Improved hydration and properties of magnesium oxysulfate (MOS) cement using sodium silicate as an additive

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Abstract

Magnesium oxysulfate (MOS) cement has many advantages, such as high early strength, low thermal conductivity, excellent fire and corrosion resistance. However, its strength is less stable and its water resistance is relatively poor, which limits its wide use in civil engineering. In this study, the MOS cement specimens with different amount of sodium silicate (SS) as an additive were manufactured before subjected to a series of laboratory tests, including dispersion tests, strength tests, SEM, XRD and Isothermal Calorimetry analysis to evaluate their modified properties. The experimental results show that an increase of the amount of SS consistently reduces the initial setting time, dispersion and fluidity performance of MOS cement paste because of the SS accelerated endothermic reaction during hydration process of MOS. An addition of the amount of SS up to 0.5% of the mass of MgO significantly increases the long-term strength and water resistance of MOS cement. This attributes to the fact that SS enhances microstructure and refines the coarse pores of hardened MOS paste, and thus forms much denser paste, although it does not change the category of hydration phase composition in hardened MOS cement.

Keywords: magnesium oxysulfate (MOS) cement, sodium silicate (SS), strength stability, water resistance, hydration process

Highlights

- Sodium silicate (SS) was used to improve the hydration and properties of Magnesium oxysulfate (MOS) cement.

- A series of systematic laboratory tests, including dispersion tests, strength tests, SEM, XRD and Isothermal Calorimetry analysis were conducted to evaluate the improved properties of MOS cement.

- Using the SS as additive, the microstructure of hardened MOS paste has been enhanced, its coarse pores refined, its long-term strength and water resistance increased significantly.

1. Introduction

Magnesium oxysulfate (MOS) cement is an air-dried magnesia cementitious material that is prepared with light-burned magnesium oxide and an aqueous solution of magnesium sulphate [1-4]. It has many outstanding characteristics, such as a short setting time, high early strength, good cohesion behaviour, low thermal conductivity, wonderful wearing capacity, excellent fire and corrosion resistance [5]. Compared with conventional Portland cement, MOS cement also consumes less energy for its production, and can be easily prepared [6]. It can be widely used for production of light weight insulation board, refractory materials, decoration materials and oil well plugging [7, 8]. However, the strength of MOS cement is unstable and its water resistance is relatively poor [9, 10], which limits its use in civil engineering. Thus, how to improve the strength stability and water resistance of MOS cement has ever been concerned in engineering practice.

The strength of MOS cement primarily varies with the category and content of its hydration products as well as the microstructures of its hardened paste. According to Demediuk and Cole [11], the hardened MOS cement paste mainly has four different phases of 5-1-3, 3-1-8, 1-2-3, and 1-1-5 of magnesium sulfate at a temperature from 30 °C to 120 °C. Urwongse and Sorrel [12] reported that the only 3-1-8 phase of $3Mg(OH)_2 \cdot MgSO_4 \cdot 8H_2O$ is stable at a normal temperature of 23±3°C, but the rest phases vary with temperature. This results in the poor strength stability of MOS cement. Mathur et al [13, 14] found that an addition of formaldehyde into MOS cement increases its initial setting time and compressive strength. Beaudoin and Ramachandran [15] studied the porosity of MOS cement and found that the high porosity of MOS is the main reason for its poor water resistance. It was known that the concentration of

SO_4^{2-} in saturated magnesium sulphate solution is only 2.93 mol/L or so, and the radius of SO_4^{2-} is approximately 3.79Å. Based on above fact the possibility of diffusion of SO_4^{2-} into the hydrated MgO layer is relatively low, which means that the reaction rate of the SO_4^{2-} with the hydration film of MgO particles by diffusion is relatively low.

Consequently much more $Mg(OH)_2$ phase is formed by MgO reacting only with water in MOS cement paste at early age, which leads to its less stable strength [15]. Accordingly some additives are used for the purpose of both inhibiting the amount of $Mg(OH)_2$ phase and increasing the content of stable magnesium sub-sulphate and eventually for improving the mechanical properties of MOS cement. Wu et al [16-19] reported that an addition of phosphoric, phosphate and citric acid could increase the compressive strength of MOS cement as a result of changing the hydration process. Wu et al [19] also studied the hydration mechanism of tartaric acid modified MOS cement. Zheng and Zhan [20] reported that citric acid can improve the strength of MOS cement effectively. Liu et al [21] found that with an increase of citric acid content, the 7-day and 55-day flexural and compressive strengths of MOS cement increase. Although above researchers have adapted different kinds of additives to increase the strength of MOS cement, they have paid less significant attention on improving both strength stability and water resistance of MOS cement.

Hence this study uses sodium silicate (SS) as an additive or modifier to the MOS cement for the purpose of changing its hydration process and improving its water resistance and strength stability. The MOS cement paste and the relevant cubic and prismatic specimens with different amount of SS additive were manufactured. A series of systematic laboratory tests, including dispersion tests, strength tests, SEM, XRD and Isothermal Calorimetry analysis were conducted on the MOS pastes and specimens to evaluate their modified workability, mechanical properties, hydration products and water resistance. This was followed by the detailed discussion and corresponding conclusion of the reported test results.

2. Experimental work

2.1 Raw materials

Magnesium oxysulphate (MOS) cement in this test was prepared by mixing magnesium sulphate heptahydrate crystals ($MgSO_4 \cdot 7H_2O$) and light burned magnesia powder (MgO) with water. The light-burned magnesium oxide (MgO) was manufactured by calcining the magnesite at 700 °C. Their chemical compositions are shown in Table 1 and Table 2. The analytical sodium silicate (SS) were adopted as an additive to the MOS cement with the citrate acid (CA) included for a comparison.

