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1  **Response to the discussion by Hongyan Ma and Ying Li of the paper "Characterisation of**

2  **magnesium potassium phosphate cement blended with fly ash and ground granulated**

3  **blast furnace slag"**

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15  **Abstract:**

16  We recently reported the first comprehensive investigation of magnesium potassium

17  phosphate cements (MKPCs) blended with supplementary cementitious materials

18  (pulverized fuel ash and granulated blast furnace slag) for the encapsulation of radioactive

19  wastes [Gardner et al., Cem. Concr. Res. 74 (2015) 78-87].  Using a combination of

20  characterization techniques, we demonstrated the important role of the reaction of the

21  supplementary cementitious materials in contributing to the development of the

22  microstructure and strength of these binder materials.  Here, we clarify aspects of our

23  experimental design, and elaborate on the interpretation of our data, following discussion by

24  Ma and Li.

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26  **Keywords:**  Microstructure (B), SEM (B), Fly ash (D), Granulated blast furnace slag (D),

27  Chemically Bonded Ceramics (D)

28

## 1. Introduction

We recently reported the first comprehensive investigation of magnesium potassium phosphate cements (MKPCs), blended with 50 wt.% fly ash (FA) and ground granulated blast furnace slag (GBFS) for the potential encapsulation of radioactive wastes [1]. Using a combination of compressive strength, X-ray diffraction (XRD), scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR) spectroscopy, we elicited the reaction of the supplementary cementitious materials in contributing to the development of the microstructure and strength of these binder materials. In this contribution, we clarify aspects of our experimental design and elaborate on the interpretation of our data, following discussion by Ma and Li [2]. For details of the materials and experimental methods, we refer the reader to our previous work [1].

## 2. Mix proportion

The motivation for our investigation of MPKCs is primarily directed toward application in the encapsulation of radioactive wastes. The mix proportions and water-to-solids ratio used in our study are common for MKPCs developed for such applications [3-7], in which high flow and controlled heat release are essential characteristics of the mix design. Our contribution [1], was therefore intended to establish the properties of a tightly controlled MKPC formulation envelope suitable for UK nuclear waste streams, rather than for civil engineering applications. As highlighted by Ma and Li [2], we appreciate that it is possible to attain higher compressive strengths, a lower porosity and lower permeability by introducing a higher $MgO$-to-$KH_2PO_4$ molar ratio ($m/p$) and with variation of water content according to [8-11]. Nevertheless, the properties of our formulations are certainly fit for the intended purpose, as elaborated below.

In the UK, the material properties taken into consideration for choosing a cement encapsulant include: chemical compatibility with the waste, controlled heat evolution during setting, radiation tolerance, aqueous stability, strength, flow properties, and cost [12]. There is no fixed strength requirement for conditioned waste packages, however static

compressive strengths between 4 to 40 MPa, as fulfilled by our formulations [1], are deemed acceptable by the Nuclear Decommissioning Authority with respect to accident performance criteria (fire, impact, water immersion) [13]. However, the strength of an encapsulant is not the overriding material requirement: the primary requirement is demonstrable compatibility with the encapsulated waste in order to achieve passive safety.  In the case of emplacement in 500 L stainless steel drums, as is common in the UK, the strength required for storage/disposal will be supplied by the stillage (overpack that contains four drums), with no load to be directly placed onto the waste  packages [13]. Therefore, the mechanical properties of the blended MKPC binder was not the dominant factor in designing our formulations [1, 14].

