Study on the Effect of Water Reducing Agent on Dolomite-based Magnesium Sulfate Cement

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Abstract. Adding different types and amounts of water reducing agent to Dolomite-based magnesium sulfate cement (DBMSC), and analysing the effect of water reducing agent on DBMSC by studying its setting time, water reduction effect and mechanical strength. On the one hand, Experimental results show that adding water reducing agent to DBMSC has a retarding effect on dolomitic magnesium sulfate cement, and reduces the hydration heat of cement; on the other hand, the water reduction effect of the water reducing agent on DBMSC prepared by light burning dolomite is not too obvious, and even the mechanical strength of DBMSC is lowered.

1. Introduction
Basic magnesium sulphate cement is a new type of gas-hardening magnesium cementitious material, which is composed of active magnesium oxide, admixture and a certain concentration of magnesium sulfate solution. At present, the magnesium oxide raw material used for preparing the basic magnesium sulfate cement is mainly the light burning powder obtained by calcining magnesite at 750 °C - 850 °C. Due to the concentrated, uneven distribution and high price of magnesite reserves is, the use of light burned dolomite powder is calcined at 850 °C for 0.5 h of widely distributed and inexpensive dolomite replaces light burning powder, greatly reducing the production cost of its productsthe basic magnesium sulfate cement.

According to the research of the previous research group, the optimum raw material molar ratio (α-MgO/MgSO₄) for preparing dolomite-based magnesium sulfate cement (DBMSC) is 4, because light burned dolomite powder contains a large amount of CaCO₃, acting as a filling in the cement slurry, resulting in a lower fluidity of the cement slurry at the molar ratio of the raw materials. Therefore, this article adds different types and amounts of water reducing agent to DBMSC, and analyses the effect of water reducing agent on DBMSC by studying its setting time, water reduction effect and mechanical strength. Finally, analysing the reasons for the influence of water reducing agent on DBMSC, and providing 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: The dolomite used to produce light burned dolomite powder is calcined at 850 °C for 0.5 hours in this study is from Baoding City, Hebei Province, and its chemical composition is shown in Table1.
Table 1. Chemical composition of light burned dolomite powder

| Component | MgO  | CaO  | SiO₂ | Fe₂O₃ | Al₂O₃ | Na₂O  | Loss on ignition |
|-----------|------|------|------|-------|-------|-------|----------------|
| Mass fraction (wt. %) | 20.6 | 31   | 0.103| 0.110 | 0.0366| 0.0195| 48.1           |

(1) Magnesium sulfate: Analysis of pure MgSO₄·7H₂O crystal is taken from Tianjin Kemiou Chemical Co., Ltd.

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

2.2. Preparation of BMSC

The content of α-MgO of light burned dolomite powder can be determined by formula (1), which is 18%. MgSO₄·7H₂O is first dissolved in water to form a magnesium sulfate solution with a mass fraction of 25.0% (H₂O / MgSO₄ molar ratio is 20.0), mixing light burned dolomite powder with sodium citrate (the content of sodium citrate is 0.5% of light burned dolomite powder), then adding the prepared magnesium sulfate solution and tap water (the DBMSC cement water-cement ratio of this study is 0.36, and H₂O contains the amount of water contained in MgSO₄·7H₂O), mixing and stirring to form DBMSC cement slurry finally. The DBMSC cement slurry is placed in a 20 mm × 20 mm × 20 mm mold, which is removed after maintenance for 1 d in an environment of a temperature of 20 °C ± 3 °C and a relative humidity of 50% ± 5%.

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

In the middle: m₁ is the mass of light burned dolomite powder before adding water, m₂ is the quality of the light burned dolomite powder reacted with water after drying, M_{MgO} and M_{H2O} are respectively the relative molecular masses of MgO and H₂O, ω(CaO) is the content of free calcium oxide in light burning dolomite.

