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Properties of fly ash blended magnesium potassium phosphate mortars: Effect of the ratio between fly ash and magnesia

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ABSTRACT

The ratio between fly ash (FA) and magnesia is an important factor for the optimum design of FA blended magnesium potassium phosphate cements (MKPCs). In this study, a high CaO content FA (CaO = 12.5 wt%) was used to partially replace magnesia at 0 wt%, 30 wt%, 50 wt%, 70 wt%, and 90 wt%, respectively. The experimental results showed that a FA replacement of 50 wt% led to the highest compressive strengths. A FA replacement of 70 wt% is considered as upper limit, as the presence of more FA caused significantly lower strength. In the plain and the FA blended MKPCs, K-struvite ($MgKPO_4 \cdot 6H_2O$) was the main hydrate. At very high FA contents, additional calcium potassium hydrogen phosphate ($CaK_3H(PO_4)_2$) was observed as well as the destabilization of K-struvite to cattiite ($Mg_3(PO_4)_2 \cdot 22H_2O$), which could be one of the main factors responsible for the lower strength of high FA blended MKPC mortars stored under water.

1. Introduction

Magnesium phosphate cements (MPCs) were first invented as dental investment or refractory material by Prosen in 1939 [1]. MPCs harden through acid-base reactions between the magnesia and phosphate acid (H_3PO_4) or soluble acid phosphates, such as ammonium dihydrogen phosphate (NH_4H_2PO4), sodium dihydrogen phosphate (NaH_2PO_4), or potassium dihydrogen phosphate (KH_2PO_4). Magnesium potassium phosphate cement (MKPC) that uses KH_2PO_4 is most commonly used, as it does not release ammonia gas [2–5], has longer setting time [4,5] and high strength [6–8]. MKPCs have been used as rehabilitation materials [4–12], as solidification/stabilization agent for low-level nuclear wastes and other wastes containing heavy metals [4,5,13–19], and as biological applications [20].

MKPC is a ternary system, consisting of $MgO\text{-}KH_2PO_4\text{-}H_2O$. The principal hardening reaction of MKPC can be described by the following equation

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O + Q_{Heat} \quad (1)$$

As shown in Eq. (1), magnesium potassium phosphate hexahydrate ($MgKPO_4 \cdot 6H_2O$, K-struvite) is the main reaction product and significant heat is released during its formation [21–23]. Thus the heat generated in large volumes of MKPC can further accelerate the setting process and make practical applications difficult [4,5]. In order to slow down the reaction rate and reduce heat generation of MKPC-based materials, a variety of methods have been employed, such as i) the use of retarders (borax, boric acid, etc.) [24,25], ii) the decrease of magnesia reactivity [26,27], iii) the increase of pH by using K_2HPO_4 and $Na_2HPO_4 \cdot 12H_2O$ [28,29], or iv) the dilution of MKPC with mineral admixtures such as fly ash (FA), wollastonite, silica fume or slag [4–7,10,12,18,30–36].

FA, a byproduct of coal-fired power generation, has been reused in Portland cement/concrete since decades [37–40]; FA has also been used in MKPC. The main advantages of FA in MKPC-based materials are (i) the reduction of the heat generated during early hydration [12,41], (ii) enhancement of the workability of fresh mixtures [12,31,35], (iii) improvement of strength [7,12,35] and (iv) the lowering material production cost. FA has been incorporated to those materials as “inert” filler replacing both magnesia and KH_2PO_4 while maintaining magnesium-to-phosphate (M/P) molar ratio unchanged [6,7,31,34–36,41], as the M/P molar ratio has a significant impact on the performance and microstructure of MKPC-based materials [8,11,42–44]. However, more and more evidence showed that FA in fact reacts in MKPC. The dissolution of low CaO FA (CaO = 2.4 wt%) and of slag glasses as well as the possible formation of a potassium aluminosilicate phase was suggested by solid -state NMR [31] in MKPC pastes with M/P molar ratio of 1.7 and water-to-binder ratio (w/b) of 0.24. These findings were confirmed recently by SEM analysis where some reaction of high CaO FA (CaO = 12.5 wt%) was observed in MKPC mortars with M/P molar ratios of 8 and 4.5 and w/b of 0.15 [12]. Also the FA composition could affect MKPC-based materials [4]. Most of the studies on the use of FA in

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Table 1
Chemical composition, mean particle size (d_{Mean}) and BET surface area (S_{BET}) of the magnesia and FA [12].

	Compound (wt.%)											d_{Mean} (μm)	S_{BET} (m^2/g)
	MgO	SiO_2	CaO	Fe_2O_3	P_2O_5	MnO	Al_2O_3	Na_2O	K_2O	TiO_2	SO_3		
Magnesia	94.66	2.28	1.78	0.85	0.29	0.15	–	–	–	–	–	23.2 ± 0.6	2.02 ± 0.22
FA	3.05	47.64	12.46	11.17	1.25	0.10	18.49	1.10	1.41	1.12	2.21	17.8 ± 0.2	7.86 ± 0.06

Table 2
Mix proportions of the MKPC mortars.

