Effect of Portland cement on Magnesium Oxysulfate Cement Using Light-burned Dolomite

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Abstract. In this research, the setting time, compressive strength, cement mortar fluidity, X-ray diffraction, scanning electron microscopy and hydration-heat release rate were adopted to assess the effect of Portland cement on magnesium oxysulfate (MOS) cement prepared by light-burned dolomite ores. The experimental results showed that adding Portland cement in MOS cement will greatly reduce its mechanical property. But, a small amounts of Portland cement in MOS cement can shorten its setting time and maintain most compressive strength meanwhile.

1. Introduction
Magnesium Oxysulfate (MOS) Cement is a new kind of magnesia cementitious material which is energy-saving, environmentally-friendly, and air-dried. It is also acknowledged to bear the advantages of light weight, high strength, good fire resistance, strong water resistance and steel protection[1-3] after adding additives such as citric acid. The MOS cement is usually prepared by mixing a certain concentration of magnesium sulfate solution with active magnesium oxide (α-MgO)[4]. Additionally, the α-MgO used in the production of magnesium cement is mainly derived from light-burned magnesite (MgCO3) nowadays[5]. However, Magnesite ores are uneven distribution. For example, 1/3 of Magnesite reserves concentrate in China around the world.

Dolomite (CaMg(CO3)2) is an important calcium and magnesium resource on Earth, it is the most common kind of rocking mineral among carbonate rocks with very abundant reserves and wide distribution around the world. Dolomite can be used as raw material (α-MgO) to prepare magnesium cement (MOC)[6-7]. Furthermore, due to the low MgO content of dolomite, the CO2 content released from dolomite which is used to prepare MOS cement during calcination process is about 1/3 of that released from the calcined magnesite. Therefore, using dolomite to replace magnesite in preparing MOS cement and its products can conform to ecological protection concept and use domestic resources effectively, which can also reduce transportation cost so as to decrease the production cost of MOS cement as well. However, the setting time of MOS cement prepared by light-burned dolomite is high according to our previous study[7], which limited its application. Therefore, shortening the setting time of MOS cement prepared by light-burned dolomite holds great significance for the popularization of MOS cement.

In this research, the compressive strength, the setting time, fluidity, X-ray diffraction analysis, scanning electron microscopy and hydration-heat release rate were adopt to assess the effect of different contents of Portland cement (by the weight of the MgO) on MOS cement.
2. Experiment

2.1 Raw materials

The dolomite ores used in this study were obtained from Hebei, China. Its main chemical compositions were determined by Semi-quantitative analysis (SQX) method and analyzed with X-ray fluorescence (XRF, ZSX Primus II) which conducted by standardless analysis, and the results are listed in Table 1. According to previous study[7], the α-MgO used in this research was obtained from light-burned dolomite with calcination time of 0.5 hour at 850 ℃. Analytical purity of citric acid (as an additive, C₆H₅O₇, CA) and magnesium sulfate heptahydrate (MgSO₄ꞏ7H₂O) were purchased from Jinan Guofeng Chemical Industry Co., Ltd. The P-O42ꞏ5R Portland cement was prepared from Qinghai Weiyuan Cement Co., Ltd, and the chemical compositions are listed in Table 2.

Table 1. Chemical compositions of dolomite ores

| Composition | MgO | CaO | SiO₂ | Fe₂O₃ | Al₂O₃ | Na₂O | CO₂ |
|-------------|-----|-----|------|-------|-------|------|-----|
| Mass fraction/% | 20.6 | 31  | 0.103| 0.110 | 0.0366| 0.0195| 48.1|

Table 2. Chemical compositions of Portland cement

| Composition | MgO | CaO | SiO₂ | Fe₂O₃ | Al₂O₃ | Others |
|-------------|-----|-----|------|-------|-------|--------|
| Mass fraction/% | 1.62 | 53.7 | 17.2 | 2.86  | 4.44  | 20.18  |

2.2 Sample preparation

MgO obtained from light-burned dolomite contains α-MgO and over-burned MgO, and only α-MgO participates into the hydration process in producing the MOS cement in the early stages[8]. The content of α-MgO derived from calcined dolomite can be determined by standard hydration method using Equation(1) according to Dong’s report[9].

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

Where \( m_1 \) and \( m_2 \) are mass of MgO before and after reacting with water for 3 hours at the temperature of 105 ℃, respectively. \( M_{MgO} \) and \( M_{H2O} \) demonstrate the molecular weight of MgO and H₂O, respectively. \( \omega(CaO) \) can be titrated by using EDTA standard solution according to Dong’s report[9].

