Study on water resistance modification of magnesium oxysulfate cement

Yafei Hao 1, Chao Li 1 and Fengqing Zhao 1, 2, *

1 Department of Chemical Engineering, Hebei University of Science & Technology, Shijiazhuang, 050018, China
2 Hebei Engineering Research Center of Solid Waste Utilization, Shijiazhuang, 050000, China

*Corresponding author e-mail: zhaofq3366@126.com

Abstract. Large-scale applications of magnesium oxysulfate (MOS) cement in civil engineering have been restricted by its defects such as low early strength and poor water resistance. In this study, some additives were used to modify MOS cement. The results show that phosphoric acid and citric acid can effectively increase the mechanical strength of MOS cement with the dosage of 0.6% and 0.3% respectively. The addition of fly ash and waste GFRP fiber contribute little for the mechanical strength of MOS cement, but has positive effect on water resistance improvement. Silica fume can significantly improve the mechanical properties and water resistance of MOS cement as well.

1. Introduction

MOS cement belongs to air-hardening cementitious material, which is prepared from magnesium oxide and magnesium sulfate solution. It has the advantages of high volume stability, light weight, low fire resistance and good decorative effect, and can be applied to many fields such as construction and decoration materials [1]. However, low strength and poor water resistance limit the application of MOS cement.

Wang Haiping [2] modified the MOS cement by adding different additives to make block stable in air which has high compressive strength. Wu Chengyou [3] used organic acid to modify the MOS cement. The softening coefficient of the cement increased from 0.40 to 1.03. Liu Tao et al. [4] found that single admixture can not improve the water resistance of MOS cement paste effectively. Some scholars [5-8] studied industrial wastes such as fly ash and silica fume to study MOS cement, and obtained desired results.

High modification costs and strengths loss have plagued the development of the MOS cement industry. Therefore, this study is aiming at modifying MOS cement materials by adding different admixtures, in order to increase mechanical strength and water resistance.
2. Experimental

2.1. Raw materials
Anhydrous magnesium sulfate: purity≥99.0%. Magnesium oxide: active MgO content 53.6% [9]. The chemical composition is shown in Table 1.

| Composition | MgO | Al₂O₃ | SiO₂ | CaO | Fe₂O₃ | Others |
|-------------|-----|-------|------|-----|-------|--------|
| Content     | 89.14 | 0.68 | 7.16 | 1.87 | 0.71 | 0.44    |

Citric acid, phosphoric acid and silica fume used in the experiment are all bought on the market. Fly ash is provided by Sijiazhuang Xibaipo power plant. Waste GFRP fiber with the length of 0–2mm is provided by Hengshui Jitong Equipment Co. Table 2 shows the chemical composition of some raw materials.

| Raw materials  | Fe₂O₃ | Al₂O₃ | SiO₂ | CaO | MgO | K₂O | SO₃ | Others |
|----------------|-------|-------|------|-----|-----|-----|-----|--------|
| Silica fume    | 7.34  | 0.47  | 82.37 | 6.06 | 3.02 | —   | —   | —      |
| Fly ash        | 5.4   | 36.51 | 49.43 | 4.66 | 0.83 | 0.87 | 0.74 | —      |

2.2. Methods

2.2.1. Preparation of MOS cement. Dissolve magnesium sulfate in water; add magnesium oxide, additives, stirring well. The prepared fresh slurry was cast in molds with a size of 40mm×40mm×160mm through vibration compaction. The specimens were then sealed with polyethylene film and air cured at room temperature. After 24h, the specimens were released from the mold and natural curing 7d. Some blocks were tested for flexural strength and compressive strength. The others were put into water and soaked for 7d before strength test.

2.2.2. Performance Test. The mechanical strength values are tested according to GB/T17671-1999. The softening coefficient is used to characterize the water resistance of the specimen. After cured for 7 days, some specimens are used to test compressive strength (Rco), the others are soaked in water for 7 days, whose average compressive strength is Rcw. The softening coefficient (Kcn) of the specimen is calculated according to the formula:

\[ Kcn = \frac{Rcw}{Rco} \]  

3. Results and discussions

3.1. Effect of phosphoric acid
The dosage of phosphoric acid ranged from 0 to 1.0%. The mechanical strength and water resistance of MOS were measured. See Fig. 1 and Fig. 2.

When the phosphoric acid content is 0.8%, the strength of the modified MOS cement reaches the highest value. Fig. 2 shows that the compressive strength of the block after soaked in water is higher with the softening coefficients above 1.0 when the dosage is at 0-0.6 %. It can be seen that the addition of phosphoric acid can improve the water resistance of MOS cement.
3.2. Effect of citric acid
The dosage of citric acid ranged from 0-1.5%. The mechanical strength and water resistance of MOS were measured. See Fig. 3 and Fig. 4.

