Study on properties of citric acid to magnesium oxysulfide cement

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Abstract. Magnesium oxysulfide cement (MOS) is an emerging building material. The application of MOS in practical engineering is affected by the low mechanical properties, which can now be modified by some admixtures. In this paper, the mechanical properties and hydration heat release of citric acid (CA)-modified MOS were studied, and the phase composition and microstructure of hydration products were analyzed by SEM and XRD. The results show that the addition of CA modified MOS can reduce MgO direct hydration of Mg(OH)2, promote the formation of a large number of needle-shaped 5Mg(OH)2 ·MgSO4 ·7H2O (5·1·7) phase crystals, and the compressive strength is greatly improved. When the CA dosage is 0.5%, the mechanics of MOS Best performance. The clotting time of the MOS modified with CA is slightly prolonged.

1. Introduction
Magnesium oxysulfide cement is a gas-hardening magnesium cementitious material prepared by mixing active magnesium oxide and magnesium sulfate [1]. MOS has the advantages of excellent performance of protective steel bars, light weight, fire resistance and high decorative value. It can be used to produce lightweight insulation boards and refractory materials [2-4]. However, the strength of magnesium oxysulfide cement is not ideal in practical use. The hydrated product structure of sulphur oxychloride cement is the main source of its strength. Studies by Dmediuk et al. [5] showed that the MgO-MgSO4-H2O ternary system produced four different phases at 30-120°C, which were 5Mg(OH)2 ·MgSO4 ·3H2O(5·1·3 phase), 3Mg(OH)2 ·MgSO4 ·8H2O(3·1·8 phase), Mg(OH)2 ·2MgSO4 ·3H2O(1·2·3 phase), Mg(OH)2 ·MgSO4 ·5H2O(1·1·5 phase). An Shengxia [6] modified the MOS with potassium chloride, which proved that potassium chloride can effectively improve the flexural strength of MOS and significantly prolong the clogging time of MOS, but it can not improve the compressive strength of MOS. Xu Changwei [7] have confirmed that the addition of water glass can effectively improve the water resistance of MOS. In this paper, the mechanical properties and setting time of citric acid modified MOS were studied. The phase composition and microstructure of hydration products were analyzed by SEM and XRD, which is important for the promotion of MOS in practical applications.

2. Experiment

2.1. Materials
(1) The magnesia used in this study is light-burned magnesia (LBM) obtained by calcining magnesite from Liaoning, China at 750°C -850°C , and the chemical composition of the powder is as
shown in Table 1. The specific surface area of the LBM was determined using the Brunauer-Emmett-
Teller (BET) method to be 13.56 m²/g.

Table 1. Chemical composition of light burned magnesia powder

| Component     | MgO | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | Loss on ignition |
|---------------|-----|-----|------|-------|-------|-----------------|
| Mass fraction/%| 81.21| 1.33| 5.67 | 0.18  | 0.52  | 11.09           |

(2) Magnesium sulfate. The magnesium sulfate (MgSO₄·7H₂O crystal) used in this study is analytically pure producing in Tianjin Kemi Europe Chemical Co, Ltd.

(3) Admixture: Sodium citrate (C₆H₅Na₃O₇·2H₂O) Phosphate, is made of Tianjin Dingshengxin Chemical Co. Ltd.

2.2. Sample preparation

The lightly burned magnesium oxide powder and magnesium sulfate heptahydrate were mixed at a molar ratio (α-MgO: MgSO₄) of 8, ball milling for 3 minutes using a planetary ball mill (fineness reaches D₉₀ <74 μm), then add 0%, 0.05%, 0.1%, 0.5% CA organic acid for mixing, the water-cement ratio (W/C) was 0.51 with water and stirred, and the mixed cement slurry was poured into a mold of 20 mm × 20 mm × 20 mm, and the mold was removed after 1 d of curing.

The compressive strength of the modified sulphur-oxygen magnesium cement is tested according to GB175—2007 《General Portland Cement》; The setting time is tested according to GB/T1346—2011 《cement Standard Consistency Water Consumption, Setting Time, Stability》; The heat release rate of cement is tested according to the direct method in GB/T12959—2008 《Test method for cement hydration heat》. The 1d and 28d sulphur magnesia cement specimens were analyzed by X-ray diffractometer (X’PROPer) for phase analysis. And the microstructure was observed on the fracture surface using a scanning electron microscope (JSM5610LV).

