Effect of boric acid and lithium chloride on magnesium oxysulfate cement

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Abstract: To reduce the production cost of magnesium oxysulfate cement(MOS) in western China and the Salt Lake region, the use of salt lake by-products such as magnesium slag, etc. to prepare raw materials for MOS has become an effective way. However, the raw material of MOS obtained through this route contains some impurities, mainly boron and lithium. Therefore, to study the effect of boron and lithium elements on the performance of MOS, boron acid and lithium chloride were used to study the effect of boron and lithium on the setting time and compressive strength of MOS. And the influence of boric acid and lithium chloride on the hydration products and microstructure of MOS was discussed. The results show: Additives (boric acid and lithium chloride) did not change the MOS hydration phase and the micro-morphology, but delayed the MOS hydration process and increased MOS initial setting and final setting time, resulting in a decrease of the MOS's early compressive strength, but had no effect on the MOS's later compressive strength.

1. Introduction

MOS is usually formed by reacting lightly burned magnesium oxide powder with a certain concentration of magnesium sulfate solution[1,2]. The cement is characterized by fast setting and hardening, good adhesion, excellent fire resistance and corrosion resistance, etc. Compared to magnesium oxychloride cement(MOC), it has the advantages of low corrosiveness to rebar, difficulty in absorbing moisture and returning to halogen, but its low mechanical strength limits its application.[3]

To improve the defect of low compressive strength of MOS cement, Wang[4] proposed that the method of adding citric acid to cement can obtain a new type of cement with a strength higher than that of MOS. Zhu[5] proposed that the addition of phosphate, sucrose and boric acid to the thiomagnesian cement can also improve the strength of MOS. Deng[1] proposed that the addition of an S-type admixture to the oxysulfur cement can significantly improve the strength of MOS, and its strength can reach 100 MPa, which is close to the strength of MOC. The admixture changed the hydration phase of the oxysulfite cement, which produced a new hydration phase. The modified MOS overcomes its shortcomings of low compressive strength and has been vigorously developed. It has been widely used in the production of interior and exterior wall decorative panels, thermal insulation panels, fireproof panels, and door cores. Plates, flower pots, containers, crafts, etc.[6] The active magnesia required to prepare the oxysulfite cement is usually obtained by calcining magnesite at 700–900°C. The calcination temperature of this active magnesia is relatively low (as compared with the heavy magnesia used for the refractory material), so it is said the light burning powder. Yet, the distribution of magnesite in the world is relatively concentrated.[7-9] For example, although China has a large amount of magnesite, about 90% is concentrated in Liaoning Province.[10-11] Therefore, this will inevitably lead to higher production costs for producing MOS products in the western region and other regions. And the magnesite resource in the...
world are always limited. So it is important to find alternative material to replace magnesite. Based on this, the search for a low-cost magnesium oxide resource to replace light-burned powder in whole or in part will contribute to the promotion of preparation of magnesium oxysulfate cement.

But the use of salt lake by-products to prepare raw materials of MOS will contain some impurities, mainly boron and lithium. Therefore, to study the effect of boron and lithium elements on the performance of MOS, boron acid and lithium chloride were used to study the effect of boron and lithium chloride on the setting time and compressive strength of MOS. And the influence of boric acid and lithium chloride on the hydration products and microstructure of MOS was discussed. At the same time, it also provides some theoretical basis for the development of MOS in western China.

2 Materials and methods

2.1 Materials

The magnesia used in this study are analytical pure light magnesium oxide (APM) and light-burned magnesia (LBM). APM is from Shanghai Tongya Chemical Technology Development Co., Ltd., in which the content of MgO is more than 98%. LBM is obtained by calcining magnesite from Liaoning, China at 750°C, and the chemical composition of the LBM analyzed with X-ray fluorescence (XRF, ZSX Primus II) is listed in Table 1. The specific surface area of the LBM was determined using the Brunauer-Emmett-Teller (BET) method to be 11.73 m²/g. The D50 and D90 of the LBM powder were analyzed using the Malvern laser method with ethanol as the dispersant to be 22 lm and 75 lm, respectively. According to Dong's[12] report, Only active MgO can react with water to form Mg(OH)₂ for 3h at 105°C. Based on this viewpoint, we can determine the content of active MgO in LBM by Eq. (1), and the content of active MgO in APM or LBM were determined to be 72% and 58%, respectively.

