

## Effect of Fineness Modulus on the Water Resistance of Magnesium Sulphide Cement Mortars

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### Abstract

The paper determines the basic properties of river sand by testing its collapse, impermeability, bulk density, water absorption, water content and mechanical properties for different fineness modulus of river sand mixed singly and in combination, and analyses the changes in the physical composition, micro-morphology, and pore size distribution of the MOS cement mortar by using XRD, SEM, and other testing equipments. The macroscopic and microscopic properties concluded that MOS855 performs best in various environments. In the water resistance, weathering and frost resistance experiments, the 517 content and MgO content of MOS cement mortar showed a decreasing trend, while the content of Mg(OH)<sub>2</sub> gradually increased. The total porosity of MOS cement mortar showed an increasing trend. MOS855 cement mortar formed a close-packing. It showed the best performance in water resistance.

### Keywords

Magnesium Sulphide Cement Mortar; Fineness Modulus; Pore Structure.

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### 1. Introduction

Cement is an important building material widely used in the construction of houses, bridges, tunnels, roads, harbours and other infrastructure. It is made from limestone, clay and other auxiliary materials through the processes of crushing, mixing and calcining. The research of cement began in the 19th century, and the earliest cement was invented by the British engineer Joseph Aspen in 1824<sup>[1]</sup>. Since the 20th century, with the acceleration of industrialisation and the development of the construction industry, the production and application of cement has been promoted and developed on a large scale<sup>[2]</sup>.

The research of cement mainly includes the basic nature of the material, preparation process, application technology, environmental issues and other aspects. In terms of the basic properties of materials, the research focuses on the chemical composition, physical properties, mechanical properties and other aspects of cement. As for the preparation process, the research focuses on the selection of raw materials, firing process, coal grinding process and other aspects. In terms of application technology, the research focus includes concrete, mortar, mixed materials, high-performance cement and other aspects<sup>[2-3]</sup>. In terms of environmental issues, the research focus includes the impact of cement production on the environment, the treatment of waste and other aspects. With the continuous development of science and technology, the research of cement is also deepening 78 and more and more new technologies, materials and processes emerge, such as high-performance cement, carbon capture technology, concrete reinforcement technology and so on<sup>[3-4]</sup>. The research and application of these new technologies and materials will further promote the development of the

cement industry and the progress of the construction industry. This paper focuses on magnesium sulphide cement mortar, so we carry out the application of magnesium sulphide cement in the construction industry<sup>[5]</sup>.

In this paper, the main purpose is to study the water resistance and pore structure of MgSO<sub>4</sub> cement, and to analyse the pore structure and blank compressive and flexural strength tests of MgSO<sub>4</sub> cement mortar specimens in immersion, freeze-thaw cycle, and hygrothermal cycle. The experimental apparatus is XRD and field emission scanning electron microscope to analyse the macrostructure of MgSO<sub>4</sub> cement<sup>[6]</sup>. The compressive strength and porosity of magnesium sulphide oxide cement specimens in water resistant environment were observed. This leads to the best proportioned mortar, which will provide a basis for the future application of magnesium sulphoxide cement mortar.

## 2. Experimental Preparation

### 2.1 Experimental Materials

Magnesite can be calcined at 850°C for 3 h to obtain MgO, and the content of reactive MgO is 63.57 wt%. The chemical compositions of both MgO and hydromagnesite were measured by laser diffraction.

Preparation of MgO cement mortar: magnesium sulphate was first dissolved in water to configure the molar ratio of MgO and magnesium sulphate to be 8:1. the water-cement ratio of the system was 0.4. then lightly burnt magnesium oxide was weighed at 0.5 wt.% citric acid, and two types of river sands with different fineness modulus were weighed according to the experimental protocol. The magnesium sulphoxide cement slurry is obtained when the MOS cement net slurry is moulded, the mixed sand is poured in and the mixer is stopped after 180 s of fast stirring. The magnesium sulphoxide cement mortar specimens can be obtained by pouring the mortar into two kinds of moulds, 40 mm×40 mm×160 mm and 40 mm×40 mm×40 mm, and waiting for 1d and then demoulding.

