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Effect of pulverized fuel ash and CO_2 curing on the water resistance of magnesium oxychloride cement (MOC)

Pingping He, Chi Sun Poon *, Daniel C.W. Tsang

Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

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ABSTRACT

This paper presents a study on the use of pulverized fuel ash (PFA) to improve the water resistance of magnesium oxychloride cement (MOC). Strength retention coefficients and volume stability were tested to evaluate the water resistance of MOC, in which the addition of PFA resulted in a remarkable improvement. The characterization of hydration products before and after water immersion was carried out using quantitative X-ray diffraction (QXRD), thermogravimetric (TG), Fourier-transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM). With the Q-XRD analysis, it was shown that the addition of PFA could result in the great increase of the amount of amorphous phase during air curing. This amorphous gel was identified as a mixture of magnesium-chloride-silicate-hydrate gel (M-Cl-S-H gel) and magnesium-chloride-hydrate gel (M-Cl-H gel) by elemental mapping scanning. It suggested that PFA could not only react with MOC to form M-Cl-S-H gel, but also change the morphology of magnesium oxychloride. The generation of insoluble M-Cl-S-H gel and M-Cl-H gel and densification of the microstructure contributed to the improvement of the water resistance of MOC. The MOC mortar expanded during air curing due to the hydration of excess MgO. Water immersion led to more expansion of MOC mortar as a result of the continuously hydration of excess MgO and the formation of $Mg(OH)_2$. Adding PFA could increase the expansion of MOC mortar during air curing, which may because the amorphous gel could remain more water and benefit to the hydration of MgO. While, the addition of PFA could decrease the expansion of cement mortar during water immersion perhaps due to the reduction of the content of excess MgO and the insoluble amorphous-gel-layer that protect the MgO from hydration. Moreover, CO_2 curing could further improve the performance of the PFA-blended MOC due to the formation of a higher content of amorphous gel.

1. Introduction

Magnesium oxychloride cement (MOC), known as Sorel's cement [1], offers the advantage of high early strength [2] and is commonly used for industrial flooring [3–5], fire protection [6] and lightweight panels [7,8]. Additional advantages are the good fire resistance [9], good resistance to abrasion [2] and low thermal conductivity [10].

However, the application of MOC for practical engineering projects has been limited by its poor water resistance. Previous studies found that the compressive strength of MOC decreased significantly when it is immersed in water for 28 days, due to the decomposition of hydration products, Phase 5 ($5\ Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$)and Phase 3 ($3\ Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$), which are the main sources of strength [11,12]. Many researchers used various additives to overcome the problem of water solubility and found that some additives were very useful, such as sulfate and phosphate [13,14]. It was proposed that phosphate could react with magnesium to produce insoluble hydrated products such as magnesium phosphate that protected the magnesium cement crystal from decomposing [15]. However, it was argued that the quantity of the insoluble phosphates was not high enough to produce a layer of the insoluble phosphates [16]. On the other hand, some studies revealed the transformation from the crystalline to gel-like Phase 5, which was believed to be the main reason for the improved water resistance of MOC when adding phosphate [13].

Although adding additives is an effective way to improve the water resistance of MOC, it increases the cost of producing the material. Therefore, using waste materials should be considered. Fly ash is a promising waste material that can significantly improve the water resistance of MOC. Previous studies found that the residual compressive strength of MOC mortars incorporating 30% fly ash cured in air for 14 days was about 80% of the initial value even after immersion in water for 28 days [11,17]. However, the mechanism of such improvement is still not well understood.

It has been reported that during natural carbonation of MOC, the Phase 5 would be transformed into Phase 3 hydration products. When Phase 3 is further carbonated, new phases would be formed as follows [18,19]:

$$5\ Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \rightarrow 3\ Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O + 2\ Mg(OH)_2 \quad (1)$$

* Corresponding author.
E-mail address: cecspoon@polyu.edu.hk (C.S. Poon).

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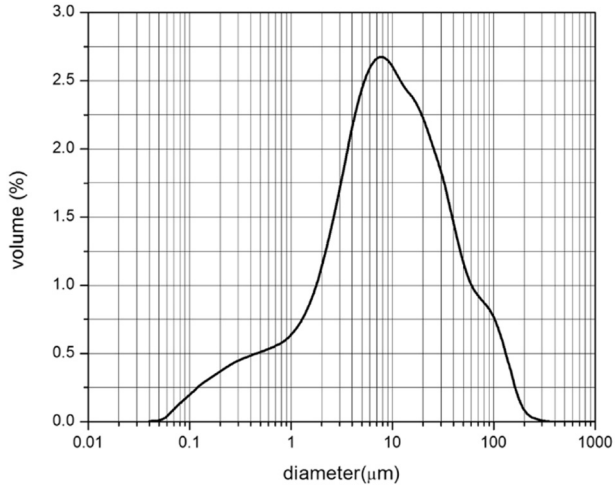

Fig. 1. Particle size distribution of PFA.

$$3\,Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O + 2CO_2 \rightarrow Mg(OH)_2 \cdot MgCl_2 \cdot 2MgCO_3 \cdot 6H_2O + 2\,H_2O \quad (2)$$

This new phase ($Mg(OH)_2 \cdot MgCl_2 \cdot 2MgCO_3 \cdot 6H_2O$) is much less soluble in water than either of Phase 5 and Phase 3, which means the carbonation may improve the water resistance of MOC. Carbon dioxide curing of concrete is distinct from natural carbonation, because the carbonation reaction occurs at early age and is used to accelerate the strength gain and to reduce the early drying shrinkage of cement products [20,21].

