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Influence of molar ratios on properties of magnesium oxychloride cement

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Abstract

A parametric study has been conducted to investigate the influences of the molar ratios of $MgO/MgCl_2$ and $H_2O/MgCl_2$ on the properties of magnesium oxychloride (MOC) cement. By an integrated assessment of the experimental studies of strength development and X-ray diffractograms, together with application of the relevant phase diagram, it is recognized that the molar ratios of $MgO/MgCl_2$ and $H_2O/MgCl_2$ can significantly affect the properties of MOC cement. For a MOC cement paste possessing a dominance of $5MgO \cdot MgCl_2 \cdot 8H_2O$ (phase 5) crystals, the molar ratios of $MgO/MgCl_2$ of 11–17 and $H_2O/MgCl_2$ of 12–18 are found to be the most favorite ranges for design purpose. The choose of the molar ratio of $H_2O/MgCl_2$ is, however, largely depends on the molar ratio of $MgO/MgCl_2$ mainly for controlling workability of paste. Therefore, the most critical parameter to be selected in the design process is the molar ratio of $MgO/MgCl_2$, although the reactivity of the MgO powder is also important. Besides, the molar ratio can also be affected by the reactivity of the MgO powder to be employed. It is believed that a molar ratio of $MgO/MgCl_2$ of 13, the most suitable one shown in this study, can be used as a starting point in the normal practice.

Keywords: Cement; Magnesia; Magnesium oxychloride; MOC; Molar ratio

1. Introduction

Magnesium oxychloride (MOC) cement, also known as Sorel cement [1], is a type of non-hydraulic cement. It is formed by mixing powdered magnesium oxide (MgO) with a concentrated solution of magnesium chloride ($MgCl_2$). Magnesium oxychloride cement has many superior properties as compared to ordinary Portland cement [2]. It has high fire resistance, low thermal conductivity, good resistance to abrasion, and unaffected by oil, grease and paints. It also has high early strength and is suitable for use with all kinds of aggregate in large quantities, including gravel, sand, marble flour, asbestos, wood particles and expanded clays. The lower alkalinity of magnesium oxychloride (pH of 10–11) compared to the higher ones of ordinary cement (pH of 12–13) makes it suitable for use with glass fiber by eliminating aging problems.

Magnesium oxychloride cement draws much research interests due to the ever increasing awareness of environmental protection [3]. One of the important issues is to recycle the waste wood in light of producing cement based wood composites. However, the lignin compounds and some other adverse chemicals contained in wood significantly retard the hydration of ordinary Portland cement. To solve the problem, magnesium oxychloride cement provides an excellent substitute of the binder [4]. Some other major commercial applications of magnesium oxychloride cement are industrial flooring, fire protection and grinding wheels. Due to its resemblance to marble, it is also used for rendering wall insulation panels, stuccos with revealed aggregates, and decorative purposes [5].

Magnesium oxide, or calcined magnesia, is normally obtained by calcinations of magnesite ($MgCO_3$) at a temperature of around 750 °C. The quality or reactivity of the formed magnesium oxide powder is largely affected by its thermal history (calcination temperature and duration) and particle size [6–8]. This in turn influences both the reaction rate and the properties of the reacted products of magnesium oxychloride cement. The setting and hardening of the magnesium oxychloride cement takes place in a through-solution reaction [9]. The four main reaction phases in the ternary MOC system are $2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ (phase 2), $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (phase 3), $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (phase 5), and lastly 9Mg

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$(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ (phase 9). Of which, the phase 3 and phase 5 may exist at ambient temperature, whereas the phase 2 and phase 9 are stable only at temperatures above 100 °C [10]. Another possible reaction product with a suitable reaction environment is magnesium hydroxide or brucite, $Mg(OH)_2$.

Therefore, optimum formation of phase 5 crystals in the hydrated MOC cement is desirable as it is widely reported that the crystals provides the best mechanical properties. The formation mechanism of the four magnesium oxychloride phases sparks vigorous discussion [11–13]. Theoretically speaking, the phase 5 can be obtainable from a molar ratio of $MgO/MgCl_2$ of 5 along with the water required by the stoichiometry of it. The mechanical strength developed largely depends on the MOC phases produced and consequently on the appropriate proportions of the starting materials. Nevertheless, the correct or theoretical proportions of the starting materials alone are not sufficient to ensure the formation of phase 5 crystals, since the reactivity of MgO can have an influence [8].

