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1 Leaching of magnesium potassium phosphate cement pastes under alkaline 2 conditions

3 Laura Diaz Caselles^{1*}, Céline Cau Dit Coumes¹, Pascal Antonucci¹, Angélique Rousselet², Adel
4 Mesbah³, Valérie Montouillout⁴

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6 ¹ CEA, DES, ISEC, DPME, SEME, LFCM, Univ Montpellier, Marcoule, France

7 ² Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux,
8 91191, Gif-sur-Yvette, France

9 ³ Univ Lyon, Université Lyon 1, Institut de Recherches sur la Catalyse et l'Environnement de Lyon,
10 IRCELYON, UMR5256, CNRS, Villeurbanne, France

11 ⁴ CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France

12 * Corresponding Author, E-mail: lauradiazcaselles@gmail.com
13

14 Abstract

15 Some legacy radioactive waste containing aluminum (Al) metal need to be stabilized and solidified
16 before their final disposal. Currently, Portland cement (PC) is extensively used for conditioning low-
17 or intermediate-level radioactive waste. However, the high alkalinity of PC leads to strong corrosion
18 of Al metal, which is associated with significant dihydrogen release. Therefore, it is important to
19 investigate alternative binders that show better chemical compatibility with Al metal. Magnesium
20 potassium phosphate cements (MKPCs), comprising equimolar amounts of MgO and KH₂PO₄, are
21 interesting candidates since their pore solution pH may fall within the passivation domain of Al metal.
22 The understanding of their long-term durability, especially under alkaline conditions, is however
23 incomplete. Hence, MKPC paste samples (with fly ash as a filler) were submitted to semi-dynamic
24 leaching tests using an alkaline solution under well-controlled conditions. The leachates were analyzed
25 over time using ICP-AES, and the leached solids were characterized by XRD, SEM/EDS, and ³¹P
26 MAS-NMR spectroscopy. Leaching induced a decrease in the content of crystalline K-struvite
27 (MgKPO₄·6H₂O), the main hydrate of the paste samples, as well as the precipitation of Ca-deficient
28 hydroxyapatite (CDHA), brucite (Mg(OH)₂) and possibly magnesium silicate hydrates. The
29 experimental data were then used as an input for numerical simulations using the reactive transport
30 code HYTEC.

31
32 **Keywords:** magnesium phosphate cement; durability; alkaline leaching; modeling;
33 hydroxyapatite
34
35

36 1. Introduction

37 Magnesium phosphate cements (MPCs) are alternative binders to Portland cement (PC) and form
38 through the reaction between magnesium oxide (MgO) and an acidic phosphate salt, such as potassium
39 dihydrogen phosphate (KH_2PO_4), sodium dihydrogen phosphate (NaH_2PO_4) or ammonium dihydrogen
40 phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) (Wagh, 2013; Wagh et al., 1997; Weill and Bradik, 1988; Xu et al., 2018). The
41 binder is referred to as magnesium potassium phosphate cement (MKPC) when KH_2PO_4 is used as the
42 phosphate source. In contact with water, dissolution and precipitation processes take place, mainly
43 yielding K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$). Secondary products such as bobierite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$),
44 cattite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$) or brucite ($\text{Mg}(\text{OH})_2$) may also form depending on the raw materials and
45 the formulation used (e.g., water-to-cement ratio, Mg/P molar ratio, addition of retarders) (Ding et al.,
46 2012; Lahalle et al., 2018; Lothenbach et al., 2019; Xu et al., 2019, 2018). When the cement initially
47 contains equimolar amounts of MgO and KH_2PO_4 , phases such as newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$),
48 phosphörrosslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$) and $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ may precede the formation of K-
49 struvite (Chau et al., 2012; Ding et al., 2012; Lahalle, 2016; Lahalle et al., 2018; Le Rouzic et al.,
50 2017) and the pore solution pH rapidly increases from 4.2 to a value close to 8.

51 MPCs are of interest in civil engineering applications, such as road repairing, due to their fast setting
52 and good bonding properties (Arora et al., 2019; Li et al., 2014; Seehra et al., 1993), but also for
53 bioengineering (Yu et al., 2016, 2010; Zhang et al., 2018) and 3D printing (Weng et al., 2019; Zhao et
54 al., 2021). They are also investigated as conditioning agents for toxic and/or radioactive waste (Buj et
55 al., 2010; Pyo et al., 2021; Torras et al., 2011). Thanks to their low alkalinity, these binders may
56 indeed offer new prospects for the stabilization/solidification of waste that is unstable in basic
57 environment. This is the case for aluminum (Al) metal, which can be encountered in legacy
58 radioactive waste (Cau Dit Coumes et al., 2014; Ionascu et al., 2014; Poras et al., 2023). At high pH,
59 Al metal is strongly corroded, with simultaneous production of dihydrogen, an explosive gas whose
60 accumulation may raise safety issues in a disposal. Several authors (Cau Dit Coumes et al., 2014;
61 Langton and Stefanko, 2011; Perona et al., 2023; Poras et al., 2023) have shown that the H_2 outgassing

62 of cemented waste packages containing Al metal can be strongly reduced by using MKPC (with a
63 Mg/P molar ratio set at 1) instead of PC.

64 Information on the long-term evolution of MKPC-based materials is still limited, especially under the
65 alkaline conditions that may be encountered in the near field of a conventional concrete produced with
66 PC or composite cement (Braney et al., 1993). A few studies have shown that immersion of MKPC
67 samples in alkaline solution may induce some microstructural and mineralogical changes (Lahalle et
68 al., 2019; Yang et al., 2000). For instance, Lahalle et al., 2019 investigated the evolution over time of
69 MKPC pastes (Mg/P molar ratio of 1) immersed in an alkaline solution mimicking the pore solution of
70 a concrete prepared with PC blended with fly ash and blast furnace slag. The solution had a pH close
71 to 13.2 and contained K (133 mmol/L), Na (from 66 to 107 mmol/L) and Ca (1 mmol/L) ions, as well
72 as chlorides (40 mmol/L) in some cases. A decrease in the content of crystalline K-struvite was
73 observed as well as the precipitation of brucite. The increase in the amorphous content was also
74 observed, likely due to the amorphization of existent K-struvite, but also to the formation of another
75 mineral, responsible for a hump in 10° - 12° 2θ range, and still unassigned. The authors also suggested
76 the possible substitution of K^{+} by Na^{+} in the structure of K-struvite, leading to the formation of
77 hazenite ($Mg_2KNa(PO_4)_2 \cdot 14H_2O$). Furthermore, the pore solution pH of the cement pastes increased
78 from 8 to 11-12. In a recent study, Xu et al., 2023 used thermodynamic modeling to predict the
79 evolution of MKPC pastes (Mg/P molar ratio of 4) exposed to alkaline solutions. K-struvite was
80 calculated to dissolve partly to form brucite and hazenite, which was then confirmed experimentally.