Besides, high purity and pressure of CO_2 gas result in rapid reaction between CO_2 and cementitious material [22]. The positive effects of CO_2 curing on the mechanical properties of cement products have attracted increasing number of studies on accelerated carbonation of Ordinary Portland cement [23,24], cement-solidified wastes [25,26], aerated lime-based mortars [27]etc.

In this study, CO_2 curing was adopted to accelerate the carbonation reactions aiming to enhance the water resistance of MOC. The objective is to identify the mechanisms of how PFA improves the water resistance of MOC, and the effect of CO_2 curing on the water resistance.

2. Experimental program

2.1. Materials

Light-burned magnesia powder (MgO) was obtained from Liaoning province, China; $MgCl_2$ used in this study was bischofite ($MgCl_2 \cdot 6H_2O$)

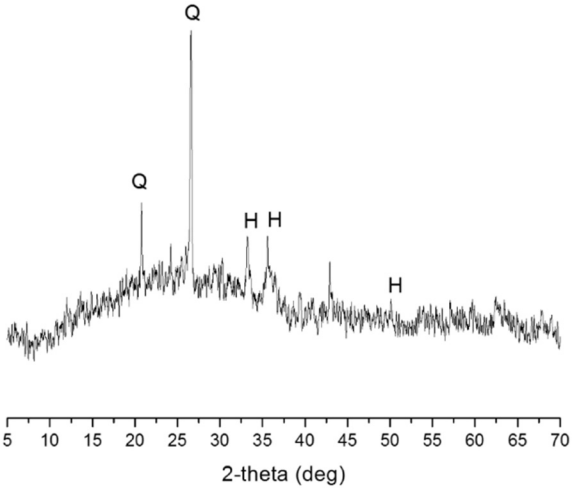

Fig. 2. X-ray diffraction pattern of the PFA. Q = quartz, H = hematite.

Table 1
Chemical characteristics of MgO and PFA.

Composition (% by mass)	MgO	PFA
MgO	94.86	
SiO_2	2.75	45.70
AlO_3	–	19.55
Fe_2O_3	0.45	11.72
CaO	1.60	12.27
Na_2O	–	1.36
K_2O	–	1.71
SO_4	0.24	1.82

with a purity of 98 wt%, produced by Qinghai, China. Class F PFA used was a pozzolanic waste material generated during the combustion of coal sourced from a local power plant in Hong Kong. The median particle size of PFA was 8.9 μm (Fig. 1). The phase compositions of PFA were shown in Fig. 2. The chemical characteristics of MgO and PFA are shown in Table 1. Standard quartz sand with particle sizes ranging from 0.5 mm to 1 mm was used as fine aggregate for preparing the mortar samples.

2.2. Mix proportions

Table 2 and Table 3 show the mix proportions of the paste and mortar specimens prepared. The specimens were cured in an environmental chamber at 25 °C and RH 55% (air curing). The CO_2 curing was conducted in a carbonation chamber with a CO_2 concentration of >99% and at a pressure of 0.1 MPa above atmospheric pressure (Total pressure 2 atm). The CO_2 pressure in the chamber was controlled by a gas regulator and kept at 0.1 MPa throughout the curing period. The PFA was used to replace MgO at dosage levels of 10%, 20%, and 30% by mass of MgO, respectively. Previous literatures suggested that the molar ratio of magnesium oxide to magnesium chloride should be >5 in order to ensure the complete reaction of magnesium chloride [28,29]. So in this study, the molar ratio of 9 was adopted. The choice of the molar ratio of $H_2O/MgCl_2$ was dependent on workability. The mix proportion of the mortar was similar to that of the paste except that standard sand was added with a sand/binder ratio of 1.5.

2.3. Sample preparation and test procedures

The required amount of magnesium chloride was first dissolved in tap water and thoroughly mixed for about 1 min in a mechanical mixer. Afterwards, magnesium oxide powder, PFA and sand (if applicable) were added and the materials were further mixed for about 3 min. The prepared materials were then cast into steel molds. The compressive strength and volume stability of MOC were determined on cubic specimens (20 × 20 × 20 mm), cylindrical (height of 285 mm; diameter of 150 mm) specimens, respectively. After casting, the specimens were covered by a plastic sheet and cured initially for 24 h at room temperature (25 °C). Then, the specimens were further cured in air for 3, 7 and 14 days, respectively. The other specimens were cured in air for 13 days followed by CO_2 curing for 1 day.

An airtight steel-cylindrical vessel was used for CO_2 curing and it was vacuumed to 0.5 bar before the CO_2 injection. The CO_2 used was

Table 2
Mix proportion of MOC paste.

Mixtures notation	Molar ratios		PFA (%, by weight of MgO)	Curing condition
	$MgO/MgCl_2$	$H_2O/MgCl_2$		
P0	9	10	–	Air curing
PF1	8.1	10	10	
PF2	7.2	10	20	
PF3	6.3	10	30	
P0C	9	10	–	13 days of air curing + 1 day of CO_2 curing
PF1C	8.1	10	10	
PF2C	7.2	10	20	
PF3C	6.3	10	30	

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