



Deposited via The University of Sheffield.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/169554/>

Version: Accepted Version

Article:

Gardner, L.J., Bernal, S.A., Walling, S.A. et al. (2018) Response to the discussion by Hongyan Ma and Ying Li of the paper "Characterization of magnesium potassium phosphate cement blended with fly ash and ground granulated blast furnace slag". *Cement and Concrete Research*, 103. pp. 249-253. ISSN: 0008-8846

<https://doi.org/10.1016/j.cemconres.2017.07.011>

Article available under the terms of the CC-BY-NC-ND licence
(<https://creativecommons.org/licenses/by-nc-nd/4.0/>).

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

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”**

4
5 Laura J. Gardner¹, Susan A. Bernal¹, Samuel A. Walling¹, Claire L. Corkhill¹, John L. Provis¹ and
6 Neil C. Hyatt^{1*}

7
8 ¹*Immobilisation Science Laboratory, Department of Materials Science and Engineering,*
9 *University of Sheffield, Sir Robert Hadfield Building, Portobello Street, Sheffield S1 3JD, UK*

10
11 **To whom correspondence should be addressed.*

12 *Email n.c.hyatt@sheffield.ac.uk, phone +44 (0) 114 222 5470, fax +44 (0) 114 222 5943*

13
14
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.

25
26 **Keywords:** Microstructure (B), SEM (B), Fly ash (D), Granulated blast furnace slag (D),
27 Chemically Bonded Ceramics (D)

28

29 **1. Introduction**

30

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

41

42 **2. Mix proportion**

43

44 The motivation for our investigation of MPKCs is primarily directed toward application in the
45 encapsulation of radioactive wastes. The mix proportions and water-to-solids ratio used in
46 our study are common for MKPCs developed for such applications [3-7], in which high flow
47 and controlled heat release are essential characteristics of the mix design. Our contribution
48 [1], was therefore intended to establish the properties of a tightly controlled MKPC
49 formulation envelope suitable for UK nuclear waste streams, rather than for civil engineering
50 applications. As highlighted by Ma and Li [2], we appreciate that it is possible to attain
51 higher compressive strengths, a lower porosity and lower permeability by introducing a
52 higher MgO-to-KH₂PO₄ molar ratio (m/p) and with variation of water content according to
53 [8-11]. Nevertheless, the properties of our formulations are certainly fit for the intended
54 purpose, as elaborated below.

55

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

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

70

71 Blended MKPC binders are under investigation as an alternative encapsulant in the UK for
72 niche intermediate level waste streams such as reactive metals (Al, Mg and U) where the
73 high pH of Portland cement-based encapsulants can promote the corrosion of Al, whilst Mg
74 and U can corrode in the presence of free water [3, 5, 15]. Corrosion of these reactive metals
75 leads to the formation of expansive corrosion products and hydrogen gas, which increases
76 the internal stress of the conditioned wasteform, and to the potential detriment of the long
77 term stability of the waste package [3, 5, 15]. To minimise corrosion of encapsulated reactive
78 metals, a low w/s ratio is therefore required. In our original study [1], we specified a w/s
79 ratio of 0.24, based on further evolution of the research conducted by Covill [4] who
80 demonstrated the mechanical and chemical stability of FA/MKPC binders with w/s ratios of
81 0.26 and 0.28, up to 360 days. No deleterious effects were observed as a result of
82 incomplete KH_2PO_4 consumption. The authors are in agreement with Ma and Li [2] that the
83 phosphate conversion to struvite-K was incomplete (as we indeed acknowledged in
84 discussion of our ^{31}P MAS NMR data [1]), however, this was not a primary objective in our
85 study.