81 Some questions remain however concerning the rate of degradation of MKPC-based materials and the
82 mechanisms controlling this degradation under such alkaline conditions. This work thus investigates
83 the durability of MKPC pastes using semi-dynamic leaching tests previously developed to understand
84 and model the degradation processes of PC hydrates (Adenot and Buil, 1992). For this purpose,
85 MKPC pastes were prepared using equimolar amounts of MgO and KH_2PO_4 and fly ash as a filler.
86 Samples were cured for 6 months under endogenous conditions. Leaching experiments were then
87 launched on monolithic samples under well-controlled conditions (pH, temperature, composition of
88 the aggressive solution), with careful analysis of both the leachates and the leached solids. Based on

89 these results, a first modeling approach was then proposed, aiming at predicting the mineralogical
 90 evolutions in MKPC pastes exposed to leaching by an alkaline solution.

91 2. Materials and Methods

92

93 2.1. Materials

94 Table 1 presents the chemical composition of the raw materials, determined by semi-quantitative X-
 95 ray fluorescence (XRF). A hard-burnt magnesium oxide (MgO) was obtained from Martin Marietta
 96 Magnesia specialties (MagChem® 10CR, purity above 98.3%). The MgO displayed a monomodal
 97 particle size distribution ($d_{10} = 4.8 \mu\text{m}$, $d_{50} = 18.9 \mu\text{m}$, and $d_{90} = 45.6 \mu\text{m}$), along with a specific
 98 surface area (BET) of $0.9 \text{ m}^2/\text{g}$. Potassium dihydrogen phosphate (KH_2PO_4) ($d_{10} = 139 \mu\text{m}$, $d_{50} =$
 99 $303 \mu\text{m}$, and $d_{90} = 566 \mu\text{m}$) was supplied by YARA (KH_2PO_4 KristaTM) and had a purity above 98%.
 100 A low calcium oxide fly ash (siliceous fly ash V, according to EN 197-1) ($d_{10} = 7 \mu\text{m}$, $d_{50} = 31 \mu\text{m}$, and
 101 $d_{90} = 163 \mu\text{m}$, specific surface area (BET) of $1.5 \text{ m}^2/\text{g}$) was obtained from EDF (power station at
 102 Cordemais, France) and comprised 10.4 wt. % quartz, 17.2 wt. % mullite, and 72.4 wt. % amorphous
 103 content, as determined XRD Rietveld analysis. Boric acid $\text{B}(\text{OH})_3$ (purity above 98%) was purchased
 104 from VWR.

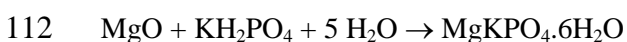
105 **Table 1** – Chemical composition of the raw materials, obtained by semi-quantitative XRF (% by weight).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	Na ₂ O	MgO	P ₂ O ₅	SO ₃	Cl
MgO	0.3	-	0.3	0.9	-	-	-	98.5	-	-	-
KH ₂ PO ₄	-	-	-	-	40.0	-	-	-	59.3	0.5	0.1
Fly ash	57.8	24.7	6.0	4.5	2.2	1.3	0.7	1.6	0.6	0.5	0.1

106

107 2.2. Preparation and curing of paste samples

108 The samples were prepared as described in Diaz Caselles et al., 2024, meaning that a MgO/KH₂PO₄
 109 molar ratio equal to 1 and a water-to-cement (w/c) weight ratio of 0.51 were used. “Cement” denotes
 110 the combination of MgO and KH₂PO₄. Such w/c ratio corresponds to the stoichiometry of the overall
 111 reaction yielding K-struvite (Eq. 1):



Eq. 1

113 To improve the rheological properties and paste stability in the fresh state, fly ash (FA) was added to
 114 the mixture, while B(OH)₃ was incorporated as a set retarder. The weight ratios of FA/c and B(OH)₃/c
 115 were set to 1 and 0.02, respectively. For the preparation of the samples, B(OH)₃ was first diluted in
 116 demineralized water using a closed reactor and a magnetic stirrer. Then, pre-mixed dried solids (MgO,
 117 KH₂PO₄ and FA) were mixed with the B(OH)₃ solution for 5 minutes in a 3-L mixer, according to EN
 118 196-1. The paste was cast into cylindrical plastic molds of 8 cm in length and 5 cm in diameter, which
 119 were tightly closed to avoid desiccation. The molds were then placed in a controlled chamber at 20 °C
 120 for the endogenous curing. Table 2 presents the mix composition of the paste samples.

121 **Table 2** - Mix composition of MKPC paste samples. Values are given in grams per 1 L of material.

	MgO	KH₂PO₄	Fly ash	Boric acid	Water^a	w/c^b
MKPC paste	131.4	443.6	575.0	11.5	293.2	0.51

122 ^a Demineralized water; ^b Water-to-cement weight ratio (cement: MgO+KH₂PO₄).

123

124 2.3. Methods

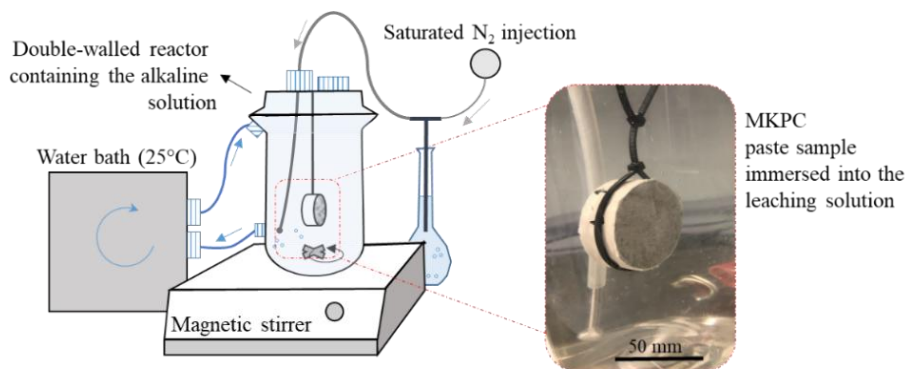
125 2.3.1. Semi-dynamic leaching tests

126 Two semi-dynamic leaching tests were performed on paste monoliths for periods of 14 days and
 127 170 days using an alkaline solution. The resulting leached solids will be referred to as MKP-14d and
 128 MKP-170d, respectively.