For the normal practice, it is believed that the chemical reactions in the system $MgO - MgCl_2 - H_2O$ is not complete and many unreacted MgO particles are expected to left in the final reaction products. While unreacted MgO particles can be treated as a filler, surplus chloride ion, however, is troublesome as it would cause corrosion problems [14] in the case of involvement of reinforcing steels. Besides, a higher water content is usually required as a lubricant for the required workability of a mixture. Therefore, excess magnesium oxide and water are suggested to be used in producing magnesium oxychloride cement to ensure the formation of phase 5 while keeping the free chloride ion to minimum. In the practical point of view, the optimal molar ratios between different components of the ternary system $MgO–MgCl_2–H_2O$ would be the most important thing to know before further formulation for commercial products with various additives and fillers [15,16]. After all, no clear guidelines are given over what is the proper molar ratios between the starting materials to achieve the best performance of MOC cement.

In this paper, a thorough parametric study of magnesium oxychloride cement is conducted to investigate the influences of the molar ratios of $MgO/MgCl_2$ and $H_2O/MgCl_2$ on the properties of the ternary MOC system. The examinations of strength development, X-ray diffractograms and phase diagram of the reaction products are used as indices in the selection of proper molar ratios for obtaining optimal magnesium oxychloride cement. While using the compositions proposed above should ensure that no significant free chloride ion remains in the pore water of the hardened cement matrix, the situation can change if equilibrium conditions change. Leaching with water can decompose phase 5 and produce enhanced levels of chloride ions. Carbonation may aggravate the situation. Therefore, components using magnesium oxychloride cements with embedded metals are not recommended for external applications.

2. Experimental programme

The three starting materials of magnesium oxychloride cement are magnesium oxide, magnesium chloride and water. The magnesium oxide used in the study was calcined magnesite powder with an averaged particle size of about 20 μm and a purity of 96%, from Jinan, Shandong Province, China. The magnesium chloride employed was hygroscopic hexahydrate ($MgCl_2 \cdot 6H_2O$) crystal with a purity of 98% from Israel. The chemical compositions of the raw materials analyzed by X-ray fluorescence spectrometer (JEOL JSX-3201Z) are listed in Table 1. The magnesium chloride hexahydrate was first dissolved into water before mixing with magnesium oxide powder to form MOC cement paste.

For the ternary system $MgO–MgCl_2–H_2O$ at ambient temperature, two molar ratios are needed to describe the system, namely, the molar ratios of $MgO/MgCl_2$ and $H_2O/MgCl_2$. The study matrix of magnesium oxychloride cement with a wide range of the molar ratios is shown in Table 2. The molar ratio of $MgO/MgCl_2$ starts from 7, which is higher than the theoretical value of 5 for phase 5, as excess MgO is expected. With a step of 2, the highest molar ratio of $MgO/MgCl_2$ reaches 19 as sufficient amount of the reaction product of magnesium hydroxide is desired for comparison purpose. The choice of the molar ratio of $H_2O/MgCl_2$, however, is limited by the possible concentration of $MgCl_2$ solution and workability (lower limit), and the rheology (upper limit) of the mixture.

For each mixture assigned in the Table 2, cubic specimens with a size of 40×40×40 mm were cast in steel moulds with vibration compaction. The strength developments of the mixtures were recorded at 3-day, 7-day and 14-day after air curing at a temperature of 25±1 °C and under a relative humidity of 60±5% in the curing room. The setting times of the fresh mixtures were assessed by using a Vicat needle according to ASTM C191. Powder samples were collected from the specimens after 14-day air curing for X-ray diffractogram measurement (Philips PW 1830) to identify the reaction products of the corresponding mixtures. The phase diagram of the ternary system $MgO–MgCl_2–H_2O$ at room temperature was plotted to help understanding the assemblages of different reaction products of magnesium oxychloride cement with different molar ratios.

