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EFFECT OF MODIFIER AND SUPERFINE STEEL SLAG POWDER ON PROPERTIES OF MAGNESIUM OXYSULFATE (MOS) CEMENT

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With the increasing of iron and steel production, the rational utilization of waste steel slag is very important. At present, it is common to use steel slag as admixture of Portland cement and concrete. In order to further investigate the effect of modifier and superfine steel slag powder on properties of magnesium oxysulfate (MOS) cement, the examinations of compressive strength, hydration products, and pore structure of various MOS cement mixtures are discussed in detail. The results show that malic acid helps the formation of $5Mg(OH)_2·MgSO_4·7H_2O$ (517 phase) and gives MOS cement a finer pore structure. Addition of superfine steel slag powder can decrease the porosity and fine the pore size in the paste.

Keywords: steel slag; magnesium oxysulfate cement; compressive strength; x-ray analysis; pore structure

INTRODUCTION

In 2019, the global crude steel output is about 1,869 billion tons, and the steel slag by - products is about as high as 280 million tons. The recovery cost of extracting metal from steel slag is high and it will reduce the utilization rate of its value if it is used as backfill. Therefore, how to use slag solid waste has been a research topic for many years by metallurgical researchers [1]. It is also a practical problem to be solved in the development of circular economy and the construction of economical and environment friendly society [2].

MOS cement is a type of air - dried cementitious material formed by the reactions between high reactivity magnesium oxide powder (normally obtained by calcinationns of magnesite at 700 °C to 900 °C) and aqueous solutions of magnesium sulfate ($MgSO_4$) [3]. MOS cement is a friendly material due to its environmental protection and energy saving properties. In addition, it has a number of better engineering performances as compared to magnesium oxychloride cement and Portland cement, such as good compatibility with many materials, good hardening speed, low thermal conductivity, high resistance to fire, abrasion and chemicals [4, 5]. As a result, it is a promising material with a wide range of industry applications, including use as binding of lightweight insulating panels, industrial flooring, fire protection, decoration and construction [6]. Moreover, MOS cement is also widely used in reinforcing steel and prefabicated structural units processed at elevated temperatures due to its low rate of steel corrosion and good insensitive to high temperatures [7].

In this paper, the influence of modifier and superfine steel slag powder on properties of MOS cement is studied, which provides theoretical basis and technical reference for improving the properties of MOS cement and expanding utilization of waste steel slag.

MATERIALS AND METHODS

Raw materials

For preparation of the MOS cement, light - burnt MgO powder with a purity of 85 %, from Haicheng, Liaoning Province, China was used. The content of active MgO used in this work was determined to be 61,6 % by the standardized hydration method mentioned in Dong et al.'s report [8]. Superfine steel slag powder with specific surface area of 610 m^2 /kg from Anshan, Liaoning Province, China. Chemical composite on of light - burned MgO and superfine steel slag powder analyzed by X - ray fluoresceence spectrometer were presented in Table 1. The magnesium oxysulfate ($MgSO_4·7H_2O$) employed was a pure analytical reagent grade crystal obtained from

Table 1 **Chemical compositions of light - burnt MgO and superfine steel slag powder / mas. %**

Materials	Light - burned MgO	Superfine steel slag powder
MgO	86,53	0,83
SiO_2	5,47	49,86
Al_2O_3	0,13	38,12
CaO	1,26	3,78
Fe_2O_3	0,43	4,52
Others	6,18	3,07

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Tianjin Biaozhunkiji Ltd., China. An ultra pure analytical reagent grade malic acid was selected as a modifier additive for MOS cement.

Sample Preparation

MOS cement paste mixtures with different combination of the raw materials were prepared, and the mixtures design are shown in Table 2.

To prepare the neat MOS cement paste, a magnesium oxysulfate water solution was prepared firstly. The malic acid was admixed with the $MgSO_4$ solution to form a clear, uniform mixture. Subsequently, the weighted MgO and superfine steel slag powder were added into $MgSO_4$ solution and blended for a few minutes to form homogenous MOS cement pastes. After mixing operations were completed, the pastes were cast into moulds.

Test methods

For each mixture assigned in Tables 2, cubic specimens with a size of 40 × 40 × 40 mm were cast in steel moulds. It was observed after 28 - day air curing at a temperature of 20 ± 2 °C in a curing room. The compression test machine (TYE - 300) having a load speed of 1,5 mm / min were selected. The crystalline phases were identified by X - ray diffraction (XRD, X'Pert PRO) technique using Cu - Kα radiation. The pore structure measurements of MOS cement paste mixtures were conducted by using a mercury intrusion porosimeter with a maximum pressure of 228 MPa. The assumed contact angle was 140 °[9], and the mercury surface tension was 485 dynes / cm.

