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Effect of Molar Ratios on Compressive Strength of Modified Magnesium Oxysulfate Cement

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Abstract

To determine the effect of molar ratios on compressive strength of magnesium oxysulfate cement (MOS), the hardened MOS cement pastes mixed with different molar ratios of $MgO/MgSO_4$ and $H_2O/MgSO_4$ were tested on the compressive strength. The examinations of strength development, phase compositions and microstructure of MOS cement are discussed in detail. The results show that these starting materials can significantly affect the compressive strength of MOS cement. The mixture with higher molar ratio of $MgO/MgSO_4$ and lower molar ratio of $H_2O/MgSO_4$ can produce more $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$(517 phase) and less $Mg(OH)_2$, which benefits the compressive strength of MOS cement.

Keywords: *magnesium oxysulfate cement, molar ratios, compressive strength, phase composition, microstructure*

1. Introduction

Magnesium oxysulfate (MOS) cement is a type of non-hydraulic cementitious material. It is formed by mixing proper ratios of magnesium oxide (MgO) powder (usually calcined at 700~900℃) with a concentrated solution of magnesium sulfate ($MgSO_4$) [1]. Similar to magnesium oxychloride (MOC) cement, MOS cement has many excellent engineering performances as compared to ordinary Portland cement. It has quick hardening properties, excellent fire-proofing, low thermal conductivity, and good resistance to abrasion and chemicals. [2-4]. As a result, it has a number of applications in architecture, including use as binders in lightweight panels, fire protection, insulating materials, and decorative purposes [5-8].

Although MOS cement features many good engineering properties, its application scope is still limited greatly for lower mechanical strength. Consequently, a lot of investigations to improve the mechanical strength of MOS cements have been carried out over the years. According to Demediuk and Cole [9], at different temperatures between 30 to 120℃, four main crystalline phases have been identified in the system of $MgO–MgSO_4–H_2O$ for MOS. They are $5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O$(or$2H_2O$) (513 phase), $3Mg(OH)_2 \cdot MgSO_4 \cdot 8H_2O$(318 phase), $Mg(OH)_2 \cdot MgSO_4 \cdot 5H_2O$(115 phase) and $Mg(OH)_2 \cdot 2MgSO_4 \cdot 3H_2O$(123 phase). However, only 318 phase appears to be stable below about 35℃. Urwong and Sorrel [10] studied the phase relationship in MOS cement carefully and identified a number of stable phases at 23℃, namely $3Mg(OH)_2 \cdot MgSO_4 \cdot 8H_2O$(318 phase), $Mg(OH)_2$, and MgO, plus $MgSO_4 \cdot nH_2O$ (n = 1, 6 and 7). In addition, metastable 115 phase, $MgSO_4 \cdot 4H_2O$ and $MgSO_4 \cdot 5H_2O$ could also be detected at

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ambient temperatures. They also indicated the impossibility of preparing MOS cement at 23°C which have more than 50wt-% of the 318 phase in cement if the starting materials are MgO and aqueous $MgSO_4$. It is because of the rapid formation of $MgSO_4 \cdot 7H_2O$ from these starting materials. These are the reasons for the low mechanical strength of MOS cement. Previous studies suggest that adjusting the crystal phase composition and minimizing undesirable phase formation may be an effective method to improve the mechanical strength of MOS cement. Very recently, according to Yu HF [11], adding phosphoric acid and phosphates can improve the compressive strength and water resistance of MOS cement by changing the hydration process of MgO and the phase composition. A new phase of $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$(517 phase) is formed, which is needle-like and insoluble in water. According to previous studies on MOC cement [12-14], the chemical reactions, reaction products, and mechanical strength of the system are drastically influenced by the starting materials. As a response to some investigations [11, 15] on the formation, structure and properties of MOS cement have been performed, but data on the compositions between the starting materials to achieve the best performance of MOS cement are rare and sparse. Additionally, the formation mechanism of 517 phase and hardening mechanism of the newly developed modified MOS cement still need further study, which is important to its industrial applications.

In the present research, a thorough study of MOS cement is conducted to investigate the effects of molar ratios of $MgO/MgSO_4$ and $H_2O/MgSO_4$ on the compressive strength of the hardened pastes. The examinations of strength development, phase compositions, and microstructure of MOS cement are discussed in detail for further studying the harden mechanism and obtaining optimal MOS cement.

