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# Effects of sodium citrate and citric acid on the properties of magnesium oxysulfate cement

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## HIGHLIGHTS

- The effects of sodium citrate and citric acid on the properties of MOS cement were studied.
- More 5 $Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ were generated when sodium citrate or citric acid was added into MOS cement.
- Sodium citrate and citric acid could reduce the total porosity of MOS cement.
- Sodium citrate and citric acid could increase the mechanical strength and water resistance of MOS cement.

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## ABSTRACT

Magnesium oxysulfate (MOS) cement is a type of green inorganic cementitious material, with the advantages of light weight, low thermal conductivity, binding ability in light-weight panels, high temperature resistance and good fire resistance; however, its application range in practical engineering is limited by its low mechanical strength. In this paper, the influences of sodium citrate and citric acid as additives on the mechanical strength, water resistance, setting time, pH change, composition and microstructure of MOS cement were investigated. The sample properties were examined by means of mechanical strength test, Vicat apparatus, pH meter, X-ray diffraction (XRD), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP). The results revealed that adding sodium citrate or citric acid could promote the large amount of 5 $Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ generation and improve the water resistance of MOS cement. The incorporation of sodium citrate or citric acid caused a reduction in the total porosity and the volume fraction of large pores (>100 nm) in MOS cement, as well as an increase in the most probable aperture and the volume fraction of small capillary pores (10 nm–100 nm). In addition, the setting time of MOS cement with sodium citrate or citric acid was longer than that without sodium citrate or citric acid.



## 1. Introduction

As an air-dried green inorganic cementitious material, magnesium oxysulfate (MOS) cement [1–3] is formed by mixing light-burned magnesia (LBM) with a concentrated solution of magnesium sulfate ($MgSO_4 \cdot 7H_2O$). MOS cement has many outstanding properties, such as its light weight [4], low thermal conductivity [5], binding ability in light-weight panels [6,7], good temperature resistance and good fire resistance [8], so it is widely applied in producing light thermal-insulating materials and fireproof materials. In recent years, MOS cement has drawn much research interest due to the gradual increase in awareness regarding environmental protection. The calcination temperature of LBM used for preparing MOS cement is much lower [9,10] than that of Ordinary Portland cement. On the other hand, magnesium resources widely exist around the world, especially in Russia, China and America. There are abundant magnesium resources in the salt lakes of China that can provide $MgSO_4 \cdot 7H_2O$ required for MOS cement, but these resources have not been effectively exploited and utilized. Research on the development of MOS cement will be conducive to the comprehensive utilization of magnesium resources.

Although it has many obvious advantages, the application of MOS cement is not widespread because of its low mechanical strength. Over the past few decades, some research has been conducted to study the hydration products and mechanical strength of

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**Table 1**
Chemical composition of LBM.

| Component | MgO | CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | Others |
|---|---|---|---|---|---|---|
| Content (wt.%) | 87.86 | 1.84 | 2.49 | 0.58 | 0.72 | 6.51 |

MOS cement. It is generally believed that $3Mg(OH)_2{\cdot}MgSO_4{\cdot}8H_2O$ (3·1·8 phase), $5Mg(OH){\cdot}MgSO_4{\cdot}3H_2O$(5·1·3 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) are the four basic magnesium salts as strength phases that exist in MOS cement paste at temperatures from 30 °C to 120 °C [11]. Kahle [12] stated that 3·1·8 phase and 5·1·3 phase could be detected simultaneously when MOS cement was cured in the steam condition. Urwongse and Sorrell [13] found that 3·1·8 phase was the main phase formed in the MgO-$MgSO_4$-$H_2O$ system at 23 °C, along with metastable 1·1·5 phase, $MgSO_4{\cdot}n\ H_2O$ (n = 7, 6, or 1), $Mg(OH)_2$ and MgO. However, the content of 3·1·8 phase in MOS cement could not exceed 50 wt% by mass, which resulted in the low mechanical strength of MOS cement. These research results indicate that it is difficult to prepare MOS cement with high mechanical strength under normal conditions.

To improve the mechanical strength, a simple and effective method is to introduce additives into MOS cement. For example, adding 0.5 wt% phosphoric acid or potassium dihydrogen phosphate [14] (by weight of LBM) could increase the compressive strength of MOS cement after 28 days of curing to over 80 MPa. The incorporation of 0.2 wt% amino trimethylene phosphonic acid [15] (by weight of LBM) could enhance the 28-day compressive strength of MOS cement to nearly 100 MPa. The flexural strength of MOS cement with 0.25 wt% sodium malate [16] (by weight of LBM) could reach 22.13 MPa when the curing time was 28 days. Even a small amount of these additives could markedly improve the mechanical strength of MOS cement by promoting the formation of the predominant strength phase of 5 $Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$ (5·1·7 phase) [17,18].

