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Tuning the phase structure and mechanical performance of magnesium oxychloride cements by curing temperature and $H_2O/MgCl_2$ ratio

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HIGHLIGHTS

- Curing temperature and $H_2O/MgCl_2$ mole ratio can tune the phase structure and mechanical strength of MOC.
- The phase 5 content increased with the increase of water ratio when cured under low temperature.
- The ternary phase diagram was used to explain the formation mechanism of phase structure.
- The compression strength of MOC was closely related to microstructure and phase structure.

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ABSTRACT

The curing temperature and $H_2O/MgCl_2$ mole ratio are the two main factors that affect the structure and mechanical performance of the magnesium oxychloride (MOC) cement. In this work, different curing temperatures and $H_2O/MgCl_2$ mole ratios were used to synthesize MOC cement. The structure of the MOC cement samples was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mechanical performance of the samples was also evaluated. The results indicated that the effect of curing temperature on the phase structure and mechanical performance of the MOC cement was closely involved with the $H_2O/MgCl_2$ mole ratio in the MgO-$MgCl_2$-H_2O ternary system. As for the mechanical properties, the compression strength was closely related to the phase structure and microstructure. When cured at 25 °C, the MOC with the $H_2O/MgCl_2$ mole ratio of 11 possessed a more dense microstructure, and higher compression strength (36.95 MPa) as compared with the MOC with the $H_2O/MgCl_2$ mole ratio of 20 (16.19 MPa). When cured at 40 °C, the MOC with the $H_2O/MgCl_2$ mole ratio of 13 exhibited more phase 5 structure, and higher compression strength (50.84 MPa) as compared with the MOC with the $H_2O/MgCl_2$ mole ratio of 20 (4.35 MPa).

1. Introduction

Many kinds of materials, such as wood [1], bamboo [2], cement and concrete [3], are widely used in construction and buildings. Among them, wood and bamboo are renewable. However, the Poor fire resistance of wood and low strength of bamboo limit their applications in many fields [1,2]. Portland cement (PC) is one of the most widely used construction and building materials [3,4]. However, PC needs to be cured under humid condition and released a large amounts of CO_2 during its production process [5,6]. In addition, the fillers could be corroded by the high pH value of PC (approximately 12–13), such as glass fibers [7]. In recent decades, MgO-based cement has been considered to be a potential substitute for PC [3]. Among all the MgO-based cements, magnesium oxychloride (MOC) cement is one of the most attractive one owing to its excellent performances, such as low alkalinity (8–10) [8], high carbon sequestration potential [9], short setting time, the ability of stabilize and solidify sewage sludge [10], high flame resistance, good mechanical strength, and excellent corrosion resistance property [11,12].

MOC cement is synthesized by hydration process of a MgO-$MgCl_2$-H_2O ternary system. The resultant product is mainly composed of magnesium chloride salts crystal phases, including the phase 5 structure [$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$] and/or the phase 3 structure [$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$] [3,13–15]. It has already been

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reported that the structure and property of MOC cement can be affected by many factors, for example, the MgO to $MgCl_2$ mole ratio, concentration of $MgCl_2$ aqueous solution, curing temperature of MOC, and the content of active MgO [13,14,16,17].

Previous studies mainly focused on improving the water resistance and mechanical properties of MOC cement by adjusting the molar ratios of raw materials and introducing different additives [18–20]. In term of water resistance, Xu et al. [21] reported that the addition of rice husk ashes and waterproof agent improved the water resistance of MOC cement. Some researchers reported that the incorporation of phosphoric acid and phosphates increased the moisture resistance of MOC cement, but decreased the mechanical property [20,22]. As for mechanical properties, prior studies reported that the mechanical properties of MOC cement were dominated by the phase 5 structure [13,23]. Karimi and Monshi [23] reported that the content of phase 5 structure increased with increasing the magnesium chloride ($MgCl_2{\cdot}6H_2O$) content from 0.5 mol to 1.9 mol. The MOC cement showed the highest compressive strength (77.86 MPa) when the magnesium chloride content was 1.5 mol after curing for 20 day. Nevertheless, only a few researches focused on the effect of curing temperature and water content of the components on the structure and properties of the MOC cement [14,15,24,25]. Li and Chau reported that the best range of $H_2O/MgCl_2$ mole ratio was 12–18 when the MOC cement cured at room temperature [25]. There was no doubt that when the curing temperature was changed (included curing in different seasons or at different locations), the results were quite different [24]. Sglavo [24] reported that the MOC cement showed very low mechanical strength (Flexural strength) when the H_2O to $MgCl_2$ mole ratio was 12 or 13, and the curing temperature was 10 °C. However, the influence of a high H_2O to $MgCl_2$ mole ratio (above 13) on the structure and properties of the MOC cement were still unknown. Moreover, the effect of curing temperature on the phase structure of the MOC cement with different water content needs to be studied as well.