Table 1 Chemical composition of magnesium sulphate $MgSO_4 \cdot 7H_2O$

Component	$MgSO_4$	$MgCl_2$	NaCl	Na_2SO_4	H_2O	others
Weight%	47.85	0.50	0.50	0.50	50.24	0.41

Table 2 Chemical composition of light-burned magnesium oxide MgO

Component	SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3	LOI
Weight%	0.40	96.50	0.85	0.19	0.21	1.85

The X-ray diffraction (XRD) pattern and particle size distribution of the light-burned MgO were shown in Figure 1 and Figure 2. Figure 1 shows that there was a small amount of Al_2O_3 in light-burned MgO powder. Figure 2 indicates that the average particle size of light-burned MgO was about 28μm. The light-burned magnesia powder MgO used for this test consists of over-burned MgO and active MgO, in which only active MgO reacts with water to form $Mg(OH)_2$ after 3 hour reaction at 105 °C [22]. On the basis of mass difference between the over burned and light burned MgO, the active MgO of the light-burned MgO used in this study was measured as 61.0% of the total mass of the light-burned MgO.
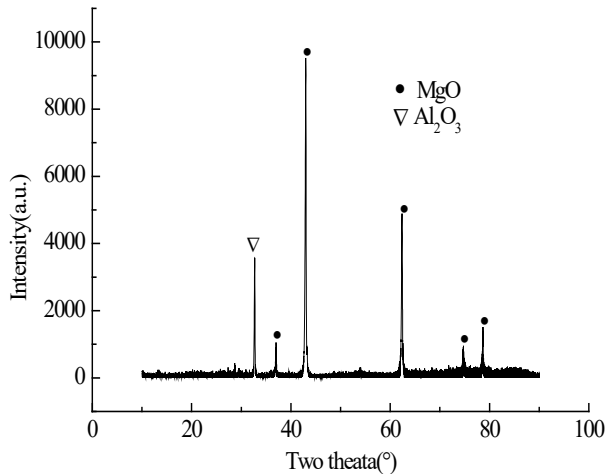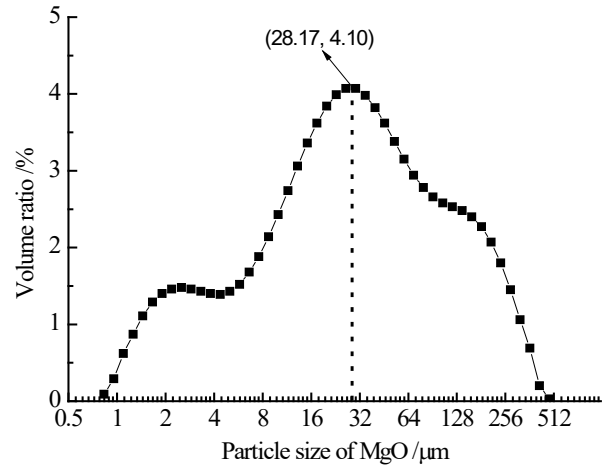

Figure1 XRD pattern of light-burned MgO   Figure 2 Particle size distribution of light-burned MgO

2.2 Experimental work

As described below, a series of MOS cement pastes, cubic and prismatic specimens with different amounts of SS were manufactured before they were subjected to six kinds of performance tests, including water dispersion, setting time, fluidity, mass loss after immersion, water resistance and strength. In order to explain the influence mechanism of SS on the above properties, Scanning Electron Microscopy (SEM), XRD, Thermogravimetry (TG) and hydration heat tests were also carried out respectively.

The light-burned MgO, magnesium sulphate MgSO$_4$·7H$_2$O and water H$_2$O were mixed with a constant molar ratio of 14:1:9 for the manufacturing of two groups of MOS cement pastes to be used for dispersion test. One group of MOS cement pastes did not contain any SS and was taken as a bench marker of the test. Another group of MOS pastes contain 0.5% of SS by the weight of MgO. The manufactured cement pastes were then placed in a container, which was filled in with a deionized water and oscillated on a magnetic stirrer, as the stirrer was rotating at a speed of 60 rotation per minute for about one minute. This was immediately followed by an observation both on the clarity of the deionized water in the container and the dispersed state of MOS cement pastes in the deionized water. Meanwhile the setting time and fluidity of MOS cement pastes with 0.5% of SS were measured in accordance with the National Testing Standard of China (GB/T1346-2001).

In addition, ten groups of the MOS cement prismatic specimens with the dimensions of 40mm×40mm×160mm and with different amount of SS were manufactured to measure their corresponding strengths and mass losses in water. Three specimens were included in one group with their measured results averaged for the group value. The specimens were demoulded 24 hours later after cast and placed in a standard curing chamber that has a temperature of 20±3 °C and relative humidity of 75%. After cured for 3 days, 7 days, 14 days, 28 days, 60 days, 90 days, 180 days and 360 days, respectively, the specimens were taken from the chamber and subjected to the compressive and flexural tests that were performed in conformity with the National Testing Standard of China (GB/T17671).