Samples	$R_{(MgO+FA)/KH2PO4}$ [1]	R_{FA} [2] (wt.%)	Binder components (referred to 1 g KH_2PO_4)				s/b [3]	w/b [4]	T_{Max} [5] (°C)	t_{Max} [6] (min)
			MgO (g)	FA (g)	KH_2PO_4 (g)	Borax (g)				
M-FA0	2.4	0	2.40	0.00	1.00	0.19	0.25	0.15	46	31
M-FA30	2.4	30	1.68	0.72	1.00	0.13	0.25	0.15	45	32
M-FA50	2.4	50	1.20	1.20	1.00	0.096	0.25	0.15	36	31
M-FA70	2.4	70	0.72	1.68	1.00	0.058	0.25	0.15	30	42
M-FA90	2.4	90	0.24	2.16	1.00	0.019	0.25	0.15	27	48

Note: [1]Base (magnesia and FA)/KH_2PO_4 mass ratio; [2]FA replacement, by weight of magnesia; [3]Sand-to-binder mass ratio; [4]Water-to-binder mass ratio; [5]Maximum temperature inside MKPC mortar during setting; [6]Reaction time corresponding to T_{Max}.

MKPC employed low CaO content (< 10 wt%) FA [4,6,7,31,34–36,41].

Based on the observed reaction of FA it was also suggested that the FA should rather replace magnesia only, which led to higher strength and a denser microstructure [12]. The ratio between FA and magnesia can be considered as one of the most important factors governing both strength and microstructure of FA blended MKPC-based materials. Thus this study aims at a deeper understanding of the interactions between magnesia, FA and KH_2PO_4 and of the effect of the FA-to-magnesia ratio on the generated heat, compressive strength, water resistance and microstructure of MKPC mortars. A FA with a high CaO content of 12.5 wt % was used to study a series of FA blended MKPC mortars where FA replaced magnesia at 0 wt%, 30 wt%, 50 wt%, 70 wt% and 90 wt%, while the magnesia plus FA to KH_2PO_4 ratio ($R_{(Magnesia\ +FA):KH2PO4}$) was kept constant at 2.4.

2. Materials and methods

2.1. Materials

The starting raw materials were dead-burnt magnesia (94 wt% purity), FA, KH_2PO_4, borax, and silica sand. The chemical compositions of the magnesia and FA determined by X-ray fluorescence (XRF) analysis are given in Table 1, together with the mean particle size (d_{Mean}) and BET surface area (S_{BET}). While the FA consisted mainly of amorphous glass, some quartz was observed by X-ray diffraction (XRD). The weight loss of the FA from 400 to 800 °C determined by thermogravimetric analysis (TGA) is 1.6%, indicating carbonate impurities.

2.2. Mortar preparation and test methods

2.2.1. Mix design

Mix proportions of the investigated MKPC mortars are provided in Table 2. The binder components included magnesia, FA, KH_2PO_4, and borax. All the mixes had same w/b ratio of 0.15, sand-to-binder ratio (s/b) of 0.25, 8 wt% borax, by weight of magnesia, and the same $R_{((Magnesia\ +FA):KH2PO4)}$ of 2.4. The FA replacements were 0 wt%, 30 wt %, 50 wt%, 70 wt%, and 90 wt%, respectively, by weight of magnesia. According to the FA replacement level, the mixtures are referred to as M-FA0, M-FA30, M-FA50, M-FA70, and M-FA90, respectively. At the FA replacement of 90 wt%, the samples showed clear expansion and cracks on the surface after final setting. The fractured surface of the FA blended MKPC mortars cured in air at 23 °C and 65% relative humidity (R.H.) for 28 days showed traces of unreacted KH_2PO_4 at the FA replacements of 70 and 90 wt% (Fig. 1).

2.2.2. Test methods for mortar

The temperature development of the MKPC mortars during setting was monitored by thermocouples as detailed in Ref. [42]. For each mix, 200 g were mixed for 2 min and immediately placed in a plastic tube, where a type K thermocouple was located at the central position. The time when the thermocouple had its first contact with the fresh mixture was taken as the starting time. The data was automatically collected at time steps of 1 s. This measurement was carried out in a room with a constant temperature of 23 °C. For compressive strength and water resistance, mixtures of the MKPC mortars were prepared by a Hobart

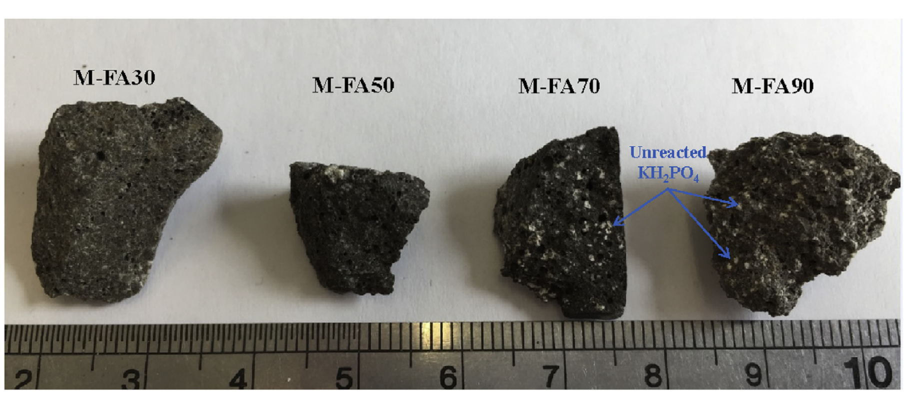

Fig. 1. Fractured surface of the FA blended MKPC mortars cured in air (23 °C and 65% R.H.) for 28 days.