![Figure 1. Effect of phosphoric acid on mechanical strength](image1)

![Figure 2. Effect of phosphoric acid on water resistance](image2)

![Figure 3. Effect of citric acid on mechanical strength](image3)

![Figure 4. Effect of citric acid on water resistance](image4)

It can be seen from Fig. 3 that citric acid significantly improved the compressive and flexural strength of the MOS cement. And with the increase of citric acid content, the strength first increases and then tends to be gentle. Fig. 4 shows that when the dosage of citric acid is more than 0.9%, the mechanical strength after soaked in water is higher than dry curing sample, and the softening coefficient is also increased.

3.3. Effect of fly ash
Fly ash is a solid waste produced from the combustion of pulverized coal in thermal power plants. It can be seen from Fig. 5 that when the amount of fly ash is between 0 and 3%, the strength of the block gradually increases. When the amount of the fly ash is above 3%, the flexural strength decreases; the
compressive strength remains stable. According to Fig. 6, the compressive strength of the block after soaking in water is higher than dry curing samples. That is to say, the addition of fly ash improved the softening coefficient of MOS cement.

**Figure 5.** Effect of fly ash on mechanical strength

**Figure 6.** Effect of fly ash on water resistance

### 3.4. Effect of waste GFRP fiber

The dosage of waste GFRP fiber ranged from 0 ~ 2.5%. The mechanical strength and water resistance of MOS were measured. See Fig. 7 and Fig. 8.

**Figure 7.** Effect of waste GFRP fiber on mechanical strength

**Figure 8.** Effect of waste GFRP fiber on water resistance

The results show that with the increase of powder fiber content, the flexural and compressive strength of blocks tends to increase. It can be seen from Fig. 8 that the compressive strength of samples after soaking in water are gradually increased with the increase of the amount of the powder, and the softening coefficient is also increased as well.
3.5. Effect of silica fume

Silica fume is an industrial dust produced from the reduction reaction of high-purity quartz and coke in a high-temperature electric arc furnace (2000°C). The particles are extremely fine, with large specific surface area and high volcanic activity, and are often used in the cement and concrete.

Figure 9 shows that the compressive and flexural strength of MOS cement is slightly increased with the increase of silica ash content. After soaking in water, the compressive strength of the sample is significantly higher than that of dry curing samples. That is to say, silica fume has significant positive effect on water resistance of MOS cement.

4. Conclusion

(1) MOS cement has characteristics of light weight, good decorative effect, suppressing frost and well rebar-protection performance, making it has more advantages on producing decoration materials. However, large-scale applications of MOS cement in civil engineering have been restricted by its defects such as low early strength and poor water resistance.

(2) In order to improve the performance of the MOS cement, additives such as phosphoric acid, citric acid can be used as effective additives. When the phosphoric acid content is 0.6% and the citric acid content is 0.3%, the mechanical strength of the MOS cement is obviously improved, and the water resistance is also improved significantly as well.

(3) Some industrial solid waste or by product can also be used as strengthening agents or modifier for water resistance for MOS. The addition of fly ash and waste GFRP fiber contribute little for the mechanical strength of MOS cement, but effective for water resistance improvement, especially, the cost can be greatly reduced. The addition of silica fume not only significantly improves the mechanical properties but also improved water resistance of MOS cement.

References
[1] Lingxiao Li, Xiongmu Chen, and Fengqing Zhao. Study on modification of magnesium oxychloride cement. Earth and Environmental Science, 2018, 170.
[2] Haiping Wang, Xueying Xiao, Jidong Wang, Quanyou Zhang, Chenggong Chang, Weixin Zheng. Modification of admixture to magnesium oxysulfate cement[J]. Journal of Salt Lake Research, 2013, 21 (1): 44-49.
[3] Chengyou Wu, Hongfa Yu, Jing Wen, Jinmei Dong. Study of phase compositions and properties of modified magnesium oxysulphate cement[J]. New Building Materials, 2013 (5): 68-72.
[4] Tao Liu, Yalin Zheng, Pei Du, Haiyan Lin, Min Han, Yujiang Wang. The preparation of high-
strength and water-resistant magnesium oxysulfate cement[J]. Sichuan Building Science, 2013, 39 (3): 214-217.

[5] Hongfa Yu. Study on Mechanism of Silica Fume Modified Magnesium Oxychloride Cement[J]. Bulletin of the Chinese Ceramic Society, 1994, 6: 58-62.

[6] Wu C, Zhang H, Yu H. The effects of alumina-leached coal fly ash residue on magnesium oxychloride cement[J]. Advances in Cement Research, 2013, 25 (5): 254-261.

[7] Hua Zhao, Yongwei Wang, Bowen Guan etc. Effect of Fly Ash on Early Properties of Magnesium Oxychloride Cement. Materials Review, 2015, 29 (18): 117-121.

[8] Chan J, Li Z J. Influence of fly ash on the properties of magnesium oxychloride cement [J]. In: Proceedings of the International Symposium of Measuring, Monitoring and Modeling Concrete Properties, 2006, (3): 347-352.

[9] Jianbo Fu. Some Factors Influencing Properties of Modified Magnesium Oxychloride Cement and its Modifying Mechanism[D]. Shan Tou University. 2005.