1. Introduction

Magnesium oxysulfate (MOS) cement is a type of magnesia-based air-hardened binding material formulated by the reaction of active magnesia and magnesium sulfate solution (Walling et al. 2016; Demediuk et al. 1957; Wu et al. 2014). Due to its low apparent density, good fire resistance, and good aesthetics, MOS can be used to produce interior and exterior decorative panels, crafts, vegetable shed skeletons, prefabricated houses, and so on (Gomes et al. 2014; Zhou et al. 2015; Lin et al. 2018). Compared with magnesium oxychloride cement, MOS cement is more suitable for the preparation of reinforced concrete as it offers excellent corrosion resistance to the steel owing to its lower Cl⁻ content (Zeng et al. 2018; Xing et al. 2017). However, this cement hardly has significant large-scale applications in civil engineering due to its long setting time and low strength, especially low early strength.

It is common knowledge that the setting speed and strength progression of cementitious material mainly depend on the speeds at which its hydration products form and its porosity decreases. Demediuk et al. (1955) reported the formation of four primary phases, i.e., 3Mg(OH)₂·MgSO₄·8H₂O (3·1·8 phase), 5Mg(OH)₂·MgSO₄·3H₂O (5·1·3 phase), Mg(OH)₂·MgSO₄·5H₂O (1·1·5 phase), and Mg(OH)₂·2MgSO₄·3H₂O (1·2·3 phase), in the MOS cement without additives within the temperature range of 30 to 120°C. Urwong and Sorrel (1980) reported the 3·1·8 phase as being the only main strength phase at room temperature, and that it is difficult to produce MOS cement with more than 50% of 3·1·8 phase content because of the mass of Mg(OH)₂ formation. According to their reports, this difficulty causes the low strength of MOS cement. Moreover, Dinnrbier et al. (2013) reported that the 3·1·8 phase is not a stable phase for the Mg(OH)₂·MgSO₄·H₂O ternary system, which can decrease the long-term strength of the concrete and even lead to cracking of the MOS cement. In our previous study, not the 3·1·8 phase, but Mg(OH)₂ was found in the hydrated MOS cement with the mole ratio of active MgO to MgSO₄ being more than 3. In recent years, many researchers have shown that the use of additives such as citric acid (CA) (Wu et al. 2014; Wang et al. 2018), tartaric acid (Wu et al. 2017), phosphoric acid (Wu et al. 2015, 2016), and their acid salts can improve the strength of MOS cement. By controlling the process of hydration of active MgO in magnesium sulfate solution, the addition of additives, such as CA, favored the formation of large amounts of the 5Mg(OH)₂·MgSO₄·7H₂O (5·1·7 phase), which resulted in MOS cements with high strength and high volume stability. However, all the reported additives that can obviously improve the compression strength of the MOS cement have strong retardation effects, and the higher the additive content, the...
longer the final setting time. For example (Wu et al., 2017), the final setting time of MOS cement with 0%, 0.13%, and 1% of tartaric acid are 2 hours, 6 hours, and 14 hours, respectively. This retardation could result in a lower strength development curve at the early stages such as 12 hours and 1 day, which will seriously reduce the production efficiency of MOS cement products.

It is widely accepted that the setting and hardening rates of magnesia-based cement can be accelerated by increasing the curing temperature, adding the appropriate early strength agent, or increasing the reaction activity of magnesia. Liu et al. (2019) reported that the early strength (at 1 day) of MOS cement at 80°C could be improved by increasing the hydration speed of active MgO. However, it also reported a drastic decrease in the water resistance and long-term strength of MOS cement because the mass of Mg(OH)₂ formed and large amounts of magnesium sulfate were not involved in the hydration process. Considering the high energy consumption and requirement for equipment, high temperature curing is not an ideal method to improve the early strength of MOS. Some inorganic salt-based early strength agents that can improve Portland cement cannot improve the early strength of MOS cement, and have a certain retardation effect. For example, An et al. (2017a, 2017b) have studied the effects of KCl and MgCl₂ on the properties of MOS cement, which shows that these inorganic salts delay the setting and decrease the strength MOS cement on the third day. Although increasing the activity of MgO, which is usually obtained by calcinating magnesite ore at a lower temperature (Chau et al., 2019), can shorten the setting time of MOS cement, the shrinkage of cement is serious and can cause cracking, and the later strength of the cement decreases (Wu et al., 2018).

Based on the above analysis, it is necessary to find a method that can improve the early strength of the cement, shorten the setting time, and does not affect its later strength, so as to increase the popularity and application of cement and improve the production efficiency of cement products. A large number of studies have shown that the addition of crystal seeds of hydration products to cement-based materials is an effective way to improve the early strength of cement. For example, C-S-H seeds are added to Portland cement (Qin et al., 2018; Wakeel et al., 1999; John et al., 2018), hydroxyapatite to calcium sulphoaluminate cement (Yu et al., 2019), and 5-phase (Mg(OH)_2·MgCl₂·8H₂O) to magnesium oxychloride cement (Zhang et al., 2017). In recent years, almost all reports on MOS cement show that the formation and interlocking of the 5·1·7 phase in the presence of additives which have obviously retardation effects, contributes the high strength of MOS cement. This seed crystal (SC) may have the potential to promote the hydration of the MOS cement paste, resulting in quick setting and high early strength development in the absence or presence of slight amounts of additives such as CA.