129 The leaching solution was prepared to mimic the pore solution of a conventional concrete prepared
 130 with PC blended with blast furnace slag and fly ash. The composition was simplified by neglecting
 131 trace elements. First, demineralized water was boiled for 1 hour at 105 °C to eliminate carbon dioxide
 132 (CO₂), followed by cooling under nitrogen atmosphere. The decarbonated water was then mixed with
 133 0.05 mol/L NaOH, 0.15 mol/L KOH (86%), and 0.001 mol/L CaO (obtained by calcining calcium
 134 hydroxide (Ca(OH)₂) in a furnace at 1000 °C for 8 hours to remove any carbonate traces). Once the
 135 reactants were dissolved, the solution pH reached a value of 13.2±0.1 at 25 °C.

136 The monolithic MKPC paste samples (one per test) were suspended in double-walled reactors (Figure
137 1). To get unidirectional diffusion through the samples, the lateral surface of the monoliths was
138 covered with an epoxy resin, leaving only the parallel end faces exposed (Figure 1). The liquid
139 volume-to-solid surface (L/S) ratio was set at 43.29 cm, and the leaching solution was maintained at
140 25 °C. To prevent carbonation, nitrogen-saturated water was injected by bubbling into the solution.
141 The leaching solution was regularly renewed to prevent the accumulation of species, and magnetic
142 stirring was applied throughout the tests to maintain uniform concentration levels. For the 14-day test,
143 the leaching solution was renewed at 2, 4, 7 and 10 days. For the 170-day test, renewals were carried
144 out at 2, 6, 14, 22, 42, 51, 59, 69, 77, 85, 94, 101, 107, 115, 127, 135, 143, 156, and 163 days. After
145 each renewal, the pH was measured in the leachates, and the solutions were then diluted by factors of
146 10, 100, and 500 using diluted HNO₃ (2 vol. % HNO₃ in ultrapure water, 18.2 MΩ.cm). All solutions
147 were stored at 4 °C until ICP-AES analyses were conducted.

148



149

150 **Figure 1** – Scheme of the device used to perform the semi-dynamic leaching tests under alkaline condition.

151 2.3.2. Hydration stoppage

152 For the mineralogical and microstructural characterizations, hydration stoppage was performed on
153 pastes after 6 months of curing by solvent exchange using isopropanol and following the RILEM TC-
154 238 SCM guidelines (Snellings et al., 2018). Residual isopropanol was removed by placing the
155 samples in a desiccator at 20 °C and 20 %R.H. for 7 days. After leaching, MKPC pastes were simply
156 rinsed with isopropanol.

157 2.3.3. *X-ray diffraction analyses*

158 XRD analyses were performed as described in Diaz Caselles et al., 2024. Therefore, analyses were
159 carried out on powder samples (particle size inferior to 63 μm). After leaching, powders were obtained
160 at various depths of the sample by scratching, step-by-step, starting from the exposed surface towards
161 the sound core. The thickness difference was determined with a digital caliper having a measurement
162 range of 0-25 mm and an accuracy of 0.001 mm. A PANalytical X'Pert Pro diffractometer with a
163 copper radiation source ($\text{Cu K}\alpha$, $\lambda = 1.54 \text{ \AA}$) and a PIXCel detector was used. Analyses were
164 performed in transmission mode using a capillary (external diameter of 0.7 mm and wall thickness of
165 0.01 mm). The anode voltage was set at 40 kV with an electric current intensity of 40 mA. Scans were
166 performed over a 5° to 120° 2θ angular range, with a step size of 2θ 0.013° and a time per step of
167 2.35 s. Pure silicon (Si) was used to extract the instrumental function. Approximately 10 wt.% Si was
168 added to each sample to evaluate the amounts of crystalline phases and amorphous. Diffrac.Suite Eva
169 and/or Highscore softwares were used for identification of phases. The Rietveld refinement was
170 performed using the Fullprof_suite program (Frontera and Rodríguez-Carvajal, 2003). The weight
171 percent content of each phase was evaluated after extracting its structure from the ICSD database and
172 performing Rietveld refinement.

173 2.3.4. *SEM/EDS analyses and optical microscopy*

174 Microstructure analyses were conducted on carbon-coated polished sections, previously soaked into
175 isopropanol, and embedded in resin, using a Scanning Electron Microscope (SEM) FEI Inspect S50
176 equipped with an Electron dispersive spectroscopy (EDS) detector (Bruker XFlash SDD 10 mm^2).
177 Images were obtained in backscattered electron (BSE) configuration at magnifications ranging from
178 50x to 2,000x. 150 EDS point analyses were performed per sample. For quantification, EDS
179 calibration was conducted using eleven reference standards: $\text{NaAl}(\text{Si}_2\text{O}_6)$, MgO (99.95% pure), Al_2O_3
180 (99.8% pure), KAlSi_3O_8 , CaSiO_3 , Ti (99.99% pure), Cr (99.96% pure), Mn (99.99%), Fe (99.95%
181 pure), FeS_2 , and GaP (99.99% pure). Moreover, pastes were characterized by optical microscopy using

182 a 4K high accuracy digital microscope (Keyence VHX-7000) combining large depth of field and high
183 resolution.

184 2.3.5. ³¹P MAS-NMR spectroscopy

185 Changes in the P environment in the MKPC pastes were investigated by solid state magic angle
186 spinning nuclear magnetic resonance (MAS NMR). ³¹P spectra were acquired on a Bruker AVANCE
187 III spectrometer (B₀ = 9.4 T) operating at 162 MHz. The spinning speed was fixed at 20 kHz and 384
188 scans were accumulated after a single short pulse ($\pi/4$) and a recycling delay of 360 s to ensure
189 complete magnetization relaxation. 2.5 mm zirconia rotors were employed. The chemical shifts were
190 referenced relative to H₃PO₄ 85%, and quantitative analyses were performed using the Dmfit program
191 developed at CEMHTI (Massiot et al., 2002).

192 2.3.6. Raman spectroscopy

193 Raman spectroscopy was used to investigate vibrational modes. Analyses were performed on powder
194 samples using a Raman XploRA Plus (Horiba) equipped with a Sincerity detector (cooled down at -
195 60°C). Raman spectra were recorded in the 1800-50 cm⁻¹ range using 10 accumulations per scan with
196 an acquisition time of 20 s per accumulation. The pairing of laser wavelength and diffraction grating
197 used was 532 nm-1800 gr/mm, with a laser intensity set at 100%.

