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The mechanical properties of magnesium oxysulfate cement enhanced with 517 phase magnesium oxysulfate whiskers

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HIGHLIGHTS

- The mechanical properties of magnesium oxysulfate cement was enhanced with 517 phase.
- 517 phase magnesium oxysulfate whiskers was formed by the addition of sodium malate.
- 517 phase was characterized by FT-IR, XRD and SEM.
- Enhancement mechanism of 517 needle phase resulted from sodium malate was proposed.

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ABSTRACT

A new magnesium oxysulfate (MOS) cement was prepared with the modification of sodium malate. The microscopic morphology of MOS cement was examined by scanning electron microscope (SEM). X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) was used to characterize the crystalline degree and molecular structure of MOS cement. The characterization results indicated that quantities of 517 phase magnesium oxysulfate whiskers were detected in the modified MOS cement. The flexural strength and water resistance of MOS cement were increased by the addition of sodium malate and the mechanism was also discussed according to the characterization results mentioned above.

1. Introduction

The magnesium oxysulfate (MOS) cement is a kind of important nonhydraulic cement, which was produced by the reaction of magnesium oxide, magnesium sulfate and water [1]. Magnesium hydroxide sulfate [$xMg(OH)_2{\cdot}yMgSO_4{\cdot}zH_2O$] phase was discovered as the main composition of MOS cement [2]. MOS cement has many potential advantages such as fire resistance, lightweight and good steel protection [3–6], therefore it can be used as fireproof materials [7], reinforcement additives [8] and building materials. However, the industrial application of MOS cement was significantly limited by its low mechanical strength, which was mainly due to the incomplete hydration reactions of magnesium oxide.

$MgCO_3$, $Mg(OH)_2$, $Mg_3Si_4O_{10}(OH)_2$ and $xMg(OH)_2{\cdot}yMgSO_4{\cdot}zH_2O$ (xyz phase) was reported as the main hydration products of MOS cement [9]. In this cementious system, $Mg(OH)_2$ was the product of incomplete hydration of magnesium oxide which caused the decrease of MOS cement's strength for its flake morphology and loose microstructure. According to the obtained results of previous works, as a complete hydration product of hydration reactions, xyz phase showed excellent mechanical strength in the cementitious system. The 513 phase, 318phase, 123 phase, 115 phase were reported as the main phases of MOS cement in the reports of Demediuk and Cole [6]. 512 phase was firstly synthesized by Yan et al. at 150 °C [10]. The existence of 235 phase was reported by Adomaviciute et al. in their studies of magnesium cement [11]. Recently, 517 phase was detected, and its crystal structure was characterized by Runcevski et al. during their studies on the modified MOS cement [12], but the modification mechanism and forming process of 517 phase were not reported.

In order to improve the strength of MOS cement, more efforts were devoted to the modification of MOS cement recently. Physical modification and chemical modification were commonly used [13]. The fly ash was used as a physical modifier on MOS cement [14]. The compressive strength of MOS cement was improved nearly 30% after modification. 517 phase was also detected in the modified samples. However, the mechanism was not given in their studies. Citric acid was used as a chemical modifier in the studies of Wu

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et al. New phase (515 phase) was formed, resulting the improvement of strength and water resistance [15]. Furthermore, the modification mechanism was proposed as the chemisorption of citric acid on the surface of MOS cement [16]. But the forming process of this chemisorption and the structure of the products were not given in their studies. Herein, sodium malate was used as a new chemical modifier for MOS cement. The hydration products were characterized by several characterizations such as X-ray powder diffraction (XRD), Fouier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM). The mechanism was also proposed in this paper.

2. Experimental

2.1. Materials and preparation

2.1.1. Materials

The light burned MgO was obtained from Haicheng of Liaoning province, China. Its activity fraction was determined according to the previous reported method [17]. Its chemical composition was also analyzed and the results were shown in Table 1. The $MgSO_4{\cdot}7H_2O$ and sodium malate were purchased from Kemiou Chemical Technology Company in Tianjin, China.

2.1.2. Preparation of MOS cement

For the preparation of MOS cement samples, 200.00 g MgO and 32.02 g $MgSO_4{\cdot}7H_2O$ were mixed with 119.38 g distilled H_2O, then a certain amount of sodium malate was added to the suspension. Six different additions of sodium malate were studied in this paper, which were listed in Table 2. These six MOS cement pastes were all stirred at the rate of 250 r/min for 10 min, monitoring of their pH values were also conducted at the same time, which were shown in Fig. 8. Then the paste was poured into six steel moulds of 10 mm × 10 mm × 60 mm and six steel moulds of 40 mm × 40 mm × 40 mm respectively. The samples were cured at 25 °C for 24 h, then demoulded and continue curing at 25 °C for 28d.

Table 1
Chemical composition of light burned MgO.

Composition	MgO	SiO_2	CaO	Fe_2O_3	Al_2O_3	Ignition loss
Amount (wt%)	86.10	6.56	1.09	0.34	0.38	6.53

Table 2
The different additions of sodium malate added to MOS cement.