In this paper, the SC is used as a modifier to accelerate the setting of MOS and improve its early strength, based on the fact that it can lead to the rapid nucleation and growth of the 5·1·7 phase crystal with or without retarders (e.g., CA). Therefore, the influence of SC on the setting time, compressive strength, volume changes of the cement with or without CA is investigated in detail. Additionally, X-ray diffraction (XRD), scanning electronic microscopy (SEM), hydration-heat release rate, and mercury intrusion porosimeter (MIP) were carried out to explain the influence mechanism of SC on the performance of MOS cement.

2. Materials and methods

2.1 Materials

The magnesia used for preparing MOS cement in this study is light-burnt magnesite (LBM), which was produced by calcination of magnesite of the Liaoning province of China at 750 to 900°C. The BET specific surface area of the LBM is approximately 14.35 m²/g. The particle size distribution (PSD) of the LBM powder was analyzed using the Malvern laser method with ethanol as the dispersant, and the analysis results (Fig. 1a) show a particle size of D₉₀ = 12 μm. According to the standard hydration method (Dong et al., 2010), the active magnesia (a-MgO) content is 55.15%. Furthermore, the chemical composition analyzed by X-ray fluorescence (XRF) is shown in Table 1. The mineralogical composi-

![Fig. 1 Particle size distribution. (a): LBM and (b): SC.](image-url)
tion of LBM detected by XRD is shown in Fig. 2 which indicates that the main minerals are magnesia (MgO), magnesite (MgCO3), quartz (SiO2) and magnesium silicate hydroxide [Mg3Si4O10(OH)2].

The SC used in this study was prepared at laboratory scale by adding 1 kg of analytical grade light magnesia (the content of active MgO is more than 99%) and 5.0 g of CA to 2.4 kg of 25% (weight %) magnesium sulfate solution. Then, the paste was placed in a sealed bag and cured for 28 days at 20 ± 3°C to promote hardening. Finally, the hardened samples were ground to high purity SC via ball milling, which is shown in the XRD pattern in Fig. 3, with D90 = 59 μm (as is shown in Fig. 1b) and a BET specific surface area of 13.80 m2/g. The SEM of the SC (Fig. 4) no longer shows the presence of needle-like shapes after the ball milling, as is reported in our previous study (Wu et al. 2018).

Analytical grade CA (C6H8O6·H2O) and magnesium sulfate (MgSO4·7H2O) used in the MOS cement were purchased from Tianjin Kemi’O Chemical Industry Technology Ltd.

### 2.2 Specimen preparation

A molar ratio of 7 for the α-MgO/MgSO4 in the MOS cement formulation was selected. The water-to-cement ratio (w/c) of the whole cement paste was kept at 0.57,
according Eq. (1). In this equation, \( m_{LBM}, m_{MS}, m_{sc}, \) and \( m_n \) are the weights of LBM, magnesium sulfate anhydrous in magnesium sulfate solution, SC, and water in magnesium sulfate solution, respectively. The different amounts of CA and SC used in the preparation of MOS cement were 0%, 0.05% and 0.5%, and 1%, 3%, and 5%, respectively, all based on \( m_{LBM} \). Firstly, a certain weight of \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \) was dissolved in a certain weight of water to form a solution. Then, the pre-weight LBM (with or without CA or SC) was mixed with the solution to form a MOS cementitious paste. Finally, this paste was cast into steel molds, and sealed and cured for 8 hours at 20 ± 3°C and a relative humidity of 50 ± 5% before demolding. Specimens with dimensions of 20 mm × 20 mm × 20 mm were prepared for measurements of compressive strength, while specimens with dimensions of 25 mm × 25 mm × 280 mm were prepared for volume change assessments.

For ease of description, the various samples were labeled “AmSn,” where \( m \) and \( n \) represent the percentages of CA and SC, respectively. For example, A005S5 represents the MOS sample with the CA and SC dosages of 0.05% and 5%, respectively.

\[
W = \frac{m_{LBM} + m_{MS} + m_{sc}}{m_n} \tag{1}
\]

2.3 Sample analysis

(1) Compressive strength

The compressive strengths of MOS cement samples after curing for 12 hours and for 1 day, 3 days, 7 days and 28 days were measured on a testing machine with a maximum force of 300 kN at a constant loading rate of 2.4 kN/s.

