

## Article

# The Effect of Doping High Volume Magnesium Sulfate on Properties of Magnesium Oxychloride Cement

Qing Huang<sup>1,2</sup>, Weixin Zheng<sup>3,4,\*</sup> , Ying Li<sup>5</sup> , Chenggong Chang<sup>3,4</sup>, Jing Wen<sup>3,4,\*</sup>, Jinmei Dong<sup>3,4,\*</sup> and Xueying Xiao<sup>3,4</sup>

- <sup>1</sup> School of Materials Science and Engineering, Shaanxi University of Technology, Hanzhong 723000, China; huangqinghq@snut.edu.cn
- <sup>2</sup> National and Local Joint Engineering Laboratory for Slag Comprehensive Utilization and Environmental Technology, Hanzhong 723000, China
- <sup>3</sup> Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China; ccg168@isl.ac.cn (C.C.); xiaoxy@isl.ac.cn (X.X.)
- <sup>4</sup> Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province, Xining 810008, China
- <sup>5</sup> China Construction Fifth Engineering Bureau Co., Ltd., Changsha 410014, China; setdownly@126.com
- \* Correspondence: zhengweixin@isl.ac.cn (W.Z.); wj580420@isl.ac.cn (J.W.); dongda839@isl.ac.cn (J.D.)

**Abstract:** The composite gelling system of chlorine and magnesium thioxide was prepared by mixing different mass fractions of magnesium sulfate solution into MOC. Detailed studies regarding the influences of magnesium sulfate replacing magnesium chloride on the setting time, compressive strength, and water resistance of magnesium oxychloride cement (MOC) have been carried out in this paper. The phase composition and micro morphology of the hydration products in the mixed system were analyzed by XRD and SEM. The results show that the addition of magnesium sulfate prolongs the setting time and reduces the compressive strength of the mixed MOC. Compared with the primordial MOC system, the water resistance of the mixed system improved, with the mixed system exhibiting optimal water resistance when the mass fraction of magnesium sulfate was 30%. The phases of the mixed system were composed of  $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  and  $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  phases. The microscopic morphology shows that the interior of air-cured MOC was composed of a large number of needle-like crystals, and continuous crystal structures have close contact and a strong bonding force. Cracks and pores appear on the surface after submerging in water, and the crystallization state of the internal crystals becomes worse. The compressive strength and water stability of MOC were closely related to the crystal morphology.

**Keywords:** magnesium oxychloride cement; magnesium oxysulfate cement; magnesium sulfate; water resistance; setting time; compressive strength



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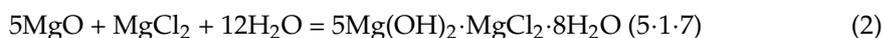
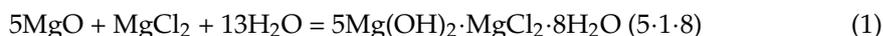


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## 1. Introduction

Cement is a very important cementitious material in civil engineering, which can be divided into two categories, calcium cement and magnesium cement, based on the composition of main elements. The magnesium cementitious material, also known as magnesium cement, can be mainly divided into three types: magnesium phosphate cement (MPC) [1], magnesium oxychloride cement (MOC) [2], and magnesium oxysulfide cement (MOS) [3]. Among these, MOC and MOS occupy the two most important types of magnesium cement. The MOC system belongs to an air-dried cementitious material that is composed of aqueous solutions of magnesium chloride and light-burned magnesium oxide powder, and was invented by French scientist Sorrel in 1867 [4]. MOS is also an air-dried cementitious material composed of magnesium oxide, magnesium sulfate, and water [5], its basic hydration feature pertains to  $\text{MgO-MgSO}_4\text{-H}_2\text{O}$  ternary system. Compared with ordinary Portland cement, MOC and MOS possess many favorable traits [6,7], such as

rapid hardening, high early strength, low thermal conductivity, good fire resistance, good wear resistance, and excellent corrosion resistance [8–10]. They are both widely used in the production of building auxiliary materials such as fireproof board and building light insulation wallboard [11–13].



MOC is widely used for high saline soil areas in Western China because of its excellent salt attack resistance [14]. This property of MOC allows for the full use of magnesium chloride generated in the process of extracting lithium from Salt Lake [8]. It can greatly solve the problem of accumulation of large quantities of magnesium resources and thus alleviates the pressure of environmental pollution in the Salt Lake area [1,3,15], therefore, the MOC system plays a vital role in promoting the comprehensive utilization of Salt Lake resources [16,17]. However, MOC also has the characteristics of poor water resistance, deformation, and corroded reinforcement [18], these affect the further development and widely application of MOC.

The  $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  (5·1·8) in MOC, which plays an important role in strength, is unstable in structure and belongs to a metastable state. The 5·1·8 can easily decompose to  $\text{Mg}(\text{OH})_2$  when immersed in water.  $\text{Mg}(\text{OH})_2$  is a layered structure, which is loosely stacked on the surface of the MOC matrix, resulting in the reduction of strength and the significant increase of porosity and moisture absorption [3,19]. These imperfections of MOC seriously hinder its application. Based on the above, the improvement of magnesium cement is imperative.