3. Results and discussion

3.1. The effect of Water Reducing agent on setting time of DBMSC

Table 2 shows the setting time of DBMSC under different water reducing agents. The main research object is the Nano superplasticizer (NF) or Polycarboxylate superplasticizer (PC). The experimental results show that adding different amounts of NF and PC will increase the setting time of dolomitic magnesium sulfate cement. The results show that the two water reducing agents have retardation effect on dolomite-based magnesium sulfate cement. According to previous studies, the initial setting time of dolomitic magnesium sulfate cement is 3.25h without Admixture. When you add 0.5%, 1%, 2% and 3% NF to dolomitic magnesium sulfate cement, its initial setting time is 3.67h, 4.17h, 4.58h and 4.83h, which is extended by 12.92%, 28.31%, 40.92% and 48.61% respectively. When you add 0.5%, 1%, 2% and 3% PC, the initial setting time is 3.45h, 3.85h, 4.05h and 4.27h, which is extended by 6.15%, 18.46%, 24.62% and 31.38% respectively. The results show that the two water reducing agents have more obvious retardation results on DBMSC with the increase of the dosage. According to relevant research, when adding the water reducing agent, the properties of the solid-liquid interface of the cement-water dispersion system (such as particle surface charge distribution, steric hindrance, etc.) are changed because of the adsorption of the water reducing agent, which makes the force between the cement particles be changed, affecting the dispersion properties of the solid particles in the liquid, resulting in retardation of the basic magnesium sulfate cement.

Figure 1 shows the heat release rate of dolomite-based magnesium sulfate cement under NP and PC water reducing agent. It can be clearly seen from the figure that when NP and PC are added, the induction period of dolomitic magnesium sulfate cement becomes longer and the acceleration period is delayed. It is found through experiments that when the admixture is not added, the induction period of DBMSC is about 7 h, and the start time of the acceleration period is about 7.9 h. When adding 3% NF,
the induction period lasts about 8.5 hours, and the acceleration period starts at about 9.8h; When adding 3% PC, the induction period lasts about 9.2 hours, and the acceleration period starts at about 9.5h. The former are respectively extended by 21.43% and 24.05% and the latter are extended by 31.42% and 20.25%. It is further verified that the two water reducing agents have a retarding effect on dolomite-based magnesium sulfate cement.

Table 2. Setting time of DBMSC under different water reducing agents

| Admixture / Content/% | Nano superplasticizer | Polycarboxylate superplasticizer |
|-----------------------|-----------------------|---------------------------------|
|                       | 0.5               | 1                  | 2                  | 3                  | 0.5       | 1                  | 2                  | 3                  |
| Initial setting time/h| 3.25              | 3.67               | 4.17               | 4.58               | 4.83      | 3.45               | 3.85               | 4.05               | 4.27               |
| Final setting time/h  | 13.17             | 13.87              | 14.42              | 14.92              | 15.1      | 15.1               | 13.56              | 13.87              | 14.13              | 14.38              |

3.2. The research of Water Reducing agent on water reduction effect of DBMSC

The water reducing effect of water reducing agent on cement is mainly expressed by water reducing rate. Figure 2 shows the influence of NP and PC water reducing agent on the water reducing effect of DBMSC. It can be seen from the figure that the highest water reduction rate of NP is only 4%, and the highest water reduction rate of PC is only 1.1%. Compared with NP, PC has no water reducing effect on dolomitic magnesium sulfate cement. The experimental results show that neither NF nor PC has obvious water reducing effect on the DBMSC mortar prepared with lightly burned dolomite. According to relevant research, the adsorption of water reducing agent molecules on the surface of cement particles plays a role in changing the surface charge distribution of cement particles, or acts as a steric hindrance, or both, which disperse the cement particles and release the water molecules encapsulated in the flocs to achieve water reduction[2]. In previous studies, it was found that the water-reducing dispersion effect of NF in basic magnesium sulfate cement was mainly caused by electrostatic repulsion effect. Figure 3 shows the Zeta potential diagram when 1% Nano superplasticizer is added to the dolomite basic magnesium sulfate cement. Compared with the potential diagram when 1% nai superplasticizer is added to the basic magnesium sulfate cement prepared by light burning powder in previous studies, the potential difference is decreased by about 1/3[3]. The content of α-mgo in the lightly burned dolomite is about 1/3 of the active magnesium oxide in the light burning powder. Therefore, the amount of NF adsorption on cement particles and their hydration products are reduced, the electrostatic repulsion effect is weakened, and the water reducing effect is reduced. The relevant scholars' research shows that PC water reducing agent molecule and SO$_4^{2-}$ have competitive adsorption relationship, the higher the concentration of SO$_4^{2-}$ is, the lower the adsorption amount of PC water reducing agent molecule is, when the SO$_4^{2-}$ concentration is 0.125mol/L, at the time, the adsorption amount of PC water reducer molecules is only 26%. In this study, the concentration of SO$_4^{2-}$ in the slurry of MgSO$_4$·7H$_2$O solution used in DBMSC is high, which reduces the ability of PC water reducing agent to disperse cement particles.