Furthermore, one 40mm×40mm×160mm prismatic specimen at age of 28 days from each group of specimens was cut into three 40mm×40mm×40 mm cube specimens for the purpose of obtaining a fresh surfaces of cube specimens and then were immersed into a deionized water in a container by a half of their 40mm depths. After these 40mm cubes in container were placed under a constant temperature environment of 20℃ for 24 hours, they were taken out from the container. The left solution in the container was put into an oven and dried at constant temperature of 100℃. After the water in the container has evaporated, the mass of some left substance in the container was weighed using a balance to obtain the mass loss rate of the samples.

In addition, other 40mm×40 mm×160mm specimens from each group were immersed in a tap water in a tank, which had the same temperature of 20±3 °C as the above curing chamber, for 14 days, before subjected to a compression test to measure their saturated compressive strengths. This saturated strength was compared with the relevant normal dry strengths of the corresponding specimens to calculate the softening coefficient using the equation (1) below as an index of the water resistance of hardened MOS cement paste.

$$K_S = \frac{f_w}{f_d}$$

(1)

Where, K_S is the softening coefficient of specimen, f_w is the compressive strength of saturated specimens, MPa；f_d is the compressive strength of dried specimens at room temperature (MPa).

After the above strength tests, the cracked sections of the tested specimens were used as fresh section for SEM observation. Some parts of SEM observed fresh sections were crushed and grinded into powder samples for XRD and TG tests. The XRD tests of the samples were performed on Purkinjie general instrument XD-3X-ray diffract meter with copper target. X-ray diffraction (XRD) adopts step scanning mode, and the peak intensity is determined by pulse counting rate. The TG test were carried on TASDT Q600 thermo-gravimetric analyzer in inert atmosphere with a heating range from 20°C to 950 °C at a heating rate of 10°C per minute. The porous characteristics of MOS cement pastes with different amount of SS at curing age of 28 days were determined by measuring evaporable water content[23]. The early hydration-heat releasing rate of MOS cement with different SS contents was measured using the Isothermal Calorimetry analyzer according to the National Testing Standard of China (GB/T 12959-2008).

3. Results and discussion

3.1 Effect of SS on dispersion of MOS paste in water

The term of dispersion here means the scattering of MOS cement particles into its surrounding water, which reflects workability and water resistance of MOS cement. Figure 3 shows the dispersion characteristics of the MOS pastes without and with 0.5% SS in deionized water. It can be seen that MOS paste without SS dispersed quickly into its surrounding water and made the deionized water become much turbid than it used to be. However, the MOS paste with SS remained a cluster shape in water and kept the water clear in the container transparent. This indicates that the dispersion of MOS paste in water has substantially reduced due to using SS as an additive. This is mainly because of the strong hydrogen bond association of silicate ion, sulphate ion and hydrogen ion in the MOS paste with SS[24]. These ions increase the consistency and cohesion of the aqueous solution on the surface of the paste in water. Therefore, addition of SS to MOS paste reduces the inward penetration rate of external water molecules, the outward diffusion and dissolution rate of powdered MgO particles and to some extent, affects workability of MOS paste, as followed below.

(a) MOS paste without SS   (b) MOS paste with SS

Figure 3 Effect of SS on the dispersion characteristics in water of MOS cement

3.2 Effect of SS on workability of MOS cement

Both setting time and fluidity are two important aspects of characterizing the workability of MOS cement paste. Figure 4 shows the variations of both setting times and fluidity of the MOS pastes with different amount of SS. It is clear that, compared with the initial and final setting times of about 0.5 and 6.0 hours, respectively, of Portland cement, those of MOS cement that was manufactured in this test and without SS are about 2.5 and 3.0 hours, respectively. In addition, an increase of the amount of SS in a MOS paste reduced its initial setting time and fluidity substantially, although it did not change the final setting time significantly. This is due to the fact that the initial setting time is closely related to the early hydration rate. In other words, Figure 4 indicates that an early hydration rate of a MOS cement paste increases with an increase of its SS content. Consequently both the hydration heat rate and pH value that changes with amount of SS are adopted to analyze the SS's early coagulation effect on MOS cement.
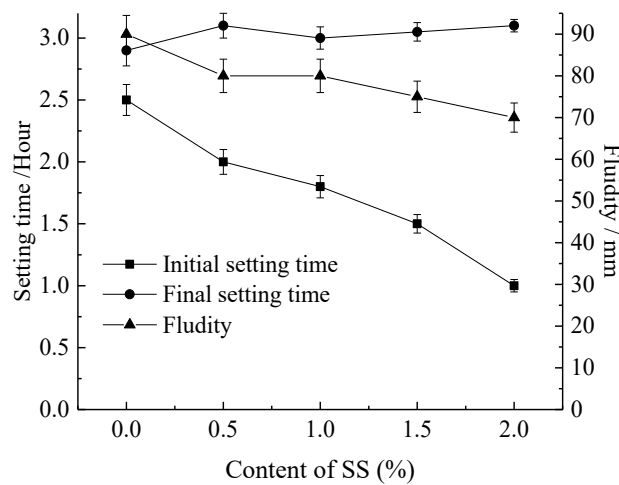