3. Results and discussions

For convenience, the following abbreviation will be used to specify the different molar ratios of each mixture. For a mixture

Table 1
Chemical compositions of the raw materials used

MgO	Components	MgO	SiO_2	SO_4	CaO	MnO	Fe_2O_3	Eu_2O_3
	Mass fraction (%)	96.58	0.766	0.162	1.408	0.137	0.774	0.116
$MgCl_2 \cdot 6H_2O$	Components	$MgCl_2$	H_2O	$CaCl_2$	NaCl	KCl		
	Mass fraction (%)	45.8	52.0	1.3	0.6	0.3		

Table 2
The study matrix of MOC cement with different molar ratios

$MgO/MgCl_2$ (M)	$H_2O/MgCl_2$ (H) 10	12	14	16	18	20	22
07	√	√	√	√			
09	√	√	√	√			
11		√	√	√	√	√	
13		√	√	√	√	√	
15			√	√	√	√	
17				√	√	√	√
19					√	√	√

with a molar ratio of $MgO/MgCl_2$ of xx and a molar ratio of $H_2O/MgCl_2$ of yy, it will be specified as Mxx/Hyy. For examples, the mixture at the top left corner in the Table 2 is specified as M07/H10, and the mixture at the bottom right corner is M19/H22.

3.1. Setting of the MOC cements

The initial setting times were mainly affected by the water content or the molar ratio of $H_2O/MgCl_2$ of the mixture. For a mixture with the same molar ratio of $H_2O/MgCl_2$, the higher the molar ratio of $MgO/MgCl_2$, the lower the water content would be. The highest water content by total weight is about 42% for the mixture M07/H16, while the lowest water content is about 25% for the mixture M13/H12. The water content of M07/H10 is about 31%, which can be further reduced by increasing concentration of $MgCl_2$ in the solution. The concentration of $MgCl_2$, however, is limited by the solubility of the magnesium chloride hexahydrate particles.

The content of $MgCl_2$ by weight of the hexahydrate crystal itself is about 46.8%, and the concentration of $MgCl_2$ of a solution with a molar ratio of $H_2O/MgCl_2$ of 10 is already 34.5%. For a $MgCl_2$ solution with a concentration higher than 35%, precipitation of hexahydrate crystal would occur easily. Besides, the molecular formula of the phase 5, $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, can be rewritten as $5MgO \cdot MgCl_2 \cdot 13H_2O$. That is, the theoretical molar ratios required by the stoichiometry of phase 5 are $MgO/MgCl_2$ of 5 and

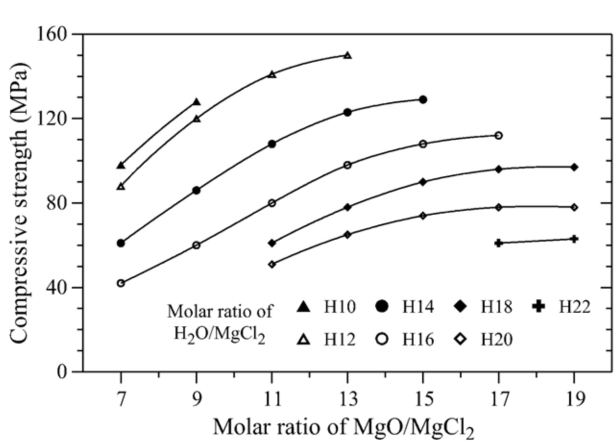

Fig. 1. Compressive strengths of different mixtures after air curing of 7 days.

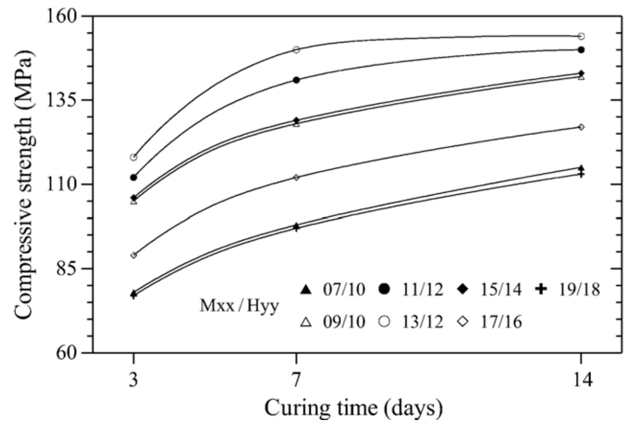

Fig. 2. Strength developments of some selected mixtures.