Figure 1. heat release rate of DBMSC under NP and PC water reducing agent

Figure 2. The influence of NP and PC water reducing agent on the water reducing effect of DBMSC
3.3. The effect of Water Reducing agent on mechanical strength of DBMSC

Figure 4 shows the compressive strength and flexural strength of dolomite-based magnesium sulfate cement prepared from dolomite under different dosages of NF or PC. The experimental results show that adding NF or PC in DBMSC can reduce the mechanical strength of DBMSC. For example, when the curing age is 28d, the compressive strength and flexural strength of DBMSC without admixture are 62.2MPa and 9.562MPa. The compressive strength and flexural strength of DBMSC with 3% NF are 40.1 MPa and 7.361 MPa, which are decreased by 35.53% and 23.02% respectively; the compressive strength and flexural strength of DBMSC with 3% PC are 42.2 MPa and 7.126 MPa, which are decreased by 32.15% and 25.48% respectively.

3.3.1. The effect of Water Reducing agent on mechanical strength of DBMSC

The mechanical strength of DBMSC depends on the type, content of hydration products, their porosity and pore distribution. Figure 5 shows the 28D XRD pattern of DBMSC prepared from dolomite under different dosages of NF or PC. Studies have shown that with the incorporation of water reducing agent, no new hydration products are formed in DBMSC. However, with the increase of the amount of water reducing agent, the peak of the main strength phase (5·1·7) of 28d is greatly reduced. However, with the increase of the amount of water reducing agent, the peak of the main strength phase (5·1·7) of 28d is greatly reduced. On the other hand, related research shows that the DBMSC contains three kinds of pores, gel pores (D ≦ 10nm), capillary pores (10nm<D ≦ 100nm) and macropores (D>100nm)[4]. Among them, the capillary pores are mainly the intergranular pores of the
hydration product 5·1·7 phase, and the macropores are unfavorable to the strength of the cement. It can be seen from figure 6 and Table 3 that the NF and PC water reducing agent change the porosity and pore distribution of DBMSC, with the increase of the amount of NF and PC water reducing agent, the porosity of cement increases, the capillary pores decrease, and the macropores increase. For example, compared with the cement without adding water reducing agent, the porosity of DBMSC with 3% PC water reducing agent is increased by 31.5%, the capillary pores are decreased by 15.95%, and the macropores are increased by 71.2%. Therefore, the incorporation of PC and NF lead to the decrease of the capillary pores, the decrease of the content of 5·1·7 phases, the increase of unfavorable macropores and the decrease of mechanical strength.

![XRD of dDBMSC with NP and PC water reducing agent](image)

**Figure 5.** XRD of dDBMSC with NP and PC water reducing agent

| sample    | average pore size | Porosity/% | <10 nm/% | 10–100nm/% | >100nm/% |
|-----------|-------------------|------------|----------|------------|----------|
| Control group | 161              | 10.19      | 0        | 81.7       | 18.3     |
| NF-3%     | 335              | 10.92      | 0        | 70.93      | 29.07    |
| PC-3%     | 87.2             | 13.4       | 0        | 68.67      | 31.33    |

![Cumulative Pore size distribution of DBMSC under NP and PC water reducing agent](image)

**Figure 6.** Vpore size distribution of DBMSC under NP and PC water reducing agent

### 4. Conclusion

In summary, the dolomite-based magnesium sulfate cement is mixed with NF or PC water reducing agent, which changes the properties of the solid-liquid interface of the cement-water dispersion system.
due to the adsorption of the water reducing agent (such as particle surface charge distribution, steric hindrance, etc.), which makes the force between the cement particles be changed, affecting the dispersion properties of the solid particles in the liquid, making the initial setting time and the final setting time be greatly increased, and the water reducing effect be poor. In addition, NF and PC water reducers have an inhibitory effect on the formation of the 5.17 phase in the hydration process of DBMSC, resulting in a large decrease in the content of the 5·1·7 phase, an increase in the porosity of the cement, a decrease in capillary pores, an increase in macropores and a great loss in mechanical strength. From a comprehensive perspective, adding PC or NF water reducing agent to DBMSC has little contribution to improving its performance, so it is not recommended to use it.

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