Figure 4 Effect of SS on setting time and fluidity of MOS cement

3.3 Effects of SS on strength development

It is well known that mechanical strength is one of the main properties of MOS cement. The compressive and flexural strengths of MOS cement specimens without and with SS were illustrated in Figure 5. It is clear that the flexural and compressive strength of MOS cement specimens without SS increased with the curing age up to 28 days and then decreased with the prolonged curing age. This is attributed to the properties and shortcoming of the MOS cement with its mechanism analysis conducted in the section 3.7. While those of the MOS cement specimens with SS exhibit relatively stable state with the prolonged curing ages. In other words, the SS addition can improve the long-term strength stability of MOS cement. However, Figure 5 also shows that, for the same curing age, the compressive and flexural strengths of MOS cement decrease with an increase of SS amount from 0.5% to 2.0. Hence, an increase of the amount of SS up to 0.5% can significantly improve the strength and strength stability of MOS cement.
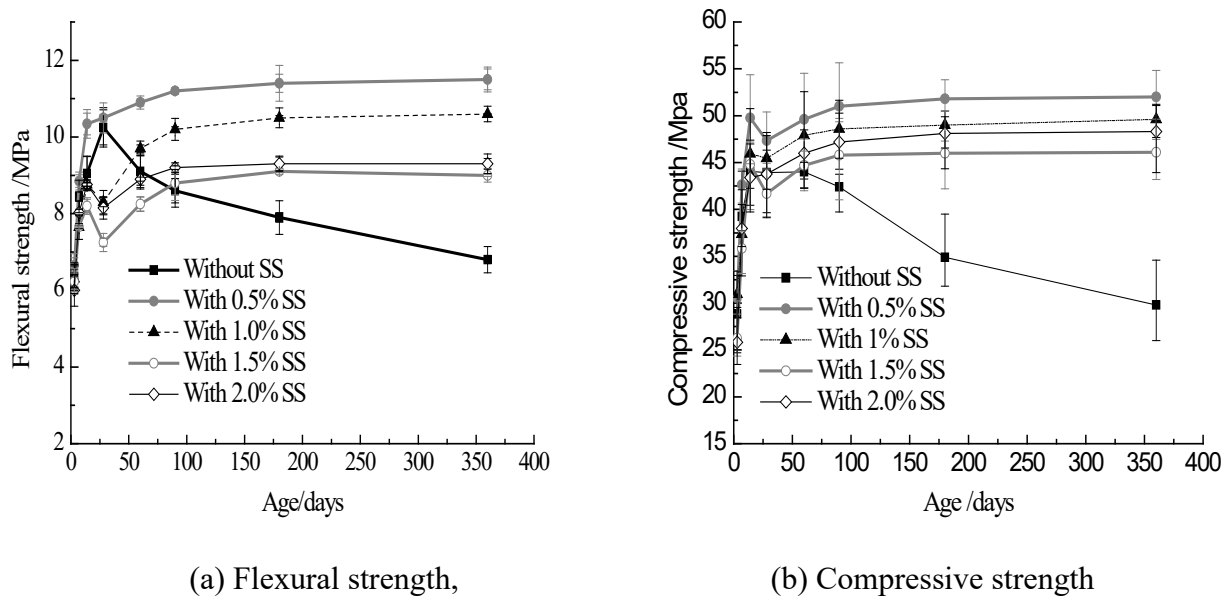

(a) Flexural strength,   (b) Compressive strength

Figure 5 Effects of SS on mechanical properties of MOS cemented materials

3.4 Effects of SS on water resistance

Immersion softening coefficient and mass loss were adopted to characterize corresponding water resistance of MOS cement. Figure 6 shows that an increase of the amount of SS up to 0.5% increased softening coefficient of MOS cement, but decreased its mass loss sharply. If the amount of SS exceeds 0.5%, however, an increase of SS decreased the softening coefficient but increased corresponding mass loss. As is well known that water resistance of MOS cement is closely related to its hydration products and porous structures, which will be analysed in following parts.
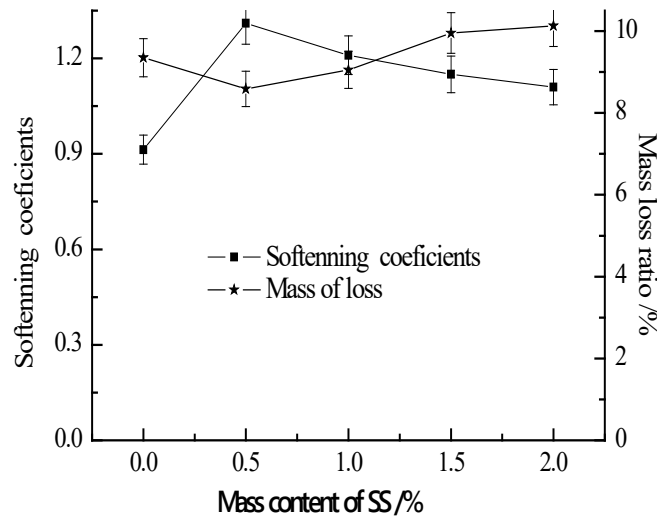
Figure 6 Effect of SS on water resistance of hardened MOS cement