$H_2O/MgCl_2$ of 13. As a result, the water content or the molar ratio of $H_2O/MgCl_2$ of the mixture M07/H10 has to be increased instead of decreased required by the stoichiometry for obtaining phase 5. Therefore, a mixture with a higher molar ratio of $MgO/MgCl_2$ can afford a higher molar ratio of $H_2O/MgCl_2$ while keeping the water content at a reasonable level in the normal practice.

3.2. Strength development

The compressive strengths of the different mixtures after air curing of 7-day are compared and shown in Fig. 1. It shows that with a fixed molar ratio of $MgO/MgCl_2$, the strength of the mixtures increases with the decrease of the molar ratio of $H_2O/MgCl_2$. Besides, with a fixed molar ratio of $H_2O/MgCl_2$, strengths change with different molar ratios of $MgO/MgCl_2$. The higher the $MgO/MgCl_2$ molar ratio, the higher the strength. The highest strength is 150 MPa for the mixture M13/H12, while the lowest strength is 42 MPa for the mixture M07/H16. Such a big difference between the maximum and minimum strength among the mixtures may due to the different microstructures and properties of the mixtures with different assemblages of the reaction products.

The mixtures having the highest 7-day strength corresponding to each molar ratio of $MgO/MgCl_2$ are M07/H10, M09/H10, M11/H12, M13/H12, M15/H14, M17/H16, and M19/H18, respectively. The strength developments of these mixtures in the first 2 weeks after casting are plotted in Fig. 2. It shows that M13/H12 has the maximum strengths at different ages, while M19/H18 has the minimum strengths. With the chemical reaction reaches plateau at the age of 7-day, M13/H12 has the fastest strength development compared with the other mixtures. It is believed that M13/H12 has the best combination of the molar ratios of $MgO/MgCl_2$ and $H_2O/MgCl_2$ for obtaining phase 5 of MOC cement.

Among the 7 mixtures compared in the Fig. 2, M07/H10 has the highest water content of 31%, while M13/H12 has the lowest one of 25%. Besides, M11/H12 has the second highest water content of 28%, but its strength is only lower than M13/H12 and much higher than those with a lower water content. For example, M17/H16 has a lower water content of 26%, but its strength is 15% less than that of M11/H12. It is, therefore, believed that the combination of the molar ratios plays a more important role than the water content itself. The differences of the phases compositions among the mixtures will be shown more clearly in the following section with the help of X-ray diffractograms and phase diagram.

3.3. Phases identification

To investigate the influences of the molar ratios on the properties of MOC cement, the X-ray diffractograms of the mixtures M07/H10, M07/12, M07/16, and M09/16 are stacked in Fig. 3. It shows that the mixture M07/H10 contains largely the phase 3 with excess MgO, while the mixture M07/H12 contains both the phase 3 and phase 5 of magnesium oxychloride. It is understood that such formulations are best avoided as phase 5 the most favorable crystalline phase. As shown in the Fig. 3, the mixture M07/H16 has mainly the phase 5 and the MgO seems almost completely consumed. It has, however, a lower compressive strength as compared to M07/H12. It may be caused by too much free water which forms large amount of pores in the matrix. With increasing of the molar ratio of $MgO/MgCl_2$, the first mixture found with the $Mg(OH)_2$ phase is M09/H16 as shown on the top row in the Fig. 3. It can be seen that the MgO is still not in excess with an obvious amount in the mixture M09/H16, which means that the amount of MgO could be further increased.