Blended MKPC binders are under investigation as an alternative encapsulant in the UK for niche intermediate level waste streams such as reactive metals (Al, Mg and U) where the high pH of Portland cement-based encapsulants can promote the corrosion of Al, whilst Mg and U can corrode in the presence of free water [3, 5, 15]. Corrosion of these reactive metals leads to the formation of expansive corrosion products and hydrogen gas, which increases the internal stress of the conditioned wasteform, and to the potential detriment of the long term stability of the waste package [3, 5, 15]. To minimise corrosion of encapsulated reactive metals, a low w/s ratio is therefore required. In our original study [1], we specified a w/s ratio of 0.24, based on further evolution of the research conducted by Covill [4] who demonstrated the mechanical and chemical stability of FA/MKPC binders with w/s ratios of 0.26 and 0.28, up to 360 days. No deleterious effects were observed as a result of incomplete $KH_2PO_4$ consumption.  The authors are in agreement with Ma and Li [2] that the phosphate conversion to struvite-K was incomplete (as we indeed acknowledged in discussion of our ^{31}P MAS NMR data [1]), however, this was not a primary objective in our study.

### 3.  Morphology

Ma and Li dispute our interpretation of the microstructure of hardened GBFS/MKPC and FA/MKPC pastes (Fig. 4 and 6, in [1]), in which a network of fine cracks was attributed to

91     desiccation of the material as a result of storage and analysis under vacuum. They speculate

92     that this microstructure *"could be formed in the growing process of struvite-K particles,*

93     *rather than due to dehydration-induced cracking"* [2]. As evidence, they show a back

94     scattered electron image (Fig 2. in [2]) of a pure MKPC paste (without the presence of

95     supplementary materials), and conjecture that the network of fine cracks, similar to those

96     observed in our study, are due to *"an assembly of poorly connected irregular particles"*.

97     Note that it is unclear as to whether Fig 2. in [2] was acquired by analysis under high

98     vacuum, as is typical in a conventional scanning electron microscope, in which case the

99     origin of the observed cracks in this image should remain moot. Nevertheless, to resolve

100     this issue, we further investigated the effect of vacuum on the microstructure of pure MKPC

101     paste (prepared according to the method of Ma and Li [2]) using a sample cured for 7 days at

102     20 °C and 95 % relative humidity. Fig. 1A shows the fracture surface of the material

103     observed using back scattered electron imaging in the low vacuum mode of a Hitachi TM

104     3030 Scanning Electron Microscope. A fracture surface was analyzed in order to exclude any

105     influence of sample grinding and polishing, as for conventional specimen preparation. Fig.

106     1B shows the fracture surface of the same material after exposure to ca. 100 mbar vacuum

107     for 12 hours at 20 °C, again observed using back scattered electrons in low vacuum mode.

108     Comparison of Fig. 1A and 1B shows, conclusively, that the fine network of cracks at issue

109     appears only after exposure to vacuum, and is not formed during the process of struvite-K

110     development, as conjectured by Ma and Li. The large cracks observed in both Fig. 1A and

111     Fig. 1B are the result of damage to the material in preparation of the fracture surface.

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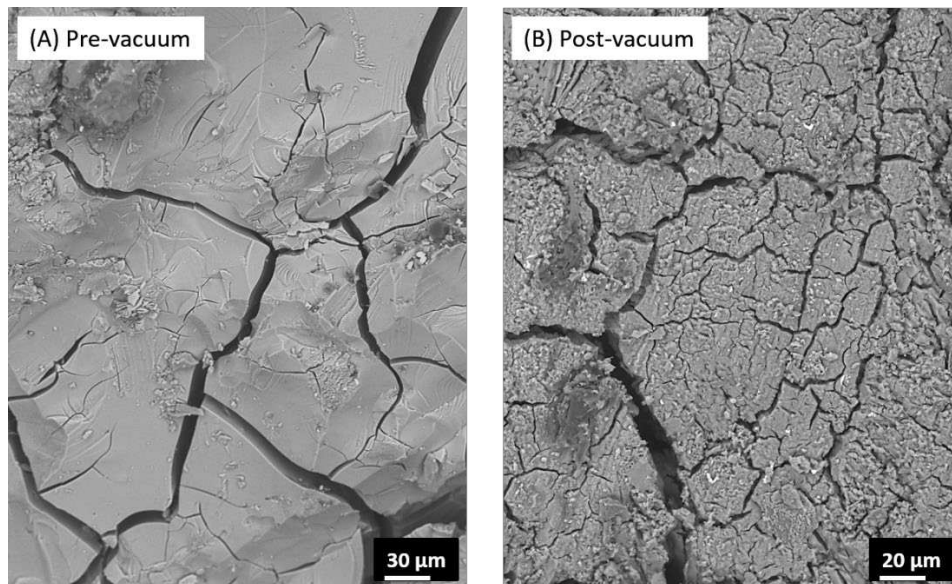
**Fig. 1. BSE micrographs of MKPC-only paste at Day 7: A) Pre-vacuum and B) Post-vacuum**