3.5 Effects of SS on porous characteristics of MOS cement

Figure 7 shows the variation of porous characteristics of MOS cement with an increase of SS content, which were evaluated by measuring the amount of evaporable water. The coarse pore here is defined as those with a diameter larger than 100 nm. The capillary pore is those with a diameter between 30 nm and 100 nm. The total porosity of a MOS cement paste is the sum of the above coarse and capillary pores. It can be seen from Figure 7 that, the coarse and capillary porosity of MOS cement paste varied significantly with the content of SS. If the amount of SS was less than 0.5%, an increase of SS obviously reduces coarse and capillary porosity. Once the amount of SS becomes larger than 0.5%, however, both coarse and capillary porosity increase steadily, which decreased its softening coefficient, but increased mass loss, as consistently as those shown in Figure 6.
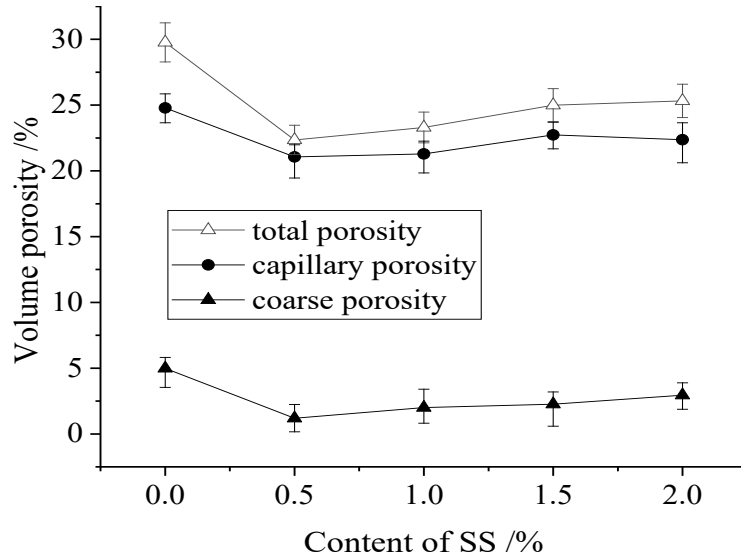
Figure 7 Volume porosity of MOS cement with different percentage of SS

3.6 Effect of SS on hydration phase composition and microstructure

The effect of SS on hydration phase composition and microstructure of hardened MOS cement at age of 28 day is shown in Figure 8. For a comparison, the XRD spectrum of MOS cement with 0.5% CA was also included in Figure 8. It is obvious that the positions of intensity peak of hydrated products of MOS cement with 0.5% of SS almost remained the same as those of MOS cement without SS. In other words, an addition of SS into MOS cement did not change its hydration phase composition. The content of $Mg(OH)_2$ phase and un-reacted MgO phase in hardened MOS cement samples with or without SS hardening are relatively high. While the stable 5-1-7 phase was formed and the content of $Mg(OH)_2$ decreases obviously in MOS cement with CA. This indicates that SS affects the properties of hardened MOS cement via changing the relative content of its hydration phases, but did not change its hydration phase composition.
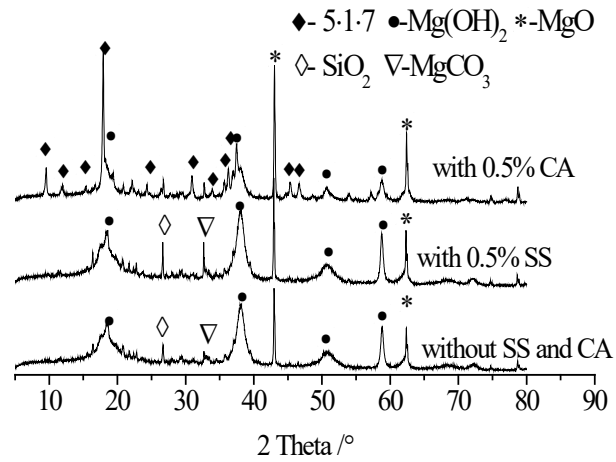
Figure 8 Effect of SS on hydration phase composition of MOS cement at 28-day age

Figure 9 shows TG and DTA (Differential Thermal Analysis) results of MOS cement without and with 0.5% SS during thermal decomposition. It can be seen that, although DTA values of MOS cement with SS was always smaller than those of the MOS cement without SS throughout the range of the temperature, their variation with the temperature were similar to each other. The peak values of the DTA of the MOS cements with and without SS during the heating process almost occurred at the same temperatures. In addition, Figure 9 shows that the total mass loss curve of MOS cement with and without SS almost coincide each other during decomposition. These findings further indicate that the phase category in hydrated MOS cement with and without SS are nearly the same in correspondence with the results shown in Figure 8.
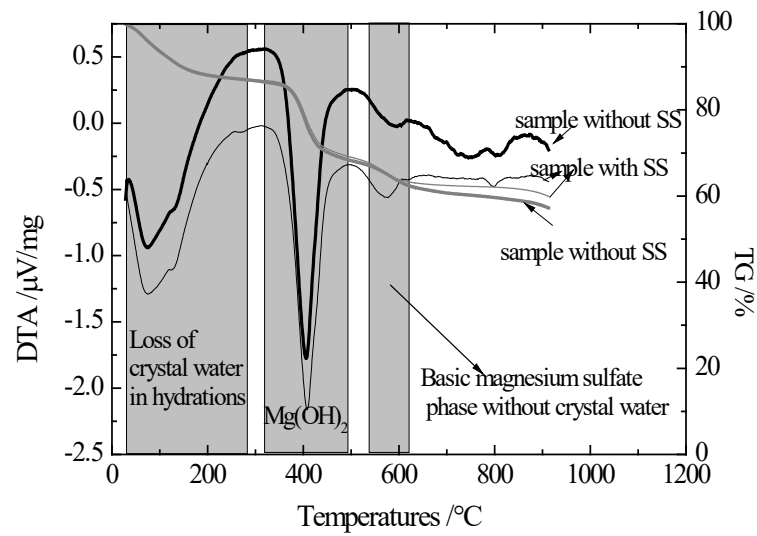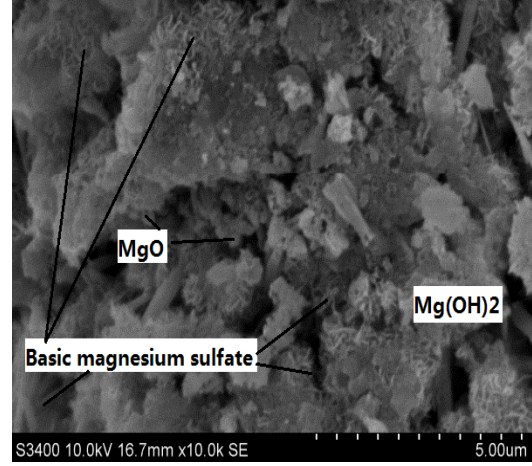
Figure 9 Effect of SS on DTA and TG results of MOS cement

