:7 phase staggered growth can be observed in T800, T900, and T1000 after 28 days of BMSC curing, and the aspect ratio of T1000 is higher than T800 and T900,
which indicates that as the calcination temperature increases, the degree of magnesia crystallinity is higher, which is more conducive to the formation of a 5·1·7 phase with a large aspect ratio. From Figs. 5(d), 5(e) and 5(f), it can be seen that when BMSC is soaked in water 120, needle-like 5·1·7 phases can be observed to grow alternately, indicating that the main phase of BMSC after soaking in water is 5·1·7. However, compared to the SEM image before immersion in water, the 5·1·7 phase whiskers are clearly not dense and slender, mainly because the 5·1·7 phase is gradually dissolved, which degrades the mechanical properties. The 5·1·7 phase whiskers of BMSC are in a tightly connected state before being soaked in water, and their microstructure is relatively loose after being soaked in water for 120 days. This indicates that one of the reasons for the decrease in strength of BMSC after soaking in water may be the change in phase crystalline state.

3.3 Pore structure

Figures 6(a) and 6(b) compare the cumulative porosities and differential pore size distributions of BMSC cured for 28 days and 30 days in water. From the figure, we can see that low-activity MgO has a higher porosity after 28 days of curing. For example, the porosity of T900 is 39.44%. This is because the hydration products of low-activity MgO are mainly 5·1·7 phases, indicating that the magnesium sulfate reaction is relatively sufficient, and the density of the 5·1·7 phase crystals (theoretical density is 1.91 g/cm³ (Wu 2014)) is greater than that of magnesium sulfate, thereby resulting in low-activity MgO with higher porosity. When BMSC is soaked in water for 30 days, it was found that the porosity of BMSC increased. The porosity values of T800, T900, and T1000 increased from 38.9%, 39.44%, and 38.88% before soaking to 39.13%, 39.94%, and 40.02%, respectively. Figures 7(a) and 7(b) show the cumulative porosities and differential pore size distributions of BMSC cured for 28 days and 120 days in water. It can be seen from the figure that the porosity of BMSC increases with the number of days of soaking in water: the values of T800, T900, and T1000 increase to 39.46%, 40.33%, and 41.72%, respectively. When compared with the porosity after 28 days of curing, the values increased by 1.42%, 2.21%, 6.82%, respectively.

Table 4 shows the pore structure characteristics of BMSC cured for 28 days and soaked in water for 30 and 120 days.

| Samples   | Porosity/% | Average pore Diameter/nm | ≤ 20 nm%/ | 20 to 100 nm% | > 100 nm% |
|-----------|------------|--------------------------|-----------|--------------|----------|
| T800d28   | 38.9       | 40.37                    | 5.55      | 87.18        | 7.27     |
| T900d28   | 39.44      | 55.40                    | 5.11      | 81.05        | 13.84    |
| T1000d28  | 38.88      | 65.73                    | 3.77      | 81.82        | 14.41    |
| T800P30   | 39.13      | 35.13                    | 10.18     | 76.29        | 13.53    |
| T900P30   | 39.94      | 50.2                     | 5.79      | 77.48        | 16.73    |
| T1000P30  | 40.02      | 69.3                     | 3.65      | 61.46        | 34.89    |
| T800P120  | 39.46      | 45.58                    | 7.75      | 86.62        | 5.63     |
| T900P120  | 40.33      | 54.01                    | 6.69      | 77.51        | 15.80    |
| T1000P120 | 41.72      | 66.19                    | 5.12      | 62.66        | 32.22    |

Fig. 6 Comparison between BMSC curing for 28 days and 30 days in water: (a) Cumulative porosity, (b) Differential pore size distribution.
intercrystalline pores (> 100 nm). When BMSC is cured for 28 days, the gel pores account for 5.55%, 5.11%, and 3.77%, respectively, and the intercrystalline pores are relatively larger. As the number of days of soaking in water increases, the proportion of gel pores of BMSC increases, and the proportion of intercrystalline pores decreases. For example, when T1000 is soaked in water for 30 days, the proportion of gel pores is 3.65%, and after 120 days of soaking in water, the proportion of gel pores increases to 5.12%. In the hydration reaction of BMSC, the more the number of high-crystallinity intensity phases generated, the more intercrystalline pores and fewer gel pores are generated. Therefore, after BMSC is soaked in water, its gel structure is no longer as dense as before, and the loose structure characteristics cause the strength of BMSC to decrease after soaking in water. By comparing the porosity and pore distribution data of T800, T900, and T1000 after soaking in water, it was found that the gel pores of T1000 after soaking in water were relatively small, and their strength was higher than that of T800 and T900. It further shows that when the MgO precursor is calcined at 1000°C, BMSC exhibits the best water resistance.

