



# Characterisation of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag



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## ARTICLE INFO

### Article history:

Received 28 August 2014

Accepted 19 January 2015

Available online 16 May 2015

### Keywords:

Microstructure (B)

SEM (B)

Fly ash (D)

Granulated blast furnace slag (D)

Chemically Bonded Ceramics (D)

## ABSTRACT

Magnesium potassium phosphate cements (MKPCs), blended with 50 wt.% fly ash (FA) or ground granulated blast furnace slag (GBFS) to reduce heat evolution, water demand and cost, were assessed using compressive strength, X-ray diffraction (XRD), scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR) spectroscopy on  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$  and  $^{39}\text{K}$  nuclei. We present the first definitive evidence that dissolution of the glassy aluminosilicate phases of both FA and GBFS occurred under the pH conditions of MKPC. In addition to the main binder phase, struvite-K, an amorphous orthophosphate phase was detected in FA/MKPC and GBFS/MKPC systems. It was postulated that an aluminium phosphate phase was formed, however, no significant Al–O–P interactions were identified. High-field NMR analysis of the GBFS/MKPC system indicated the potential formation of a potassium-aluminosilicate phase. This study demonstrates the need for further research on these binders, as both FA and GBFS are generally regarded as inert fillers within MKPC.

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## 1. Introduction

Magnesium potassium phosphate cement (MKPC) is a clinker-free acid–base cement, in which the mechanical strength development is a direct result of the rapid formation of cementitious hydrogel type products [1]. The chemical reaction resulting in the formation of MKPCs (Eq. (1)) is based on the dissolution of MgO and  $\text{KH}_2\text{PO}_4$  reacting in solution to form struvite-K ( $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ ), which is isostructural to struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) [2] and is naturally cementitious. In 2003, struvite-K was classified as a distinct mineral species by the Commission of New Mineral and Mineral Names, International Mineralogical Association (CNMNM-IMA) after it was discovered naturally in two locations; Binntal, Switzerland and the Styria region of Austria [3].



When compared to conventional Portland cements, MKPCs have advantageous properties including near-neutral pH, low water demand, low drying shrinkage and high early compressive strength [4]. These properties make MKPCs remarkably versatile, and this cementing system has been used for rapid repair of damaged roads, bridges and runways [5], in conditioning various nuclear waste streams containing reactive metals [6,7] and in dental castings with antibacterial properties [8].

In practical application, MKPC binders are frequently blended (up to 50 wt.% replacement) with fly ash (FA) from the coal combustion

process to reduce their production cost, reduce water demand of the paste, and lower the exothermic output of the acid–base reaction which avoids cracking of the hardened paste. The inclusion of FA in MKPC enhances the workability of the binder via the “ball-bearing effect” of the spherical particles [6,9–11]. Several studies [6,12,13] based on FA/MKPC blended binders have suggested that FA simply acts as a diluent or inert filler, that modifies the aesthetics of MKPC to be compatible to traditional Portland cement, which has been deemed important for rapid-repair applications [9]. Conversely, others hypothesise that FA replacement promotes high mechanical strength in FA/MKPC binders, as a consequence of the formation of a secondary amorphous phase containing silicon-phosphate bonds [12,14]. This is commensurate with the work of Wilson and Nicholson [1], who suggested that aluminosilicate glass can react with phosphoric acid to form a strong phosphate bonded cement. It is conceivable that the glassy aluminosilicate fraction of the FA reacts in the initially acidic environment of the MKPC, forming a secondary phase intermixed with struvite-K. If this occurs, it could result in a matrix of higher density that would be more impermeable to water, have a higher mechanical strength [15,16] and provide additional sites for sorption of radionuclides, which would be of importance for application in the encapsulation of radioactive wastes. However, previous studies have not identified additional crystalline or amorphous reaction products, for example by powder X-ray diffraction or Fourier transform infrared spectroscopy, although the compressive strength and setting characteristics were altered in MKPC with the inclusion of FA [17].

Ground granulated blast furnace slag (GBFS) produced in the iron-making process is a FA alternative that could be used as a diluent within MKPC binders. GBFS/MKPC blended binders are novel and little open

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literature is available concerning their properties. However, it should be noted that crystalline and amorphous blast furnace slags have been previously employed as filter/sorbent materials to remove phosphates from wastewater systems such as constructed wetlands and soil infiltration systems [18–20]. As such, it is conceivable that slag–phosphate interactions could occur within this system and potentially lead to the formation of secondary reaction products.