Many scholars have shifted their focus to the influence of various impurities and admixtures on the characteristics of MOC with the deepening of research. Previous studies [20,21] have found that the foamed fireproof board was prepared by mixing magnesium sulfate solution and magnesium chloride solution in the MOC system, which overcomes the disadvantages of moisture absorption and halogen in MOC. Research also found that [22] properties of the mixed system, in which the mixed system was prepared using a different ratio of magnesium sulfate solution and magnesium chloride solution as common raw materials and adding potassium dihydrogen phosphate as a modifier, were greatly changed, showing good water resistance after soaking in water for 28 days. There have already been many reports [8,23–27] on the improvement of MOC performance by adding phosphoric acid and phosphate. Results [10,23,24] have also shown that the addition of phosphoric acid and phosphate can greatly enhance the water resistance of MOC. Although MOC and MOS belong to the same type of cement, however, what are the reasons and crux for the improvement of performance in a mixed system, especially water resistance? There has been little attention to the hydration products and micro-morphology after they form a mixed system. In addition, MOC has relatively higher compressive strength than MOS, while MOS has relatively better water resistance than MOC. Whether doping high volume magnesium sulfate to MOC can greatly improve the water resistance and slightly decrease the compressive strength of MOC or not is a worthy question for further research.

Based on the above,  $\text{MgSO}_4$  was added into the MOC system, the  $\text{MgCl}_2$  in MOC was partially or completely replaced by  $\text{MgSO}_4$  in this study, without adding any modifier, the influence of  $\text{MgSO}_4$  on the setting time, compressive strength, and water resistance of the generated mixed system were studied in detail.

## 2. Experimental

### 2.1. Raw Materials and Specimen Preparation

Light-burnt MgO powder was produced by calcining magnesite in Liaoning province, China. The activity fraction of light-burnt MgO powder was 50 wt% tested via the hydration method [4,10]. The chemical composition was analyzed by X-ray fluorescence (XRF, Arl Quant) is shown in Table 1. Reagent grade  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MgCl}_2$  were supplied by Kemiou Chemical Technology Company, Tianjin, China.

**Table 1.** The chemical composition of light-burned magnesia powder.

Compound	MgO (Magnesium Oxide)	MgO <sub>a</sub> (Active Magnesium Oxide)	CaO (Calcium Oxide)	Al <sub>2</sub> O <sub>3</sub> (Aluminium Oxide)	SiO <sub>2</sub> (Silicon Dioxide)	Fe <sub>2</sub> O <sub>3</sub> (Ferric Oxide)	Ignition Loss
Content/wt%	85.92	55.05	1.24	1.31	6.03	0.55	4.84

a: active magnesium oxide.

The investigated MOC was fabricated by mixing MgO:MgCl<sub>2</sub>:H<sub>2</sub>O at molar ratios of 6:1:15 and 7:1:18. Meanwhile, 0 wt%, 30 wt%, 50 wt%, 70 wt%, and 100 wt% mass fractions of MgSO<sub>4</sub> were completely dissolved in magnesium chloride solution, and then mixed with MgO at the stirring rate of 250 r/min for 15 min. The paste was then poured into steel molds with the size of 20 mm × 20 mm × 20 mm, cured at 25 ± 1 °C and 65% RH for 24 h. Lastly, the specimens were released from the mold, and the curing of the specimens resumed at 25 ± 1 °C and 65% RH for another 24 h.

## 2.2. Specimen Characterizations

The compressive strength of cured MOC samples were evaluated by a Universal Testing Machine (CMT5105) with a maximum force of 300 kN, and a loading speed of 3mm/min, according to the test standard (GB9341-2000, China). The compressive strength was also evaluated after air curing at 3 days, 7 days, and 28 days, and submerging the samples in water for 3 days, 7 days, and 28 days, respectively. Moreover, the compressive strength of each samples was used to calculate the softening coefficient via Equation (1) and each test was repeated six times to ensure repeatable data.

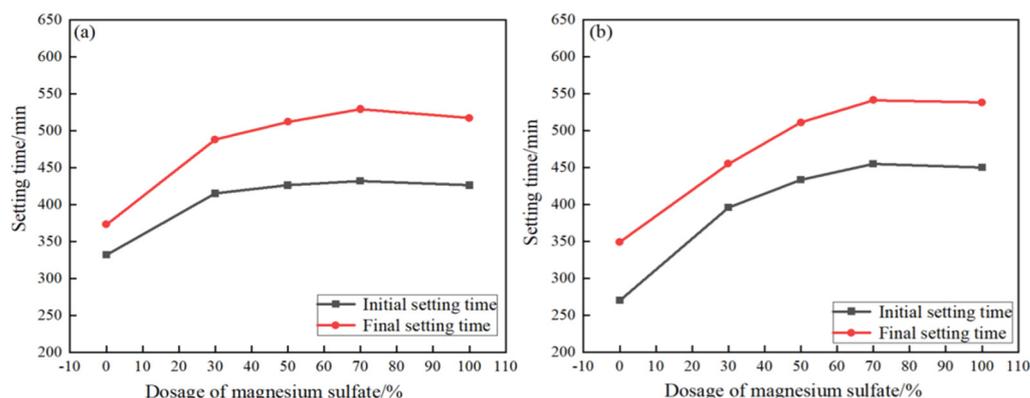
$$R_f = R_{(w, n)} / R_{(a, 14)} \quad (3)$$

