Effect of Different Additives Addition on Basic Magnesium Sulfate Cement Composite Sheet

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Abstract. Study the effects of different admixtures and different dosages on Basic Magnesium Sulfate Cement (BMS) composite sheets, the effects of sodium citrate and phosphoric acid on the flexural strength and compressive strength of basic magnesium sulfate cement sheets were studied, XRD and SEM were used to analyze the composition and microstructure of hydration products. The results show, the addition of admixtures has a great influence on the properties of composite sheets. Adding the corresponding proportion of admixture to the plate, the mechanical properties are significantly improved. Therefore, the properties of sheet metal can be greatly improved by choosing appropriate additives.

1. Introduction

The main raw materials of Basic Magnesium Sulfate Cement (BMS) are magnesium oxide (MgO) and magnesium sulfate (MgSO₄·nH₂O). From its composition, it is similar to Magnesium Oxysulfate Cement (MOS). All belong to MgO-MgSO₄·H₂O ternary cementitious system. The difference is that the basic magnesium sulfate cement is a magnesium cementitious material which is superior in strength, water resistance, salt resistance and anti-aging property by the admixture technology. From the previous studies¹⁻², it was confirmed that the main strength phase of the basic magnesium sulfate cement was 5Mg(OH)₂ · MgSO₄ · 7H₂O (5-1-7 phase). Deng Dehua believes that adding a predetermined admixture to MOS can increase its strength and achieve a strength of 100 MPa. The strength of MOS and MOC is similar, even higher than that of MOC, because the admixture is added to form a new hydration phase, ie BMS.

In this paper, basic magnesium sulfate cement powder was prepared by direct ball milling, and a certain amount of sodium citrate and phosphoric acid were used as admixtures to prepare basic magnesium sulfate cement composite sheet. Study on its compressive strength, flexural strength and phase change under different dosages. The influence of different admixtures and different dosages on basic magnesium sulfate cement composite sheet is analyzed. The purpose is to find the best admixture and dosage to improve the mechanical properties of basic magnesium sulfate cement composite sheet, and provide some technical and theoretical guidance for the promotion of basic magnesium sulfate cement and its products.

2. Experiment

2.1. Raw material

(1) Light burned dolomite powder: All of them are produced by Dashiqiao, Liaoning Province. Its chemical composition is shown in Table 1. Due to the different storage time of light burned magnesia powder, the content of active oxidation (a-MgO) was determined according to rapid water law.
Table 1. Chemical composition of light burned dolomite powder.

| Component | MgO  | CaO  | SiO$_2$ | Fe$_2$O$_3$ | Al$_2$O$_3$ | I.L. |
|-----------|------|------|---------|-------------|-------------|------|
| Mass fraction (wt. %) | 80.20 | 1.30 | 6.07 | 0.41 | 0.15 | 11.87 |

(2) Magnesium sulfate: Analysis of pure MgSO$_4$·7H$_2$O crystal is taken from Tianjin Kemiou Chemical Co., Ltd.

(3) Admixture: Sodium citrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O), Phosphate, is made of Tianjin Dingshengxin Chemical Co., Ltd.

(4) Sawdust: Poplar sawdust.

2.2. Preparation of BMS

At present, magnesium cement is mostly prepared by mixing magnesium or magnesium sulfate solution with light burning powder [2]. In order to make BMS better promoted, this paper uses direct ball milling to prepare BMS powder. When the content of sodium citrate and phosphoric acid is 0.1%, 0.33%, 0.5% and 1% of cement, the residual sieve of square-hole sieve with light-burned powder, magnesium sulfate and ball milling for 5-10 minutes to 180 microns according to a certain mix ratio is less than 10%.

2.3. Preparation of BMS sheet

Mixing BMS powder, wood chips and water in a certain proportion. The cement mortar mixer was stirred at low speed for 1 minute, stirred at high speed for 30 seconds, and stirred to form a slurry. The slurry was layered into a 40 mm × 40 mm × 160 mm steel test mold, and a glass fiber mesh cloth was laid. The distance between the mesh cloth and the lower surface of the test piece was 5 ± 0.3 mm. Shaping by vibration for 1 minute on the shaking table of cement mortar, sealed with fresh-keeping film, and maintained at room temperature for 1 day before demoulding, and continued to be maintained in the indoor atmosphere until the prescribed age.

3. Results and discussion

3.1. Effect of different dosage of phosphoric acid on the strength of BMS sheet

Figure 1. Effect of different content of phosphoric acid on the strength of composite Sheets.

Figure 1. shows the effect of different dosages on the strength of BMS composite sheets when phosphoric acid is used as an additive. It can be seen that the addition of additives has a great influence on the strength of composite sheets. It can be seen from Figure 1. (a) that the compressive strength of BMS composite sheets increases with age. When phosphoric acid was not added, the compressive strength of BMS composite sheet at 3d and 28d was 10.22MPa and 17.32MPa, respectively. When phosphoric acid is added, the compressive strength increases first and then decreases with the increase of phosphoric acid content. The compressive strength is the highest when the dosage is 0.33%, the compressive strength values of 3d and 28d are 12.54 MPa and 40.67 MPa,
respectively. Compressive strength of BMS composite sheet increased by 22.7% and 134.8% respectively on 3d and 28d compared with that without phosphoric acid. It can be seen from Figure 1. (b) that the increasing trend of flexural strength of BMS composite sheet is similar to that of its compressive strength when phosphoric acid is added, when the content of phosphoric acid is 0.33%, the flexural strength is the highest, the compressive strength of 3d and 28d increased by 8% and 75.9% respectively. Therefore, phosphoric acid has an obvious effect on improving the mechanical properties of BMS cement composite sheets.