The MgO:MgSO<sub>4</sub>:H<sub>2</sub>O of the specimen was 8:1:20 and 0.5% citric acid was added. Three sets of control experiments were carried out on two kinds of fineness modulus of river sand according to the relative content of 0%+100%, 50%+50%, 100%+0% for compounding.

### 2.2 Lightly Burnt Magnesium Oxide Powder

Lightly burnt magnesium oxide powder comes from magnesite in Haicheng, Anshan City, Liaoning Province, calcined at 750°C-850°C. After crushing and grinding to 200 mesh, the powdered material with a certain content is obtained, and the chemical composition of light burnt magnesium oxide is shown in Table 1.

**Table 1.** Chemical composition of lightly burnt magnesium oxide (%)

Numbler	SiO <sub>2</sub>	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Loss
Loss Content	7.35	1.79	82.47	0.43	0.54	7.42

### 2.3 Magnesium Sulphate

Magnesium sulphate heptahydrate is in the form of crystals, the composition of which is shown in Table 2.

**Table 2.** Chemical composition of magnesium sulfate heptahydrate (%)

Numbler	MgSO <sub>4</sub>	MgO	Mg	Fe	Cl	Pb	As
Loss Content	≥48.59	≥16.20	≥9.80	≤0.0015	≤0.014	≤0.0006	≤0.0002

## 2.4 Sulphuric Acid

98% concentrated sulfuric acid, when used in accordance with a certain molar ratio and lightly burned magnesium oxide powder mixed reaction, so that part of the MgO reaction into  $\text{MgSO}_4\text{-H}_2\text{O}$ , and then add water to prepare magnesium sulfate cement. In addition, you can also dilute concentrated sulfuric acid to a certain concentration and then mix it with lightly burnt magnesium oxide powder to prepare magnesium sulfate cement or alkaline magnesium sulfate cement.

## 2.5 Citric Acid

The additive used is citric acid (CA), also known as citric acid, molecular formula for  $\text{C}_6\text{H}_8\text{O}_7$ . colourless, odourless but acidic crystals, easy to dissolve in water, white crystalline particles at room temperature, density  $1.542 \text{ g/cm}^3$ , citric acid is an essential additive in this experiment, the melting point of 153-159 degrees Celsius, higher than  $175^\circ\text{C}$ , it will be divided into interpretation and release of water and carbon dioxide. Citric acid can dissolve 59% in water at  $20^\circ\text{C}$ , and its pH is 2.1 in 2% water.

## 2.6 Fine Aggregate

The sand used in the test is natural river sand with specific gravity of 2.9 and water absorption rate of 2.7%, which is divided into two kinds of sand with fineness modulus of 2.45 (fineness modulus range of 2.3-3.0) and 1.93 (fineness modulus range of 1.6-2.2) in accordance with the national requirements, of which the stacking density of the medium sand is  $1,146.5 \text{ kg/m}^3$ , and that of fine sand is  $1,616 \text{ kg/m}^3$ , which meets the requirements of the specification "Ordinary Concrete".  $\text{m}^3$ , which is in line with the specification "Standard for Quality and Test Methods of Sand and Stone for Ordinary Concrete" (JGJ52-2006). In the following, the fineness modulus of 2.45 is called A, and the fineness modulus of 1.93 is called B.

## 2.7 Experimental Apparatus

The experimental instruments used in this experiment are all the equipment of Liaoning University of Science and Technology, including mixer, curing machine, drying box, press, and XRD.

## 2.8 Test Methods

According to the purpose of the experiment, the main MOS cement mortar's collapse, bulk density, water content, water absorption, compressive strength, flexural strength, and characterise the durability of MOS cement mortar by determining the water resistance, weathering resistance, frost resistance, and then use XRD detection to analyse the hydration products of MOS cement mortar test methods are as follows.

Mechanical properties are the key to measure the performance of cement, in order to ensure the accuracy and stability of the data, each group of experiments were tested using three parallel specimens, and the average of the test results was the final result. The mechanical properties were tested with reference to the requirements of the national standard GB/T 17671-199, and a rectangular specimen of  $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$  was used for flexural resistance, and a cubic specimen of  $40 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$  was used for compressive resistance, and a microcomputer controlled electro-hydraulic servo universal testing machine with the model number of WAW-1000B, a maximum test force of 1000 N, and a falling displacement of 0.5 mm/s was used for the testing of the cement. microcomputer WAW-1000B with a maximum test force of 1000 N and a falling displacement of 0.5 mm/s was used to test the specimen.

