Construction and Building Materials 123 (2016) 719–726

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Experimental study of magnesium phosphate cements modified by metakaolin

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HIGHLIGHTS

- The MK-MPC mortar yielded a higher one-hour compressive and flexural strength than MPCs.
- The introduction of MK largely prolonged the setting time of MPCs up to 52 min.
- The addition of MK improved the water resistance of MPCs.
- Mechanisms of hydration products of MK-MPC system were proposed.

ARTICLE INFO

Article history:
Received 1 June 2016
Received in revised form 27 June 2016
Accepted 15 July 2016

Keywords:
Magnesium phosphate cement
Metakaolin
Setting time
Mechanical property
Microstructure

ABSTRACT

Magnesium phosphate cements have the characteristics of fast setting and high early strength, which have been extensively used as rapid repair materials in civil engineering. However, Magnesium Phosphate Cement (MPCs) were also reported to have the disadvantage of water instability and short setting time which was difficult to control. The present research was carried out to evaluate the properties of magnesium phosphate cement with high dosage of metakaolin (MK). Different contents of metakaolin were used to replace magnesium to prepare magnesium phosphate cement. The experimental results showed that the successive additions of MK led to a cumulative increase in setting time to a maximum of 52 min for the compositions investigated, and the intensity of the exothermic reactions was also reduced by MK. Moreover, the additions of MK also improved the strengths of the specimens greatly at the early age, and the compressive strength at 1 h can reach 65.7 MPa. Meanwhile, the water resistance of MPC mortar was also investigated by the form of strength retention, and the results revealed that the addition of MK improved the water resistance after curing for 28 days and 56 days. The improvement mechanism was discussed based on the micro-analysis of XRD, SEM along with energy dispersive spectrometer (EDS). The phase analysis revealed the promotion effect of MK on the hydration of MPC, and confirmed the formation of a new gel. From the microstructural and compositional analyses, the gel was identified as aluminum phosphate ($AlPO_4$), which increased the density of the cement.

1. Introduction

Magnesium Phosphate Cement (MPC) was invented and developed in the 19th century. Since 1970s, it has been investigated as one type of rapid-repair structural materials and through continuous improvements [1,2]. It is well known for its fast setting and high early compressive strength characteristics and attracted much attention in the fields of dental and bone restorations [3], rapid repair to damaged concretes [4–6], and refractories and hazardous waste management [7–9]. However, as an acid-base reaction material, certain issues regarding MPCs are still remaining in the engineering applications: (1) the rapid reaction makes the setting time too short to be cast in the construction; (2) the vast heat is hard to disperse timely in the large-scale pouring; (3) the cost is higher than the traditional Portland cement; (4) the water resistance is poor; and (5) unpleasant ammonia gas may be released to cause pollutions to the surroundings during its setting and hardening stages [10–14]. In some common practice, retarders such as borax, boric acid or sodium triphosphate (STP) were normally used to control the setting time and reduce the intensity of the exothermic reactions during the initial setting, however, which may cause a reduction on its mechanical strength, especially in the early period [15,16]. To reduce the high cost, fly ash was

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http://dx.doi.org/10.1016/j.conbuildmat.2016.07.092
0950-0618/

added to this type of cement, but it was found that high content of fly ash would cause a dramatic reduction on the early strength of MPC [17,18]. To improve the water resistance, Gai et al. [19] introduced silica and cellulose into this cement system which could enhance its water resistance to some extent, but also had negative effects on the mechanical strength of hardened mortar. In general, although continuous efforts had been done to solve these remaining issues, an effective means to control setting time and resultant properties is still missing.

According to previous research [20], pozzolanic material had already been proved as a material which leads to high-early strength, low porosity, high temperature resistance and well chemical corrosion resistance. Among others, metakaolin was a candidate material [21,22]. The metakaolin (MK, $Al_2O_3{\cdot}2SiO_2$) is a kind of thermal alteration product made by kaolin calcined and dehydrated at the temperature of 500–980 °C [23], forming the anhydrous aluminum silicate with a strong reactive activity. Some early studies [24,25] found that the mixture of alumina with phosphate acid could yield amorphous gelatinous substance of aluminum phosphate ($AlPO_4$) at temperatures greater than 150 °C, which had a denser microstructure. Moreover, according to Fan [26], small addition of active alumina to MPC system had positive effects on its setting properties and significantly enhanced its mechanical properties and improved its water resistance. Thus, it is reasonable to assume that similar effect could happen in the MK which has active alumina. Also, from the economic and ecological perspective, MK is a natural-sourced mineral which is much cheaper than magnesia, thus this proposed research on the addition of MK to MPC systems should have a broader impact.