Analytical purity of trisodium citrate dihydrate (as an additive, C₆H₅Na₃O₇ꞏ2H₂O, CA) and magnesium sulfate heptahydrate (MgSO₄ꞏ7H₂O) were purchased from Tianjin Dingshengxin Chemical Industry Co., Ltd.

Here, m₁ and m₂ are mass of LBM before and after reacting with water for 3 h at 105°C, respectively.

\[ W_{(MgO)} = \left( \frac{m_1 - m_2}{m_1} \right) \times \frac{M_{MgO}}{M_{H₂O}} \times 100\% \]  

-----(Eq.1)

Table 1. Chemical composition of lightly-burned magnesia powder

| Component  | MgO  | CaO  | SiO₂ | Al₂O₃ | Fe₂O₃ | CO₂   |
|------------|------|------|------|-------|-------|-------|
| Mass fraction (wt. %) | 80.20 | 1.30 | 6.07 | 0.15  | 0.41  | 11.87 |

2.2 Sample preparation

The a-MgO/ MgSO₄ molar ratio for the magnesium-oxysulfide cement set in this study was 7. CA is an additive added in an amount of 1% of the mass of APM or LBM. The content of boric acid is 1% of the mass of APM or LBM. The content of lithium chloride is in accordance with the mass of lithium in lithium chloride as 0.25% of the mass of APM or LBM. First, MgSO₄ꞏ7H₂O is dissolved in water to form a magnesium sulfate solution having a MgSO₄ content of 25%. Second, the weighed sodium citrate dissolved in a certain mass of magnesium sulfate solution to form a mixed solution. Next, the active magnesium oxide and boric acid or lithium chloride were added to a certain mass of magnesium sulfate solution, and the mixture was stirred to form a MOS cement paste. Finally, the paste into the 20 × 20 × 20 mm³ of the steel mold, the temperature is 20 °C ± 2 °C, relative humidity of 35% ± 5% of the environment, maintenance 24h demolition.

Symbol Description: The blank sample of raw material LBM is labeled LBM control, the sample added with boric acid is labeled as LBM B-1%, and the label added with lithium chloride is LBM
Li-0.25%. The blank sample of raw material APM is marked as APM control. Samples of boric acid are labeled as APM B-1% and lithium chloride is labeled as APM Li-0.25%.

2.3 Sample analysis
Compressive strength of MOS cement with reference to the provisions of GB / T17671-1999 prescribed method, the maximum load of 300kN constant stress automatic cement pressure testing machine, the loading speed of 0.3kN/s test its age compressive strength. Test specimens of finished strength, grind to D90<35μm. The crystal phase composition was tested in an X-pert Pro with a Cu target (λ= 0.15418 nm), accelerated pressurization setting Is 30 kV, the range of 2θscan is 5~70°. MOS samples were analyzed by scanning electron microscopy (SEM, JSM-6300). Hydration of cement hydration measurement using TY12959-08 hydrometer in accordance with the provisions of GB / T12959-2008 direct method of measurement. The cement coagulation time, according to Chinese standard methods, the use of Vicat apparatus determination: initial setting time is defined as the initial pouring needle to the distance from the bottom mold 5±1mm experienced specimen. Final setting time for the diameter of 5mm final coagulation needle can not leave obvious signs of time.

3 Results and discussion

3.1 Effect of Boric Acid and Chloride Oxidation on the Setting Time of MOS Cement
The setting time of cement is one of the important performance indicators of cement. Figure 1 shows the effect of boric acid and lithium chloride on the MOS setting time. It can be seen from the picture that boric acid and lithium chloride retard the initial setting and final setting time of MOS cement, and the retardation effect of boric acid is more obvious. For LBM, the initial setting and final setting time of the control were 268 min and 603 min, respectively. With the addition of lithium chloride, the initial and final setting times were increased by 9.7% and 9.6%, respectively. After the addition of boric acid, the initial and final setting times were increased by 66.1% and 47.6%, respectively. For APM, the initial setting and final setting time of the control were 337 min and 811.9 min, respectively. With the addition of lithium chloride, the initial setting and final setting times increased by 2.4% and 3.6%, respectively. After the addition of boric acid, the initial and final setting times increased by 74.5% and 28.7%, respectively. Thus, we found that the retardation effect of boric acid on APM is more pronounced than that of LBM. The reason for this phenomenon is mainly related to the MOS hydration process, and we will examine and explain in detail in 3.2 later.