Table 2 **Mixtures design of the MOS cement pastes**

Sample number	(MgO: $MgSO_4$: H_2O) [a]	Superfine steel slag powder [b] / mas. %	Malic acid [b] / mas. %
M0	9 : 1 : 20	0	0
M1	9 : 1 : 20	0	0,5
M2	9 : 1 : 28	0	0,5
M3	9 : 1 : 20	10	0,5

a – Molar ratio
b – By weight of light – burned MgO

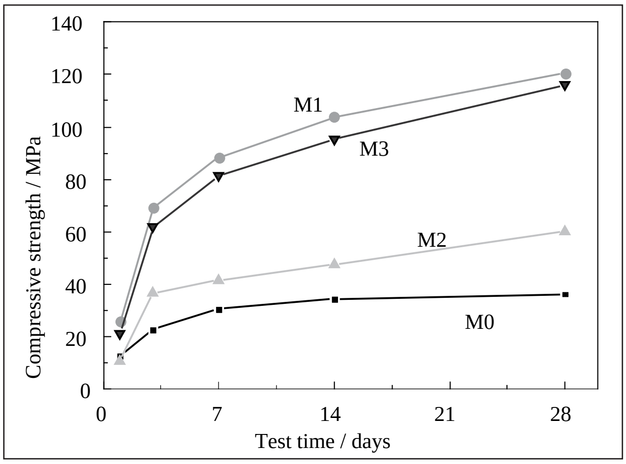

Figure 1 Compressive strength of MOS cement

RESULTS AND DISCUSSION

Compressive strength

The compressive strength of different MOS cement mixtures after 28 - day air curing for 3, 7, 14 and 28 days are illustrated in Figure 1. It shows that with a fixed molar ratio of MgO : $MgSO_4$ and H_2O : $MgSO_4$, the control sample of M0 has low compressive strength of about 30 MPa after 28 - day air curing. Compared with the control sample, the compressive strength of the modified sample M1 is improved significantly by adding malic acid as an additive. The compressive strength is over 110 MPa after 28 - day air curing, which is nearly four times the control sample. This means that malic acid can boost the compressive strength of MOS cement significantly. From Figure 1 also can be seen that the compressive strength of M3 with an addition of 10 % superfine steel slag is similar to the sample M1.

Pore structure

Porosity, pore size distribution and critical pore radius of MOS cement mixtures at 28 - day air curing are shown in Figure 2 and Figure 3.

From Figure 2 can be seen that the critical pore radius shift to the left side of finer pore size for the sample with malic acid. Thus, the lower porosity and finer pore radius of modified MOS cement paste result in the bet-