## 2.9 Durability

### (1) Water Resistance

Water resistance is the basic property of durability, and most durability tests are based on water resistance. In the water resistance test, deionised water was used, and the sizes of the specimens used were  $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$  for the flexural specimen and  $40 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$  for the compressive specimen. After the specimens were made in accordance with the ratio above, they were

put into the conservation environment at a temperature of 25°C and a humidity of 65% RH for 28 days, and then put into the water and immersed for 7, 14 and 28 days, and then immersed in water for 7, 14 and 28 days, and then immersed in water for 7, 14 and 28 days, the softening coefficient of the specimen is tested at three immersion ages, and the softening coefficient is calculated with reference to Equation 2.6, which characterises the water resistance of the specimen by the softening coefficient.

$$R_f = \frac{R_w}{R_a} \quad (1)$$

Where: for the softening coefficient of the specimen; for the compressive strength of the specimen at a certain age of immersion, in MPa; for the compressive strength of the specimen after 28 d of normal maintenance, in MPa.

### (2) X-ray diffraction test (XRD)

The composition of the physical phase in the MOS was qualitatively analysed using an X'Pert powder type X-ray diffractometer (tube pressure = 40 kV, tube current = 40 mA, scanning angle from 5° to 85°, scanning rate 0.2 s/step) with a Cu target (CuK $\alpha$ 1,  $\lambda = 0.15406$  nm), and the Topas 6.0 software was used for the quantitative analysis of the components was carried out by adding an internal standard (15 wt% ZnO), and the content of amorphous and unidentified crystalline phase substances that may be present in the system was calculated according to the following equation (2).

$$ACn = \frac{1 - \frac{W_{st}}{R_{st}}}{100 - W_{st}} \quad (2)$$

Where: is the weight fraction of added ZnO is the weight fraction of ZnO calculated by Rietveld.

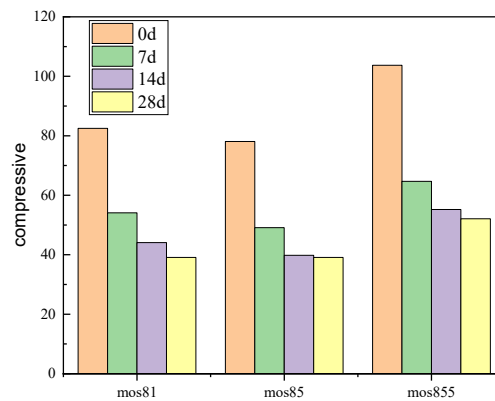
### (3) Microscopic morphology (SEM)

The weathering samples with different molar ratios as well as different fineness modulus compounding were made into thin slices, and the moisture in the samples was dried by using a vacuum drying oven with the temperature set at 40°C, and the microscopic morphology of the MOS cement mortar-resistant samples at the gravel and the MOS cementitious was observed by using a scanning electron microscope (SEM, SIGMA HD). The acquired electron microscope images were analysed for total porosity and pore structure in the transition zone of the ITZ interface by Image Pro Plus software.