It has been reported that sodium citrate (SC) and citric acid (CA) can have positive effects on the mechanical strength of MOS cement, but there is still a lack of research regarding the hydration products, micro morphology and pore structure of MOS cement after modification. In this work, we incorporated SC and CA as additives into MOS cement to improve the mechanical strength and water resistance. The effects of SC and CA on the qualitative and quantitative composition, micro morphology, setting time and pH value of MOS cement were discussed in detail. Additionally, mercury intrusion porosimetry (MIP) was used to study the differences in the pore structure between MOS cement with and without additives.

## 2. Experiment

### 2.1. Raw materials

The LBM used in this experiment was prepared by calcination of magnesia from Haicheng, China at 800 °C. The chemical composition of LBM containing 62.07 wt% reactive MgO(α-MgO) [19,20] is given in Table 1 and the particle size distribution curve of LBM is shown in Fig. 1. $MgSO_4{\cdot}7H_2O$, SC and CA are chemical reagents, from Ruijinte Chemical Co., Ltd. (Tianjin, China).

### 2.2. Specimen preparation

To obtain MOS cement specimens, the α-MgO/$MgSO_4$ molar ratio and water to binder ratio (w/b) were fixed at 10 and 0.47, respectively. According to the calculated results, a magnesium sulfate solution was first prepared by dissolving $MgSO_4{\cdot}7H_2O$ in water. Second, SC or CA was added at 0.5 wt% by weight of LBM to the magnesium sulfate solution to form a clear mixed solution. Then, premeasured LBM was stirred with mixed solution to form MOS cement paste, which was packed into PVC molds. After hardening for 24 h, the MOS cement specimens were removed from the molds ($40 \times 40 \times 160\ mm^3$, $40 \times 40 \times 40\ mm^3$) and cured in a room under controlled conditions of 22 ± 2 °C and 60 ± 5% humidity.

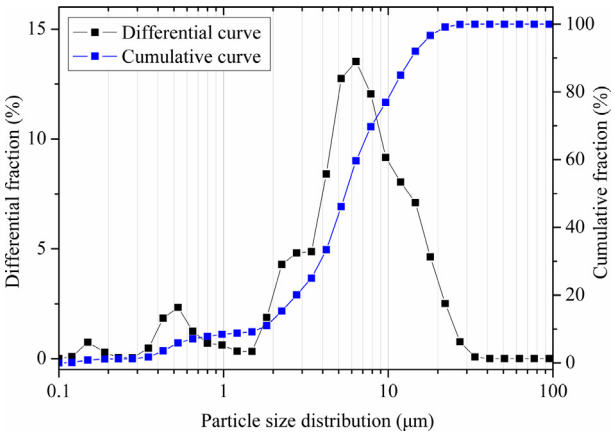


**Fig. 1.** Laser particle size distribution curve of LBM.

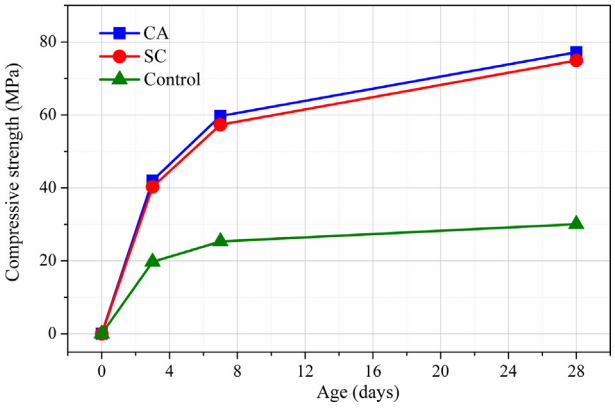


**Fig. 2.** Compressive strength of MOS cement with and without additives at different curing ages.

### 2.3. Testing method

For the flexural strength test, three MOS cement specimens of each group at 3, 7 and 28 days were measured using a machine with a maximum force of 100 KN at a loading rate of 50 N/s [21]. The compressive strength of MOS cement with three replicates at 3, 7 and 28 days was detected on a testing machine having a maximum force of 300 KN at a loading rate of 2400 N/s [22].

The identification of crystalline composition of MOS cement was determined on an X-ray diffractometer (XRD, D8 Discover, CuKα radiation) from 5° to 70° (2θ) with 0.017° step size and a count time of 2 s per step. The particle size of the samples for XRD tests was controlled to less than 74 μm. The quantitative phase analysis of specimens was performed by Rietveld method [23–25] using the Topas5.0 software package. The fractured surface morphology of MOS cement before and after water immersion was observed by scanning electron microscopy (SEM, ΣIGMA HD) after gold coating. AutoPoreIV9510 with a maximum pressure of 60,000 psia was used to measure the pore structure of MOS cement