Serial number	P1	P2	P3	P4	P5	P6
Sodium malate (wt%)[a]	0	0.25	0.5	0.75	1	1.25

[a] Calculated by the mass fraction of MgO.

2.2. Measurement

2.2.1. Strength test of MOS cement

Microcomputer control electron universal testing machines (CMT6104, Sans, China) was used for testing the flexural strength of MOS cement samples (10 mm × 10 mm × 60 mm), which have cured at 25 °C for 7d and 28d respectively. In addition, half of these samples were used for strength test after being submerged in distilled water at 25 °C for 7d. Then the softening coefficient was calculated by Eq. (1) as follow:

$$Rf = \frac{R(w,7)}{R(a,28)} \tag{1}$$

where R_f is softening coefficient, $R_{(w,\ 7)}$ is the strength of samples which have submerged in distilled water at 25 °C for 7d, $R_{(a,\ 28)}$ is the strength of samples which have cured at 25 °C for 28d.

2.2.2. Microporous structure test of MOS cement

When comparing with the methods of mercury intrusion porosimetry (MIT) and N_2 adsorption, the method of water absorption ratio can be used to test the samples with larger shape, and the data collected by this method are closer to the real microporous structure of integral samples. While MIT and N_2 adsorption method are usually used to test the samples with tiny shapes, the data collected by these two methods may lack of integrity. Thus the microporous structure of MOS cement samples (40 mm × 40 mm × 40 mm), which have been curing for 56d at 25 °C were tested according to the method of water absorption ratio reported by Yan et al. [18]. Firstly, the samples were kept in constant humidity of 65% for 4d at 25 °C and recorded the mass as m_B. Then the samples were dried at 105 °C for 48 h and recorded the mass as m_0. Next five surfaces of the samples were sealed by scotch tape after drying. Submerged another surface in distilled water at 25 °C for 24 h and recorded the mass of 0.25 h, 1 h, 24 h as $m_{0.25}$, m_1, m_{24} respectively. Finally, the microporous structure parameters of these MOS samples were calculated by Eq. (2) to Eq. (5) as follow:

$$K_a = \left(\frac{m_1 - m_0}{A}\right)^2 \cdot \frac{1}{3600} \tag{2}$$

$$K_m = \frac{m_B - m_0}{m_{24} - m_0} \tag{3}$$

$$\alpha = \frac{\ln\left[\frac{\ln\left(\frac{m_{24}-m_1}{m_{24}-m_0}\right)}{\ln\left(\frac{m_{24}-m_{0.25}}{m_{24}-m_0}\right)}\right]}{\ln 4} \tag{4}$$

$$\ln\lambda = \frac{\ln\left[\ln\frac{m24-m0}{m24-m1}\right]}{\alpha} \tag{5}$$

where K_a (cm^2/s) is integral porosity, which refers to the quantities of micropores. A is the cross section area of MOS cement sample. K_m is differential porosity, which refers to the relative quantities of micropores. α refers to the uniformity of micropores. λ refers to the size of micropores.

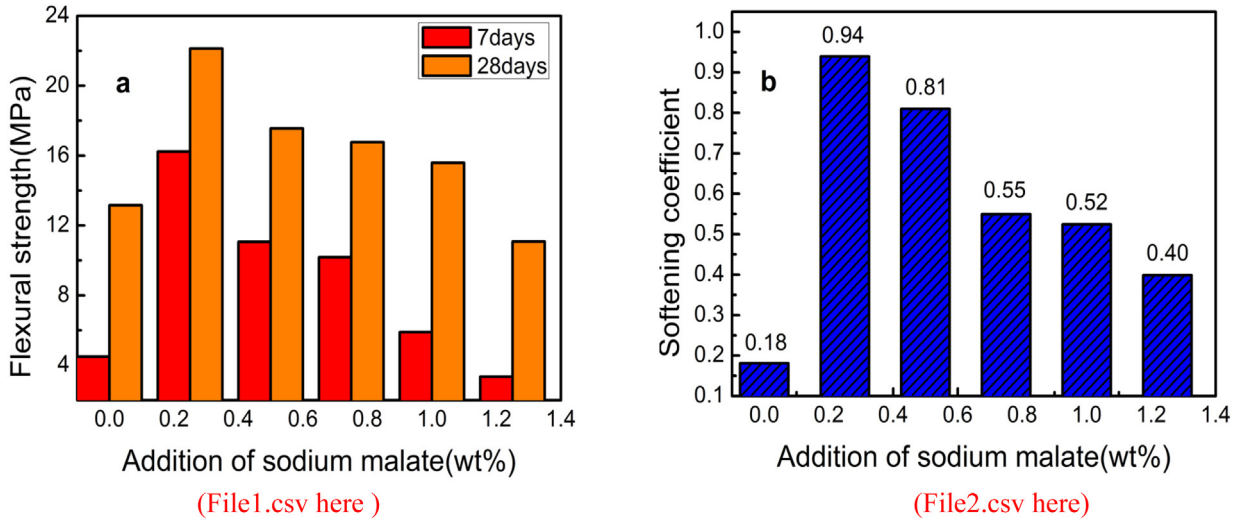

Fig. 1. Effect of sodium malate addition on the mechanical properties of MOS cement.