The X-ray diffractograms of the mixtures M13/H12, M13/16, M17/16, and M19/22 are shown in Fig. 4 to examine why M13/H12 has the highest strength. From the bottom row in the Fig. 4, X-ray diffractogram of the mixture M13/H12 shows the sharpest peaks of phase 5 and the lowest amorphous base as compared to others in the Figs. 3 and 4. That means the degree of crystallization of phase 5 in the mixture M13/H12 is more complete. As expected, the MgO content of the mixture M13/H12 is in excess and residual MgO is found. Obvious $Mg(OH)_2$ phase in the M13 series is found when the molar ratio of $H_2O/MgCl_2$ is larger than 16. For both series M17 and M19, the $Mg(OH)_2$ phase is found in all of the mixtures with different molar ratios of $H_2O/MgCl_2$. As also shown in the Fig. 4, the amount the $Mg(OH)_2$ phase in the mixture M19/H22 would be even larger than the phase 5.

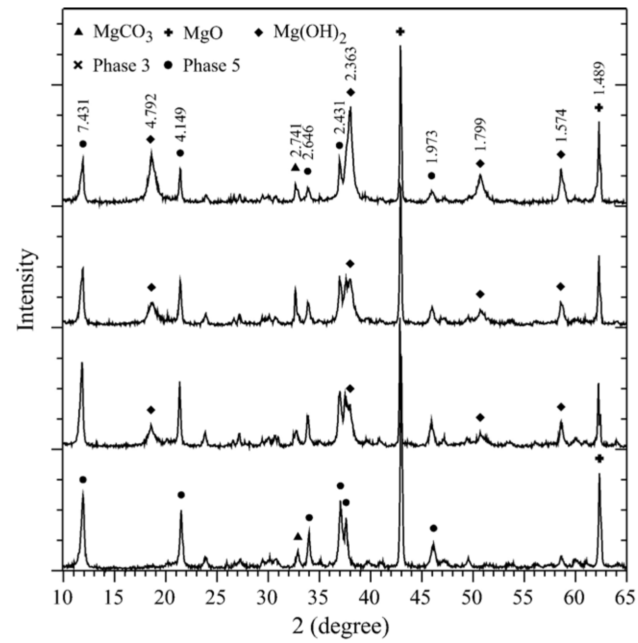

Fig. 4. XRD spectrograms of the mixtures (from bottom to top): M13/H12, M13/H16, M17/H16, and M19/H22.

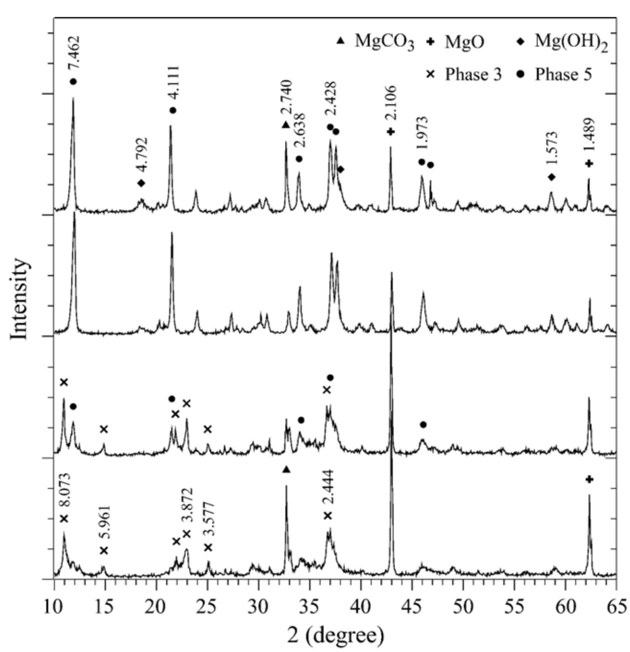

Fig. 3. XRD spectrograms of the mixtures (from bottom to top): M07/H10, M07/H12, M07/H16, and M09/H16.