where  $R_f$  corresponds to the softening coefficient of MOC,  $R_{(w, n)}$  is the strength of the sample after submerging in water for  $n$  days,  $R_{(a, 28)}$  indicates the compressive strength of the MOC sample, which has been cured for 28 days. The setting time was determined using a Vicat apparatus at 20 ± 2 °C according to the test standard (GB/T1346-2001, China). XRD spectra were fitted by Bruker AXS (2006) Topas 4.2 software (Bruker Company, Billerica, MA, USA), where the scanning range was 5–70°, and the scanning rate was 12.0°/min. Analytically pure Al<sub>2</sub>O<sub>3</sub> was selected as the internal standard sample, and a 10 wt% internal standard sample was added to quantitatively analyze the MOC, at a scanning rate of 2.4°/min. Phase content was quantitatively analyzed using the Rietveld method [28]. Moreover, the microstructures of the samples were observed by a scanning electron microscope (SEM, SU8010/X-Max). The accelerating voltage was 20 kV and the resolution was 3.5 nm.

## 3. Results and Discussion

### 3.1. Setting Time

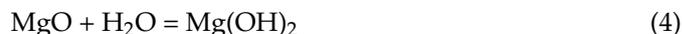
The setting time of MOC and MOS is related to the hydration rate of magnesium oxide and the process of the crystalline forming phase in general [29]. The effect of magnesium sulfate with different mass fractions on the setting time of MOC under different ratios is shown in Figure 1a,b, respectively. It can be concluded from Figure 1a that the initial setting time of the slurry was extended from 332 to 426 min, which was extended for 28.3% with the mass fraction of MgSO<sub>4</sub> increasing from 0% to 50 wt% under the ratio of 6:1:15. Meanwhile, the final setting time was extended from 373 to 512 min, which was prolonged by 37.3%. When the mass fraction of MgSO<sub>4</sub> in MOC was 100%, in the pure MOS system, the initial setting time was extended from 426 to 432 min and extended by 1.3% compared with MOC with 70% MgSO<sub>4</sub>. The final setting time was extended from 517 to 529 min, which was prolonged by 2.2%.



**Figure 1.** The setting time of MOC at different mass fractions of MgSO<sub>4</sub> (a): 6:1:15; (b): 7:1:18.

Compared to the pure MOC system, the setting time of the slurry also shows a continuous growth trend with the addition of MgSO<sub>4</sub> under the ratio of 7:1:18 (Figure 1b). When the mass fraction of MgSO<sub>4</sub> increases from 30 wt% to 70 wt%, the initial setting time of the slurry was extended from 396 to 455 min, which was prolonged by 14.8%. The final setting time was prolonged from 455 to 541 min, an increase of 18.9%. The initial setting time in pure MOS system, compared with MOC with 70 wt% MgSO<sub>4</sub>, was lengthened from 450 to 455 min, an extension of 1.1%. The final setting time was extended from 538 to 541 min and extended by 0.5%. Additionally, the setting time of cement paste at the ratio of 6:1:15 was longer than that at the ratio of 7:1:18, the analysis shows that the increase of water content leads to the prolongation of setting time.

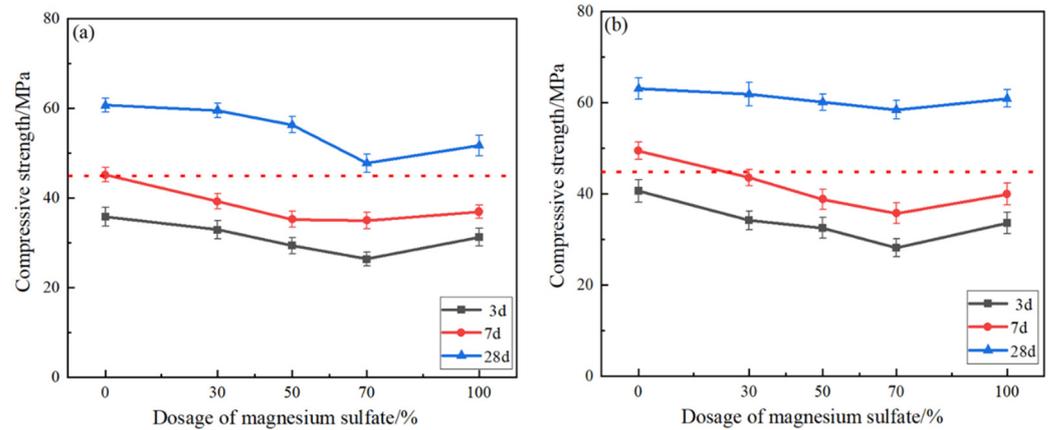
It can also be seen that the pure MOC system has a faster condensation and hardening rate and a shorter condensation time, while the pure MOS system has a slower condensation and hardening rate and a longer hardening time. The setting time of the slurry is closely related to the molar ratio of cements. When the concentration of MgCl<sub>2</sub> in MOC system is high, the formation of hydration products is promoted, and the setting time is short. With the increase of the mass fraction of MgSO<sub>4</sub>, the concentration of MgCl<sub>2</sub> decreases gradually. Due to the fact that SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> interfere with each other in the slurry, the formation rate and crystallization rate of hydration products becomes slower, and the setting time of the slurry is prolonged [22]. The specific chemical mechanism is shown as Equations (4)–(6). When the mass fraction of MgSO<sub>4</sub> is greater than 70 wt%, the concentration of Cl<sup>-</sup> in the slurry decreases, the increase of SO<sub>4</sub><sup>2-</sup> concentration promotes the formation of 5·1·7 phase, and the setting time of the slurry shortens. However, due to the low concentration of MgSO<sub>4</sub> and the low consistency of the slurry, the setting time of MOS is longer than that of MOC.