4. Influence of mineral admixtures on BMSC after soaking in water

4.1 Compressive strength

By studying the effect of different active magnesium oxides on the performance of BMSC after soaking in water, it was found that T1000 has the best water resistance. Therefore, MgO obtained by calcination at 1000°C was selected as the raw material, and a ratio of MgO:MgSO₄:H₂O = 5:1:20 was used. BMSC was prepared by adding 10% fly ash and 20% silica fume. It was soaked in water for 30 days to test its compressive strength and pore distribution. Table 5 shows the compressive strength and softening coefficient of BMSC soaked in water for 30 days when the calcination temperature is 1000°C mixed with fly ash and silica fume. It can be found that the compressive strength of BMSC mixed with mineral admixtures decreased after being soaked in water for 30 days. The compressive strength of T1000 after curing in air for 28 days is 103 MPa. After the addition of 10% fly ash and 20% silica fume, the strength drops to 99.78 MPa, 83.8 MPa, 82 MPa, and 75.5 MPa, respectively. This is mainly due to the crystal expansion stress and deformation volume caused by the secondary hydration of excessive MgO. T1000 achieved a compressive strength of 72.23 MPa and a softening coefficient of 0.7 when soaked in water for 30 days. When mineral admixtures are added, the softening coefficient values of T1000-10%FA-P30, T1000-20%FA-P30, T1000-10%SF-P30, and T1000-20%SF-P30 are 0.79, 0.88, 0.75, and 0.81, respectively, compared with when no mineral admixture is added. Adding fly ash and silica fume can increase the softening coefficient.

|                  | T1000-10%FA | T1000-20%FA | T1000-10%SF | T1000-20%SF |
|------------------|-------------|-------------|-------------|-------------|
| Curing for 28 days/MPa | 99.78       | 83.8        | 82          | 75.5        |
| Soak in water for 30 days/MPa | 78.82       | 73.74       | 61.5        | 61.12       |
| Softening factor  | 0.79        | 0.88        | 0.75        | 0.81        |

Fig. 7 Comparison of of BMSC after 28 days of curing and 120 days of soaking in water: (a) Cumulative porosity, (b) Differential pore size distribution.
The compressive strength of BMSC after soaking in water is higher than that without fly ash, which shows that adding fly ash and silica fume can improve the water resistance of BMSC, mainly because the addition of mineral admixtures helps in the formation of the MSH gel phase and reduces the crystal expansion stress. On comparing the water resistance of the same mineral admixture with different contents, it was found that the softening coefficient increased with an increase in the mineral admixture content. For example, the softening coefficient of T1000-10%FA-P30 and T1000-20%FA-P30 was 0.79 and 0.88, respectively, and it was found that adding fly ash improved the water resistance of BMSC better than silica fume. When the fly ash content was 10%, the improvement performance of BMSC was better than that of other contents. This is because the fly ash acts as a micro-aggregate, filling the internal pores of the BMSC, making the internal structure more compact, and therefore having better water resistance.

4.2 Hydration phase composition and micro-structure

Figure 8 shows the XRD pattern of T1000 with different mineral admixtures after soaking in water for 30 days. It can be seen that the hydration products of T1000 after 30 days of soaking in water are mainly 5·1·7 phases. On adding mineral admixtures, fly ash, and silica fume, the hydration products of BMSC after soaking in water for 30 days are still 5·1·7 phase, and no diffraction peaks of other new hydration products are seen. However, the peak value of the hydration product of BMSC with mineral admixtures after being soaked in water for 30 days is significantly higher than that of BMSC without mineral admixtures. This further shows that the addition of mineral admixtures can promote the formation of 5·1·7 phases in BMSC hydration products, which highlights the importance of the role of mineral admixtures in the microaggregates of BMSC and in improving its water resistance.

Figure 9 shows the SEM image of T1000 with different mineral admixtures after 30 days of soaking in water. From Fig. 9(a), it can be observed that after 30 days of soaking without adding mineral admixture, the main phase is the needle-like 5·1·7 phase. From Figs. 9(b) and 9(c), it can be observed that a large number of needle-like 5·1·7 phase whiskers are bonded with fly ash and silica fume particles after being soaked in water for 30 days with mineral admixtures, and the overall appearance is tight. The connected state and aspect ratio of the 5·1·7 phase whiskers are greater than that of T1000P30. Therefore, the addition of mineral admixture, fly ash, and silica fume can improve the water resistance of BMSC.