86

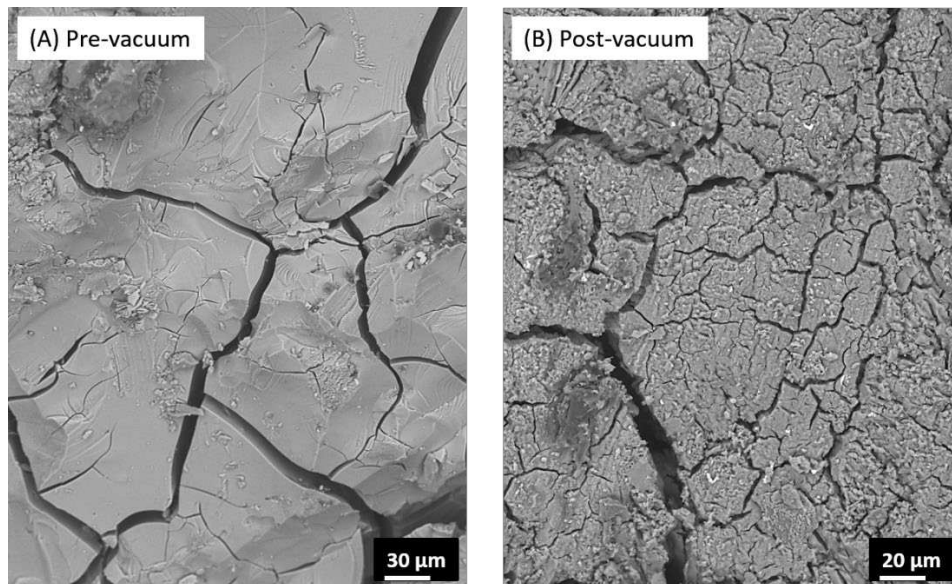
87 **3. Morphology**

88

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

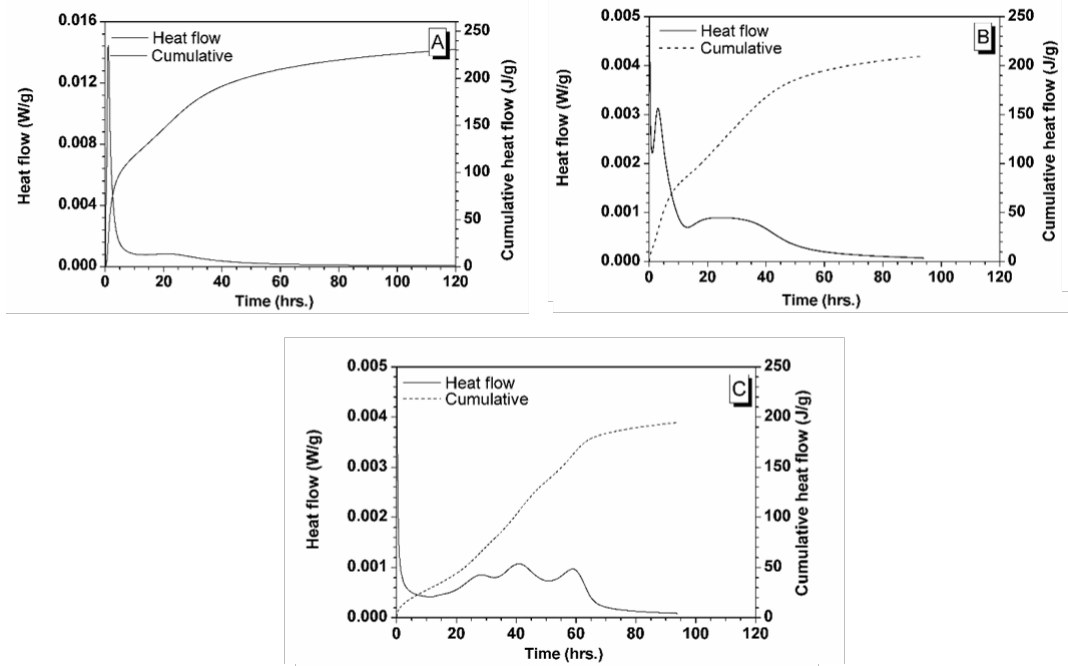
91 desiccation of the material as a result of storage and analysis under vacuum. They speculate
92 that this microstructure *“could be formed in the growing process of struvite-K particles,*
93 *rather than due to dehydration-induced cracking”* [2]. As evidence, they show a back
94 scattered electron 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.