Figure10 shows the SEM images of MOS cement with and without SS cured in air and in water immersion condition for the same curing age of 28 days. It can be seen from Figure10 (a) that a large amount of flaked $Mg(OH)_2$ phase and stubby basic magnesium sulfate phase were formed in hardened MOS cement that had no SS. In addition the corresponding structure of the hardened MOS cement with no SS becomes looser after 14-days' air curing and 14 days' water immersion, as shown in Figure10 (b). However it was observed from Figure10 (c) that there were much more refined flake crystal $Mg(OH)_2$ to form the more compact structures for the MOS cement with SS. This is why up to 0.5% of SS can improve the water resistance of hardened MOS cement paste.
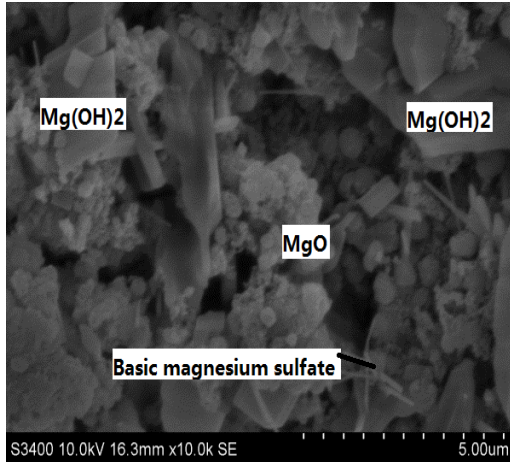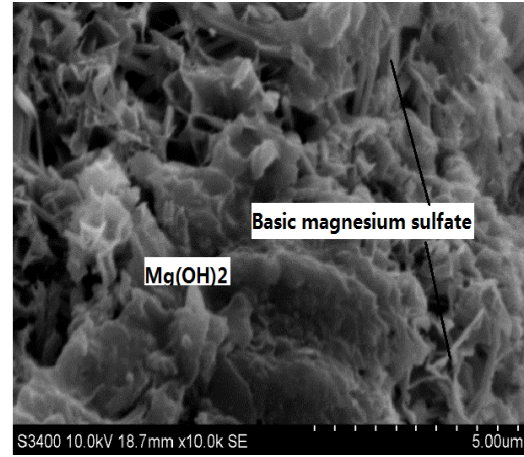
(a) No SS cured 28 days in air　　　　(b) No SS cured 14 days in water and 14 days in air
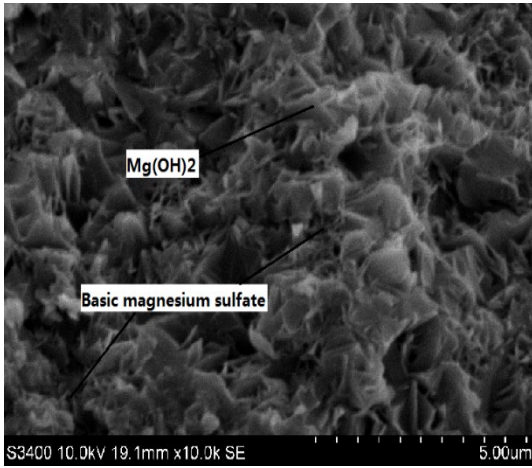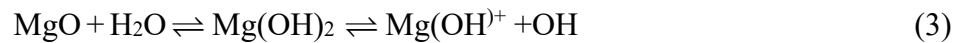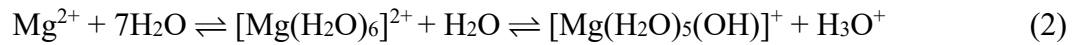
(c) With SS cured 28 days in air　　　　(d) With SS cured 14 days in water and 14 days in air

Figure10 SEM images of hardened MOS cement cured under different conditions

3.7 Effect of SS on hydration process of MOS cement

Actually before mixed with MgO, the $MgSO_4 \cdot 7H_2O$ dissolved in water and magnesium ions soon was leached in the form of $[Mg(H_2O)_6]^{2+}$ in the solution and then hydrolyzed to form $[Mg(OH)(H_2O)_5]^+$ as demonstrated in the following Eq.(2) :

$$Mg^{2+} + 7H_2O \rightleftharpoons [Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+ \qquad (2)$$

$$MgO + H_2O \rightleftharpoons Mg(OH)_2 \rightleftharpoons Mg(OH)^+ + OH \qquad (3)$$