Fig. 8 30-day XRD pattern of T1000 with different mineral admixtures soaked in water.

Fig. 9 SEM image of T1000 added with different mineral admixtures soaked in water for 30 days: (a) T1000P30, (b) T1000-20%FA-P30, (c) T1000-20%SF-P30.
4.3 Pore structure

Figure 10 shows the porosity and pore distribution of T1000 with different mineral admixtures for 30 days. Table 6 shows the pore structure characteristics of the T1000 mineral admixtures soaked in water for 30 days. It can be seen that after T1000 series BMSC specimens are soaked in water for 30 days, their porosity with mineral admixtures gradually decreases. For example, the porosity of the control group T1000-P30 is 38.01%, while that of T1000-10% FA-P30 and T1000-20% FA-P30 is 33.91% and 33.76%, respectively, which is 10.79% and 11.18% less compared to the control group. The porosity of T1000-10%SF-P30 and T1000-20%SF-P30 is 33.96% and 34.79%, respectively, which is 10.66% and 8.47% less compared to the control group. With an increase in the mineral admixture content, the porosity of the BMSC specimens gradually increased after being soaked in water. The porosity of the BMSC specimen affects its water resistance. The smaller the porosity, the smaller the water absorption inside the BMSC specimen, indicating that the structure is complete and more compact, and the damage is less; therefore, its water resistance is better. In addition, the particle size of fly ash is smaller than that of silica fume and can be evenly distributed to fill the pores inside the specimen. Therefore, the water resistance of BMSC after the addition of fly ash is better than that after adding silica fume. Therefore, it is shown that the addition of mineral admixtures can further optimize the pore structure of BMSC, reduce the volume deformation caused by expansion stress, and improve its water resistance.

Table 6 Pore structure characteristics of T1000 BMSC specimens with different mineral admixtures, soaked in water for 30 days.

| Sample          | Porosity/% | Average pore Diameter/μm | ≤ 20 nm/μm/% | 20 to 100/μm/% | > 100 nm/μm/% |
|-----------------|------------|--------------------------|-------------|---------------|--------------|
| T1000-P30       | 38.01      | 69.20                    | 3.65        | 61.46         | 34.89        |
| T1000-10%FA-P30 | 33.91      | 90.32                    | 3.67        | 50.24         | 46.09        |
| T1000-20%FA-P30 | 33.76      | 116.31                   | 4.12        | 36.53         | 59.35        |
| T1000-10%SF-P30 | 33.96      | 76.07                    | 9.22        | 52.65         | 38.16        |
| T1000-20%SF-P30 | 34.79      | 78.14                    | 8.42        | 53.18         | 38.40        |

5. Conclusions

This study describes the influence and improvement of different active magnesium oxide on the water resistance of BMSC cement. Based on the experimental results, the following conclusions are drawn.

1. MgO activity has an important influence on the water resistance of BMSC. After soaking in water, the compressive strength of BMSC showed a decreasing trend with an increase in MgO activity. The BMSC prepared from low-activity (T1000) MgO exhibited the best water resistance. This is because the BMSC hydration product prepared by low-activity MgO is mainly a 5-1-7 phase, while the MgSO₄ in the 5-1-7 phase is mostly insoluble in water, and there is less free MgSO₄ in BMSC; thus, the phase does not change.

2. The BMSC specimens were soaked in water over time. After 120 days, the low-activity MgO gel pores accounted for the smallest proportion, and the intercrystalline pores accounted for a larger proportion. In the hydration reaction of BMSC, the more the number of high-crystallinity intensity phases generated, the more intercrystalline pores and fewer gel pores are generated. Therefore, T1000 showed better water resistance.

3. The softening coefficient behavior of BMSC prepared by adding mineral admixtures to low-activity (T1000) MgO after being soaked in water for 30 days was as follows: the softening coefficient increased with an increase in the mineral admixture.

Fig. 10 T1000 added with different mineral admixtures for 30 days: (a) Porosity, (b) Differential pore size distribution.
content. Both fly ash and silica fume can improve the water resistance of BMSC and increase its water resistance.

Acknowledgments
This study was supported by the National Natural Science Foundations of China (Grant no. 52002202 and 51662035), the Applied Fundamental Research Project of Qinghai Province (Grant no. 2019-ZJ-7005) and the West Light Project of Chinese Academy of Sciences.

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