2. Materials and Methods

2.1. Raw Materials

The magnesium oxide used in the current study was light-burnt MgO powder with a purity of 85%, from Haicheng, Liaoning Province, China. 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 [16]. The magnesium oxysulfate ($MgSO_4 \cdot 7H_2O$) employed was a pure analytical reagent grade crystal obtained from Tianjin Biaozhunkiji Ltd., China. An ultra pure analytical reagent grade citric acid ($C_6H_8O_7$) was selected as modifier additives for MOS cement. The chemical compositions of the raw materials in wt.% are presented in Table 1.

Table 1. Chemical Compositions of Light-burnt MgO and Fly Ash /wt.%

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Others
light-burnt MgO	3.09	1.3	0.16	0.33	81.0	14.03

The crystalline phases of light-burnt MgO powder identified by X-ray diffraction (XRD) are in stacked in Figure 1. The XRD peaks of crystalline MgO are clearly seen and small XRD peaks for $MgCO_3$ appear in the pattern. A small amount of residual $MgCO_3$ is due to low calcinations temperature of caustic magnesia.

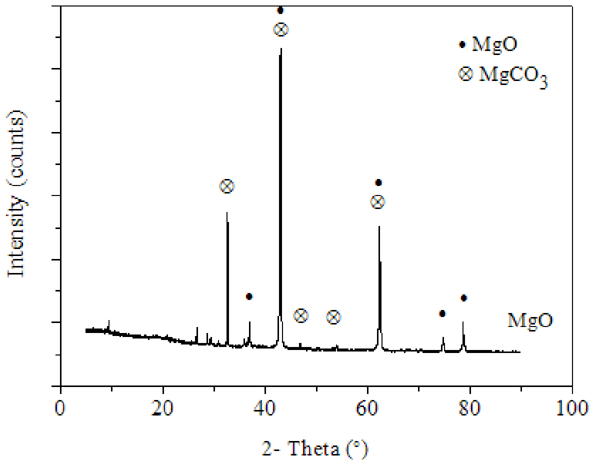


Figure 1. XRD Patterns of the Raw Materials

2.2. Sample Preparation

Targeting the effects of molar ratios of $MgO/MgSO_4$ and $H_2O/MgSO_4$ on the compressive strength, MOS cement paste specimens with wide ranges and different combinations of the raw materials were prepared, and the specimen matrices are shown in Tables 2.

Table 2. Mixtures Design of the MOS Cement Pastes with Different Molar Ratios

Sample number	$[MgO/MgSO_4/H_2O]$ [a]	Citric acid [b] (%)	Sample number	$[MgO/MgSO_4/H_2O]$ [a]	Citric acid [b] (%)
A1	5/1/18	0.5	C1	9/1/18	0.5
A2	5/1/20		C2	9/1/20	
A3	5/1/24		C3	9/1/24	
A2	5/1/28		C4	9/1/28	
B1	7/1/18		D1	11/1/18	
B2	7/1/20		D2	11/1/20	
B3	7/1/24		D3	11/1/24	
B4	7/1/28		D4	11/1/28	

[a] Molar ratio..
[b] By weight of light-burned MgO.

Deionized water was used for the production of MOS cement pastes. First, a magnesium oxysulfate water solution was prepared. The $MgSO_4{\cdot}7H_2O$ salt was dissolved in deionized water to form the solutions with different molar ratios of $H_2O/MgSO_4$. For the modified version, the citric acid was admixed with the $MgSO_4$ solution to form a clear, uniform mixture. Then, the MgO powder was added into $MgSO_4$ solution and blended for a few minutes to produce MOS cement paste. After mixing operations were completed, the pastes were cast into moulds.

2.3. Test Methods

For each mixture assigned in Tables 2, cubic specimens with a size of 40×40×40 mm were cast in steel moulds with vibration compaction. The strength development of the mixtures were recorded at 1, 3, 7, 14 and 28 days after air curing at a temperature of 20 ± 2℃ and under a relative humidity of 60 ± 5% in the curing room. The concrete compression test machine (TYE-300) and a load of 1.5mm/min were selected. The crystalline phases were identified by X-ray diffraction (XRD, X'Pert PRO) technique using Cu-Kα radiation. The morphology and microstructure of MOS cement samples were characterized by scanning electron microscopy (SEM, Quanta 200) on a fractured surface with gold coating.