112



113
114 **Fig. 1. BSE micrographs of MKPC-only paste at Day 7: A) Pre-vacuum and B) Post-vacuum**
115

116 The difference discussed by Ma and Li [2] concerning the crystallite size of struvite-K is an
117 interesting point, and can be explained by the formulation design, using the mechanism they
118 propose. In the blended MKPC binders, supplementary cementitious materials (FA, GBFS)
119 were added at 50 wt. %, which effectively diluted the reactants in the system and retarded
120 the acid-base reaction. The reaction duration of the MKPC-only and blended MKPC binders
121 was monitored using isothermal calorimetry; the MKPC-only (0.24 w/s) was observed to
122 reach completion after 50 hours, whilst the reaction of the FA/MKPC and GBFS/MKPC
123 binders continued until approximately 80 hours, as shown in Fig. 2. This difference could
124 explain why larger crystallites are only observed in the blended MKPC binders. Hall *et al.*,
125 [16] described similar microstructural effects when the retarder was changed to boric acid,
126 and heterogeneous crystal sizes were observed alongside “large, well-formed crystals” in
127 magnesium ammonium phosphate cements (MAPCs). This concurs with the findings
128 described by Popovics *et al.* [17], who found that in MAPCs without a retarder (such as
129 borax) the crystals could be up to one-half smaller than corresponding samples with a
130 retarder. The microstructures of the MKPC-only pastes were not reported in [1], as in
131 practical applications in the UK nuclear industry, supplementary cementitious materials will
132 always be utilised to reduce cost and ensure that the grouts pass UK plant acceptance tests,
133 which are based on flow/fluidity, heat of hydration, bleed and set times [18].
134



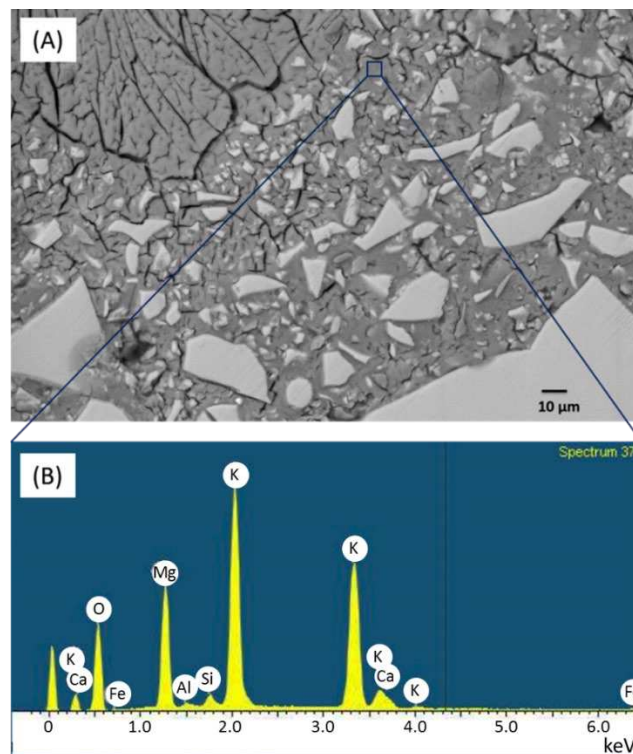
135
 136 **Fig. 2. Normalized isothermal calorimetry traces of A) MKPC-only, B) FA/MKPC and C)**
 137 **GBFS/MKPC pastes**

138 **4. Synergy mechanism**

139
 140 Ma and Li propose an alternative interpretation of aspects of the reaction mechanism of FA
 141 and GBFS with MKPC, proposed in our study [2], including the supposition of different
 142 reaction products. We show that this interpretation is inconsistent with careful
 143 interpretation of the full data set previously presented, together with additional
 144 supplementary data [1].