When light-burned MgO was mixed with the magnesium sulphate solution (either with or without SS), it was slightly soluble in water as its slow hydration reaction to form water-insoluble $Mg(OH)_2$　as

shown in the Eq.(3). During hydration process, pH values varies, as shown in Figure 11. It can be seen that the concentration of OH⁻ increases in early stage, which further confirms what demonstrated in Eq.(3). Figure 11 also shows that the first pH peak value of the MOS with SS was greater than those of MOS without SS.
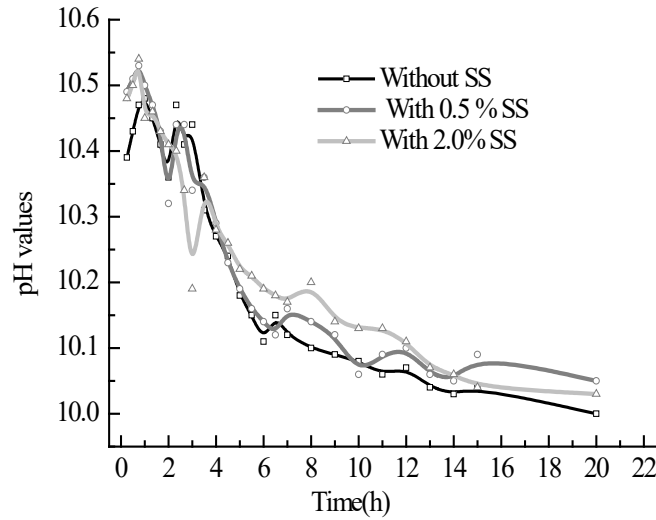

Figure 11 pH values of MOS cement with and without SS

When the concentration of OH⁻ was over saturated, the neutralization reaction between $[Mg(OH)(H_2O)_5]^+$ and OH⁻ occurred, as indicated in Eq.(4).

$$MgO + H^+ \rightarrow [Mg(H_2O)_6]^{2+} + OH^- \rightleftharpoons [Mg(H_2O)_5(OH)]^+ \tag{4}$$

In term of chemical reaction kinetics, soluble $[Mg(H_2O)_5(OH)]^+$ ion in Eq.(4) easily diffused in solution to increase the dissolution rate of MgO and thus promoted much more $[Mg(H_2O)_5(OH)]^+$ to be formed. However insoluble $Mg(OH)_2$ simultaneously formed, according to Eq.(3), and that easily accumulated in the surface of MgO particle to decrease the corresponding reaction rate.

The 70-hour heat evolution and accumulative heat of MOS cement with different amount of SS were measured by Isothermal Calorimetry and the results were shown in Figure 12. It can be observed from Figure12 (a) that the early hydration process can be divided into five stages. The first stage (OA) was taken as initial hydration period. Then stage AB was denoted as dormant period. And then stage BC is named as accelerated period until the second peak C. Next stage CD is called deceleration period and finally stage DE is stable period.
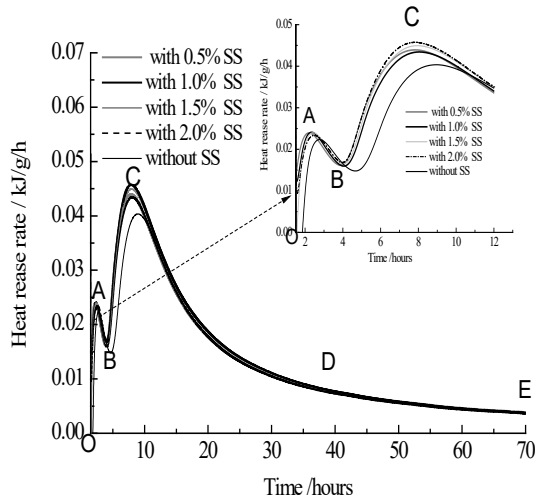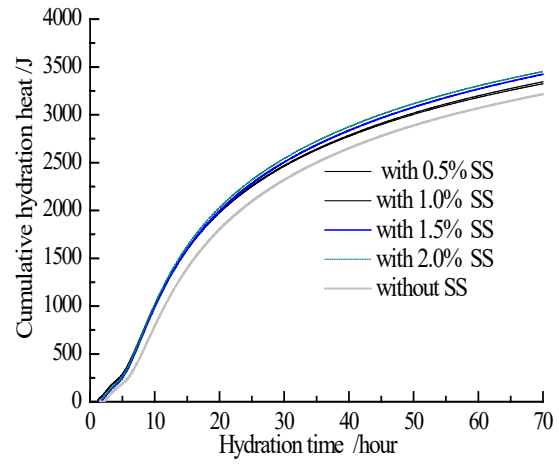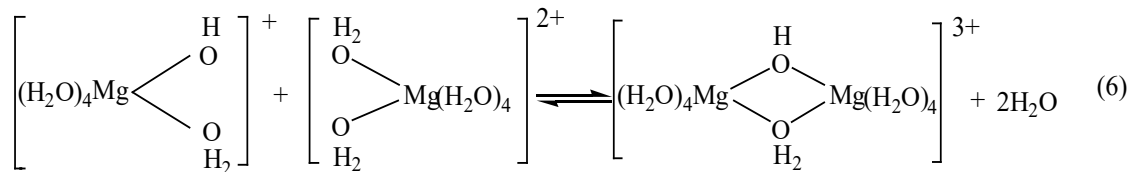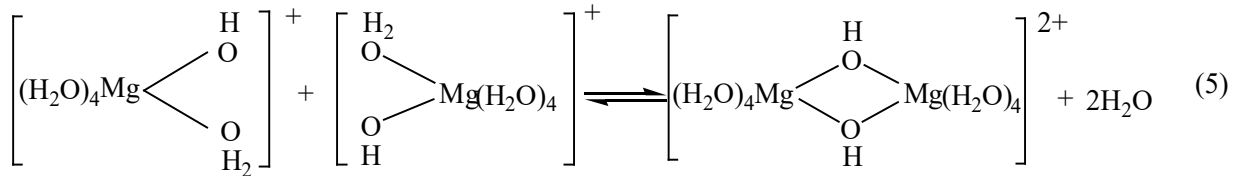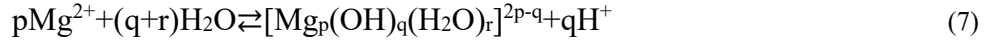
(a) Heat release rate   (b) Cumulative heat