3. Results and Discussion

3.1. Compressive Strength Development

The compressive strength of MOS cement depends mainly on the crystal phase composition, microstructure, and appropriate proportions of the starting materials. To investigate the influences of the molar ratios of MOS cement on the compressive strength, the different MOS cement pastes were prepared with regard to $MgO/MgSO_4$ molar ratios (5, 7, 9 and 11) and $H_2O/MgSO_4$ (18, 20, 24 and 28). The choice of the molar ratios, however, is limited by the rheology (upper limit) and the workability (lower limit) of the mixture, thus limited by the concentration of $MgSO_4$ solution and the content of active MgO in light-burnt MgO powder. At the same time, citric acid selected as modifier additive in the amounts of 0.5wt.% of MgO. The composition of the cement paste considered here is reported in Table 2.

The compressive strength of the MOS cement with different molar ratios of $MgO/MgSO_4$ and $H_2O/MgSO_4$ at air curing age of 7 days are compared and plotted in Fig.2. It shows that the compressive strength is influenced significantly by the molar ratios of $MgO/MgSO_4$ and $H_2O/MgSO_4$. The effect of molar ratios on compressive strength of MOS cement is in good agreement with the results of previous works on MOC cement. Compressive strength of MOS cement pastes increased with the increasing $MgO/MgSO_4$ molar ratio (lower than 11) when the molar ratio of $H_2O/MgSO_4$ was fixed. When the molar ratio of $MgO/MgSO_4$ was fixed, lower molar ratio of $H_2O/MgSO_4$ (the higher concentration) yielded higher strength. The highest strength is 107.6Mpa for the mixture D2, while the lowest strength is 19.4Mpa for the mixture A3.

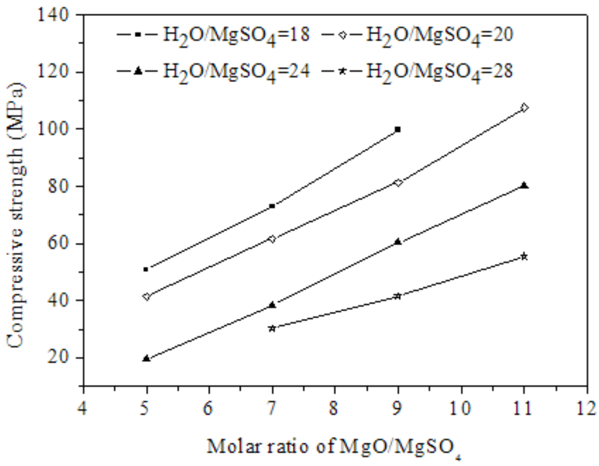


Figure 2. Compressive Strength of Different MOS Mixtures at Air Curing Age of 7 Days

The strength developments of these mixtures in the first 4 weeks after casting are plotted in Figure 3. It shows that mixture D2 has the maximum strength at different ages, while mixture D4 has the minimum strengths. When the chemical reaction reaches plateau at the age of 7 days, D4 has the fastest strength development compared with the other mixtures. It is believed that D4 has the best combination of the molar ratios of $MgO/MgSO_4$ and $H_2O/ MgSO_4$ for obtaining 517 phase of MOS cement.

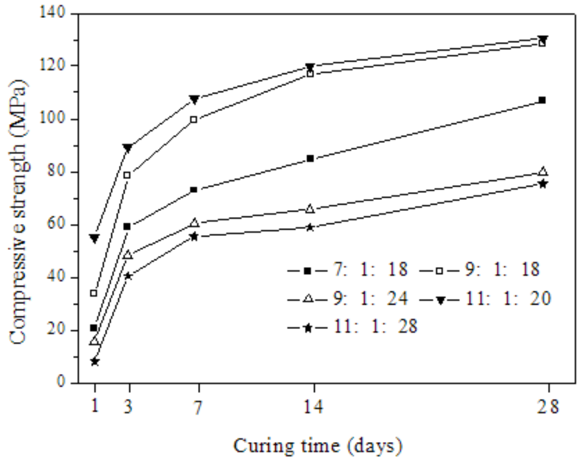


Figure 3. Compressive Strength Development of Some Selected Mos Mixtures Before Air Curing Age Of 28 Days