198 2.3.7. Porosity characterization

199 Porosity accessible to water was determined as described in Diaz Caselles et al., 2024 and following
200 European Standard NF P 18-459 (2022). Three cylindrical paste samples (2 cm high and 5 cm in
201 diameter) were used after 6 months of curing and before leaching. First, the samples were placed in a
202 vacuum desiccator at 25 mbar for 4 hours. Then, they were covered with demineralized water while
203 maintaining the 25 mbar vacuum pressure for a minimum of 44 hours. Drying was conducted in a
204 controlled chamber at 38 °C and 10% R.H. to prevent K-struvite dehydration (Lahalle et al., 2019;
205 Lothenbach et al., 2019). Arithmetic average result is presented with a 95% confidence interval.

206 2.3.8. *pH estimation*

207 The Rainbow indicator was purchased from German Instruments. This indicator was used to estimate
208 the pH of cement pastes before and after leaching. The color of this indicator changes from orange (pH
209 4-6) to yellow (pH 6-8), green (pH 8-10), purple (pH 10-12), and blue (pH 12-14). To assess the pH of
210 the paste samples, the indicator was applied to the cross-section of either fractured pieces or sliced
211 samples. Pictures of the sprayed surfaces were taken several minutes later once the indicator solution
212 had dried.

213 2.3.9. *Modeling*

214 One-dimension (1D) model (i.e., unidirectional diffusion) was used to simulate the leaching of MKPC
215 paste. Modeling was performed using reactive transport code HYTEC (version 4.7.4) (van der Lee et
216 al., 2003) as described in Diaz Caselles et al., 2024. General Eq. 2 describes the concentration
217 variation of species i in a unit volume, taking into account transport by diffusion through the pore
218 network, and participation to chemical reactions (using the geochemical module CHESS) (De Windt
219 and Badreddine, 2007).

$$220 \frac{\partial \omega c_i}{\partial t} = \nabla \cdot (D_e \nabla c_i) - \frac{\partial \omega \bar{c}_i}{\partial t} \quad \text{Eq. 2}$$

221 c_i and \bar{c}_i are the mobile and immobile concentrations of a specie per unit volume. ω and D_e are the
222 porosity and the effective diffusion coefficient, respectively. Transport and chemistry are coupled
223 through a sequential iterative algorithm, which simultaneously considers the altered layers due to
224 mineral dissolution, and the associated ion release from the cement paste. Furthermore, changes in
225 local porosity due to dissolution or precipitation of minerals lead to changes in D_e . The retroactive
226 effect of chemistry on mass transport is incorporated through the implementation of a modified
227 version of Archie's law, as described by Eq. 3 (De Windt and Badreddine, 2007).

$$228 D_e(\omega) = D_e(\omega_0) \left(\frac{\omega - \omega_c}{\omega_0 - \omega_c} \right)^\alpha \quad \text{Eq. 3}$$

229 ω_0 is the initial porosity and ω_c is the critical porosity threshold under which diffusion stops
230 (considered as zero in the model). α is an empirical Archie's coefficient, which commonly ranges from

231 1.5 to 4.0 in the modeling of cementitious materials under leaching (Adenot and Buil, 1992; De Windt
 232 and Badreddine, 2007; De Windt and Devillers, 2010; Neithalath et al., 2006). In this study, the
 233 Archie's power was set to 2.0.

234 The computational domain was defined by two zones as presented by Diaz Caselles et al., 2024 (cf.
 235 Fig. 2). This means that zone I corresponded to the MKPC paste sample, and zone II to the reactor
 236 containing the alkaline leaching solution. The experimental liquid volume-to-solid surface (L/S) ratio
 237 of 43.29 cm was reproduced by the geometry definition of each domain (note that the code assumes a
 238 depth of 1 m in the z-axis). The node sizes were set at 100 μm in the paste and in the first 10 mm of
 239 the reactor (zone B in Fig. 2 in Diaz Caselles et al., 2024). The node size in the rest of the reactor
 240 (zone C) was set at 1 mm. The leaching solution comprised 0.13 mol/L KOH, 0.05 mol/L NaOH and
 241 0.001 mol/L portlandite, to obtain the same concentrations as in the experimental leaching solution.
 242 The diffusivity coefficient of the leaching solution was set at $1.0 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$, and $1.0 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ in
 243 the zones B and C to simulate an agitated solution, and to reduce the computation time. No boundary
 244 conditions were defined in this model. Additionally, the leaching solution was renewed at the same
 245 frequency as in the leaching experiments. The chemical reactions were computed by assuming local
 246 thermodynamic equilibrium and utilizing the B-dot model for the calculation of activity coefficients
 247 due to the high values of ionic strength (superior to 1).

248 For this simulation, the thermodynamic CHESS database (version 2.5) was used and enriched with
 249 thermodynamic data for magnesium phosphate phases presented by Lothenbach et al., 2019, Xu et al.,
 250 2020, and Xu et al., 2023. The minerals considered in the model are presented in Table 3.

251 **Table 3** – Thermodynamic data at 25 °C and 1 bar.

Species	Reaction	Log $K_{\text{formation}}$	Vol (kg/m ³)	Ref.
K-struvite	$\text{Mg}^{2+} + \text{HPO}_4^{2-} + \text{K}^+ + 6\text{H}_2\text{O} \rightarrow \text{MgKPO}_4 \cdot 6\text{H}_2\text{O} + \text{H}^+$	-1.36	1870.2	(Lothenbach et al., 2019)
Cattiite	$3\text{Mg}^{2+} + 2\text{HPO}_4^{2-} + 22\text{H}_2\text{O} \rightarrow \text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O} + 2\text{H}^+$	-1.61	1640.5	(Lothenbach et al., 2019)
$\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$	$2\text{Mg}^{2+} + 2\text{HPO}_4^{2-} + \text{K}^+ + 15\text{H}_2\text{O} \rightarrow \text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O} + \text{H}^+$	4.03	1810.6	(Lothenbach et al., 2019)
Phosphorösslerite	$\text{Mg}^{2+} + \text{HPO}_4^{2-} + 7\text{H}_2\text{O} \rightarrow \text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$	4.69	1740.3	(Lothenbach et al., 2019)
Newberyite	$\text{Mg}^{2+} + \text{HPO}_4^{2-} + 3\text{H}_2\text{O} \rightarrow \text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	5.61	2121.1	(Lothenbach et al., 2019)
$\text{MgKPO}_4 \cdot \text{H}_2\text{O}$	$\text{Mg}^{2+} + \text{HPO}_4^{2-} + \text{K}^+ + \text{H}_2\text{O} \rightarrow \text{MgKPO}_4 \cdot \text{H}_2\text{O} + \text{H}^+$	-1.37	2668.7	(Lothenbach et al., 2019)