The reaction of supplementary cementitious materials (SCMs), FA and GBFS, at the pH and chemical speciation conditions reached within MKPC binders, is largely unclear; detailed chemical or microstructural characterisation of secondary cementitious phases forming in FA/MKPC or GBFS/MKPC binders has not yet been reported, and there is a lack of evidence regarding whether or not the dissolution of FA or GBFS particles occurs (and to what extent) within MKPC-based binders. It is therefore imperative to develop an in-depth mechanistic understanding of the role of FA and GBFS within the phase assemblage of MKPC binders.

In this study, FA/MKPC and GBFS/MKPC binders were investigated via mechanical testing (compressive strength), XRD, SEM,  $^{25}\text{Mg}$  magic angle spinning (MAS) NMR,  $^{27}\text{Al}$  MAS NMR,  $^{29}\text{Si}$  MAS NMR,  $^{31}\text{P}$  MAS NMR,  $^{31}\text{P}\{^1\text{H}\}$  cross polarisation (CP/MAS) NMR and  $^{39}\text{K}$  MAS NMR spectroscopy techniques, with the aim of providing the first detailed characterisation of these systems.

## 2. Experimental programme

### 2.1. Materials

MgO was sourced from Richard Baker Harrison Ltd in the form of Dead Burnt Magnesia (DBM) at 90% purity.  $\text{KH}_2\text{PO}_4$  was provided by Prayon UK as Food Grade E340 MKP, and the certificate of analysis purity was >99%. FA was supplied by CEMEX as PFA BS EN 450-1S [21]. Ground granulated blast furnace slag (GBFS) from Scunthorpe Steelworks was supplied by Hanson Cements according to the established specifications of Sellafield Limited for use in the UK nuclear industry, and is a blend of finely-ground and coarser-ground materials. Granular boric acid ( $\text{H}_3\text{BO}_3$ ) was sourced from Fisher Scientific UK (CAS number 10043-35-3, laboratory grade) with a purity of >99.5%, and used as a retarder. The chemical compositions of MgO, FA and GBFS determined by X-ray fluorescence (XRF) oxide analysis are given in Table 1. The powder properties (particle size distribution, fineness, specific surface area and density) are reported in Table 2.

### 2.2. Mix design

The formulations used throughout this study involve the addition of boric acid as a setting retarder to ensure that a workable paste is formed, as without a retarder similar magnesium phosphate systems have been reported to set within 20 min [22], which is not desirable for large-scale industrial applications. The addition of dead-burnt MgO (low reactivity) and supplementary cementitious materials (FA or GBFS; which act as diluents) has also been reported to further extend the setting time of the acid–base reaction [6,23]. The formulations to produce blended

**Table 1**  
Composition of raw materials determined by XRF oxide analysis (precision  $\pm$  0.1 wt.%).

Compound (wt.%)	MgO	FA	GBFS
$\text{Na}_2\text{O}$	<0.1	1.1	0.4
MgO	88.9	1.7	7.9
$\text{Al}_2\text{O}_3$	1.7	25.2	12.0
$\text{SiO}_2$	4.3	50.2	36.6
$\text{P}_2\text{O}_5$	<0.1	0.3	<0.1
$\text{K}_2\text{O}$	0.1	3.6	0.7
CaO	2.1	2.4	40.2
$\text{Fe}_2\text{O}_3$	1.5	9.3	0.4
<b>Total</b>	<b>98.8</b>	<b>93.8</b>	<b>98.3</b>

**Table 2**

Characterisation of raw materials using PSD, Blaine fineness, BET surface area and density measurements.

Material	$d_{10}$ ( $\mu\text{m}$ )	$d_{50}$ ( $\mu\text{m}$ )	$d_{90}$ ( $\mu\text{m}$ )	Blaine fineness ( $\text{m}^2/\text{kg}$ )	BET ( $\text{m}^2/\text{kg}$ )	Density ( $\text{kg}/\text{m}^3$ )
MgO	$3.2 \pm 0.1$	$24.4 \pm 0.3$	$63.8 \pm 0.6$	$329 \pm 16$	$563 \pm 72$	$3471 \pm 1$
FA	$2.7 \pm 0.1$	$14.0 \pm 0.3$	$66.1 \pm 3.5$	$560 \pm 10$	$2258 \pm 10$	$2329 \pm 5$
GBFS	$1.6 \pm 0.1$	$16.0 \pm 0.1$	$1465 \pm 15$	$497 \pm 17$	$993 \pm 72$	$2885 \pm 5$

MKPC pastes are shown in Table 3; a 1.7 MgO:1  $\text{KH}_2\text{PO}_4$  molar ratio (based on previous research [6]) with a water-to-solids (w/s) ratio of 0.24 was used, with additions of 50 wt.% of either FA or GBFS, and 2 wt.%  $\text{H}_3\text{BO}_3$ .