3. Results and discussion

3.1. Effect of sodium citrate on mechanical properties of MOS

Figure 1. Compressive strength of MOS under different CA dosage

The mechanical properties of cement are one of the important indicators reflecting the application of cement in practical engineering. Figure 1 is a graph showing the compressive strength of MOS under different CA dosages. The results show that with the increase of CA dosage, the compressive strength of MOS shows an upward trend. When the CA content is 0.1%, the compressive strength of 1d and 3d is higher than that of 0.5% CA. The 7d intensity is almost the same as the 0.5% dosage. This is because the incorporation of CA provide an effect of delaying the setting time. The early solidification rate of 0.5% CA was slower than that of 0.1% CA, so the early strength of 0.5% CA was lower than 0.1% CA. When the CA content is 0.5%, the compressive strength of 28d is the highest, the
compressive strength of 28d can reach 76.5MP, and the strength of 28d is 42.7MP higher than that of the control group, and the strength increase is about 127%. Because in the absence of CA, the following reactions will occur in the MOS system:

\[
\text{MgO}^{\text{solid}} + (x+1)\text{H}_2\text{O} \rightarrow \left[\text{Mg(OH)}(\text{H}_2\text{O})_x\right]^{\text{surface}} + \text{OH}^{-}\text{(aq)}
\]

\[
\left[\text{Mg(OH)}(\text{H}_2\text{O})_x\right]^{\text{surface}} + \text{OH}^{-}\text{(aq)} \rightarrow \text{Mg(OH)}_2^{\text{solid}}
\]

The addition of CA inhibits the formation of Mg(OH)_2 and promotes the formation of the 5·1·7 phase, thereby increasing the mechanical properties of MOS.

3.2. Effect of CA on MOS hydration products and micromorphology

![Figure 2.XRD patterns of MOS with different Ca dosages after curing 1(a).28(b) days](image)

(a) (b)
As can be seen in Figure 2, in the case where the CA content is 0.05%, 0.1%, or 0.5%, the diffraction peak height of the 5·1·7 phase in the XRD pattern of MOS is significantly increased. It is not directly related to the solubility of CA in magnesium sulfate solution. It is obvious that CA is suitable as a modifier for MOS cement. At the same time, we observed that the change of Mg(OH)$_2$ diffraction peak is also very obvious. In the sample which absence of CA, MgO directly hydrates to form Mg(OH)$_2$. After the addition of CA, the Mg(OH)$_2$ diffraction peak gradually decreases, and the diffraction peak of the 5·1·7 phase as the main intensity phase gradually increases, which is consistent with the above strength theory.

According to the SEM image in Figure 3, the number of needle-shaped 5·1·7 crystals in the image (a, b) without CA is very small, and with the increase of CA content, needle-shaped 5·1·7 crystal content increased significantly.

### 3.3. Effect of CA on MOS hydration heat release and setting time

Figure 4 shows the effect of different CA dosages on MOS setting time. The experimental results show that the addition of CA has a significant effect on delaying coagulation. For example, when no CA admixture is added, the initial setting time of MOS is 2h, and the initial setting time of MOS after adding 0.05%, 0.1%, and 0.5% CA is 2.5h, 3.75h and 4h, respectively, which is extended by 25%, 87.5% and 100%. As the amount of CA increased, the clogging time of MOS also showed an increasing trend. The final setting time of MOS also conforms to this law. When no CA admixture was added, the final setting time of MOS was 4.75h, and the final setting time of MOS after adding 0.05%, 0.1% and 0.5% CA was 5.5h, 7.5h and 8h, they were extended by 15.8%, 57.9% and 68.4% respectively.
Figure 5 shows the effect of different CA dosages on the heat release rate and cumulative heat release of MOS cement. The experimental results show that with the increase of CA dosage, the duration of induction period of MOS is obviously prolonged, and the acceleration period is delayed. For example, as shown in Figure 5(a), the MOS induction period duration of undoped CA is about 2.4h, and the MOS induction period duration of 0.5% CA is about 5.6h, which is extended by 133%. Therefore, as the amount of CA increases, the setting time of MOS is greatly shortened, which is consistent with the above conclusion. In Figure 4(b), the total amount of hydration heat release of the control group before 14h is higher than that of the sample with CA added. This may be due to the fact that without the addition of CA, MgO directly hydrates to form Mg(OH)₂, only a very small number of 5ꞏ1ꞏ7 phases are generated. In Figure 4(b), the total hydration heat of MOS is observed for about 24h. It can be seen that when the CA content is 0.1%, the total heat release is higher than 0.5% CA MOS. This is due to the fact that in the early stage of hydration around 1d, the 5ꞏ1ꞏ7 phase produced by 0.1% CA MOS hydration is more than that produced by 0.1% CA, so the heat release is greater, which corresponds to the 1d compressive strength theory mentioned above. With the continuation of hydration, the cumulative heat release of MOS with CA in Figure 4(b) was significantly higher than that of control group in about 48 hours. It can be inferred that the addition of CA promoted the hydration of MgO to form 5ꞏ1ꞏ7 phase. At the same time, the retarding effect of CA on MOS is more obvious when the content of CA is increased to 0.5%, which leads to the total heat release of hydration at about 48h is lower than that of 0.1% CA.

4. Conclusion

(1) CA as a modified admixture can effectively improve the mechanical properties of MOS. The increase in compressive strength is most obvious in the case of 0.5%, and the 28d compressive strength can reach 76.5MP.

(2) With the increase of the amount of CA admixture, the hydration induction period of the modified sulphur oxychloride cement is prolonged. The acceleration period lags, prolongs its condensation time, and delays the progress of its hydration reaction. When the dosage of CA admixture is 0.5%, the initial and final setting time of modified sulphur oxychloride cement is extended to 2h and 3.25h, respectively, and the duration of induction period is about 5.6h.

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