3. 2. Hydration Products

The X-ray diffractograms of mixtures B2, C2 and C4 are shown in Figure 4. It shows that the crystalline phases of these mixtures (at the 28 days curing age) are primarily composed of $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ (517 phase), $Mg(OH)_2$, residual MgO, and $MgCO_3$ that originated from the raw materials. The results from XRD (in Fig.4) also show that in MOS cement mixtures, with a fixed molar ratio of $MgO/MgSO_4$ of 9, cement paste C2 (with lower molar ratio of $H_2O/MgSO_4$ of 20) exhibits stronger peak intensity of 517 phase and weaker peak intensity of $Mg(OH)_2$ than the mixture C4 (with higher molar ratio of $H_2O/MgSO_4$ of 28). In addition, for a fixed molar ratio of $H_2O/MgSO_4$ of 20, the mixture C2 (with higher molar ratio of $MgO/MgSO_4$ of 9) exhibits stronger peak intensity of 517 phase and weaker peak intensity of $Mg(OH)_2$ than the mixture B4 (with lower molar ratio of $MgO/MgSO_4$ of 7). Moreover, with higher amounts of $MgO/MgSO_4$, the amount of residual MgO in the cement increased slightly. This indicates the amount of MgO is not completely reacted and that increasing the molar ratio of $MgO/MgSO_4$ leads to even more MgO not consumed by the reactions. The residual MgO could act as fillers in hardened MOS cement paste and benefit to the strength. These results indicate that lower molar ratio of $H_2O/MgSO_4$ (higher concentration brine) and higher molar ratio of $MgO/MgSO_4$ are favorable to the formation of 517 phase, and the higher the molar ratio of $H_2O/MgSO_4$, the more Mg $(OH)_2$ is produced. Hence, the specimen C2 with rational formulation would have better crystal formation and more compact microstructure compared to the other specimens.

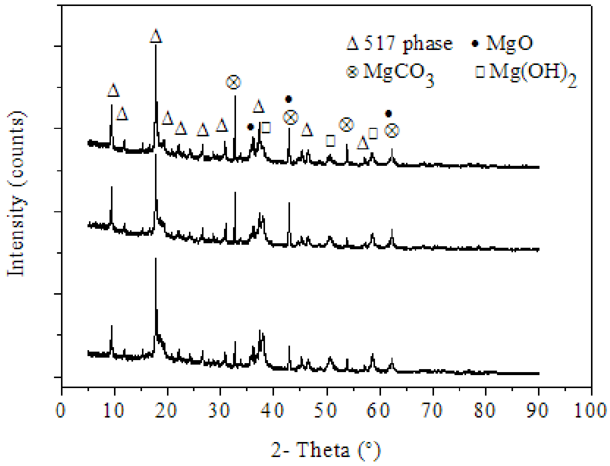
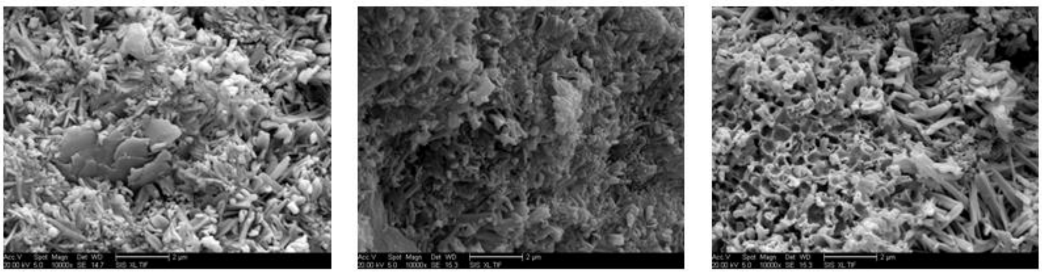


Figure 4. XRD Patterns of the Mos Mixtures with Different Molar Ratios Mgo/Mgso$_4$ and H$_2$o/Mgso$_4$ at the 28days (From Bottom to Top, C4, C2, B2 Respectively)