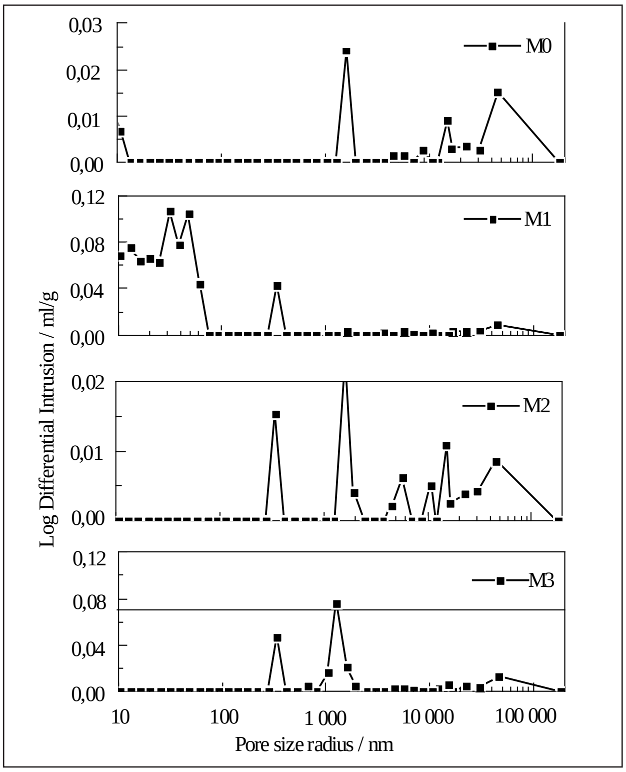

Figure 2 Differential pore distribution curve of MOS cement

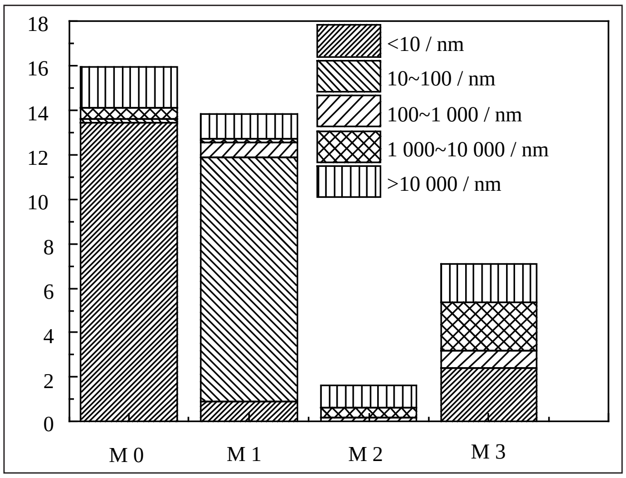

Figure 3 Porosity and pore distribution of MOS cement pastes

ter pore structure than that of the control sample without malic acid. Figure 3 shows that the porosity decreases from 15,94 % to 12,87 % for the modified sample M1 compared with the control sample M0.

From Figure 2 and Figure 3 also can be seen that the porosity and pore size of the hardened modified MOS cement paste are influenced significantly by the molar ratio of H_2O : $MgSO_4$ for the same molar ratio of MgO : $MgSO_4$. For example, although the sample M2 has lower porosity of 1,66 % than the sample M1 of 12,87 %, but the volume of pore size larger than 100 nm were 100 % which higher than the sample M1 of 14,05 %. And the critical pore radius of sample M2 was larger than the sample M1. This means that higher molar ratio of H_2O : $MgSO_4$ can greatly increase the proportion of harmful large pores. The modified MOS cement paste incorporated with 10 % superfine steel slag powder by weight of MgO has the lowest porosity of 7,10 % and the volume of pore size larger than 1 000 nm reduced from 11,26 % to 10,03 %. This implies that superfine steel slag powder can function as a filler in the paste, thus decreasing the porosity and improving pore structure of MOS cement.

Hydration products

From Figure 4, X-ray diffraction (XRD) can be seen that these mixtures at the air curing age of 28 days are primarily composed of 517 phase, $Mg(OH)_2$, residual MgO, and $MgCO_3$ that originated from the raw materials. The results indicate that malic acid are favorable to the formation of 517 phase. For fixed molar ratio of MgO:$MgSO_4$ of 9, cement paste M1 exhibits stronger peak intensity of 517 phase and weaker peak intensity of $Mg(OH)_2$ than the mixture M2.

CONCLUSIONS

The XRD results indicate that modifier additive of malic acid, lower molar ratio of H_2O : $MgSO_4$ and addition of superfine steel slag powder are favorable to the formation of 517 phase and less $Mg(OH)_2$ produced in the hydrate products, which are benefit to compressive strength.

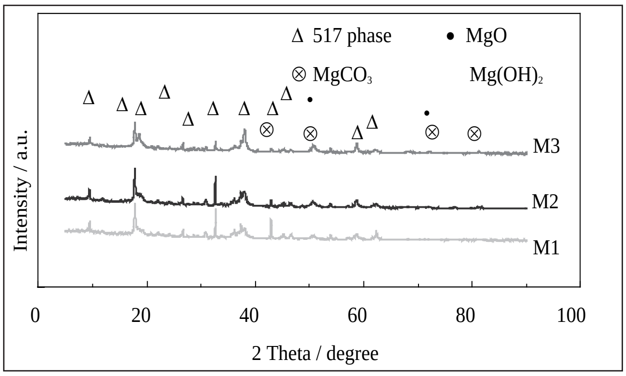

Figure 4 XRD patterns of modified MOS cement with different molar ratios

MOS cement paste with small amount malic acid becomes denser and with finer pore diameter. Higher molar ratio of H_2O : $MgSO_4$ can greatly increase the proportion of harmful large pores. Superfine steel slag powder plays a good filling role between the needle rod 517 phase, thus decreasing the porosity.

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Note: X. D. Wang is responsible for English language, Harbin, China