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Experimental investigation on the properties and microstructure of magnesium oxychloride cement prepared with caustic magnesite and dolomite

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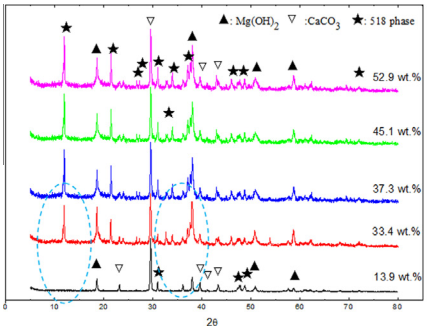
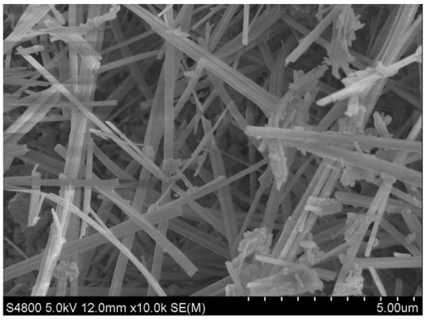
HIGHLIGHTS

- We made magnesium oxychloride cements with caustic magnesite and dolomite.
- The minimum of active MgO in magnesium oxychloride is suggested by 33.4 wt.%.
- We defined two very important parameters in $MgO–MgCl_2–H_2O$ system, K_1 and K_2.
- The water resistance coefficient of magnesium oxychloride is not related with the compressive strength.

GRAPHICAL ABSTRACT





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ABSTRACT

Magnesium oxychloride cements (MOCs) with different amount of active magnesium oxide were prepared with caustic magnesite and dolomite. The fluidity, compressive and flexural strength were measured. After that, the MOCs were analyzed by XRD and SEM. The results indicated that MOCs prepared with caustic magnesite and dolomite obtained a good engineering performance. The result suggested that the minimum active MgO content used in MOCs should be 33.4 wt.%. At the same time, this study shows that the water resistance coefficient of MOC is concerned with the balance of hydration and hydrolysis reactions which provides two main modification approaches, improving the hydration rate or preventing the reverse reaction. Meanwhile, it is shown in the experiment that there is no significant relationship between the water resistance coefficient and the compressive strength of MOCs.

1. Introduction

In 1867, Sorel discovered a new type of cementitious material which was named Sorel cement [1]. Sorel cements are also called magnesium oxychloride cement (MOC) because it is a ternary system of $MgO–MgCl_2–H_2O$. In present applications and researches, the MgO was provided by caustic magnesite or dolomite while the $MgCl_2$ is often from brines. This solution brings out many advantages. Such as, the calcination temperature of magnesite and dolomite (750–800 °C) is much lower than ordinary Portland cement (OPC) production (1000–1450 °C). On the other hand, there are lots of salt lakes (such as Qinghai Lake) in west-China [2], which contains large amounts of high-purity, easy-to-exploit

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magnesium salts, for example, potassium chloride (KCl) and magnesium chloride ($MgCl_2$). These sources provide considerable amounts of $MgCl_2$ needed in the MOC production and prevent Mg pollution at the same time. Considering the low carbon footprint, low energy, fire resistance, proper adhesion, rapid setting, excellent bonding capacity and high strength performances over other cement, Sorel cement or MOC has been used in many fields [3–8].

The same with OPC, MOC obtains the strength via chemical reaction and hydration products. The possible hydration products of MOC include various crystalline phases of magnesium, as shown in Eqs. (1)–(4) [9–12]. Previous study revealed that phases 3 and 5 (P3 and P5) exist at room temperature, and phases 2 and 9 (P2 and P9) can be observed at temperature over 100 °C. While the composition of the three constituents in P2 (P212, P214 or P215) and P9 (P914, P915 or P916) are variable, the crystalline phases remaining in the hydrates are P3 and P5 with fixed composition under practical application conditions. During the hydration process, these hydrates play a similar role as calcium silicate hydrate (CSH) in OPC, which are the most important of the constituent phases for strength development. However, compared to OPC, both the compressive and flexural strength developed by P3 and P5 are much higher than that by CSH.

$$\begin{aligned}&2Mg(OH)_2\cdot MgCl_2\cdot 2H_2O\\&2Mg(OH)_2\cdot MgCl_2\cdot 4H_2O\\&2Mg(OH)_2\cdot MgCl_2\cdot 5H_2O\quad(\text{Phase}\,2)\end{aligned}\tag{1}$$

$$3Mg(OH)_2\cdot MgCl_2\cdot 8H_2O\quad(\text{Phase}\,3)\tag{2}$$

$$5Mg(OH)_2\cdot MgCl_2\cdot 8H_2O\quad(\text{Phase}\,5)\tag{3}$$

$$\begin{aligned}&9Mg(OH)_2\cdot MgCl_2\cdot 4H_2O\\&9Mg(OH)_2\cdot MgCl_2\cdot 5H_2O\\&9Mg(OH)_2\cdot MgCl_2\cdot 6H_2O\quad(\text{Phase}\,9)\end{aligned}\tag{4}$$