According to previous study[7], The molar ratios of α-MgO/MgSO₄ of MOS cement were set to 4 in this research. The mixture designs of MOS cement are shown in Table 3 (the citric acid and Portland cement content were the mass percentage of magnesium oxide). Firstly, MgSO₄ꞏ7H₂O was dissolved in deionized water to form a 25.0% magnesium sulfate solution (the molar ratio of H₂O/MgSO₄ is 20)[3]. Then, according to Table 3, we mixed a certain magnesium oxide, CA and Portland cement evenly, and by adding the prepared magnesium sulfate solution, the MOS cement is formed. Eventually, we removed MOS cement paste to steel molds with dimensions of 20 mm × 20 mm × 20 mm, cured at 20±3 ℃ for around 24 hours before demolding.

Table 3. Mixture designs of MOS cement prepared by light-burned dolomite

| Test number | Molar ratios (α-MgO/MgSO₄) | Citric acid (%) | Water cement ratios (W/C) | Portland cement content (%) |
|-------------|----------------------------|----------------|--------------------------|----------------------------|
| A1          | 4                          | 0.5            | 0.357                    | 0                          |
| A2          | 4                          | 0.5            | 0.357                    | 1                          |
2.3 Analyzing the Sample
The f-CaO in light-burned dolomite was tested by using EDTA standard solution according to Dong et al.’s report[10]. The setting time of MOS cement were tested via a Vicat apparatus according to the GB/T 1346-2011 standard used in China. The compressive strength of MOS cement was examined by a testing machine with the maximum load of 300 kN and a loading rate of 0.3 kN/s according to cement strength test standard methodology (GB175-2007). The hydration-heat release rate of MOS cement mortar (the weight ratio of standard sand to MgO was set to 2) derived from light-burned dolomite was determined via a tester for cement hydration heat (YT12659-16) according to the GB/T 12959-2008 used in China: Test methods for heat of hydration of cement. The fluidity of MOS cement mortar (the weight ratio of standard sand to MgO was set to 2) was determined by GB/T 2419-2005 standard.

Additionally, the crystal-phase compositions of MOS cement were examined by X-ray diffractometer with CuKα radiation (λ = 0.15419 nm) over a 20 range from 5° to 70°. The microstructure and Energy-Dispersive X-ray Spectroscopy results of MOS cement were tested by using Scanning Electron Microscopy (SEM, JSM-5610LV) on fractured surfaces after gold plating.

3 Results and Analysis

3.1 Effects of Portland cement on setting time of MOS cement prepared by light-burned dolomite
Setting time is one of the important properties of cement which can directly reflect the hardening rate of cement. Figure 1 shows that the setting time of MOS cement prepared by light-burned dolomite with different amounts of Portland cement. It can be clearly seen that the setting time of MOS cement decreased gradually after adding Portland cement in MOS cement. For example, the final setting time of MOS cement were 15.67h, 15.38h, 14.5h, 13.75h and 12.37h as the content of Portland cement were 0%, 1%, 3%, 5% and 10% respectively.

The hydration of magnesium oxide with magnesium sulfate solution prepared by light-burned dolomite would directly affect the hydration-heat release rate of MOS cement[7]. As shown in Figure 2, adding Portland cement in MOS cement could short its induction period and bring forward its acceleration period. For instance, the induction period of MOS cement without Portland cement was about 9.72h, however, it was about 3.7h for induction period of MOS cement containing 10% Portland cement, decreasing about 61.93%. This once more verifies the setting time of MOS cement was shortened after mixing Portland cement.

![Figure 1. Setting time of MOS cement after mixing different amounts of Portland cement](image_url)
3.2 Effects of Portland cement on compressive strength and fluidity of MOS cement prepared by light-burned dolomite

According to previous study\cite{7}, the main strength phase of MOS cement prepared by light-burned dolomite is the needle-like 5Mg(OH)$_2$·MgSO$_4$·7H$_2$O (5·1·7) crystal phase. Figure 3 shows the compressive strength of the MOS cement with different contents of Portland cement. The experimental results show that the compressive strength of A3 after curing for 1d was better than other samples’ compressive strength. For example, the compressive strength of A3 was 11.7 Mpa after curing for 1d, but 10.8Mpa and 3.3Mpa for A1 and A5 respectively. According to 3.3.1 analysis, the setting time of MOS cement decreased gradually after adding Portland cement. Comparing A1 with A3, the setting and hardening time of A3 was shorter than A1, which resulted in the higher compressive strength of A3. However, in comparison with A5, A3 had more 5·1·7 crystal phase content than A3 done. therefore, the compressive strength of A3 after curing for 1d was higher than other samples’ compressive strength.