### 3.2. Compressive Strength

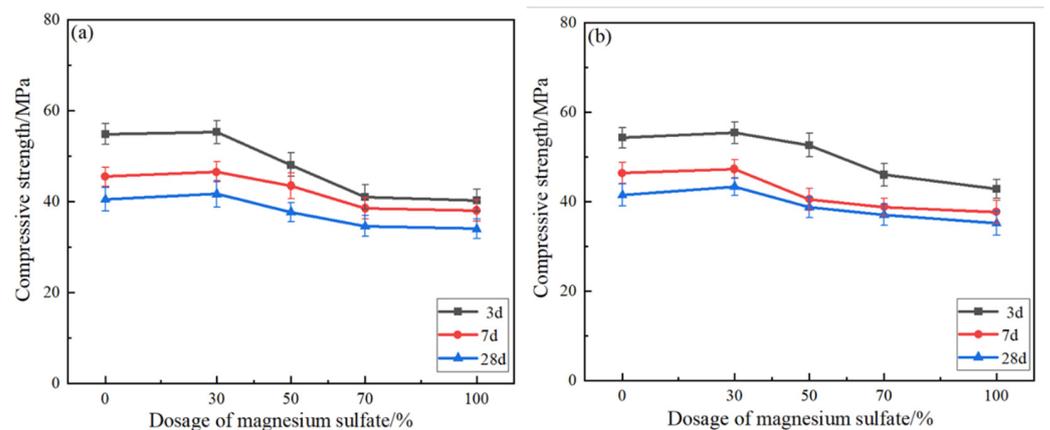
Strength was one of the main indexes to evaluate the properties of cementitious materials [30–33]. Figure 2 shows the relationship between the compressive strength of MOC cement mixed with different mass fractions of MgSO<sub>4</sub> under different ratios. It can be concluded from Figure 2 that when curing in air, the compressive strength of the specimen decreases firstly and then increases with the increase of the mass fraction of MgSO<sub>4</sub>. When the mass fraction of MgSO<sub>4</sub> was 70 wt%, the compressive strength reached the lowest. The compressive strength of system with the 100 wt% mass fraction of MgSO<sub>4</sub> decreases by 38.67% compared with MOC without MgSO<sub>4</sub> at the age of 3 days (Figure 2a). This means that the compressive strength of the pure MOC system was 38.67% higher than that of the pure MOS system, when the age was 28 days. Compared with MOC without MgSO<sub>4</sub>, the mass fraction of MgSO<sub>4</sub> increases to 30 wt%, the compressive strength decreases

by 1.88%, and the mass fraction of  $\text{MgSO}_4$  increases to 50 wt%, while the compressive strength decreases by 7.81%. The mass fraction of  $\text{MgSO}_4$  in MOC increases to 70 wt%, the compressive strength decreases to the lowest, which is 58.17 MPa, and the compressive strength decreases by 10.03% (Figure 2b). Therefore, the pure MOC system has the highest compressive strength. The pure MOS system, however, has relatively lower compressive strength. When  $\text{MgSO}_4$  was added to the MOC system, the compressive strength of the MOC system can be reduced. However, the compressive strength of the MOC system is higher than 42.50 MPa after 28 days air curing, which is satisfactory for application according to the Standard of GB175-2007.



**Figure 2.** The compressive strength of MOC with different mass fractions of  $\text{MgSO}_4$  at air curing (a): 6:1:15; (b): 7:1:18.

Figure 3 shows that the compressive strength of the specimen decrease with the increase of the mass fraction of  $\text{MgSO}_4$  after soaking in water. Compared with MOC without  $\text{MgSO}_4$ , when the mass fraction of  $\text{MgSO}_4$  increases to 30 wt%, the compressive strength has a small range of variation. While the mass fraction of  $\text{MgSO}_4$  increases to 70 wt%, the compressive strength decreases significantly by 22.68% at the age of 3 days (Figure 3a). It can also be seen that under the ratio of 7:1:18, the change trend of compressive strength in MOC was consistent with Figure 3a, and with the increase of the mass fraction of  $\text{MgSO}_4$  during the same soaking period (Figure 3b).

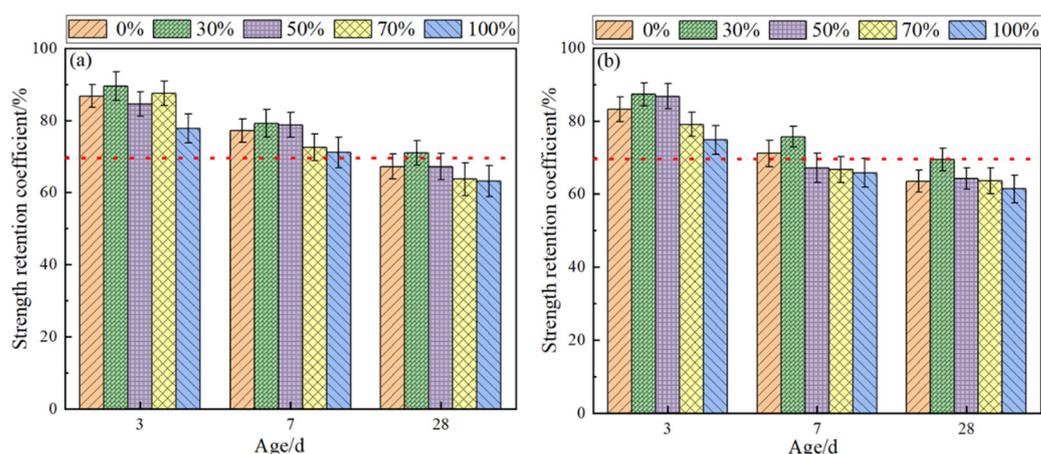


**Figure 3.** The compressive strength of MOC with different mass fractions of  $\text{MgSO}_4$  after water immersion (a): 6:1:15; (b): 7:1:18.