## 3. Effect of Fineness Modulus on Water Resistance of Magnesium Sulphate Cement Mortar

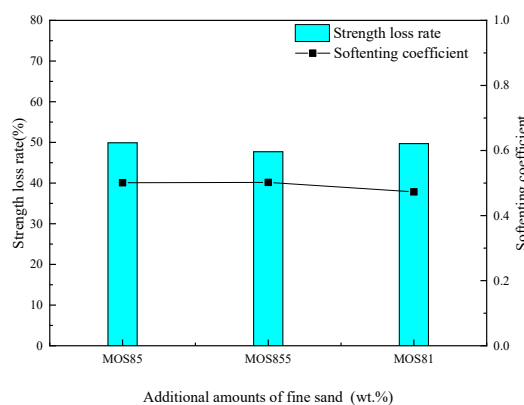
### 3.1 Mechanical Property Changes

Figure 1 shows the effect of fineness modulus and immersion age on the compressive strength of magnesium sulfide oxide cement mortar. The compressive strength of MOS85, MOS855 and MOS81 at day 0 was 78.1MPa, 82.5 MPa and 103.7MPa, respectively. The compressive strength of MOS85, MOS855 and MOS81 at day 0 showed the largest decrease in compressive strength when they were immersed for 7d, and at this time their compressive strengths were 49.1MPa, 64.7MPa, 55.2MPa, and 14d when they were immersed, 55.2MPa; at 14d of immersion, the compressive strengths of MOS85, MOS855, and MOS81 are 39.8MPa, 54.1MPa, and 52.1MPa, respectively; at 28d of immersion, the compressive strengths of MOS85, MOS855, and MOS81 are 28.4MPa, 39.1MPa, and 39.1MPa, respectively, which can be seen that the MOS855 has the highest compressive strength in all immersion cycles, in order to explain this result, the compositional composition and microstructure of magnesium sulphoxide cement mortar specimens were subsequently analysed in this paper.



**Figure 1.** Compressive strength of magnesium sulphate cement mortar specimens with different fineness modulus immersed in distilled water for 7d, 14d, 28d

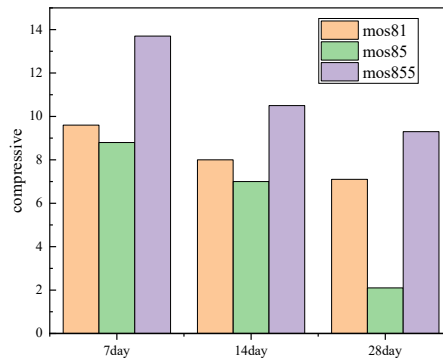
Figure 2 shows the effect of fineness modulus on the softening coefficient and rate of strength loss of magnesium sulphate-oxygen cement mortar immersed in distilled water for 28d. It can be seen that the softening coefficients of MOS85, MOS855, and MOS81 immersed in distilled water for 28 d were 0.501, 0.502, and 0.473, respectively. The softening coefficients of magnesium sulphate-oxygen cement mortar showed a tendency to increase and then decrease with the admixture of fine sand, and the highest softening coefficient of MOS cement mortar immersed in distilled water for 28 d was MOS855, and the lowest softening coefficient was MOS81. The strength loss rate of MOS85, MOS855 and MOS81 immersed in distilled water for 28 d was 49.9%, 47.7% and 49.7% respectively, with the mixing of fine sand, the strength loss rate of magnesium sulphate cement mortar changed in the opposite way to the softening coefficient, showing a trend of decreasing and then increasing. The lowest strength loss rate of magnesium sulphate-oxygen cement mortar immersed in distilled water for 28 d was similar for specimens MOS85, MOS855 and MOS81. This indicates that MOS855 specimen, i.e., magnesium sulphate cement mortar specimen with 50% fine sand admixture has relatively better water resistance.



**Figure 2.** Softening coefficient and rate of strength loss of magnesium sulphate cement mortar specimens with different fineness modulus immersed in distilled water for 28d