Figure 12 Effect of SS on heat release of MOS cement paste

It is obvious that reaction in Eq.(2) promoted the first peak stage (OA). Then the insoluble $Mg(OH)_2$ was formed in Eq.(3) and coated on the surface of MgO particles, which prevented it from further reaction to a certain extent. Thus the hydration process entered the decline stage (AB), as shown in Figure 12 (a). With the process of hydrolysis reaction in Eq.(2), H_3O^+ ion concentration in solution increased and promoted to form a great amount of $[Mg(OH)(H_2O)_5]^+$ which made hydration process enter the accelerated period (BC). During this period the $[Mg(OH)(H_2O)_5]^+$ was polyhedral cationic ions taking Mg^{2+} as central ion in connection with OH^- and H_2O by coordination bond. With an increase of concentration of mononuclear $[Mg(OH)(H_2O)_5]^+$, its ligand OH^- was attracted by central Mg^{2+} of neighbouring $[Mg(OH)(H_2O)_5]^+$ to form its ligand by the established hydroxyl bridge which linked two or much more single-core polyhedral ions together as Eqs.(5) and (6). Conversely two central or more Mg^{2+} in $[Mg(OH)(H_2O)_5]^+$ can also be connected by sharing a H_2O ligand to form multi-core $[Mg_p(OH)_q(H_2O)_r]^{2p-q}$ as shown in Eq.(7).

$$\left[(H_2O)_4Mg\begin{array}{c}H\\O\\ \\O\\H_2\end{array}\right]^+ + \left[\begin{array}{c}H_2\\O\\ \\O\\H\end{array}Mg(H_2O)_4\right]^+ \rightleftharpoons \left[(H_2O)_4Mg\begin{array}{c}H\\O\\ \\O\\H\end{array}Mg(H_2O)_4\right]^{2+} + 2H_2O \quad (5)$$

$$\left[(H_2O)_4Mg\begin{array}{c}H\\O\\ \\O\\H_2\end{array}\right]^+ + \left[\begin{array}{c}H_2\\O\\ \\O\\H_2\end{array}Mg(H_2O)_4\right]^{2+} \rightleftharpoons \left[(H_2O)_4Mg\begin{array}{c}H\\O\\ \\O\\H_2\end{array}Mg(H_2O)_4\right]^{3+} + 2H_2O \quad (6)$$

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$$pMg^{2+}+(q+r)H_2O\rightleftarrows[Mg_p(OH)_q(H_2O)_r]^{2p-q}+qH^+ \tag{7}$$

These finally formed multi-core $[Mg_p(OH)_q(H_2O)_r]^{2p-q}$ in Eq.(7) associate with SO_4^{2-} to generate basic magnesium sulfate colloidal particles which gradually grew to be hydration crystals with larger aspect ratio. Finally the hydration rate begun to decrease over relatively long period as was called deceleration stage CD and stable stage DE in Figure12(a).

From Figure 12(a), it was observed that SS shortened the stage (OA) and stage (BC) and promoted the reactions in Eq.(2) and Eq.(3). It can also be seen from Figure 12 (b) that SS increases the early heat release rate and cumulative hydration heat of MOS cement. With an increase of SS content early heat release rate of MOS cement obviously increased, while the corresponding cumulative heat changed little. This finding can explained why SS reduced the initial setting time and paste fluidity of MOS cement shown in Figure 4. Furthermore, an addition of SS accelerated the reactions in Eq.(2) and (3) to increase the crystalline of basic magnesium ions in MOS cement paste. This helps to form the much refined and stable basic magnesium sulfate phase in hardened MOS cement.

4. Conclusion

From the analysis and discussion of the above experimental results, the following conclusions can be drawn below.

(1) An increase of SS as additive to MOS cement consistently reduces the dispersion and fluidity of MOS cement paste in water and effectively shortens its initial setting time. An up to 0.5% increase of SS significantly increases the long-term strength stability and water resistance of MOS cement.

(2) SS does not change the category of hydration phase composition in hardened MOS cement, but an up to 0.5% increase of SS does promotes the developments of better crystalline hydration products, refines the coarse pores, and thus forms much denser structures. This eventually leads to the improvement of water resistance and strength stability of MOS cement.

(3) SS accelerates the endothermic reaction in MOS cement paste by promoting the development of much more $[Mg(H_2O)_5(OH)]^+$, and hence increases the hydration process and the total hydration rate of early MOS cement paste. With SS content increase, the early heat release rate of MOS obviously increases, while cumulative heat changes little.

(4) In order to improve both water resistance and strength stability, the combined effects of SS with citrate acid or with phosphoric acid needs to be investigated and the corresponding compound modifying

mechanism needs further study by means of quantitative analysis techniques. Additionally further investigation is required to determine what to be the much stable refined crystal products in MOS cement with SS.

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Conflict of interest

Mingfang Ba received funding from Natural Science Foundation of China. Yanling Ma received the funding from Guangdong Province of China. The rest authors declare that they have no conflict of interest.

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