### 3.3. Water Resistance

The composition and structure of hydration products were the fundamental factors affecting the water resistance of magnesium cementitious materials [34]. Figure 4 is the softening coefficient diagram of MOC with different mass fractions of  $\text{MgSO}_4$  under different

ratios. It was observed that the addition of  $\text{MgSO}_4$  increases the softening coefficient of a cement system when compared with the pure MOC and pure MOS systems. Additionally, the softening coefficient of MOC firstly increases and then decreases with the increased mass fraction of  $\text{MgSO}_4$ . When the mass fraction of  $\text{MgSO}_4$  increase ranges from 0% to 30 wt%, the softening coefficient increases significantly, while when the mass fraction of  $\text{MgSO}_4$  increase ranges from 30 wt% to 100 wt%, the softening coefficient decreases gradually (Figure 4a). Therefore, the system has the highest softening coefficient when the mass fraction of  $\text{MgSO}_4$  is 30 wt% at all curing ages with 71.0%. It is reported that the MOC can have excellent water resistance when the softening coefficient is higher than 70.0% [35]. The variation tendency of the softening coefficient of MOC was consistent with Figure 4a, and with the increase in the mass fraction of  $\text{MgSO}_4$  (Figure 4b). Thus, it is concluded that the water resistance of a cementitious system has been improved with the incorporation of  $\text{MgSO}_4$ . In particular, when the mass fraction of  $\text{MgSO}_4$  is 30 wt%, the mixed cementitious material shows best water resistance.

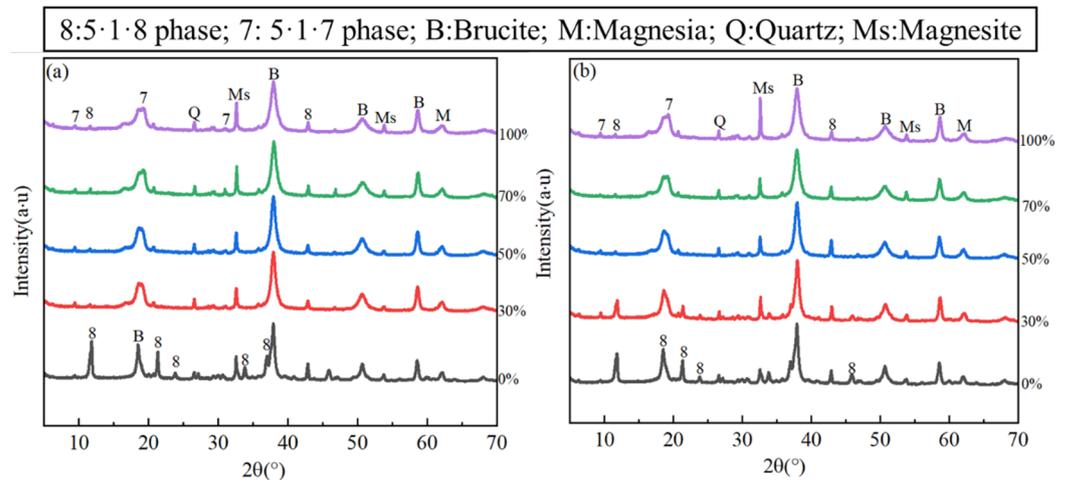


**Figure 4.** The softening coefficient of cement with different mass fractions of  $\text{MgSO}_4$  (a): 6:1:15; (b): 7:1:18.