3.2 Effect of Boric Acid and Chloride Oxidation on the Hydration Process of MOS Cement

![Figure 1. Setting time of MOS after mixing boric acid or lithium chloride](image-url)
Figure 2. Heat release rate of MOS after mixing boric acid or lithium chloride (a:LBM; b:APM).

The hydration history and the setting time of cement are closely related and mutually corroborated. According to Wu et al.\cite{9} report, the hydration process of MOS cement can be divided into five periods: pre-induction, induction, acceleration, deceleration, and stationary. Fig. 2 shows the MOS hydration heat release curve. From Fig. 2, it can be clearly seen that the addition of boric acid and lithium chloride delayed the MOS hydration process compared to the blank sample. The effect of boric acid was most obvious. For Figure 2(a), boric acid makes the induction period of MOS up to 20.5 hours, while the induction period of blank sample is only about 9.7 hours. Therefore, the acceleration period, deceleration period and plateau period of MOS cement are also correspondingly delayed. Similarly, the phenomena reflected in Figure 2(b) and Figure 2(a) are consistent. However, since the Mg activity in APM is higher than the activity of Mg in LBM, the rate of heat release and the time of MOS cement are correspondingly accelerated. In summary, the main reason for adding boric acid and lithium chloride to increase the setting time of MOS cement is that the additive delays the MOS hydration process. In addition, compared to the LBM specimens, the main reason for the longer cement setting time of the APM specimens is: the water-cement ratio of the APM specimens is greater than the water-cement ratio of the LBM specimens.

3.3 Effect of Boric Acid and Chloride Oxidation on Compressive Strength of MOS Cement

Figure 3. Compressive strength of MOS after mixing boric acid or lithium chloride.
The compressive properties of cement are also one of the important indicators of cement performance. Figure 3 shows the compressive strength of MOS. It can be seen that the addition of boric acid and lithium chloride both reduce the compressive strength of MOS, and the effect of boric acid is the most obvious. For the LBM specimens, the 3d and 28d strengths of the blank specimens were 38.5 MPa and 80 MPa, respectively. After the addition of boric acid, the strength of MOS at 3d and 28d was 23.6 MPa and 73.5 MPa, respectively, decreased by 31.9% and 8.1%. After the addition of lithium chloride, the strengths of MOS at 3d and 28d were 34.4 MPa and 79 MPa, respectively, which did not change substantially. For the specimens of APM, the effect of boric acid on the initial compressive strength of MOS is very obvious, mainly because boric acid prolongs the setting time of MOS. The above viewpoint will be further proved in 3.4.

3.4 Effects of Boric Acid and Chloride Oxidation on Hydration Products and Micromorphology of MOS Cement

![Figure 4](image-url)

**Figure 4.** XRD diffractogram of MOS after mixing boric acid or lithium chloride (a:LBM; b:APM)

![Figure 5](image-url)

**Figure 5.** EM images of MOS cement after mixing boric acid or lithium chloride (a:LBM control b:LBM Li-0.25% c:LBM B-1%)

Figure 4 shows the XRD diffraction pattern of MOS. It can be seen that the addition of boric acid and lithium chloride did not change the MOS phase. For APM samples, a small amount of Mg(OH)₂ production is mainly due to the high molar ratio of MgO/MgSO₄, leaving MgO remaining in the early hydration period, resulting in the gradual conversion of MgO to Mg(OH)₂ at the later stage of MOS hydration. This is also the reason why the compressive strength of the APM specimen is slightly lower than that of the LBM specimen. Figure 5 shows the SEM of MOS. It can be seen that the main crystalline phase of MOS is pin-like after the addition of boric acid and lithium chloride. Therefore, the admixture did not change the morphology of the MOS hydrate phase(5Mg(OH)₂·MgSO₄·7H₂O, 517 phase).
4 conclusion
This dissertation mainly studies the effect of boric acid and lithium chloride on MOS performance, and has obtained several conclusions:

1. The incorporation of boric acid and lithium chloride did not change the hydrated phase and the micromorphology of MOS.
2. Boric acid and lithium chloride delay the hydration process of MOS, and boric acid delay effect is obvious.
3. Boric acid and lithium chloride increase the initial setting and final setting time of MOS.
4. Boric acid and lithium chloride reduce the early compressive strength of MOS, but have no effect on the compressive strength of MOS in the later period, among which boric acid has a great influence on the early compressive strength.

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