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The hydration mechanism and performance of Modified magnesium oxysulfate cement by tartaric acid

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HIGHLIGHTS

- Effects of tartaric acid (TA) on performance of MOS cement have been studied.
- XRD, SEM, EIS and MIP were used to examine effects of TA on MOS cement.
- The main strength phase of MOS cement with TA is $5Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$ crystal phase.
- TA can retard the hydration rate of MOS cement.
- Adding TA can improve strength and decrease shrinkage of MOS cement.

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ABSTRACT

Magnesium oxysulfate (MOS) cement has the advantages of light weight, low alkalinity, fire resistance, and good decorative value. Large-scale applications of MOS cement in civil engineering have been restricted by its low strength, which can be improved by adding some proper additives. Here, the effects of tartaric acid on the setting time, compressive strength, flexural strength, and deformation of MOS cement have been studied. Fourier transform infrared spectra, pH changes, hydration-heat release rate, and impedance have been observed to determine the effects of tartaric acid on the hydration process of MOS cement. To a certain extent, the addition of tartaric acid extends the setting time of MOS cement by improving the stability of the hydration film of active MgO in magnesium sulfate. X-ray diffraction, scanning electron microscopy, and mercury intrusion porosimetry were used to examine the hydration products and pore-size distribution of MOS cement. The analysis results indicate that the main reason for the high strength of MOS cement with tartaric acid is that the addition of tartaric acid can promote the formation of the needle-like high-strength phase of $5Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$ and inhibit the formation and growth of the $Mg(OH)_2$ crystal phase.

1. Introduction

Magnesium oxysulfate (MOS) cement is a type of air-dried magnesia cementitious material prepared using active magnesium oxide and an aqueous solution of magnesium sulfate [1,2]. Magnesium oxysulfate (MOS) cement can be used for producing light insulation boards and fire-resistive materials because of outstanding merits such as light weight, good fire resistance, and low thermal conductivity [3–5]. MOS cement has good steel-protection properties resulting from its lower Cl^- content, which enable its use in preparing reinforced concrete. However, in recent years, the large-scale applications of MOS cement in civil engineering have been restricted by its low strength.

The compressive strength of MOS cement is primarily dependent on the category and content of magnesium subsulfate in MOS cement as well as on the porosity. According to Demediuk's report [6], four types of magnesium subsulfate exist in ternary systems (MgO-$MgSO_4$-H_2O) between 30 °C and 120 °C: $5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$ (5·1·3 phase), $3Mg(OH)_2{\cdot}MgSO_4{\cdot}8H_2O$ (3·1·8 phase), $Mg(OH)_2{\cdot}2MgSO_4{\cdot}3H_2O$ (1·2·3 phase), and $Mg(OH)_2{\cdot}MgSO_4{\cdot}5H_2O$ (1·1·5 phase). In 1980, Urwong and his colleague [7] studied phase relations in MOS cement prepared using a solution of MgO and sulfuric acid (H_2SO_4), and they found that $Mg(OH)_2$, unreacted $MgSO_4{\cdot}nH_2O$ (n = 1,6, or 7), and the 3·1·8 phase are stable at a

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temperature of 23 ± 3 °C. They also suggested that the reason for the low compressive strength of MOS cement is that it is difficult to prepare MOS cement with the content of the 3·1·8 phase greater than 50% at room temperature. At room temperature, the concentration of SO_4^{2-} in saturated magnesium sulfate solution is approximately 2.93 mol/L, which is far lower than that of Cl^- (9.02 mol/L) in saturated magnesium chloride solution. The hydration radius of SO_4^{2-} is approximately 3.79 Å, which is greater than that of Cl^- (3.31 Å) [8]. Based on the two above reasons and the experimental data of the phase composition of MOS cement, the probability of diffusion of SO_4^{2-} into the hydrated MgO layer and its reaction with MgO is less than that of Cl^- in MOC cement; consequently, more $Mg(OH)_2$ is produced by MgO reacting only with water in MOS cement. It is known that cement with a higher $Mg(OH)_2$ content has lower compressive strength and tends to crack. Beaudoin [9] studied the effects of porosity on MOS cement and speculated that high porosity was the main reason for its lower strength compared to MOC cement. However, in our previous study [10], even with a low water-cement ratio, the compressive strength of MOS cement was significantly less than that of MOC cement.