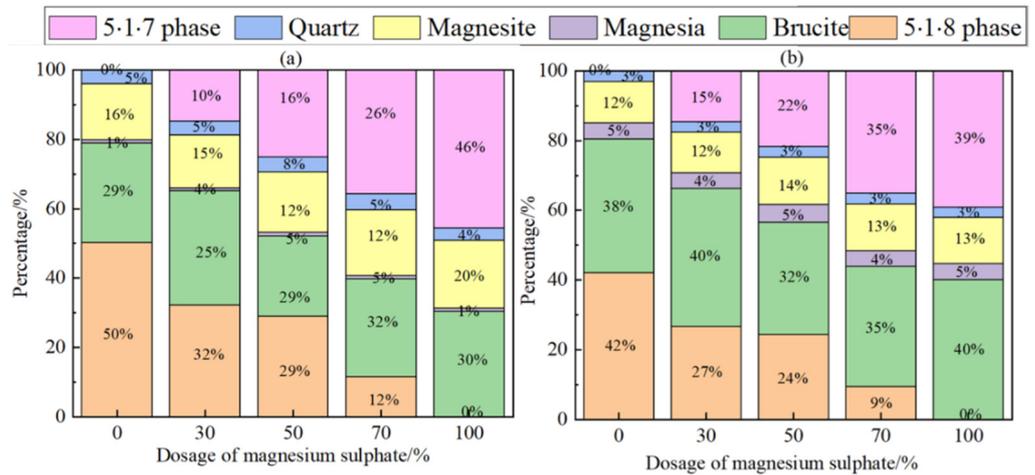
### 3.4. XRD Analysis

Figure 5a,b were the phase diagrams of the MOC system with the mix ratio of 7:1:18 after curing in air for 28 days and soaking in water for 28 days, respectively, and then mixed with different mass fractions of  $\text{MgSO}_4$ . The software Topas 4.2 has been adopted to analyze the phases and summarize the results in Figure 6a and b, respectively. It can be observed from Figure 5 that the main strength phase of the pure MOC system was 5·1·8 phase and the hydration product of the pure MOS system was 5·1·7 phase after 14 days of air curing or water immersion. When  $\text{MgSO}_4$  solution was added to the pure MOC system, the main hydration product phases of the mixed system were 5·1·8 and 5·1·7, which existed simultaneously. In addition, they also contained unreacted  $\text{MgO}$ , a small amount of  $\text{SiO}_2$ ,  $\text{MgCO}_3$ , and a large amount of  $\text{Mg(OH)}_2$ . Among them,  $\text{Mg(OH)}_2$  was the hydration product, and the other phases stem from unreacted raw materials and impurities.

The content of 5·1·8 phase gradually decreases from 50% to 0% with the increase of the mass fraction of  $\text{MgSO}_4$  (Figure 6a). The content of 5·1·7 phase increases from 0% to 46% with the increase of the mass fraction of  $\text{MgSO}_4$ . The content of  $\text{Mg(OH)}_2$  generally decreases firstly and then increases with the increase of the mass fraction of  $\text{MgSO}_4$ . This may be due to the addition of  $\text{MgSO}_4$  causing the growth of 5·1·8 phase and 5·1·7 phase to compete with each other, which hinders the production of  $\text{Mg(OH)}_2$ . In addition, the content of  $\text{Mg(OH)}_2$  was as high as 30–40%. The foremost reason was that the mix ratio selected in this study provides excess water.



**Figure 5.** The XRD patterns of cement with different mass fractions of  $MgSO_4$  (a): Air curing for 28 days; (b): Water immersion for 28 days.



**Figure 6.** The content of phases in cement with different mass fractions of  $MgSO_4$  (a) Air curing for 28 days; (b) Water immersion for 28 days.

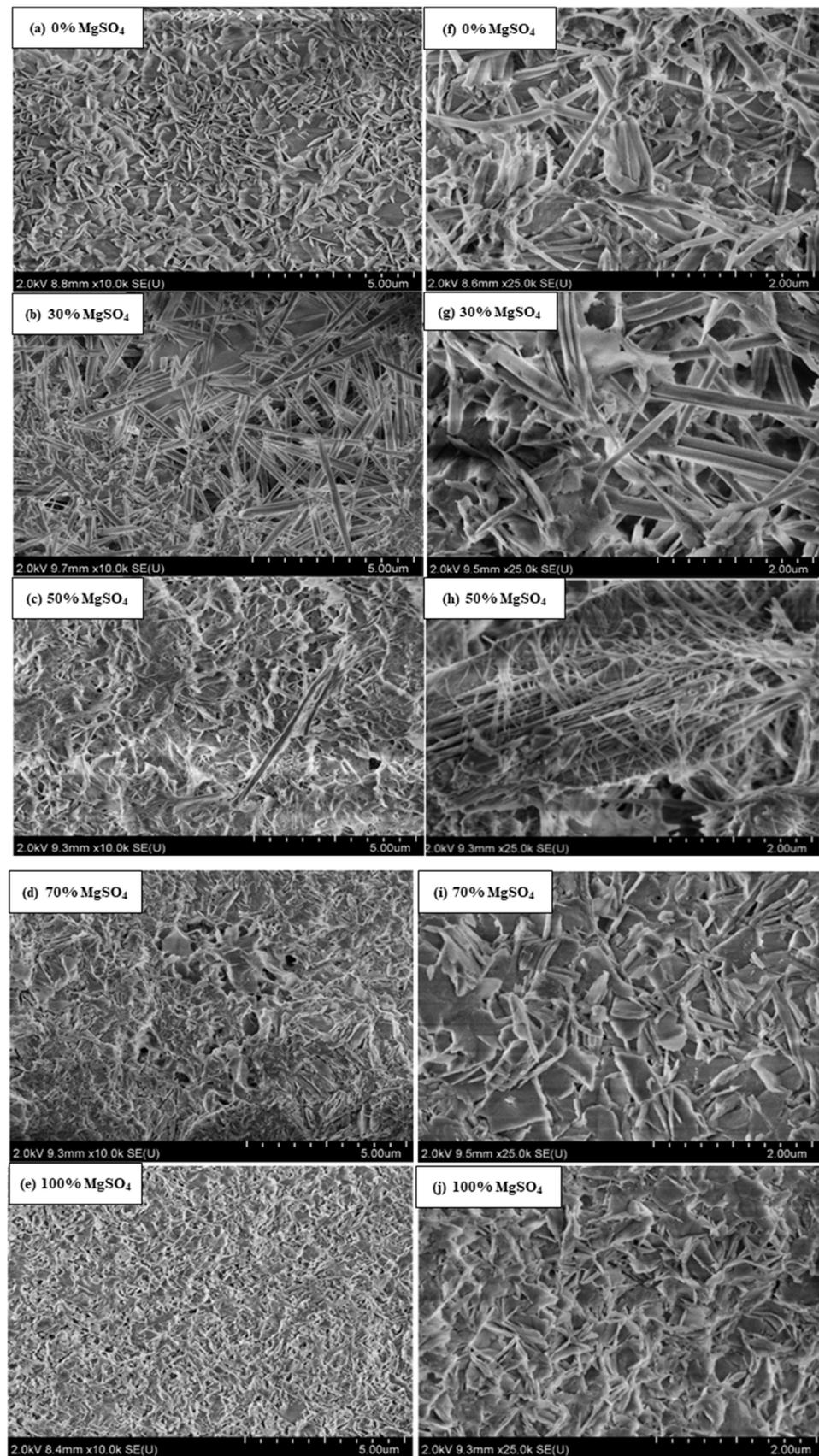
It was worth noting that the content of the main hydration product phases (5·1·8 and 5·1·7) in the mixed system was lower compared with the pure MOC system. Meanwhile, the compressive strength of the mixed system was lower than that of the pure MOC system. It could be concluded that the different concentrations of  $SO_4^{2-}$  and  $Cl^-$  in the solution causes a difference in the growth order and amount of hydration products 5·1·8 and 5·1·7. Therefore, there was no connection structure between crystals and the low mechanical properties in the mixed system.