Farringtonite	$3\text{Mg}^{2+} + 2\text{HPO}_4^{2-} \rightarrow \text{Mg}_3(\text{PO}_4)_2 + 2\text{H}^+$	-2.23	2761.2	(Lothenbach et al., 2019)
Bobierite	$3\text{Mg}^{2+} + 2\text{HPO}_4^{2-} + 8\text{H}_2\text{O} \rightarrow \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} + 2\text{H}^+$	0.66	2129.9	(Lothenbach et al., 2019)
Magnesium orthophosphate tetrahydrate	$3\text{Mg}^{2+} + 2\text{HPO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow \text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+$	-1.14	2380.6	(Lothenbach et al., 2019)
$\text{CaK}_3\text{H}(\text{PO}_4)_2$	$\text{Ca}^{2+} + 3\text{K}^+ + 2\text{HPO}_4^{2-} \rightarrow \text{CaK}_3\text{H}(\text{PO}_4)_2 + \text{H}^+$	2.24		(Xu et al., 2020)
brucite ($\text{Mg}(\text{OH})_2$)	$\text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{H}^+$	-16.29	2367.83	Chess v.2.5
Hydroxyapatite	$3\text{HPO}_4^{2-} + 5\text{Ca}^{2+} + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 4\text{H}^+$	7.56		(Janot and Ilschner, 2001)
Hazenite	$2\text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ + 2\text{HPO}_4^{2-} + 14\text{H}_2\text{O} \rightarrow \text{Mg}_2\text{NaK}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O} + 2\text{H}^+$	-0.64		(Xu et al., 2023)
OCP	$8\text{Ca}^{2+} + 6\text{HPO}_4^{2-} + 5\text{H}_2\text{O} \rightarrow \text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O} + 4\text{H}^+$	22.87		(Janot and Ilschner, 2001)
CDHA	$9\text{Ca}^{2+} + 6\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5\text{OH} + 6\text{H}^+$	12.79		(Janot and Ilschner, 2001)
Portlandite	$\text{Ca}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{H}^+$	-22.80	2245	Chess v2.5

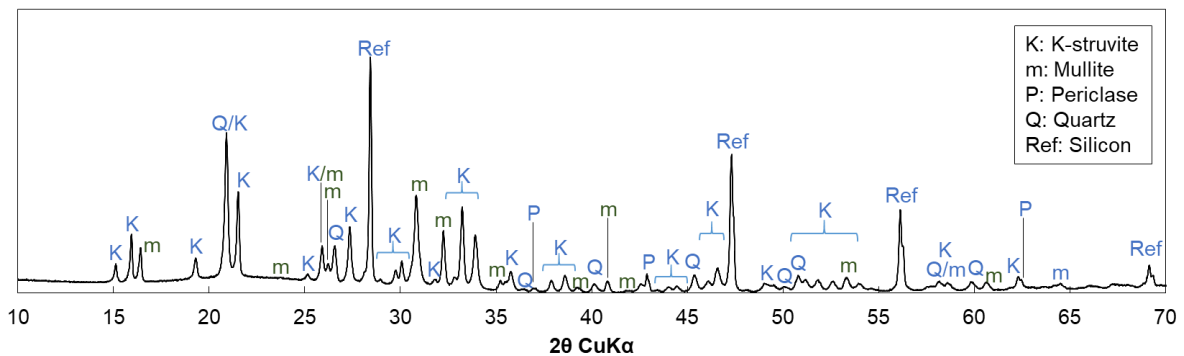
252

253 3. Experimental results

254 3.1. Reference paste characterization

255 The MKPC paste sample after curing and before leaching was the reference material and is referred to
 256 as MKP-ref. Figure 2 presents its XRD pattern after 6 months of endogenous curing.

257



258

259 **Figure 2** – XRD pattern of MKP-ref plotted in the selected range 10 °-70 ° 2θ.

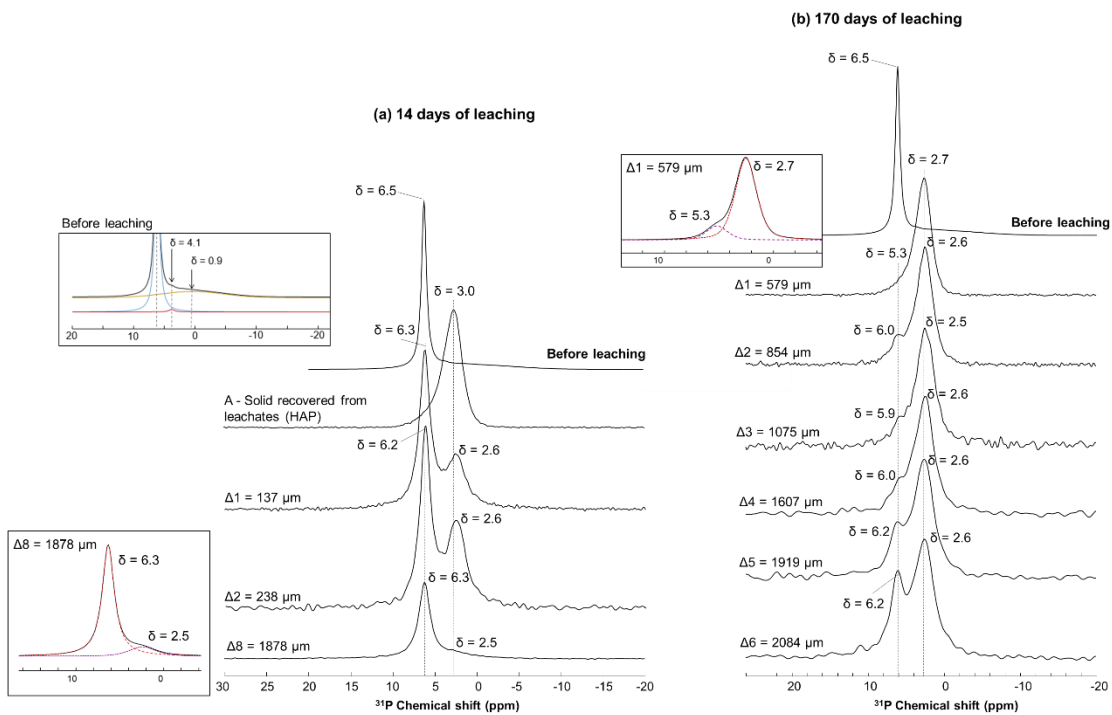
260

261 MKP-ref was composed of K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$), along with residual MgO (periclase), quartz,
 262 mullite (an alumino-silicate mineral), and an amorphous content (Figure 2). The presence of quartz
 263 and mullite were attributed to fly ash. The amorphous content is likely associated with the glassy
 264 structure of the fly ash and potentially with the presence of amorphous phosphate phases (e.g.,

265 amorphous K-struvite, boro-phosphates) (Ding et al., 2012; Lahalle et al., 2019). The mineralogical
 266 assemblage of the paste was estimated by Rietveld refinement and comprised 53.8% K-struvite,
 267 33.6 wt.% amorphous, 8.2 wt.% mullite, 2.6 wt.% quartz, and 1.8 wt.% periclase (Diaz Caselles et al.,
 268 2024). Therefore, the mullite-to-quartz ratio was 3.