For the preparation of MOC, since they are both abundantly available in China, either caustic magnesite or dolomite has been used as the MgO source in literatures. For example, Ji [13] reported a light MOC foamed material produced by caustic magnesite with an active MgO content of 79.18 wt.%. Wang et al. [14] stated that the difference of active MgO affected the deformability and strength of MOCs. Chau et al. [15] and Wen et al. [2] announced that they produced a high strength MOCs used the caustic magnesite. However, Wang and Li reported that high compressive strength would increase the fragility of cement concrete [16], which will put the construction into hazardous conditions. Therefore, to reduce the content of active MgO in MOCs and decrease the compressive strength seems necessary.

One natural approach to reduce the compressive strength is to use another caustic mineral, dolomite, which contains less active MgO. Wang et al. [17] and Yu et al. [18] announced that MOCs produced by caustic dolomite powder could obtained a stable hydrate gel phase and microstructure, and the undercalcined limestone (calcium carbonate, $CaCO_3$) maybe have special effects in cementitious materials [19]. Meanwhile, because of the limited content of active MgO in caustic dolomite, some researchers advocated that the engineering performance of MOCs cannot meet the specification requirements [20]. To solve this issue, researchers replaced the caustic dolomite with some parts of caustic magnesite showing a practical proposal to produce MOCs. However, no more studies were published about the mixed use of these two types of caustic mineral powders.

Therefore, to reduce the strength of MOCs and the fabricating cost, both caustic dolomite and magnesite powders are used to produce MOCs in this paper. The mechanical performances, crystalline phases and microstructure were examined systemically. Furthermore, the influence of active MgO oxide and the ratio of MgO or H_2O to $MgCl_2$ on the properties and microstructures was discussed. These findings will highlight the feasibility of the development of MOCs, eco-friendly.

2. Experimental

2.1. Raw materials

The used active magnesium oxide (defined as α-MgO) in this paper is caustic dolomite (α-MgO purity = 13.88 wt.%, Qinghai Institute of Salt Lakes, Chinese Academy of Science, China) and caustic magnesite (α-MgO purity = 52.93 wt.%, Haicheng LingHai magnesia company, Liaoning, China). As well, the brines were prepared with tap water and bischofite ($MgCl_2\cdot 6H_2O$) with a content of 98 wt.%, produced by Qinghai salt industry Co., Ltd. According to the recently study [12], the phosphoric acid with a purity of 85 wt.% was used as the water resistance modifier.

2.2. Specimens preparation

Two groups of MOCs specimens were prepared in this research: the first group used the water/powder ratio at 0.46 for all seven cases and the second group kept the magnesite/dolomite ratio as 6:4 for all the nine cases. Table 1 shows the composition of the MOCs pastes. For all specimens, the producing process is given out in Fig. 1. The water locked in the bischofite ($MgCl_2\cdot 6H_2O$) structure should be converted into the whole used water to avoid the effect on the water–powder ratio. The mixed specimens were feed into steel molds and then cured in air at room temperatures.

2.3. Test methods

The fluidity of MOC pastes was measured in terms of GB/T 8077–2000 [21], seeing Fig. 2(a). In this measurement, the fluidity is indicated with the average flow diameter of the paste on the glass after 30 s. The flexural strength of the cured MOC pastes (160 × 40 × 40 mm) was investigated with a SANSY Universal Testing Machine (span = 100 mm, loading speed = 1 mm/min), while the compressive strength was detected by a punching machine(2.42 ± 0.1 kN/s) on 40 × 40 × 40 mm cubes, as Fig. 2(b) and (c) showing.

To evaluate the water resistance of MOCs, MOC samples were immersed in water for 3 days and then compressive strength was measured. The water resistance coefficient was defined as follows.

$$\mathrm{WRC}=\frac{\text{Compressive strength immersed in water}}{\text{Compressive strength cured in air}}\tag{5}$$

where WRC = water resistance coefficient (the higher WRC is, the better water resistance it has). If the WRC > 1.0, it means the strength of MOCs still develops in immersion condition which indicates the MOCs with a desired water resistance

Table 1
Composition and the sample number of MOCs.

Sample number	Caustic magnesite/caustic dolomite, by weight	K_1 (MgO/$MgCl_2$, by mole)	Water/powder, by weight	Phosphoric acid/powder, by weight
NO-1	0:10	7	0.46	1%
NO-2	2:8			
NO-3	4:6			
NO-4	5:5			
NO-5	6:4			
NO-6	8:2			
NO-7	10:0			
NO-0.36	6:4		0.36	
NO-0.38			0.38	
NO-0.40			0.4	
NO-0.42			0.42	
NO-0.44			0.44	
NO-0.46			0.46	
NO-0.48			0.48	
NO-0.57			0.57	
NO-0.58			0.58	