The content of  $Mg(OH)_2$  increases after adding  $MgSO_4$  solution in the system after water immersion, while the content of 5·1·8 phase and 5·1·7 phase decreases when compared with the pure MOC system and the pure MOS system. This was indicative that the main strength phases in the system had undergone the transformation and produced a certain amount of  $Mg(OH)_2$  with poor mechanical properties. The water resistance of the mixed system was improved compared with the pure MOC system and the pure MOS system. The most likely reason was that 5·1·8 phase and 5·1·7 phase were transformed into a certain amount of  $Mg(OH)_2$  that accurately fills the pores formed by the overlapping of 5·1·8 phase and 5·1·7 phase, which render the structure of the mixed system more dense and show better water resistance.

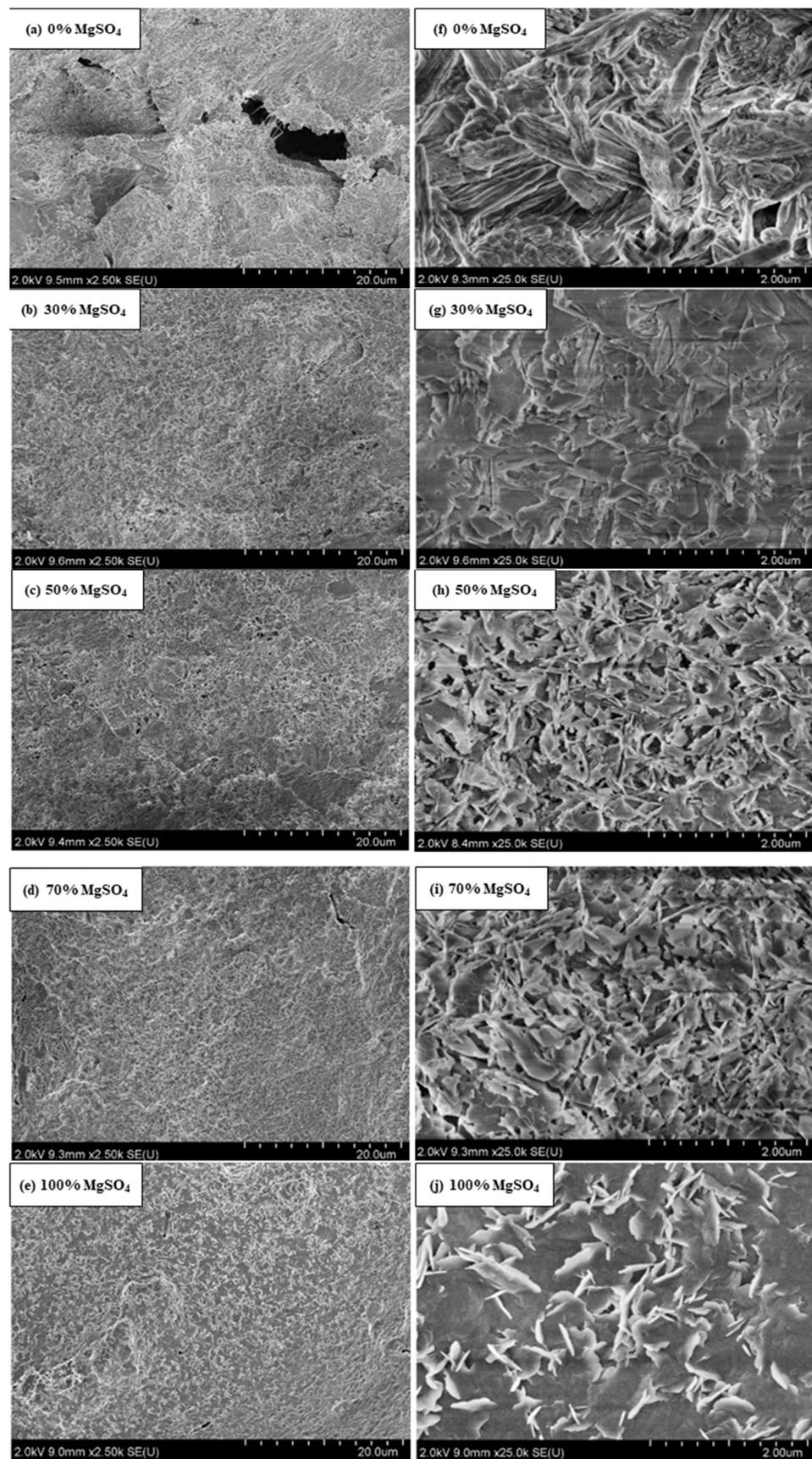
### 3.5. SEM Images

The SEM images with different mass fractions of  $\text{MgSO}_4$  cured in air for 28 days are shown in Figure 7. It can be seen that the different mass fractions of  $\text{MgSO}_4$  have an obvious influence on the micro morphology of magnesium cementitious material. It can be observed that the matrix surface structure of the mixed system was loose compared with the pure MOC and MOS systems (Figure 7a–e). Meanwhile, there are pores in the matrix, which was one of the reasons for the reduction of compressive strength of the mixed system. When the matrix was further enlarged, it was found that the MOC system mainly contains a large number of needle-rod crystals dispersed in gelled crystals, forming a continuous structure with high compactness and a strong connection between crystals (Figure 7f–j). The pure MOS system was mainly composed of a large number of flake crystals, granular crystals, and gelled crystals. When adding  $\text{MgSO}_4$ , increasing the mass fraction of  $\text{MgSO}_4$  to 50 wt%, the hydration products of the mixed system have a poor crystallization state, the internal crystals change to become long and needle-shaped, the size distribution range of the needle-shaped crystals becomes wide, and the degree of cross-linking between crystals was reduced. When the mass fraction of  $\text{MgSO}_4$  continued to increase to 70 wt%, there were not only rod-like crystals, but also flake crystals. This further leads to the reduction of the cross-linking degree of the mixed system and the less dense structure, which renders the compressive strength of the mixed system lower.

The SEM images with different mass fractions of  $\text{MgSO}_4$  soaked in water for 28 days are shown in Figure 8. It can be seen that the substrate surfaces of the pure MOC system and the pure MOS system were uneven, pores appeared and obvious traces of erosion appeared after soaking in water (Figure 8a–d,f). When adding  $\text{MgSO}_4$ , the surface of the matrix structure of the mixed system became denser with the increase of the mass fraction of  $\text{MgSO}_4$ . The matrix of the pure MOC