269 Figure 3 shows the ^{31}P MAS-NMR spectrum obtained from MKP-ref after 6 months of curing (see
 270 spectrum in the top), and Table 4 presents the quantitative estimations resulting from the
 271 decomposition of ^{31}P MAS-NMR spectra (Diaz Caselles et al., 2024).

272



273

274 **Figure 3** – ^{31}P MAS-NMR spectra obtained before (MKP-ref), and after leaching (MKP-14d and MKP-170d). δ
 275 indicates the chemical shift.

276

277 **Table 4** - ^{31}P site fractions (mol. %) estimated for MKP-ref.

MKPC paste	Attribution	Chemical shift (ppm)	FWHM (ppm)	^{31}P fraction (%)
Before leaching	K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$)	+6.5	0.7	76
	Residual KH_2PO_4	+4.1	1.0	1
	Broad hump *	+0.9	10.2	23

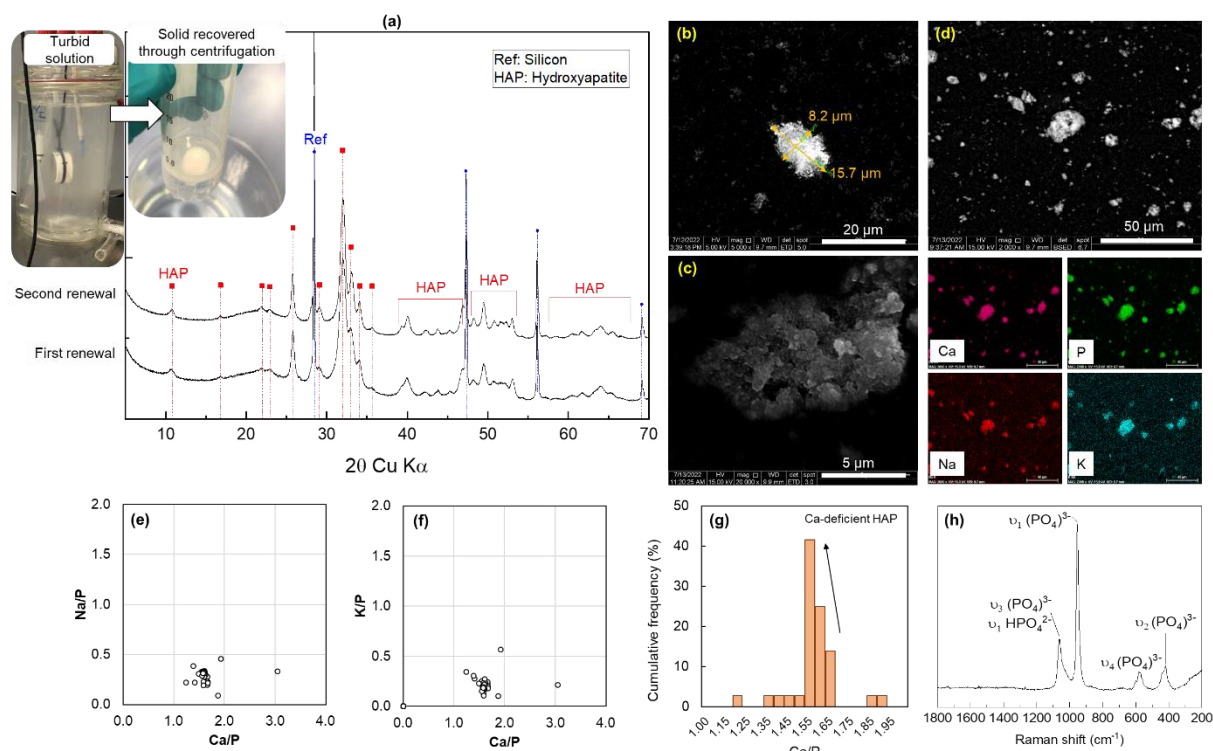
278 *This signal was not clearly assigned.

279 The ^{31}P MAS-NMR spectrum of MKP-ref exhibited three different ^{31}P chemical environments (see top
280 spectrum in Figure 3). The resonance at $\delta = +6.5$ ppm was attributed to K-struvite (Gardner et al.,
281 2015; Lahalle et al., 2018; Viani et al., 2017). A minor ^{31}P resonance at $\delta = +4.1$ ppm (1% of the ^{31}P
282 fraction) was attributed to residual KH_2PO_4 , which was not detected by XRD due to its low content
283 (Gardner et al., 2015; Lahalle et al., 2018). This indicates that KH_2PO_4 was not completely consumed
284 after the 6-month curing period. The resonance at $\delta = +0.9$ ppm could not be assigned with certainty.
285 This resonance might correspond to one or several contributions of poorly crystallized phosphate
286 phases, including (i) $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, (Lahalle et al., 2018; Xu et al., 2022), (ii) lünebergite
287 ($\text{Mg}_3\text{B}_2(\text{PO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$) (Lahalle et al., 2018), (iii) an anhydrous, poorly crystallized
288 orthophosphate $\text{Mg}_3(\text{PO}_4)_2$ (Viani et al., 2017), and/or (iv) hydrated magnesium phosphate phases
289 ($\text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$) (Kongshaug et al., 2001). In two recent papers, Viani et al., 2021, 2017 showed that
290 hardening of a MKPC paste occurs through an amorphous-to-crystalline transformation, involving two
291 distinct amorphous precursors of the final crystalline product (K-struvite), characterized by broad
292 resonances at 3 ppm and 1.8 ppm. The authors suggested that, in analogy with the sol-gel processing
293 of ceramics, the amorphous precursors may bear some structural motifs of K-struvite, the final
294 crystalline phase.