(2) Setting time

The setting time of the MOS cement paste was tested using a Vicat apparatus at 20 ± 3°C according to the Chinese National Standard (China GB/T 1346-2011). The initial setting time was defined as when an initial needle with a diameter of 1 mm penetrated the sample to a point 3-5 mm from the bottom of the mold. The final setting time was defined as when a 5 mm cap ring left no visible mark after being placed on the surface of the MOS paste samples.

(3) Volume changes

The dimensional changes of the MOS cement at different ages were studied by measuring the edge-length changes of the paste samples (25 mm × 25 mm × 280 mm) cured at 20 ± 3°C and relative humidity of 50 ± 5%. The length change rates (LCR) were calculated according to Eq. (2):

\[
\text{LCR} = \frac{L_n - L_i}{L_i} \times 100\% \tag{2}
\]

where \( L_n \) and \( L_i \) denote the edge lengths of the MOS cement samples cured for \( n \) days and 1 day, respectively.

(4) XRD and SEM analyses

The crystallized phases of hydration products were identified by an X-ray diffractometer (D/max-2500PC) with CuKα radiation (\( \lambda = 0.15419 \text{ nm} \)) and 30 kV acceleration voltage, at a condition of over 20 range of 5 to 70 degrees on paste powder (D90 < 45 μm). The detector adopts a scintillation counter. The sample holder type is non-reflective plexiglass, the current is 200 mA, the slit width is 1 mm, and the 0-20 linkage continuous scanning mode has a scanning speed of 8 degrees/min. Finally, the XRD pattern is imported into the “Highscore” software, and the type of the product is determined by comparison with a standard diffraction peak. The microstructure of the MOS cement samples cured in air was characterized using SEM (JSM-5610LV) on the fractured surfaces after gold coating.

(5) Hydration heat release rate, AC impendence, and MIP test

The hydration heat release rate of the MOS cement paste at different times was tested at a constant temperature of 20°C by a four-channel isothermal calorimeter (Cal-metrix-I-cal 4000HPC). In a typical sample (e.g., A0S0) test, 20 g LBM and 18.9 g magnesium sulfate solution with a mass fraction of 25% were mixed rapidly, and then the uniform paste was placed into a polypropylene sample pool with a volume of 125 ml. Sample pools containing the MOS paste were put into the calorimeter and the heat release rate at each time was recorded. The AC impedance of the MOS mortar having a standard-sand-to-LBM weight ratio of 3 was measured using RST5200 electrochemical workstation with two 40 mm × 40 mm stainless-steel plate electrodes at an of AC frequency greater than 10 KHz. The porosity and pore distribution of MOS cement cured in air for 8 hours and 28 days were measured with the mercury intrusion porosimetry (MIP) method using an automatic mercury porosimeter (Auto Pore IV 9500). The pressure range of the instrument is 1.38 kPa to 228 MPa, wherein the contact angle of mercury with the substance is 135°, and the testable aperture range is 5 nm to 1100 μm; Mercury is non-wetting to most solid materials and requires additional pressure to allow it to enter the solid pores. For the cylindrical hole model, the size and pressure of the holes that mercury can enter are in accordance with the Washburn equation. By controlling the different pressures, the volume of mercury in the press-in holes can be measured, and thus a cumulative distribution curve or a differential curve corresponding to the pore size of the different pressures can be obtained. Crushed samples from hardened pastes at given age (28 days) were ground to powder and covered by KBr to be used in FT-IR measurements. A Fourier Transform IR (FT-IR) was used, within the range from 400 to 4000 cm⁻¹ (Nicolet 6700). The sample was scanned 32 times with a resolution of 4 cm⁻¹ by scanning through the transmission method.
3. Results and discussion

3.1 Effects of SC on compressive strength

The effects of SC on MOS cement with 0%, 0.05%, and 0.5% CA are shown in Figs. 5a, 5b, and 5c. Because the compressive strength of MOS cement with 0.5% CA is lower than 0.5 MPa, which is also lower than the limit of detection of the testing machine, no strength data for 12 hours could be shown in Fig. 5c. Although CA could ensure high late compressive strength, it may cause strong retardation of the hydration process, resulting in low early strength, especially before 1 day.

Reducing the amount of CA will improve the early strength of MOS cement, but its later strength will be significantly reduced. Therefore, reduction of CA content alone is not an effective step to improve the mechanical properties of MOS cement. The 12 h compressive strength of MOS cement increases significantly after the addition of SC, especially when CA is not added or is added in small quantities. For example, when 5% SC was added to the MOS cement without CA, the 12 h compressive strength increased from 3 MPa to 21.5 MPa, and the 28 d strength increased by approximately 1.96 times from 33.8 MPa to 66.5 MPa. When 5% SC was added to the MOS cement with a CA content of 0.05%, the 12 h compressive strength of MOS cement increased by approximately 3.24 times and the 28 d compressive strength increased by 63% to 85.8 MPa, which is higher than the strength of 76.5 MPa of MOS cement with 0.5% CA content and without SC. However, when the CA content was 0.5%, the 12 h compressive strength of MOS cement still did not reach a detectable value, and the 1 d compressive strength decreased with the increase of SC. For example, after the 5% SC was added to the MOS cement with 0.5% CA, the 1 d compressive strength decreased by approximately 33%.