The difference discussed by Ma and Li [2] concerning the crystallite size of struvite-K is an interesting point, and can be explained by the formulation design, using the mechanism they propose. In the blended MKPC binders, supplementary cementitious materials (FA, GBFS) were added at 50 wt. %, which effectively diluted the reactants in the system and retarded the acid-base reaction. The reaction duration of the MKPC-only and blended MKPC binders was monitored using isothermal calorimetry; the MKPC-only (0.24 w/s) was observed to reach completion after 50 hours, whilst the reaction of the FA/MKPC and GBFS/MKPC binders continued until approximately 80 hours, as shown in Fig. 2. This difference could explain why larger crystallites are only observed in the blended MKPC binders. Hall *et al.,* [16] described similar microstructural effects when the retarder was changed to boric acid, and heterogeneous crystal sizes were observed alongside "large, well-formed crystals" in magnesium ammonium phosphate cements (MAPCs). This concurs with the findings described by Popovics *et al.* [17], who found that in MAPCs without a retarder (such as borax) the crystals could be up to one-half smaller than corresponding samples with a retarder.  The microstructures of the MKPC-only pastes were not reported in [1], as in practical applications in the UK nuclear industry, supplementary cementitious materials will always be utilised to reduce cost and ensure that the grouts pass UK plant acceptance tests, which are based on flow/fluidity, heat of hydration, bleed and set times [18].
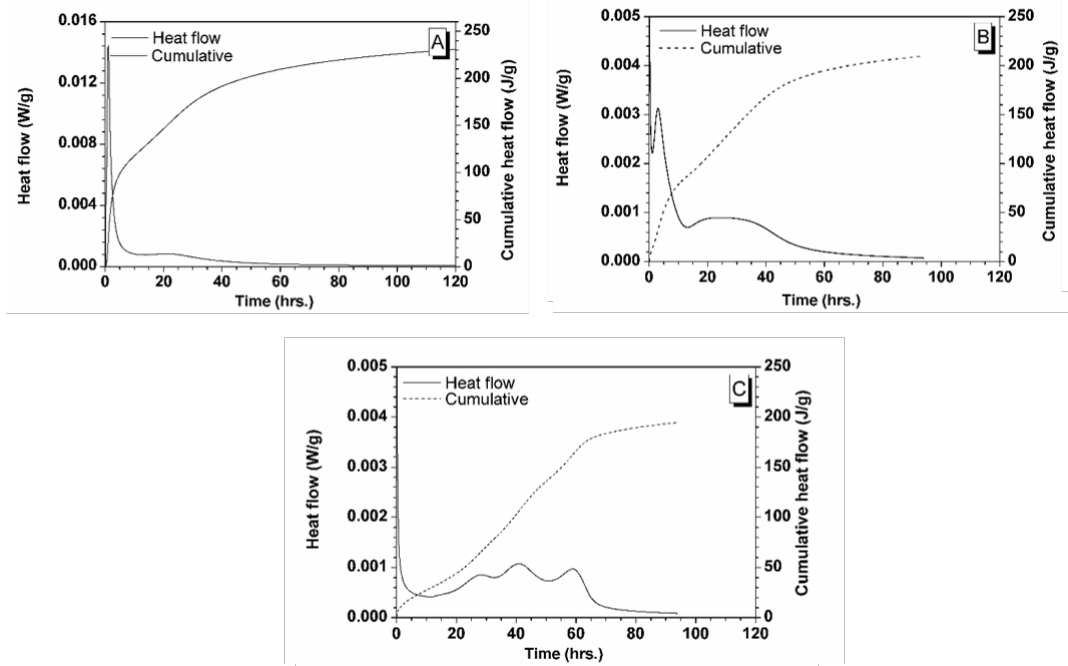
**Fig. 2. Normalized isothermal calorimetry traces of A) MKPC-only, B) FA/MKPC and C) GBFS/MKPC pastes**