295 3.2. *Leaching tests: experimental results*

296 3.2.1. *Precipitate recovered from leachates*

297 The leaching solution became visibly turbid upon immersion of paste samples, indicating the
298 formation of a precipitate in the solution (Figure 4-a). Subsequently, after each renewal, solid and
299 liquid phases were separated through centrifugation to isolate any precipitate that might have formed.
300 During the first two renewals, the precipitate was easily recovered. From the third renewal onwards,
301 the clarity of the leaching solutions improved over time. The recovered precipitate was rinsed with
302 ethanol, dried at 38 °C for 24 h, and identified by XRD as hydroxyapatite (HAP) with low crystallinity
303 (Figure 4-a).



304
 305 **Figure 4** – Characterization of HAP (a) XRD patterns (range 5 °-70 ° 2θ), (b) SE image, (c) zoomed-in of an
 306 agglomerate of HAP crystals, (d) BSE image and EDS elemental mapping, (e) EDS semi-quantitative analyses
 307 Na/P vs. Ca/P, (f) K/P vs. Ca/P atomic ratios, (g) Distribution of Ca/P atomic ratios, and (h) Raman spectrum.

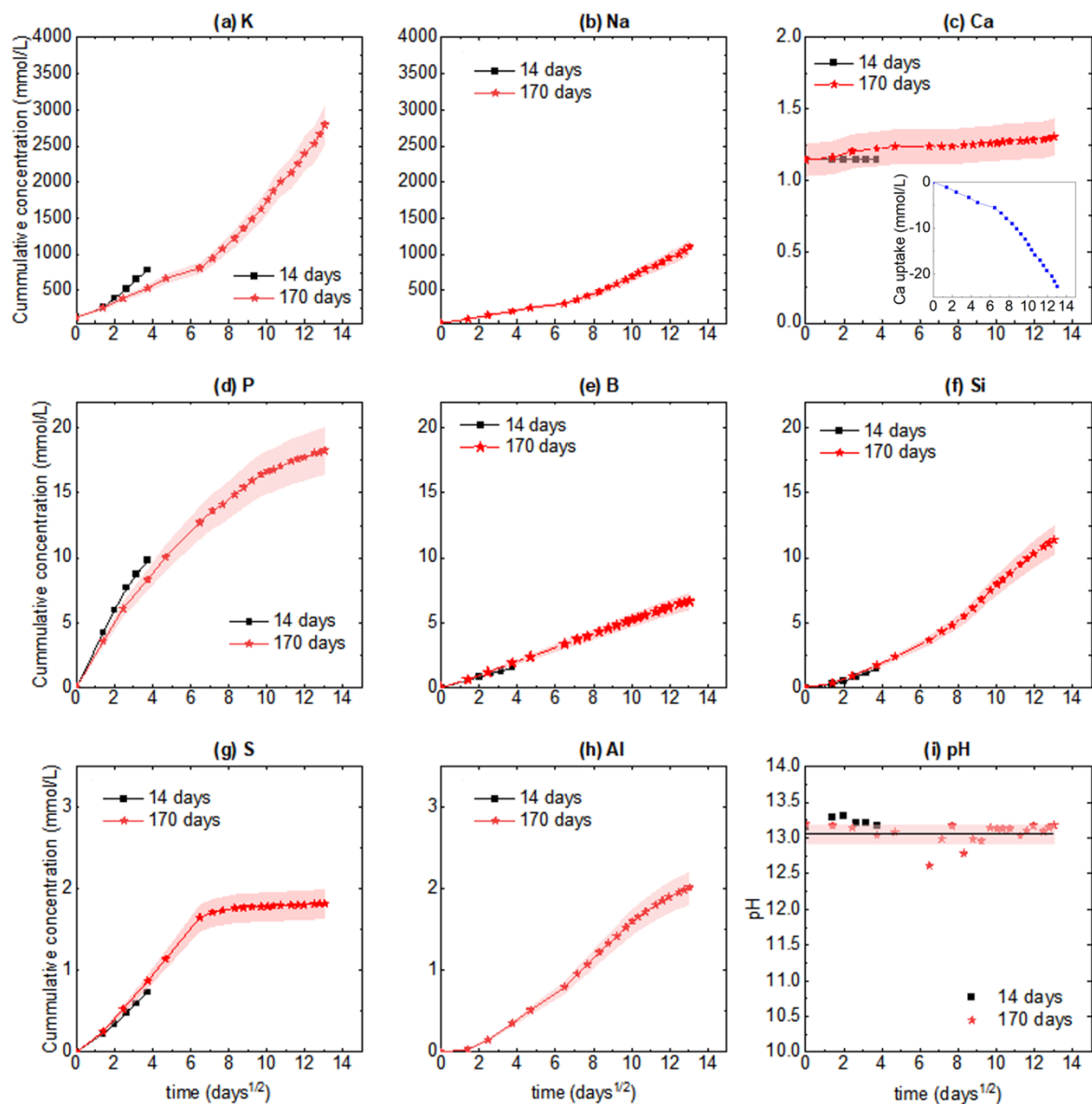
308 HAP particles, of approximately 16 μm long and 8 μm wide, consisted of agglomerates of
 309 micrometer-sized crystals (Figure 4-b and c). EDS analyses showed the presence of Ca, P, Na and K in
 310 the HAP particles, which suggests the uptake of alkalis by HAP (Figure 4-d, e and f), as already
 311 observed by Stoll and Neuman, 1956. By suspending pure HAP in solutions containing KCl and NaCl
 312 at various concentrations, these authors observed indeed an uptake of Na, which was higher than that
 313 of K. Na ions entered the crystal surface of HAP by replacing Ca ions, whereas K ions remained in the
 314 hydration shell of HAP. The HAP particles obtained in the current study had a Ca/P ratio of 1.59±0.11
 315 (arithmetic mean value with a confidence interval of 95 %) (Figure 4-g), suggesting the precipitation
 316 of Ca-deficient HAP (CDHA) (the Ca/P ratio of stoichiometric HAP is 1.67), possibly due to the
 317 uptake of Na.

318 Figure 4-h presents the Raman spectrum of the collected precipitate. The spectrum exhibited distinct
 319 bands, including the symmetric stretching mode (ν1) of phosphate at 960-962 cm⁻¹, which

320 corresponds to the tetrahedral $(\text{PO}_4)^{3-}$ group (P–O bond) typically reported in HAP (Penel et al., 1998;
321 Wilson et al., 2005). The ν_4 and ν_2 bending modes (O–P–O bond) produced bands of weak intensity
322 in the regions of $570\text{--}625\text{ cm}^{-1}$ and $400\text{--}490\text{ cm}^{-1}$, respectively. The band at $1000\text{--}1095\text{ cm}^{-1}$ could be
323 assigned to the ν_3 $(\text{PO}_4)^{3-}$ domain (Penel et al., 1998), but also to the ν_1 mode of hydrogen phosphate
324 (HPO_4^{2-}) present in CDHA (Elliot, 1994; Wilson et al., 2005).