The precursors (MgO,  $\text{KH}_2\text{PO}_4$ , SCMs and  $\text{H}_3\text{BO}_3$ ) were mixed initially for 10 min in a Kenwood benchtop mixer at low speed. Afterwards, the slurry was transferred to a high shear Silverson mixer and mixed for an additional 10 min at 4000 rpm to achieve a homogenous paste. The binders were poured into centrifuge tubes or steel moulds and cured for 28 days in an environmental chamber at 20 °C and 95% relative humidity until testing.

### 2.3. Analytical methods

Compressive strength was determined from triplicate 50 mm cube specimens after 3, 7 and 28 days of curing using a Controls Automax 5.0 machine at a loading rate of 0.25 MPa/s. Paste samples cured for 28 days were crushed and subsequently ground using an agate mortar and passed through a 63  $\mu\text{m}$  sieve prior to powder XRD analysis using a STOE STADI P diffractometer with an image plate detector and Cu  $\text{K}\alpha$  radiation (1.5406 Å); diffraction patterns were collected between  $10^\circ < 2\theta \leq 50^\circ$ . SCM-blended MKPC samples were polished and carbon coated for analysis using a Jeol JSM 6400 SEM at a 20 kV accelerating voltage and a working distance of 15 mm. Elemental maps were collected using a Link ISIS EDS (energy dispersive X-ray spectrometer) detector.

Solid-state NMR spectra were collected on a Varian VNMRS 400 (9.4 T) spectrometer using either a probe for 4 mm o.d. zirconia rotors ( $^{27}\text{Al}$ ,  $^{31}\text{P}$ ) or 6 mm o.d. zirconia rotors ( $^{29}\text{Si}$ ).  $^{27}\text{Al}$  MAS NMR spectra were collected at 104.198 MHz and a spinning speed of 14 kHz, employing a pulse width of 1  $\mu\text{s}$  ( $25^\circ$ ), a relaxation delay of 0.2 s, and with a minimum of 7000 scans.  $^{29}\text{Si}$  MAS NMR spectra were collected at 79.435 MHz at a spinning speed of 6.8 kHz and employed a pulse duration of 4.7  $\mu\text{s}$  ( $90^\circ$ ) and a relaxation delay of 1.0–5.0 s, with a minimum of 1200 scans.  $^{31}\text{P}$  MAS NMR spectra were collected at 161.874 MHz at a spinning speed of 10.0 kHz with a pulse duration of 4.4  $\mu\text{s}$  ( $90^\circ$ ) and relaxation times of 10 and 300 s, with a minimum of 110 and 4 scans, respectively.  $^{31}\text{P}\{^1\text{H}\}$  CP/MAS NMR spectra were collected at 161.874 MHz at a spinning speed of 10 kHz with a pulse duration of 4.4  $\mu\text{s}$ , acquisition time of 30.0 ms at a recycle time of 1.0 s, and a minimum of 120 scans.  $^{27}\text{Al}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  chemical shifts are referenced to external samples of 1.0 M aqueous  $\text{Al}(\text{NO}_3)_3$ , tetramethylsilane (TMS), and 85%  $\text{H}_3\text{PO}_4$ , respectively.

Solid-state NMR spectra for  $^{25}\text{Mg}$  and  $^{39}\text{K}$  nuclei were collected on a Bruker Advance III 850 (19.96 T) spectrometer using 4 mm o.d. zirconia rotors.  $^{25}\text{Mg}$  MAS NMR spectra were collected at 52.05 MHz at a spinning speed of 10.0 kHz with a pulse duration of 5.0  $\mu\text{s}$  ( $90^\circ$ ) and recycle time of 2.0 s for 5800 scans.  $^{25}\text{Mg}$  MAS NMR chemical shifts were

**Table 3**

Formulation of MKPC pastes based on a 0.24 water/solids ratio, using a 500 g batch size to  $\pm$  0.1 g precision [24].

Blend	MgO (g)	$\text{KH}_2\text{PO}_4$ (g)	$\text{H}_2\text{O}$ (g)	FA (g)	GBFS (g)	$\text{H}_3\text{BO}_3$ (g)
MKPC	132.3	262.8	96.0	–	–	9.8
FA/MKPC	77.8	154.6	96.0	165.0	–	6.6
GBFS/MKPC	77.8	154.6	96.0	–	165.0	6.6

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