In this study, different MOC cement were prepared under different curing temperatures (8 °C, 25 °C, 40 °C, and 55 °C) with a range of water content (H_2O to $MgCl_2$ mole ratio) from 11 to 20. The micro-topography and quantitative composition of the MOC cement were investigated by using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The mechanical performances (harness and compression strength) of the MOC cement were also evaluated by using a hardness tester and a universal machine, respectively.

2. Materials and experiment

2.1. Materials

The magnesium oxide (MgO, 96% purity, 65% activity) was provided by Guangzhou Danlin Trade Co., Ltd (Guangdong, China). The Magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$, 98% purity) was purchased from Beijing Chemical Works (Beijing, China).

2.2. Preparation of the MOC cement

Firstly, 1 mol of $MgCl_2{\cdot}6H_2O$ was dissolved in different amount of distilled water [H_2O to $MgCl_2$ mole ratio ($H_2O/MgCl_2$) was 13, 15, 18, and 20]. Then, 5 mol of MgO was added to the solution and stirred at low speed (100 rpm) for 2 min and high speed (300 rpm) for 3 min to obtain a homogeneous mixture. Secondly, the mixture solution was poured into the mold (40 mm × 40 mm × 40 mm) and sealed with a polyethylene film. Finally, the above solution (in the mold) was oven-dried at different temperatures (8 °C, 25 °C, 40 °C and 55 °C) for 24 h to cure, and stored at room temperature for 24 h. It has been reported that the phase 5 structure lost two water molecules at about 72 °C and the phase 3 structure started to decompose at about 80 °C [14,24]. Therefore, the curing temperatures used in this experiment were below 70 °C. All the MOC cement samples are listed in Table 1. They were named as M (T-R), where T was represented temperature, R was represented $H_2O/MgCl_2$ mole ratio.

2.3. X-ray diffraction (XRD) analysis

The structure of the MOC cement samples was investigated by a XRD analyzer (Bruker D8 ADVANCE, Germany) with Cu Kα radiation at 40 kV and 40 mA at a rate of 4°/min. The scanning range was from 5° to 90°. All the formulations were grinded into powder (about 200 mesh) before testing. The component and quantitative analysis of specimens were carried out by EVA software.

2.4. Scanning electron microscopy (SEM) analysis

The fracture surface of the MOC cement samples was observed by a SEM analyzer (Hitachi S-3400N II, Japan) with an accelerating voltage of 5 kV. The fracture surface of the samples was sputter-coated with gold layer.

2.5. Mechanical properties

The mechanical performance of the MOC cement samples were evaluated by the hardness and compression strength. The hardness of all the samples was evaluated by a hardness tester (TH210, China). The surface of the specimen was polished by an abrasive paper before testing. Six replicates (40 mm × 40 mm × 40 mm) were tested for each group. The compression strength of the MOC cement samples was evaluated by a universal machine (WD W-50, China) at a loading rate of 5 mm/min. Six replicates (20 mm × 20 mm × 20 mm) were tested for each group.

3. Results and discussion

3.1. Structure analysis

Fig. 1 shows the XRD patterns of different MOC cement samples under various curing temperatures and different water ratios. It can be observed that the phase 3 structure and phase 5 structure in the MOC cement samples varied under different curing temperature and water ratios. In Fig. 1a (curing temperature was 8 °C), when $H_2O/MgCl_2$ mole ratio was 11, the sample only contained the phase 3 structure. Whereas both phase 3 and phase 5 structures were produced as $H_2O/MgCl_2$ mole ratio was 12 and 13. However, when $H_2O/MgCl_2$ mole ratio increased to 15, 18 and 20, the phase 3 structure disappeared and only phase 5 structure was produced. This result was different from the previous report that the MOC cement cured at low temperature (5 °C) would generate the phase 3 structure [24]. It was noteworthy in Fig. 1b (curing temperature was 25 °C) and Fig. 1c (curing temperature was 40 °C) that the major phase structure (phase 5 structure) in the MOC cement samples did not change too much as the variety of $H_2O/MgCl_2$. Only a little amount of phase 3 structure appeared when $H_2O/MgCl_2$ mole ratio was 11 and 12 under these two curing temperature conditions. As the curing temperature further increased to 55 °C (Fig. 1d), the phase 3 and phase 5 structures coexisted when $H_2O/MgCl_2$ mole ratio was 11, 12, 13 and 15, while the phase 5 structure gradually decreased with the increasing $H_2O/MgCl_2$ mole ratio (18 and 20).

Fig. 2 is the relation schema of mineralogical phases, temperature, and the water ratio. It can be observed in Fig. 2 that the