## 4. Synergy mechanism

Ma and Li propose an alternative interpretation of aspects of the reaction mechanism of FA and GBFS with MKPC, proposed in our study [2], including the supposition of different reaction products. We show that this interpretation is inconsistent with careful interpretation of the full data set previously presented, together with additional supplementary data [1].

The Ca present in the FA/MKPC formulations was reported to be associated with the calcium silicate impurity ingrained with the MgO particles, which is evident in the corresponding micrograph (Fig. 4 in [1]) where a lighter region is visible around the unreacted MgO. It is not believed that the Ca impurities present in the MgO in either the FA/MKPC or GBFS/MKPC binders contributed to the formation of additional phases, however, we appreciate that reference to "Ca present in the MKPC matrix" could have been misinterpreted. To clarify, the "MKPC matrix" referred to the bulk sample rather than the cementitious component (struvite-K).

155     In our original study, we identified the presence of an aluminosilicate phase as a result of

156     partial dissolution and reaction of FA and GBFS supplementary materials [1]. Ma and Li

157     dispute our interpretation of back scattered electron images and associated X-ray maps in

158     [1], in which we show incorporation of Al and Si in the binding matrix (Fig. 4 and Fig. 6 in

159     [1]). Their interpretation is that the observed X-ray emission, associated with Al and Si in

160     these maps, is attributed to *"the unreliability/noise of this technique"*. Incongruously, they

161     cite as evidence the back scattered electron image and X-ray map of an MKPC-only paste,

162     produced with MgO containing <1 wt. % $Al_2O_3$ (Fig. 1 in [15]). With respect to these data,

163     they interpret the background emission in their X-ray maps, within the energy window

164     expected for Al K$\alpha$ and Si K$\alpha$ lines, as demonstrating the absence of these elements within

165     the binding matrix of our materials. However, as shown by the example EDX spectrum in Fig.

166     3, acquired from the binding matrix of an GBFS/MKPC sample prepared in [1], the presence

167     of measurable Al and Si K$\alpha$ emission lines, above the background, verifies the presence of

168     these elements in accordance with our interpretation.
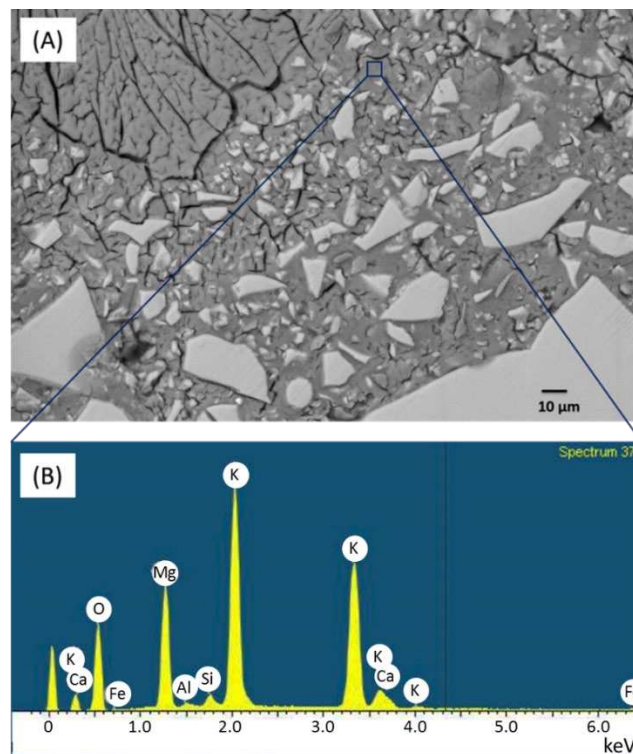