It can be clearly observed that the compressive strength of MOS cement after curing for 28d gradually decreased after mixing Portland cement. As shown in Figure 3, the compressive strength of MOS cement after curing 28 days without Portland cement was 62.2 MPa, but 9.2 MPa for MOS cement with 10% content of Portland cement, decreasing about 85.2%. Figure 4 shows the XRD diffractogram of MOS cement with different amounts of Portland cement after curing 28 days. It is obvious that the peaks of 5·1·7 crystal phase gradually decreased as the content of Portland increased, which could account for the decreased compressive strength of MOS cement after mixing Portland cement. Similarly, as shown in Figure5(a-c), the needle-like 5·1·7 crystal phase of MOS cement gradually reduced as the content of Portland cement increased. In addition, it can be clearly seen that CaSO$_4$·2H$_2$O and (CaO)$_x$·(SiO$_2$)$_y$·(H$_2$O)$_z$ gradually increased after adding Portland cement. As shown in Figure 2, the P·O42·5R Portland cement in this research contained 53.7% CaO. And we can observed from Figure4 and Figure5 that there was little needle-like 5·1·7 crystal phase for A5, but some CaSO$_4$·2H$_2$O and (CaO)$_x$·(SiO$_2$)$_y$·(H$_2$O)$_z$ appeared. According to previous study\cite{7}, we can infer that the hydration process of A5 is often undertaken by reactions of Equations (2-4). However, the 5·1·7 crystal phase is main strength phase of MOS cement prepared by light-burned dolomite, and CaSO$_4$·2H$_2$O in MOS cement can reduce its compressive strength\cite{7}. Therefore, the compressive strength of MOS after curing for 28d decreased following the increased content of Portland cement.

Figure 6 shows the fluidity of MOS cement prepared by light-burned dolomite after mixing different contents of Portland cement. It can be clearly seen that the fluidity of MOS cement deceased after mixing Portland cement. For instance, the MOS cement mortar fluidity without Portland cement was 211.9mm, but the MOS cement mortar fluidity with 10% Portland cement was 145.6mm, decreasing about 31.29%. On one hand, according to EquationsII, III and IV, when the content of Portland cement in MOS cement mortar increases, the water molecules and SO$_4^{2-}$ in MOS cement react with CaO and SiO to from CaSO$_4$·2H$_2$O and (CaO)$_x$·(SiO$_2$)$_y$·(H$_2$O)$_z$, which result in low compressive strength and poor cement mortar fluidity. On the other hand, higher content of CaO in Portland cement (Table 2) will cause MOS cement to harden faster\cite{7}, which result in poor fluidity of MOS after adding Portland cement.
(x+n)CaO+ySiO₂+(z+n)H₂O→(CaO)_x(SiO₂)_y(H₂O)_z+(Ca(OH)₂)_n \hspace{1cm} (2)
CaO+H₂O→Ca(OH)₂ \hspace{1cm} (3)
Ca(OH)₂+MgSO₄+2H₂O→2CaSO₄.2H₂O+Mg(OH)₂ \hspace{1cm} (4)

Figure 3. Compressive strength of MOS cement after mixing different amounts of Portland cement

Figure 4. XRD diffractogram of MOS cement after mixing different amounts of Portland cement

Figure 5. EM images of MOS cement after mixing different amounts of Portland cement
(a: with 0% Portland cement   b: with 3% Portland cement   c: with 10% Portland cement)
4 Conclusions
This test study the effect of Portland cement on MOS cement prepared by light-burned dolomite. According to the mentioned results, we can clearly draw the following conclusions:

(1) The compressive strength of MOS cement gradually decrease as the content of Portland cement increase.

(2) The Portland cement can shorten the setting time of MOS cement.

(3) Adding Portland cement in MOS cement can make its fluidity worse.

Above all, adding Portland cement in MOS cement will greatly reduce its mechanical property. But, a small amounts of Portland cement in MOS cement can shorten its setting time and maintain most compressive strength meanwhile. Therefore, the study on the effect of Portland on MOS cement prepared by light-burned dolomite could represent a great significance for popularization of MOS cement.

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