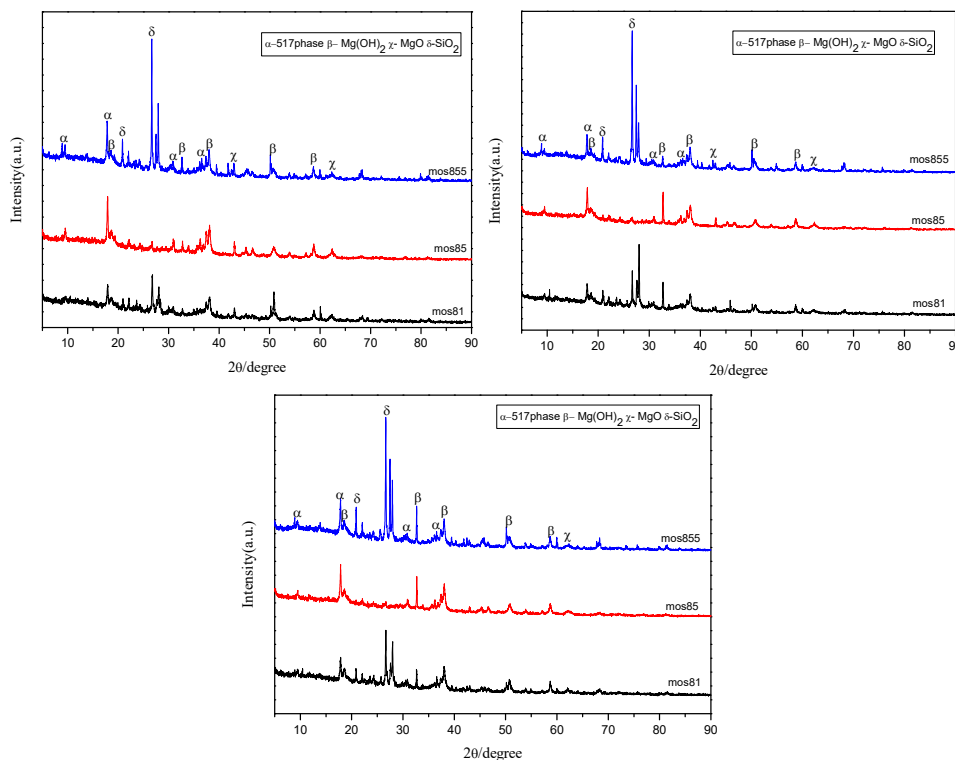
Figure 3 shows the effect of fineness modulus and age of immersion on the flexural strength of MOS cement mortar. It can be seen that the flexural properties of MOS cement mortar decreased gradually with the increase of soaking time, and the flexural strengths of MOS85, MOS855, and MOS81 were reduced to 2.1MPa, 9.3MPa, and 7.1MPa, respectively, at 28d, when their rates of strength loss were 76.13%, 32.12%, and 53.13%, respectively. With the incorporation of fine sand, the flexural strength

of magnesium sulphate cement mortar showed a tendency of increasing first and then decreasing, with the highest flexural strength of MOS855 and the lowest of MOS85 at 28d, which is consistent with the results of compressive strength.



**Figure 3.** Flexural strength of magnesium sulphate cement mortar specimens with different fineness modulus immersed in distilled water at 7d, 14d, 28d

### 3.2 Microstructure Characterisation



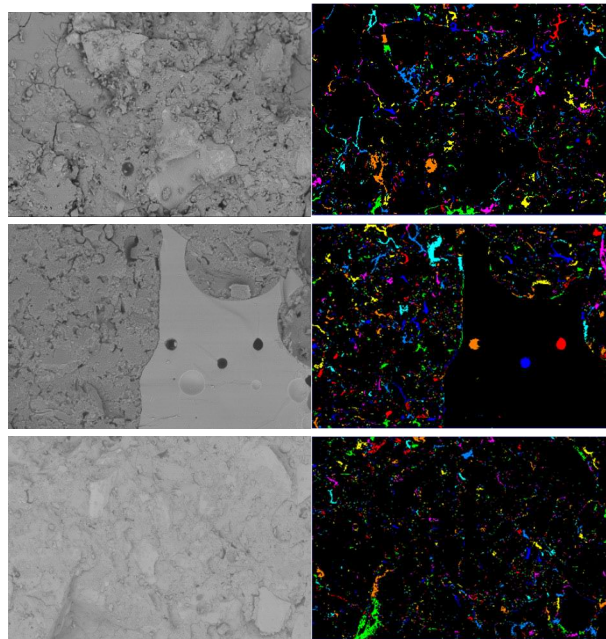
**Figure 4.** XRD patterns of magnesium sulphoxide cement mortar specimens with different fineness modulus immersed in distilled water for 7d, 14d and 28d

Figures 4 show the XRD patterns of magnesium sulphate cement mortar specimens of different fineness modulus after immersion in distilled water for 7 d, 14 d and 28 d, respectively. From Figures 4, it can be found that there is a significant difference in the percentage of  $Mg(OH)_2$  and 517 with the increase in soaking time, and Table 2 was produced based on the differences, from which it can be seen that after soaking in distilled water, the content of MgO in the specimens MOS85, MOS855, and MOS81 decreases, whereas the content of  $Mg(OH)_2$  starts to increase, and the content of 517 slightly

decreased. We found that MgO starts to transform to Mg(OH)<sub>2</sub> under water-resistant condition, which makes the content of Mg(OH)<sub>2</sub> increase. While 517 is converted from Mg(OH)<sub>2</sub>, this process also inhibits the decomposition of 517 under the condition of immersion in distilled water, so the strength decreases slightly.