The above results show that the early and late strengths of the MOS cement without CA or with less CA content can be significantly improved by the addition of SC, while the early strength of MOS cement with high content of CA was reduced by the addition of SC. In other words, to improve the early strength of MOS cement without reducing its late strength, SC can be added at a lower CA content (e.g., 0.05% by weight of LBM).

3.2 Effects of SC on setting time

The setting time of cement affects the production efficiency of cement products and reflects the formulation rate of cement hydration products. Figure 6 shows the initial and final setting times of different samples. It can be seen that the initial and final setting times of cement increase with the increase in CA content. For example,
after the addition of 0.5% CA, the initial and final setting times extend to 4.5 hours and 11.5 hours from 1.8 hours and 3 hours, respectively, which is consistent with the observations of previous reports (Liu et al. 2010). After the addition of SC, the initial setting time of cement can be shortened to various time periods, which means the formation rate of early hydration products is accelerated. For instance, the initial and final setting times were shortened to 2 hours and 3.5 hours from 3 hours and 5.5 hours, respectively, after the addition of 5% SC to the MOS cement with 0.05% CA. Although the initial setting time is slightly shortened after the addition of SC in MOS cement with 0.5% CA, the final setting time is prolonged by 1 hour, which means the rate of formation of hydration products in the MOS cement will be reduced after the initial setting.

Considering with the effects of SC on the early strength of MOS cement, the production efficiency of cement products can be significantly improved by adding SC under the condition of low CA content (e.g., 0.05%).

3.3 Effects of SC on volume changes

Figure 7 shows the length changes of MOS cement under different curing times. It can be seen that with the extension of curing time, the cement shrinks continuously, and adding both SC and CA to the cement can decrease its shrinkage. The shrinkage of MOS cement (a type of air-hardened binding material) during the curing mainly involves chemical shrinkage and dry shrinkage. Between them, the degree of chemical shrinkage is related to the degree of hydration of cement and the type of hydration products. The higher the degree of hydration and the denser the hydration products, and the greater the chemical shrinkage. For example, as previously reported, the addition of CA in MOS cement reduces its hydration rate, and the hydration phase changes from Mg(OH)₂ to the 5·1·7 phase with lower density. As the amount of CA increases, chemical shrinkage decreases. The drying shrinkage is mainly caused by capillary shrinkage, which in turn is caused by evaporation of water in the cement. The higher porosity and the lower the strength of the pore wall (matrix), the larger the drying shrinkage. For the same amount of CA, the total shrinkage decreases after the addition of SC, which is bound to be closely related to the porosity, hydration degree, and composition of hydration products (which affect the strength of the pore wall) after the addition of seed crystal.

To analyze the influence mechanism of 5·1·7 phase seed crystal on the compressive strength, setting time, and volume changes of MOS cement, the composition and morphology of hydration products, the hydration heat rate, and pore structure characteristics of the cementitious paste were adopted.

3.4 Effects of SC on hydration products and microstructure

Figure 8 shows the XRD patterns of MOS cement cured for 12 hours and 28 days with and without SC. It can be seen that after curing for 12 hours, the hydration products of MOS cement without CA or SC are not the 5·1·7 phase products, but Mg(OH)₂. Although the diffraction peak of Mg(OH)₂ disappears, when CA is added to the MOS cement (Fig. 7a), the intensity of the ensuing 5·1·7 phase is weaker than that of the cement with SC (Fig. 7b). To verify if the addition of SC promotes the formation of the new 5·1·7 phase at an early age of the cement, SEM analysis was performed. As shown in Fig. 9, for the sample of A0S0 (Figs. 9a and 9b), a large amount of flaked Mg(OH)₂ appears in the pores, while the needle-shaped 5·1·7 phase was not only small, but also very short. When SC was added (Figs. 9c and 9d), there was nearly no Mg(OH)₂, but a large number of needle-shaped 5·1·7 phase crystals appeared in the pores. As the amount of CA increases, chemical shrinkage decreases. The drying shrinkage is mainly caused by capillary shrinkage, which in turn is caused by evaporation of water in the cement. The higher porosity and the lower the strength of the pore wall (matrix), the larger the drying shrinkage. For the same amount of CA, the total shrinkage decreases after the addition of SC, which is bound to be closely related to the porosity, hydration degree, and composition of hydration products (which affect the strength of the pore wall) after the addition of seed crystal.