Therefore, the present paper is concerned with the effects of MK on the MPCs, with particular emphasis on the improvements of strength and performance. For this purpose, the microstructures and compositions of new MK-MPC specimens were studied and the hydration products were examined using X-ray diffraction (XRD) and Scanning Electronic Microscopic-Energy Dispersive Spectrometer (SEM-EDS).

2. Experimental details

2.1. Raw materials

The MK-MPC mortar was prepared as a mixture of magnesium oxide (MgO), MK, ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$), sand, water reducer, and borax ($Na_2B_4O_7{\cdot}10H_2O$) in diverse proportions. The magnesia powder with average particle size of 1.05 μm was calcined at about 1500 °C for about 6 h, and a purity of 89.5% was achieved in the Taishan Refractory Plant of Shanghai. The ammonium dihydrogen orthophosphate and borax used in the previous research were in the industrial grade provided by Fine Chemical Plant of Wujiang, Jiangsu province, China. Natural river sand with the maximum size of 5 mm was used in the experiments to prepare the MPC mortar. The MK with specific surface area of 18 m^2/g was provided by Chaopai Co., Ltd of Hunan province of China. The chemical compositions of the raw materials in the preparation of the mortar are listed in Table 1.

2.2. Specimen preparation

For each specimen, the weight ratio of water to solid (*W*/*C*) which consists of magnesia, MK, ammonium dihydrogen orthophosphate and sand was fixed at 0.12, and the mass ratio of phosphates to metal oxide (magnesium and MK, P/(P + MK)) (*M*/*P*) was always 2.5. The MPC mortar was prepared using a fixed content of borax (3.5% of the weight of metal oxide) with a sand/binder ratio of 1.0. Table 2 summarizes these mixing parameters. The mixing procedure can be divided into two steps: (i) dry-mixing of the powders consisting of magnesia, MK, borax, water reducer and sand for 3 min; (ii) further mixing after water introduced into the mixture for 2 min. After mixing, the mixed fresh mortars were casted into the molds immediately and were demoded one hour later.

2.3. Property measurements

Considering that MPC is mainly used for repair and as grout material, the fluidity and setting time of the fresh paste were tested. For each mixture, the heat evolution during its exothermic setting and hardening reactions were monitored by the automatic temperature recorder. Meanwhile, the setting time was recorded by using a modified Vicat needle according to the ASTMC187 standard. The flowing table test (standard UNE-EN 1015-3) as demonstrated in Fig. 1 was conducted to check the spread diameter of the MK-MPC slurry. In this test, a platform type mold with an initial diameter of 100 mm was placed on a plate glass, and the slurry was poured into it and then lifted vertically. The spread diameter of the mortar was measured in two perpendicular directions, and the mean values were recorded.

The compressive strength and flexure strength of the hardened MK-MPCs mortar were measured using the MTS servo hydraulic testing machine at a speed of 1 mm/min. The specimens were poured into the molds with the dimension of 40 × 40 × 40 mm for measuring the compressive strength and 40 × 40 × 160 mm for measuring flexure strength. The strengths of mortar samples with three replicates under different curing condition were tested at the ages of 1 h, 1 d, 7 d and 28 d. For the samples cured in water, it was kept in water after demolding. Before strength testing, the water curing samples were taken out of water and dried in air for 2 h (room temperature is around 20 °C). The strength retention (*Sr*) is defined as the ratio of the compressive strength of the water curing sample to that of the air curing one, which is used to reflect

Table 2
Mixing proportions of MPC mortars.

Group	Mix proportions (wt%)		P/(M + MK)	W/C	B/O (%)
	MgO	MK			
A0	100	0	1/2.5	0.23	3.5
A30	70	30	1/2.5	0.23	3.5
A40	60	40	1/2.5	0.23	3.5
A50	50	50	1/2.5	0.23	3.5
A60	40	60	1/2.5	0.24	3.5

Table 1
Chemical compositions of magnesia and MK.

Raw material	Mass fraction of the sample (%)									
	MgO	Al_2O_3	SiO_2	P_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	SO_3	N_2O
Magnesia	90.5	1.3	4.91	0.11	1.44	1.2	–	–	–	–
MK	–	43.9.	49.4	–	0.27	0.51	–	0.23	0.14	1.52