**Table 3.** Content of each substance in the environment of soaking distilled water

	materialistic	7d	14d	28d
mos81	MgO	19%	17%	16%
	Mg(OH) <sub>2</sub>	33%	35%	37%
	517	48%	48%	48%
mos855	MgO	16%	15%	13%
	Mg(OH) <sub>2</sub>	30%	35%	34%
	517	54%	50%	53%
mos85	MgO	17%	16%	12%
	Mg(OH) <sub>2</sub>	29%	32%	37%
	517	54%	51%	51%



**Figure 5.** Comparison of SEM treatments of magnesium sulphate-oxygen cement mortar specimens of different fineness modulus immersed in distilled water (a-MOS855, c-MOS85, e-MOS81 before treatment, b-MOS855, d-MOS85, f-MOS81 after treatment)

Figure 5 SEM treatment control plots of MOS cement mortar specimens of different fineness modulus immersed in distilled water for 30 days. From Figure 3.12 which shows the total porosity of the specimens after, it can be found that the minimum total porosity of MOS cement mortar is 4.1437 per cent for 50 per cent fines sand mixing, the maximum total porosity of the mortar is 5.4598 per cent for full mixing of fines sand and the total porosity of the mortar without mixing of fines sand is 4.8214 per cent. Combining the comparison graphs before and after SEM treatment and the MIP total porosity graphs shows that MOS855 in distilled water immersion for 30 days environment has the

least porosity, the least destroyed pore structure, and relatively less destruction of the 517 terms, thus obtaining the best performance of MOS855.

#### 4. Conclusion

When medium sand and fine sand each accounted for 50%, the MOS cement mortar showed better water resistance, weather resistance and frost resistance. The physical properties of MOS85, MOS855 and MOS81 fine three kinds of cement mortar gradually decreased with the increase of soaking time, while the 517 content decreased and the pore structure was gradually destroyed. The compressive strength of MOS855 reached 39.1MPa at 28d of immersion, the softening coefficient reaches 0.502, strength loss rate reaches 47.7%, flexural strength reaches 9.3 MPa, and the relative content of 517 in MOS cement mortar is 53%.

Quantitative analysis by XRD shows that the 517 content and MgO content in the MOS cement mortar show a decreasing trend in the water resistance experiments, while the content of  $Mg(OH)_2$  gradually increases.

#### References

- [1] L. Urwongse, C.A. Sorrell, Phase relations in magnesium oxysulfate cements [J]. *J. Am. Ceram. Soc.* 1980, 63 (2):523–526.
- [2] Caijun Shi, A. Fernández Jiménez, Angel Palomo, New cements for the 21st century: The pursuit of an alternative to Portland cement [J]. *Cement and Concrete Research*, 2011, 41(8):750-763.
- [3] Demediuk, Cole WF. Hueber, HV. Studies on magnesium and calcium oxychlorides[J]. *Australian Journal of Chemistry*, 1955, 8(2):215-233.
- [4] T. Runċevski, C.Y. Wu, H.F. Yu, B. Yang, R.E. Dinnebier, Structural characterization of a new magnesium oxysulfate hydrate cement phase and its surface reactions with atmospheric carbon dioxide[J]. *J. Am. Ceram. Soc.* 2013, 96(11): 3609–3616.
- [5] Nan Wang, Hongfa Yu, Wanli Bi, et al, Effects of sodium citrate and citric acid on the properties of magnesium oxysulfate cement[J]. *Construction and Building Materials*, 2018, 169 : 697-704.
- [6] T. Demediuk, W.F. Cole, A study of magnesium oxysulfate [J]. *Aust. J. Chem.* 1957, 10 (3) :287–294.