3.2. Effect of different dosage of sodium citrate on the strength of BMS sheet

![Figure 2](image)

(a) Compressive strength
(b) Flexural strength

Figure 2. Effect of different dosage of sodium citrate on the strength of composite Sheet.

Figure 2. shows the effect of different dosage of sodium citrate on the strength of BMS composite sheet. It can be seen that the addition of additives has a great influence on the strength of composite sheets. It can be seen from Figure 2.(a) that the compressive strength of BMS composite sheets increases with age. When sodium citrate was not added, the compressive strength of 3d and 28d was 10.25 MPa and 17.35 MPa, respectively. When sodium citrate is added, the compressive strength increases first and then decreases with the increase of the content of sodium citrate, when the dosage is 0.5%, the compressive strength is maximum, compressive strength values for 3d and 28d are 27.2MPa and 38.8MPa, respectively. Compressive strength of BMS composite sheets at 3d and 28d increased by 165% and 123.6% respectively compared with that without sodium citrate. From Figure 2. (b), it can be seen that the increasing trend of flexural strength of BMS composite sheet is similar to that of its compressive strength when phosphoric acid is added. When the content of phosphoric acid is 0.5%, the flexural strength is the highest, the compressive strength of 3d and 28d increased by 105% and 107%, respectively. Therefore, sodium citrate has a significant effect on improving the mechanical properties of BMS composite sheets.

3.3. Effect of sodium citrate on hydration products of BMS composite sheet

![Figure 3](image)

Figure 3. XRD pattern of different dosages of sodium citrate.
Figure 3. is an XRD pattern of different amounts of sodium citrate. It can be seen from the figure that the diffraction peaks of 5·1·7 phase and MgO are higher when 0.5% sodium citrate is added. Compared with the sodium citrate of more than 0.5% admixture, although the diffraction peak of 5·1·7 phase is high, there are also some diffraction peaks of Mg(OH)₂. Combining with figs. 1 and 2, it can be seen that when the admixture increases to a certain extent (0.33%), its strength decreases.

During the test, it was found that the admixture of additives had obvious retarding effect. When 0.5% of sodium citrate were added, the plate could not be demoulded normally because of the slow increase of strength. It can be seen that the admixture has a certain inhibitory effect on the hydration of a-MgO in the magnesium cement. The more the amount of the admixture, the more obvious the inhibition effect, which inevitably leads to the slow formation of the strength phase. Therefore, the admixture is not as good as possible. In this experiment, it is most preferable when the amount of sodium citrate is 0.5%.

Table 2. Phase change of composite sheets at different dosages (topas 4.2 fit).

| Admixture dosage/% | 517phase /% | Mg(OH)₂ /% | MgCO₃ /% | MgO /% |
|--------------------|-------------|------------|----------|--------|
| 0.1                | 65.52       | 9.74       | 11.56    | 11.17  |
| 0.33               | 73.03       | 8.61       | 7.52     | 10.84  |
| 0.5                | 76.66       | 10.08      | 6.91     | 5.48   |

Table 2. shows the results of quantitative analysis by topas 4.2. When the dosage is 0%, no 5·1·7 phase is formed in the hydration product, but a large amount of Mg(OH)₂ is formed. Therefore, it is a basic magnesium sulfate cement mixed with an admixture. Composite sheets have poor mechanical properties. When admixture is added, a large amount of 5·1·7 phase is formed, Mg(OH)₂, MgCO₃, and the remaining MgO is significantly reduced. Therefore, the admixture can effectively improve the mechanical properties of the basic magnesium sulfate cement composite sheet. When the admixture content is 0.5%, the resulting 5·1·7 phase is the most, and the remaining MgO content is the least. Therefore, the admixture can induce a-MgO to form a complexation reaction [3]-[5] as shown, and form a 5·1·7 phase.

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

(1)

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

(2)
Figure 5. Effect of sodium citrate on the morphology of BMS
(a, b control, c, d with 0.33% sodium citrate).

It can be seen from Figure 5. (a), (b) that the main hydration phase of BMS without adding an additive is Mg(OH)$_2$ crystal. Its micro-structure is relatively loose and has many pores, which is the main reason for the low strength of basic magnesium sulfate cement. When 0.33% of the admixture was added, the main hydration phase of BMS changed from Mg(OH)$_2$ to 5·1·7 phase. It can be seen from Figure 5. (c), (d) that the microstructure of the BMS hydrated with the admixture is dense, and there are a large number of needle-shaped 5·1·7 crystals at the pores, and the 5·1·7 phase is alkali. The high-strength phase in the magnesium sulfate cement, a large amount of 5·1·7 formation is the main reason for significantly improving the strength of the BMS composite sheet.

4. Conclusion
In conclusion, the addition of additives has a great influence on the properties of BMS composite sheets. When 0.33% of phosphoric acid is added to the plate as admixture, its compressive strength and flexural strength increase most significantly. When 0.5% sodium citrate is added to the plate as an admixture, its compressive strength and flexural strength increase most significantly. It can be seen that the appropriate amount of admixture has a significant effect on improving the mechanical properties of BMS cement composite plate. However, the excessive admixture has a certain inhibitory effect on the hydration of a-MgO in magnesium cement. The more the amount of admixture is, the more obvious the inhibition effect is, resulting in the slow formation of the strength phase. It can be seen that the selection of the appropriate amount of admixture can be greatly improve the performance of BMS sheet.

Acknowledgement
This study was supported by the National Natural Science Foundations of China (Grants no. 51662035) and applied fundamental research project of Qinghai Province (Grants no.2019-ZJ-7005) the Science and Key R&D and transformation planned project of Qinghai province (Grants no. 2019-NN-159) and S&T Foundation Platform of Qinghai Province(Grants no. 2018-ZJ-T01) and the teaching team of civil engineering safety technology of Qinghai University (Grants no. TD1804).
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