According to the studies of compressive strength development and X-ray diffractograms, the morphology of the samples with fractured surface of mixtures B2, C2, and C4 were selected for the microstructure study shown in Figure 5. It can be seen that the SEM image of the samples B2, C2, and C4 show reasonable agreement with the X-ray diffractograms corresponding to crystalline phase of MOS cement. It also can be seen that the microstructures of B2 and C2 are mainly composed of 517 phase, The crystals of the mixture B2 is generally in needle and plate shape. As compared to the sample B2, the microstructure of the mixture C2 is more homogenous, more compact, and contains interlaced needle-shaped crystals. The interlaced needle-shaped crystal and the resulting mechanical interlocking is believed to be responsible for the strength development of MOS cement. In addition, the image of mixture C4 occupied with plenty of flaky $Mg(OH)_2$ crystal with a loose structure except 517 phase. These indicate that more 517 phase and $Mg(OH)_2$ phase produced and more MgO residual as fillers, and the microstructure of sample C2 becomes more compact than the other samples.



(a) (b) (c)

Figure 5. SEM Images of the Mos Mixtures with Different Molar Ratios of Mgo/Mgso$_4$ And H$_2$o/Mgso$_4$ At The 28days (a) B2, (b) C2, (c) C4

4. Conclusions

A detailed parametric study of the effects of molar ratios of $MgO/MgSO_4$ and $H_2O/MgSO_4$ on the compressive strength of MOS cement was conducted. The lower molar ratio of $H_2O/MgSO_4$ (higher concentration brine) and higher molar ratio of

$MgO/MgSO_4$ are favorable to the formation of 517 phase, and the higher the molar ratio of $H_2O/MgSO_4$, the more $Mg(OH)_2$ is produced. The mixture with higher molar ratio of $MgO/MgSO_4$ and lower molar ratio of $H_2O/MgSO_4$ could produce more 517 phase and less $Mg(OH)_2$ which benefits the compressive strength of MOS cement. The MOS cement with rational formulation can have better crystal formation, more compact microstructure, and optimal compressive strength.

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References

[1] T. Demediuk, W. F. Cole and H. V. Hueber, J. Aust. Chem., vol. 2, no. 8, **(1955)**.
[2] T. A. Plekhanova, J. Keriene, A. Gailius and G. I. Yakovlev, Constr. Build. Mater, vol. 9, no. 21, **(2007)**.
[3] C. Y. Wu, H. F. Yu, J. Wen and J. M. Dong, New. Build. Mater, vol. 5, **(2013)**.
[4] G. Z. Li, Y. Z. Yu, J. Q. Li, Y. Z. Wang and H. S. Liu, Cem. Concr. Res., vol. 33, **(2003)**.
[5] X. Zhou and Z. Li, Constr. Build. Mater, vol. 1, no. 27, **(2012)**.
[6] A. Ozturk and M. Timucin, Adv, Appl, Ceram, vol. 7, no. 110, **(2011)**.
[7] Y. Li, H. F. Yu, J. M. Dong, H. X. Qiao and M. J. Wang, Chin. Ceram. Soc., vol. 4, no. 29, **(2010)**.
[8] C. K. Chau, J. Chan and Z. J. Li, Cem. Concr. Compos., vol. 4, no. 31, **(2009)**.
[9] T. Demediuk and W. F. Cole, J. Aust. Chem., vol. 10, **(1957)**.
[10] L. Urwong and C. A. Sorrell, J. Am. Ceram. Soc., vol. 10, no. 63, **(1980)**.
[11] C. Y. Wu, H. F. Yu, H. F. Zhang, J. M. Dong, J. Wen and Y. S. Tan, Mater. Struct., vol. 10, **(2013)**.
[12] Z. J. Li and C. K. Chau, Cem. Concr. Res., vol. 37, **(2007)**.
[13] Y. Karimi and A. Monshi, Ceram. Int., vol. 7, no. 37, **(2011)**.
[14] V. M. Sglavo, F. De Genua, A. Conci, R. Ceccato and R. Cavallini, J. Mater. Sci., vol. 20, no. 46, **(2011)**.
[15] T. Runčevski, C. Y. Wu, H. F. Yu, B. Yang and R. E. Dinnebier, J. Am. Ceram. Soc., vol. 11, no. 96, **(2013)**.
[16] J. M. Dong, H. F. Yu and L. M. Zhang, J. Salt. Lake. Res., vol. 18, **(2010)**.