When CA was added (Figs. 9e and 9f), it was found that there were a lot of MgO particles on the cement surface, which indicated that the addition of CA delayed the hydration of MgO in the magnesium sulfate solution. After the addition of SC in the MOS cement with 0.05% CA (Figs. 9g and 9h), a large number of needle-shaped
5·1·7 phase crystals appeared among the MgO particles. Considering that the SCs were not needle-shaped after ball milling, as is shown in Fig. 4, it was proved that the addition of SC could promote the in situ growth of the 5·1·7 phase crystals on the SC surface. At an early age, a large number of new 5·1·7 phase crystals grow on the SC surface in situ, which not only improves the early strength of the cement, but also increases the strength of the pore wall of the cement pores, thereby reducing the early dry shrinkage.

Figure 10 is the FTIR spectra of MOS cement with and without SC. As can be seen clearly, for the sample of A0S0 (Fig. 10a), a strong absorption peak of stretching vibration of O–H (δO–H) in Mg(OH)2 appears at approximately 3700 cm⁻¹, which further confirms Mg(OH)2 was formed after curing for 8 hours. For the MOS cement with CA, however, nearly no absorption peak appears at 3700 cm⁻¹ due to the retarding effect of CA. However, the peak of δO–H becomes weaker after the addition of SC, especially for A0S5 and A005S5, which results from the inhibition of Mg(OH)2 formation by the formation and growth of the new 5·1·7 phase crystals on the surface of SC. Although SC can inhibit the formation of Mg(OH)2 and promote the formation of 5·1·7 phase in the early hydration of MOS cement as CA does, it has no obvious retardation effect on the MOS cement. Instead, it only has a certain accelerating effect.

As is shown in Figs. 8c and 8d, the diffraction peak of Mg(OH)2 can also be seen in the MOS cement without CA or with 0.5% CA after curing for 28 days. After the addition of SC, the intensity of the diffraction peak of Mg(OH)2 in the MOS cement decreased and that of 5·1·7 phase increased distinctly, which results in a higher late strength of the MOS cement. Thus, an important inference can be drawn: based on the fast formation of the 5·1·7 phase and the inhibition of the formation of Mg(OH)2, the addition of SC in MOS cement without CA or with a small amount of CA can improve both early and late strengths without causing retardation effects in the MOS cement.

3.5 Effects of SC on hydration heat and AC impedance

Figure 11 shows the hydration release rate curves of different MOS cement samples. The curve can be divided into five stages, i.e., pre-induction period, induction period, acceleration period, deceleration period, and stabilization period, similar to the hydration heat release law of Portland cement.

In the MOS cement without any admixture, the exo-

![Figure 11](image-url)

Fig. 8 XRD patterns of MOS cement. [(b), (d)]: with 5·1·7 phase crystal seeds; [(a), (c)]: without 5·1·7 phase crystal seeds. The results after curing for 8 hours are shown in (a) and (b) while (c), (d) show the results after curing for 28 days. (P: 5·1·7 phase; MH: Mg(OH)2; MO: MgO; MC-MgCO3).
thermic energy in the pre-induction and induction peri-
dods is mainly expended from the dissolution of MgO in
magnesium sulfate, and the reaction formula is shown in
Eq. (3). When the concentration of ions in the liquid
phase (e.g., OH⁻) reaches a certain super-saturation level
of Mg(OH)₂ or 5·1·7 phase, the hydrate product nucleus
is formed. When this nucleus multiplies into a certain
number, the induction period ends and the acceleration

Fig. 9 SEM images of MOS cement with and without SC after curing for 8 hours. [(a) and (b): A0S0; (c) and (d): A0S5; (e)
and (f): A005S0; (g) and (h): A005S5].
period begins, i.e., the hydrate product begins to precipitate and grow continuously, accompanied by the further dissolution of MgO. The addition of CA leads to the complexation of MgO with citrate ion. This complexation reduces the reaction ability of the MgO hydration film with OH⁻ in the liquid phase [Eq. (4)] (Wu et al. 2017). Therefore, higher pH (i.e., higher super-saturation) is needed for the crystallization of hydration products, which requires a longer induction period and slower setting and hardening rates of cement. Considering that Mg(OH)₂ has lower solubility than the 5·1·7 phase, the required concentration of OH⁻ for the formation of Mg(OH)₂ is significantly lower than that of 5·1·7 phase, low concentration of OH⁻, i.e., in the absence of CA, is prior to the formation of Mg(OH)₂. As seen in the results of the phase analysis in Section 3.1 the strength of MOS cement without additives is significantly lower than that with CA.