145
 146 The Ca present in the FA/MKPC formulations was reported to be associated with the calcium
 147 silicate impurity ingrained with the MgO particles, which is evident in the corresponding
 148 micrograph (Fig. 4 in [1]) where a lighter region is visible around the unreacted MgO. It is not
 149 believed that the Ca impurities present in the MgO in either the FA/MKPC or GBFS/MKPC
 150 binders contributed to the formation of additional phases, however, we appreciate that
 151 reference to “Ca present in the MKPC matrix” could have been misinterpreted. To clarify,
 152 the “MKPC matrix” referred to the bulk sample rather than the cementitious component
 153 (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. % Al₂O₃ (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 α and Si K α 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 α 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 $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ as reaction products in
190 our FA/MKPC and GBFS/MKPC formulations [2]. Formation of significant $\text{Ca}_3(\text{PO}_4)_2$ 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 $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ 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 $^{31}\text{P}\{^1\text{H}\}$ CP MAS NMR [1]. As a result, this feature cannot be attributed to the presence of
198 $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the blended MKPC binders, whilst characteristic resonances expected of
199 $\text{Ca}_3(\text{PO}_4)_2$ are not observed in our ^{31}P MAS NMR. From these data, we can rule out the
200 formation of significant $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ 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

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

211

212 **Acknowledgements**

213 LJG is grateful to the Nuclear Decommissioning Authority for sponsorship, under supervision
214 by the National Nuclear Laboratory. NCH wishes to acknowledge the Royal Academy of
215 Engineering, the Nuclear Decommissioning Authority and EPSRC for funding support
216 (EP/L014041/1 and EP/N017617/1). CLC is grateful to the University of Sheffield for the
217 award of a Vice Chancellor's fellowship and EPSRC for the award of an Early Career Research
218 Fellowship (EP/N017374/1). This research was performed in part at the MIDAS Facility, at the
219 University of Sheffield, which was established with support from the Department of Energy
220 and Climate Change.

221

222 **Literature cited**

223 [1] L.J. Gardner, S.A. Bernal, S.A. Walling, C.L. Corkhill, J.L. Provis, N.C. Hyatt, Characterisation of
224 magnesium potassium phosphate cements blended with fly ash and blast furnace slag, *Cement and*
225 *Concrete Research*, **2015**, vol. 74, pp. 78-87.

226 [2] H. Ma, Y. Li, Discussion of the paper "Characterisation of magnesium potassium phosphate
227 cement blended with fly ash and ground granulated blast furnace slag" by L. J. Gardner, *Cement and*
228 *Concrete Research*, **2016**, vol. In review.

229 [3] M. Hayes, I.H. Godfrey, Development of the use of alternative cements for the treatment of
230 intermediate level waste, *Waste Management Conference; AZ, USA, Feb 25 - Mar 1; 2007*, On-
231 line/CD ROM proceedings.

232 [4] A. Covill, *Novel encapsulants for intermediate level waste in the UK nuclear industry*, Unpublished
233 thesis, Department of Materials Science and Engineering, University of Sheffield, **2010**.

234 [5] A. Covill, N.C. Hyatt, J. Hill, N.C. Collier, Development of magnesium phosphate cements for
235 encapsulation of radioactive waste, *Advances in Applied Ceramics*, **2011**, vol. 110, pp. 151-156.