system was mainly formed by interweaving rod crystals and flocculent crystals with a loose structure (Figure 8f–j). The pure MOS system was mainly composed of flower flake crystals with a low cross-linking degree. When  $\text{MgSO}_4$  was added, the matrix surface was composed of a large number of flake crystals and particle crystals accompanying the increase of the mass fraction of  $\text{MgSO}_4$ . However, the flake crystals were intertwined and overlapped to form a dense matrix structure. Therefore, after adding  $\text{MgSO}_4$ , the water resistance of the mixed system was better than that of the two pure systems. The main reason for the improvement of water resistance was the recrystallization of hydration products during immersion, which change the micro morphology of the crystals. It was also shown that the water stability of the hydration products of magnesium cementitious materials was closely related to the crystal morphology [9,10,23,36].



**Figure 7.** The SEM images of cement with different mass fractions of  $\text{MgSO}_4$  after air curing for 28 days.



**Figure 8.** The SEM images of cement with different mass fractions of  $\text{MgSO}_4$  after water immersion for 28 days.

#### 4. Conclusions

The effect of doping high volume  $\text{MgSO}_4$  on the setting time, compressive strength, and water resistance of magnesium oxychloride cement was studied in detail, and the following conclusions are obtained:

- (1) Compared with the pure MOC system, the incorporation of  $\text{MgSO}_4$  extended the setting time and showed an obvious retarding effect. Due to the fact that  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  interfere with each other in the slurry, the formation rate and crystallization rate of hydration products become slower, and the setting time of the slurry was prolonged.
- (2) The compressive strength of MOC was reduced by adding  $\text{MgSO}_4$ .
- (3) The addition of  $\text{MgSO}_4$  can improve the water resistance of MOC. MOC showed the best water resistance when the mass fraction of  $\text{MgSO}_4$  was 30 wt%.
- (4) The hydration products of MOC were mainly composed of 5·1·8 phase, 5·1·7 phase, and  $\text{Mg}(\text{OH})_2$ . The 5·1·8 phase and 5·1·7 phase were the main strength support for the mixed system.
- (5) The  $\text{MgSO}_4$  in the MOC system can significantly change the micro morphology. The compressive strength and water resistance stability of cement specimens were closely related to the crystal morphology.
- (6)  $\text{MgSO}_4$  is good for use in MOC and the proper content is 30 wt%.

**Author Contributions:** All authors discussed and agreed upon the idea, and made scientific contributions: writing—original draft, Q.H. and W.Z.; investigation, Y.L. and C.C.; Conceptualization, J.W.; Methodology, X.X.; writing—review and editing, W.Z. and J.D. All authors have read and agreed to the published version of the manuscript.

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