169

170     **Fig. 3. A) BSE micrograph and B) EDX point analysis of GBFS/MKPC prepared in [1]**

171

172     Further evidence in support of our interpretation is to be found in the multinuclear NMR

173     data published in our original study [1]. The dominant source of Al and Si in our

174  formulations is derived from GBFS and FA.  The published ^{27}Al MAS NMR data show the

175  appearance of an additional resonance in the $Al^{VI}$ region centered at -9.5 ppm for our

176  GBFS/MKPC formulation, and the appearance of an additional resonance in the $Al^{IV}$ region

177  centered at 14 ppm for our FA/MKPC formulation [1].  Neither resonance is present in the

178  spectra of the isolated FA and GBFS material.  Likewise, the published ^{29}Si MAS NMR data of

179  our GBFS/MKPC formulation shows the appearance of an additional resonance between −90

180  to −112 ppm, indicative of a highly cross-linked $Q^4$ type site, which was not observed in the

181  spectrum of the isolated GBFS material [1].  We could not reliably identify changes in the [29]Si

182  MAS NMR spectrum of the FA/MKPC formulation, compared to the isolated FA material, due

183  to paramagnetic relaxation of the NMR signal associated with the high Fe content of the fly

184  ash.  The chemical shift of these new resonances, is consistent with plausible reaction

185  products arising from reaction of FA and GBFS with the MKPC binder, as discussed in our

186  original article [1].  Collectively, these data demonstrate reaction of the supplementary

187  cementitious materials disputed by Ma and Li.

188

189  Ma and Li conjecture the formation of $Ca_3(PO_4)_2$ and $CaHPO_4 \cdot 2H_2O$ as reaction products in

190  our FA/MKPC and GBFS/MKPC formulations [2].  Formation of significant $Ca_3(PO_4)_2$ would be

191  expected to contribute three distinct resonances between 6 to − 4 ppm in the ^{31}P MAS NMR

192  spectrum [19], whereas formation of significant $CaHPO_4 \cdot 2H_2O$ would contribute a single

193  sharp resonance between 1.6 to 2.0 ppm [20-22].  The published ^{31}P MAS NMR spectra

194  show resonances located at 6.2 ppm (struvite-K), 3.6 ppm ($KH_2PO_4$) and a low intensity

195  shoulder between -4 to 4 ppm [1]. The latter feature was assigned to an amorphous

196  phosphate phase that has no hydrogen interactions, as confirmed by cross polarization

197  [31]P[^{1}H] CP MAS NMR  [1]. As a result, this feature cannot be attributed to the presence of

198  $CaHPO_4 \cdot 2H_2O$ in the blended MKPC binders, whilst characteristic resonances expected of

199  $Ca_3(PO_4)_2$ are not observed in our ^{31}P MAS NMR.  From these data, we can rule out the

200  formation of significant $Ca_3(PO_4)_2$ and $CaHPO_4 \cdot 2H_2O$ reaction products, as conjectured by Ma

201  and Li [2].

202

203  This discussion serves to further emphasize that, although the principal role of FA and GBFS

204  in blended MKPC binders is as a filler and diluent, partial dissolution of the aluminosilicate

205  fractions of both the FA and GBFS component leads to the formation of secondary reaction

products, which contribute to strength development [1].  We highlight the need to utilize a suite of complementary characterization techniques to understand the complex mechanisms involved in MKPC binder formation.  In particular, it is evident that exploitation of multinuclear solid state NMR is essential, in order to reliably ascertain and interpret the reaction of supplementary cementitious materials in MKPC blends.

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