After the addition of SC in the MOS cement, the hydration heat release rate increases and the duration time decreases in the induction period with the increase of SC content. For example, in the MOS cement with 0.05% CA, the induction period was shortened from 3.61 hours to 3.50 hours, 2.85 hours, and 1.17 hours, when the SC content was 1%, 3%, and 5%, respectively. Considering more 5·1·7 phases and almost no Mg(OH)₂ formation after hydration for 8 hours, as is analyzed in Section 3.4, it can be inferred that the super-saturation required for the formation of the 5·1·7 phase nucleus is decreased, and the formation of the 5·1·7 phase nucleus is increased in the induction period by the addition of SC. With the increase of SC content, the number of active sites for in situ nucleation of the new 5·1·7 phase increases [Eq. (5)], the content of the 5·1·7 phase nu-

![Fig. 10 FTIR of MOS cement with and without SC after curing for 8 hours.](image1)

![Fig. 11 Effects of CA [(a)] and of SC [(b), (c), (d)] on hydration heat release rates of MOS cement.](image2)
cleus formed in the induction period increases, and the initial setting time of the MOS cement decreases.

From Fig. 11, it can also be seen that the hydration rate of cement containing SC decreases significantly during the acceleration period, especially for the MOS cement with CA. This may be due to the competition between the liquid-ion nucleation and growth on the SC surface [Eq. (5)] and on the MgO surface [Eqs. (4) and (6)]. The nucleation on the SC surface (secondary nucleation) consumes the early nucleating agent [Eq. (5)], which inhibits the hydration of the new MgO caused by primary nucleation and growth [Eqs. (4) and (6)] (Wu et al. 2018). Because the formation of the 5·1·7 phase promoted by the addition of SC and the formation of Mg(OH)$_2$ was inhibited, the hydration release rate barely decreased at the accelerated stage of MOS cement without CA. The hydration heat release of the formation of 5·1·7 by the reaction of MgO with magnesium sulfate solution was higher than that of the formation of Mg(OH)$_2$. As shown in Fig. 12, although the cumulative heat release of MOS cement with CA at an early age was lower than that without CA, the later (after hydration time more than 24 hours) cumulative heat release became higher than that of the MOS cement without CA because of the continuous formation of the 5·1·7 phase. Therefore, the formation of the 5·1·7 phase instead of Mg(OH)$_2$ caused by the addition of SC in the MOS cement without CA compensates the decrease of hydration exothermic rate caused by the inhibition of primary nucleation and growth on MgO surface.

Figure 13 illustrates the AC impedance of different cements at different hydration times. Because the frequency of AC used in this study is 10 kHz, the AC impedance value of cement can be approximately equal to the pore solution resistance of the cementitious paste (Hafiane et al. 2000; Liu et al. 2010). It can be seen that the more the amount of CA, the slower the increase in resistance of the pore solution. It is further proved that with the increase of CA, the rate of increase of the solid volume and the rate of decrease of porosity of the cementitious paste are reduced, i.e., CA has a strong retardation effect. In addition, except for the cement without CA, the resistance of the pore solution increases with the addition of SC, which proves that liquid ions (such as SO$_4^{2-}$ and Mg$^{2+}$) react more adequately, and that more basic magnesium sulfate phase (mainly refer to 5·1·7 phase) and less Mg(OH)$_2$ are formed in the MOS cement with SC.

3.6 Effects of SC on pore structure
The mechanical strength and volume stability of MOS cement may be related to its pore structure, besides the category and content of the hydration product. Figure 14 shows the cumulative porosity (330 μm - 5 nm) of the MOS cement with and without SC after curing for 8 hours (Fig. 14a) and 28 days (Fig. 14b). As can be seen in the figures, the addition of SC does not decrease the porosity of MOS cement, but instead increases it, especially for the cement with 0.05% CA. However, as summarized in Table 2, the relative content of the gel pore (< 20 nm) decreased and the average pore diameter increased after the addition of SC. For example, after curing for 8 hours, the cumulative porosity of MOS cement with 0.05% CA increased to 37.07% from 25.62%, and that of the relative content of gel pore decreased to 36.29% from 70.32%. As in our previous report (Liu et al. 2019), the gel pore was derived from poor crystalli-
zation-precipitated products such as magnesium sulfate (MgSO₄·nH₂O). As analyzed from Fig. 13, although the porosity of A005S5 is lower than that of A005S0, the pore solution impendence is higher at 8 hours, which is an indication that more Mg²⁺ and SO₄²⁻ ions in magnesium sulfate solution participate in the reaction that produces the 5·1·7 phase with higher degree of crystallization. Therefore, the MOS cement with more 5·1·7 phase after the addition of SC has a higher average pore and low gel pore content. With the extension of hydration time, the average pore size of MOS cement increases, which further proves that with the hydration process, the crystallinity of hydration products increases continuously, especially with the addition of SC. Therefore, the increase of crystallinity of hydration products by adding SC can improve the 28 d compressive strength. Furthermore, the increasing porosity of MOS cement with SC may be because the density of 5·1·7 phase is higher than that of MgSO₄·nH₂O, which resulted in a smaller solid volume.

Above all, based on the XRD, SEM and MIP analyses results, it can be seen that the hydration product type (such as 5·1·7 phase or Mg(OH)₂) and relative content in hydrated MOS cement are more important influence factors of the strength and volume stability of MOS cement than the pore structure.