- 236 [6] C. McCague, L. Wang, Y. Bai, Magnesium phosphate cement as a potential alternative for
237 encapsulation of nuclear wastes containing aluminium *31st Cement and Concrete Science*
238 *Conference*; London, UK, 12-13 September 2011; **2011**.
- 239 [7] W. Montague, M. Hayes, L.J. Vandeperre, Strength - formulations correlations in magnesium
240 phosphate cements for nuclear waste encapsulation *The American Ceramic Society's 37th*
241 *International Conference on Advanced Ceramics and Composites* FL, USA, January 27 - February 1,
242 2013; **2014**, 34.
- 243 [8] F. Qiao, C.K. Chau, Z. Li, Property evaluation of magnesium phosphate cement mortar as patch
244 repair material, *Construction and Building Materials*, **2010**, vol. 24, pp. 695-700.
- 245 [9] A.-j. Wang, Z.-l. Yuan, J. Zhang, L.-t. Liu, J.-m. Li, Z. Liu, Effect of raw material ratios on the
246 compressive strength of magnesium potassium phosphate chemically bonded ceramics, *Materials*
247 *Science and Engineering: C*, **2013**, vol. 33, pp. 5058-5063.
- 248 [10] C.K. Chau, F. Qiao, Z. Li, Microstructure of magnesium potassium phosphate cement,
249 *Construction and Building Materials*, **2011**, vol. 25, pp. 2911-2917.
- 250 [11] H. Ma, B. Xu, J. Liu, H. Pei, Z. Li, Effects of water content, magnesia-to-phosphate molar ratio and
251 age on pore structure, strength and permeability of magnesium potassium phosphate cement paste,
252 *Materials & Design*, **2014**, vol. 64, pp. 497-502.
- 253 [12] Nuclear Decommissioning Authority, *Geological Disposal Package evolution status report 2010*,
254 *NDA Report no. NDA/RWMD/031*, **2010**.
- 255 [13] Nuclear Decommissioning Authority, *Waste package specification and guidance documentation:*
256 *WPS/700 500 litre drum waste package specification: explanatory material and design guidelines*,
257 **2008**.
- 258 [14] L.J. Gardner, V. Lejeune, C.L. Corkhill, S.A. Bernal, J.L. Provis, M.C. Stennett, N.C. Hyatt, Evolution
259 of the phase assemblage in magnesium potassium phosphate cement binders at 200 and 1000 °C,
260 *Advances in Applied Ceramics*, **2015**, vol. 114, pp. 386-392.
- 261 [15] A. Setiadi, N.B. Milestone, J. Hill, M. Hayes, Corrosion of aluminium and magnesium in BFS
262 composite cements, *Advances in Applied Ceramics*, **2006**, vol. 105, pp. 191-196.
- 263 [16] D.A. Hall, R. Stevens, B. El-Jazairi, The effect of retarders on the microstructure and mechanical
264 properties of magnesia–phosphate cement mortar, *Cement and Concrete Research*, **2001**, vol. 31, pp.

265 455-465.

266 [17] S. Popovics, N. Rajendran, M. Penko, Rapid hardening cements for repair of concrete, *Materials*
267 *Journal*, **1987**, vol. 84, pp. 65-73.

268 [18] Radioactive Waste Management, *RWM HAW Innovation and Delivery: A review of cement*
269 *powders security of supply, specifications and disposability issues. NDA Report No. NDA/RWM/144*,
270 **2016**.

271 [19] A.P. Legrand, H. Sfihi, N. Lequeux, J. Lemaître, ³¹P Solid-State NMR study of the chemical setting
272 process of a dual-paste injectable brushite cements, *Journal of Biomedical Materials Research Part B:*
273 *Applied Biomaterials*, **2009**, vol. 91B, pp. 46-54.

274 [20] A.K. Cheetham, N.J. Clayden, C.M. Dobson, R.J.B. Jakeman, *Correlations between ³¹P NMR*
275 *chemical shifts and structural parameters in crystalline inorganic phosphates*, in: *Journal of the*
276 *Chemical Society, Chemical Communications, The Royal Society of Chemistry*, **1986**, pp. 195-197.

277 [21] S. Hayakawa, K. Tsuru, H. Iida, C. Ohtsuki, A. Osaka, ³¹P MAS-NMR studies of phosphate salts
278 formation on calcium-containing oxide glasses in a simulated body fluid, *Journal of the Ceramic*
279 *Society of Japan*, **1996**, vol. 104, pp. 1000-1003.

280 [22] W.P. Rothwell, J.S. Waugh, J.P. Yesinowski, High-resolution variable temperature phosphorus ³¹P
281 NMR of solid calcium phosphates, *Journal of the American Chemical Society*, **1980**, vol. 102, pp.
282 2637-2643.

283