In view of the analysis above, the inhibition of the production or growth of the $Mg(OH)_2$ crystal phase and the increase in the content of magnesium subsulfate are effective methods to improve the mechanical strength of MOS cement. It is difficult to decrease the amount of $Mg(OH)_2$ in MOS cement by increasing the concentration of magnesium sulfate solution because of the limited saturated concentration. The addition of additives is one of the frequently used and effective methods to improve the properties of cement materials. For example, adding phosphoric acid, amino trimethylene phosphonic acid and citric acid [3,10,11], can significantly improve the compressive strength and water resistance of MOS cement by promoting the formation of the $5Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$ phase. Similarly, phosphoric acid and phosphate were used to improve the water resistance of MOC cement by changing the crystal habit of $5Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O$ [12–14]. Tartaric acid (TA) is often be used as retarder in Portland cement because it can delay the hydration rate of tricalcium silicate and tricalcium aluminate through adsorption and complexation with the initial hydration product of C-S-H gel and ettringite [15,16]. The influence of TA on the early hydration and mortar performance of Portland cement-calcium aluminate cement-anhydrite ternary systems was also investigated, and the results indicated that TA delayed the formation of ettringite by poisoning the growth of the crystalnucleus [17].

In the present study, TA is used as a modifier in MOS cement based on the consideration that it may change the hydration process of MgO in magnesium sulfate solution and promote the formation of magnesium subsulfates such as $5Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$. Therefore, the effects of TA on setting time, hydration product, compressive and flexural strength, and deformation have been investigated in detail. Additionally, the mechanism by which TA modifies MOS cement is discussed.

2. Materials and experimental procedures

2.1. Raw materials

The magnesia used in this study is light-burned magnesia (LBM) obtained by calcining magnesite from Liaoning, China at 750 °C, and the chemical composition of the LBM analyzed with X-ray fluorescence (XRF, ZSX Primus II) is listed in Table 1. The specific surface area of the LBM was determined using the Brunauer-Emmett-Teller (BET) method to be 11.73 m^2/g. The D50 and D90 of the LBM powder were analyzed using the Malvern laser method with ethanol as the dispersant to be 22 µm and 75 µm, respectively. Magnesium oxide in LBM included both over-burned MgO and active MgO, and only active MgO was hydrated and converted

Table 1
Chemical composition of LBM.

Component	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	CO_2
Mass fraction (wt.%)	80.20	1.30	6.07	0.15	0.41	11.87

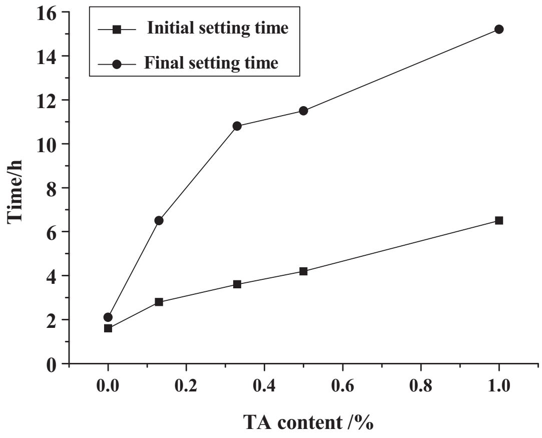

Fig. 1. Setting time of MOS cement with different TA contents.

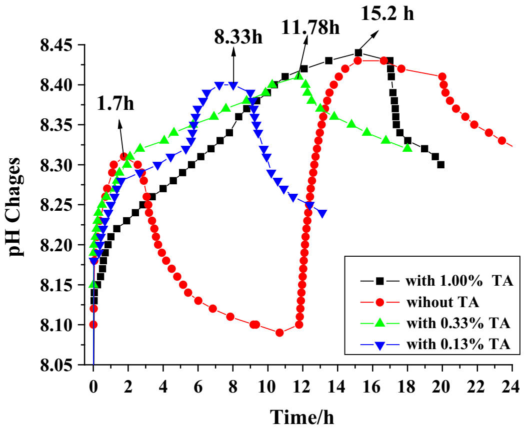

Fig. 2. pH changes of MOS cement samples with and without TA.

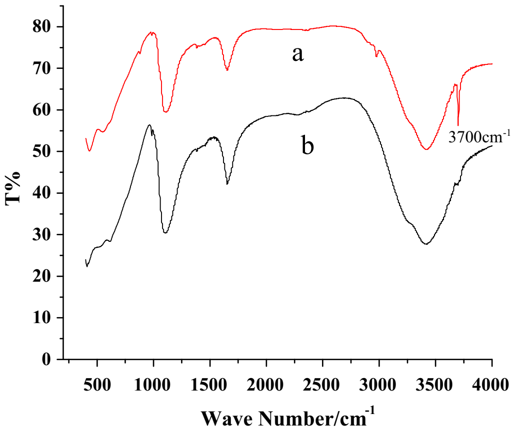

Fig. 3. FTIR spectra of MOS cement without TA (a) and with 1%TA (b) after hydration for 12 h.