4. Conclusion

In this study, the influences of SC on the performance of MOS cement with and without CA were investigated. Based on the analysis results in previous sections, the following conclusions can be drawn:

(1) Both early and later strengths of the MOS cement can be improved by adding SC without or with small quantities of CA. The early strength of MOS cement improves because of the in situ nucleation and growth of the new 5·1·7 phase by the addition of SC at an early age. The later strength improvement results from the relatively decreasing content of Mg(OH)₂ with low cementing performance.

(2) The setting time of MOS cement can be shortened by the addition of SC. The addition of SC to MOS cement with low CA content (e.g., 0.05%) can significantly improve the production efficiency of MOS-based products without the reduction of its mechanical strength.

(3) The addition of SC improves the volume stability of

Table 2 Statistics of pore distribution of MOS cement with and without SC after curing for 8 hours and 28 days.

| Samples  | Porosity (%) | Average pore diameter (nm) | < 20 nm (%) | 20 to 100 nm (%) | > 100 nm (%) |
|----------|--------------|----------------------------|-------------|-----------------|-------------|
| A0S0-8 h | 22.65        | 16.08                      | 66.61       | 14.34           | 19.05       |
| A0S0-28 d| 21.04        | 16.10                      | 60.36       | 19.92           | 19.72       |
| A0S5-8 h | 26.84        | 21.05                      | 50.00       | 30.88           | 19.12       |
| A0S5-28 d| 26.05        | 164.72                     | 22.68       | 18.63           | 58.68       |
| A005S0-8 h| 25.62        | 12.00                      | 70.32       | 11.85           | 17.82       |
| A005S0-28 d| 23.40        | 66.16                      | 29.83       | 27.43           | 42.72       |
| A005S5-8 h| 37.07        | 33.88                      | 36.29       | 28.71           | 35.00       |
| A005S5-28 d| 29.11        | 183.71                     | 11.46       | 21.37           | 67.17       |
| A05S0-8 h | 36.13        | 27.21                      | 35.05       | 54.06           | 10.89       |
| A05S0-28 d| 31.21        | 64.03                      | 10.00       | 65.73           | 24.27       |
| A05S5-8 h | 36.96        | 41.88                      | 27.60       | 40.31           | 32.00       |
| A05S5-28 d| 32.73        | 153.75                     | 7.18        | 25.57           | 67.25       |

Fig. 14 Cumulative porosities of MOS cement with and without SC after curing for (a) 8 hours and (b) 28 days, with D being the pore diameter (nm).
MOS cement as the pore wall strength is increased by prompting the formation of more 5:1:7 phases among the MgO particles and cement matrix-pore interface.

To obtain more details about the effects of SC on the performance of MOS cement, the effects of different particle size, micromorphology, and impurity content of SC on the performances of MOS cement need further studied via different synthetic methods. Moreover, whether the MOS cement modification technology based on crystal seed technology can be applied in low temperature projects and low-grade or active magnesia ore (such as light-burnt dolomite) for MOS cement product needs to be further studied.