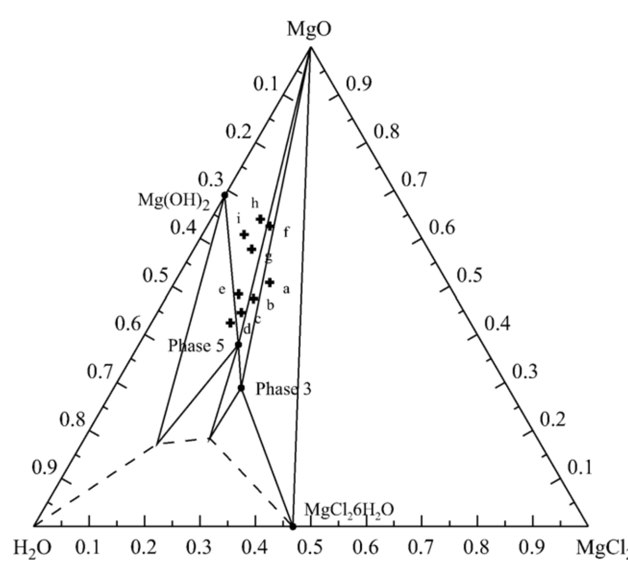

Fig. 5. The ternary $MgO–MgCl_2–H_2O$ system at room temperature (the dashed line indicates the approximate limits of homogeneous gel formation): a — M07/H10, b — M07/H12,c — M07/H14, d — M07/H16, e — M09/H16, f — M13/H12, g — M13/H16, h — M17/H16, and i — M19/H22.

To further understand the assemblages of the different phases in the mixtures, the phase diagram of the ternary system MgO–$MgCl_2$–H_2O at room temperature is plotted in Fig. 5 with the indices of the mixtures examined in the Figs. 3 and 4. It shows that the mixture M07/H10 (point a) is lying in the compatibility triangle MgO – phase 3 – hexahydrate, the mixture M07/H12 (point b) lying in the compatibility triangle MgO – phase 5 – phase 3, and the mixture M07/H16 lying in the compatibility triangle $Mg(OH)_2$ – gel – phase 5. From the phase diagram, it can be predicted that the main reaction products of the mixtures M07/H10, M07/H12 and M07/H16 should be mainly the phase 3, the combination of the phases 3 and 5, and mainly the phase 5, respectively. The predicted assemblages of the reaction phases of the mixtures are confirmed by the measurements of X-ray diffractograms as shown in the Fig. 3. In addition, the composition points of the mixtures M17/H16 and M19/H22 are very close to the phase $Mg(OH)_2$, and large amounts of Mg $(OH)_2$ are also identified from the X-ray diffractograms as shown in the Fig. 4. The results from the strength measurements, X-ray diffractograms and phase diagram construction agree very well to each other.

4. Conclusions

A detailed parametric study of magnesium oxychloride cement with a wide range of molar ratios of MgO/$MgCl_2$ and H_2O/$MgCl_2$ is conducted. The strength development, X-ray diffractograms and phase diagram are utilized in finding the influences of the molar ratios on properties of MOC cement. The basic requirements for obtaining high performance MOC cement are to ensure the production of phase 5, minimize of unreacted $MgCl_2$ content, and obtain a reasonable workability with an appropriate setting time. To achieve the goals, excess MgO content is required in the ternary system MgO–$MgCl_2$–H_2O of MOC cement. The experimental results show that any mixture with a molar ratio of MgO/$MgCl_2$ lower than 11 has a prolonged setting time and more phase 3 produced. The amount of $Mg(OH)_2$ phase in the mixture can be dominant if the molar ratio of MgO/$MgCl_2$ is higher than 17.

In the current study, the best combination of the molar ratios for MOC cement is MgO/$MgCl_2$ of 13 and H_2O/$MgCl_2$ of 12. By an integrated assessment of the experimental studies on strength development, phase diagram and X-ray diffractograms, it is recommended that the optimal application ranges of the molar ratios for the ternary system of MOC cement are MgO/$MgCl_2$ from 11 to 17, and H_2O/$MgCl_2$ from 12 to 18. The choose of the molar ratio of H_2O/$MgCl_2$ is, however, largely depended on the molar ratio of MgO/$MgCl_2$ as excess water is required for desired workability. Therefore, the most critical molar ratio to be selected in the design process of MOC cement is MgO/$MgCl_2$. As a result, a molar ratio of MgO/$MgCl_2$ of 13, as found the best in this study, would be a suitable starting point for the normal application of magnesium oxychloride cement.

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