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References
An, S. X., Xiao, X., Li, Y., Wen, J. and Chang, C. G., (2017a). “Effects of potassium chloride on the property of magnesium oxysulfate cement.” New Building Materials, (11), 79-83.
An, S. X., Xiao, X., Li, Y., Wen, J., Zheng, W. X., Chang, C. G., Dong, J. M. and Huang, Q., (2017b). “Setting, hardening characteristics and microstructure of magnesium oxysulfate and magnesium oxychloride mixed cementitious system.” Bulletin of the Chinese Ceramic Society, 36(8), 2607-2613.
Chau, C. K. and Li, Z. J., (2008). “Accelerated reactivity assessment of light burnt magnesium oxide.” Journal of the American Ceramic Society, 91(5), 1640-1645.
China GB/T 1346-2011, (2011). “Test methods for water requirement of normal consistency, setting time and soundness of the Portland cement.” National Standard GB/T 1346-2011 of the People's Republic of China. Beijing, China: Standardization Administration of China. (in Chinese)
Demediu, T., Cole, W. F. and Hueber, H. V., (1955). “Studies on magnesium and calcium oxychlorides.” Australian Journal of Chemistry, 8(2), 215-233.
Demediu, T. and Cole, W. F., (1957). “A study of magnesium oxysulfate.” Australian Journal of Chemistry, 10, 287-294.
Dinnbrier, E. R., Pannach, M. and Freyer, D., (2013). “3Mg(OH)2·MgSO4·8H2O: a metastable phase in the system Mg(OH)2·MgSO4·H2O.” Zeitschrift für Anorganische und Allgemeine Chemie, 639(10), 1827-1833.
Dong, J. M., Yu, H. F. and Zhang, L. M., (2010). “Study on experimental conditions of hydration methods of determining active magnesium oxide content.” Journal of Salt Lake Research, 1838-1841.
Gomes, C. E. M. and Camarini, G., (2014). “Magnesium oxysulfate fiber cement.” Key Engineering Materials, 600, 308-318.
Hafiane, Y., Smith, A. and Bonnet, Y., (2000). “Electrical characterization of aluminous cement at early ages the 10 Hz - 1 GHz frequency range.” Cement and Concrete Research, 30(2), 1057-1062.
John, E., Matschei, T. and Stephan, D., (2018). “Nucleation seeding with calcium silicate hydrate: a review.” Cement and Concrete Research, 113, 74-85.
Lin, Q., Gao, X. J. and Chen, T. F., (2018). “Recycling of raw rice husk to manufacture magnesium oxysulfate cement based lightweight building materials.” Journal of Cleaner Production, 191, 220-232.
Liu, C. S., Huang, Y. and Zheng, H. Y., (2010). “Study of the hydration process of calcium phosphate cement by AC impedance spectroscopy.” Journal of the American Ceramic Society, 82(4), 1052-1057.
Liu, P. P., Wu, C. Y., Luo, K. J., Chen, C., Chen, Y. J., Zhang, H. F. and Yu, H. F., (2019). “Effects of the curing temperature on the performance of glass fiber reinforced basic magnesium sulfate cement.” Ceramics-Silikáty, 63(1), 32-44.
Qin, L., Gao, X. J. and Zhang, A. L., (2018). “Potential application of Portland cement-calcium sulfoaluminate cement blends to avoid early age frost damage.” Construction and Building Materials, 190, 363-372.
Urwong, L. and Sorrell, C. A., (1980). “Phase relations in magnesium oxysulfate cements.” Journal of the American Ceramic Society, 63(9-10), 523-526.
Wakeel, E. I. A., Korashy, S. A. E., Hemaly, S. A. E. and Uossef, N., (1999). “Promotion effect of C-S-H phase nuclei on building calcium silicate hydrate phases.” Cement and Concrete Composites, 21(3), 170-180.
Walling, S. A. and Provis, J. L., (2016). “Magnesium-based cements: a journey of 150 years, and cements for the future?” Chemical Reviews, 116(7), 4170-4204.
Wang, N., Yu, H. F., Bi, W. L., Tan, Y. S., Zhang, N., Wu, C. Y., Ma, H. Y. and Shi, H., (2018). “Effects of sodium citrate and citric acid on the properties of magnesium oxysulfate cement.” Construction and Building Materials, 169, 697-704.
Wu, C. Y., Chen, C., Zhang, H. F., Tan, Y. S. and Yu, H. F., (2018). “Preparation of magnesium oxysulfate cement using magnesium-rich by products from the production of lithium carbonate from salt lakes.” Construction and Building Materials, 172, 597-607.
Wu, C. Y., Chen, W. H., Zhang, H. F., Yu, H. F., Zhang, W. Y., Jiang, N. S. and Liu, L. X., (2017). “The hydration mechanism and performance of modified magnesium oxysulfate cement by tartaric acid.” Construction and Building Materials, 144, 516-524.
Wu, C. Y., Yu, H. F., Dong, J. M. and Zheng, L. N., (2014). “Effects of material ratio, fly ash, and citric acid on magnesium oxysulfate cement.” ACI Materials Journal, 111(3), 291-297.
Wu, C. Y., Yu, H. F., Zhang, H. F., Dong, J. M., Wen, J.,
and Tan, Y. S., (2015). “Effects of phosphoric acid and phosphates on magnesium oxysulfate cement.” *Materials and Structures*, 48(4), 907-917.

Wu, C. Y., Yu, H. F. and Zhang, H. F., (2016). “Preparation and properties of modified magnesium oxysulfate and cement derives from waste sulfuric acid.” *Advances in Cement Research*, 28(3), 178-188.

Xing, S. N., Wu, C. Y., Yu, H. F., Jiang, N. S. and Zhang, W. Y., (2017). “Research on A3 steel corrosion behavior of basic magnesium sulfate cement.” *IOP Conference Series: Earth and Environmental Science*, 94(1), 012037.

Yu, J. C., Qian, J. S., Tang, J. Y., Ji, Z. W. and Fan, Y. R., (2019). “Effect of ettringite seed crystals on the properties of calcium sulfoaluminate cement.” *Construction and Building Materials*, 207, 249-257.

Zeng, X., Yu, H. F. and Wu, C. Y., (2018). “Experimental study on shear destruction of BMSC concrete beam.” *Journal of Harbin Engineering University*, 39(7), 40-44.

Zhang, X., Ge, S. J., Wang, H. N. and Chen, R. Y., (2017). “Effect of 5-phase seed crystal on the mechanical properties and microstructure of magnesium oxychloride cement.” *Construction and Building Materials*, 150, 409-417.

Zhou, X. M. and Li, Z. J., (2012). “Light-weight wood-magnesium oxychloride cement composite building products made by extrusion.” *Construction and Building Materials*, 27(1), 382-389.