325 3.2.2. *Leachates characterization*

326 Figure 5 shows the evolution of the cumulative concentrations of K, Na, Ca, P, B, Si, S and Al in the
327 leachates (in mmol/L) (i.e., total concentrations of soluble species measured in the leachates) and of
328 pH as a function of the square root of time (in days^{1/2}). The Mg concentration always remained below
329 the detection limit of the ICP-AES method (10 ppb). The red envelope represents the experimental
330 analytical error. The subfigure in Figure 5-c plots the Ca concentration consumed from the initial
331 solution. This means the difference between the Ca concentration measured in the leachates and the
332 initial concentration in the leaching solution. Table 5 presents the initial composition of MKP-ref
333 alongside with the cumulative leached element concentrations determined for each leaching period,
334 expressed in mmol/g of paste. The leached fraction is presented as a percentage for each element,
335 assuming an experimental paste density of $1,876.2\text{ kg/m}^3$, which was obtained by total porosity
336 accessible to water experiments.



337

338 **Figure 5** – Cumulative concentrations (in mmol/L) measured in the leachates as a function of the square root of
 339 time ($\text{days}^{1/2}$). (a) K, (b) Na, (c) Ca, (d) P, (e) B, (f) Si, (g) S, (h) Al, and (i) pH evolution. The analytical error is
 340 estimated to be 10 %.

341

342

343

344

345

346

347 **Table 5** – Initial and leached elemental concentrations (given in mmol/g of MKPC paste) and pH values
 348 determined at 25 °C.

		K	Na	Ca	Al	B	Fe	Mg	P	S	Si	pH	
	days	Initial concentration	2.8	0.1	0.3	1.9	0.13	0.6	2.4	2.6	0.04	3.8	13.2±0.1
Leaching time	14	Leached concentration	-	-	-	0.01	0.03	0.0	0.0	0.2	0.02	0.03	13.2±0.1
		Leached fraction (%)	-	-	-	0.33	26.5	0.0	0.0	8.7	40.1	0.87	-
	170	Leached concentration	-	-	-	0.0	0.13	0.0	0.0	0.4	0.04	0.26	13.1±0.1
		Leached fraction (%)	-	-	-	2.4	100	0.0	0.0	16.3	100	6.91	-

349 *K and Na leached concentrations are not presented as their quantification fell into the 10% error associated*
 350 *with the ICP-AES technique. Ca concentrations were below the ICP-AES detection limit.*

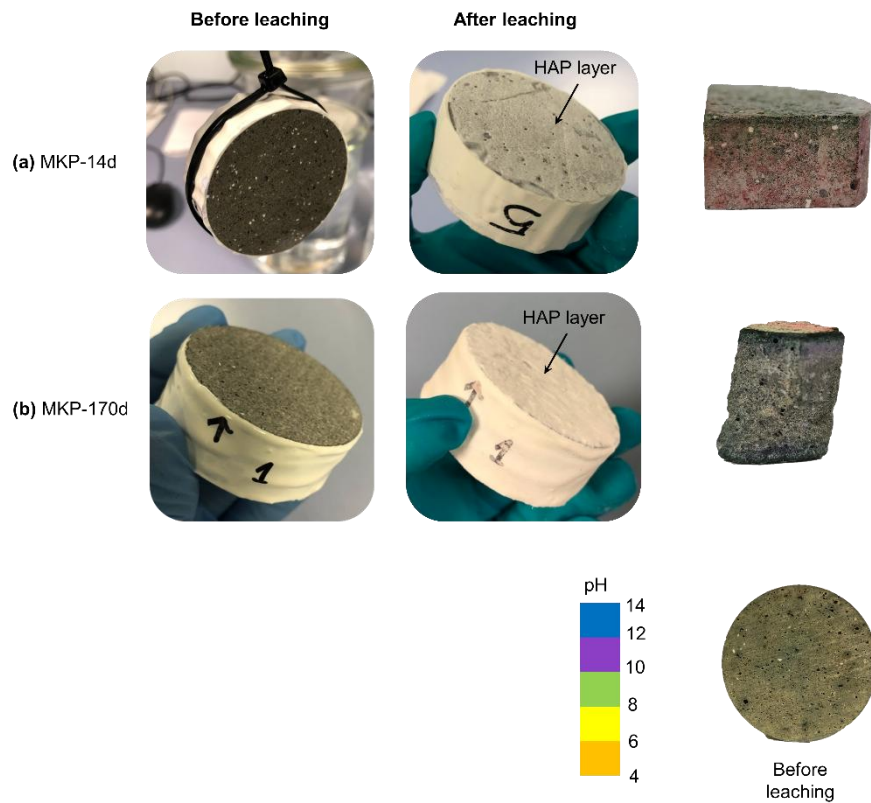
351 The two leaching experiments provided rather well repeatable results. Soluble phosphates (excluding
 352 P that precipitated as CDHA) were released in the leachates, albeit at a decreasing rate over time. The
 353 cumulative concentration of B in the leachates increased linearly versus the square root of time,
 354 suggesting that its release was controlled by diffusion through the pore network of the cement paste.
 355 Mass balance calculations in Table 5 show that B may be depleted by the end of the 170-day leaching
 356 test. The leached Si, S, and Al resulted from dissolution of fly ash and/or impurities present in the raw
 357 materials. Si and Al cumulative concentrations exhibited similar evolution with time, while S was
 358 fully depleted after approximately 36 days of leaching. Unlike the other elements, calcium was
 359 significantly depleted from the leaching solution due to the precipitation of CDHA evidenced in
 360 section 3.2.1.

361 3.2.3. *Characterization of leached solids*

362 After leaching, paste samples presented thin white layers coating their exposed surfaces (Figure 6).
 363 The thickness of each sample was measured using a digital caliper with a measurement range of 0-
 364 25 mm and an accuracy of 0.001 mm. There was no observable interface retreat or expansion on the
 365 exposed surfaces of the leached solids. Despite the absence of any retreat or expansion, the exposed
 366 surfaces of the leached solids exhibited pronounced brittleness, and material deposited on these
 367 surfaces could be easily removed, especially after 170 days of leaching.

368 The Rainbow indicator was sprayed onto the cross-sections of the leached pastes. The color
369 transformation from greenish to purple-blue indicated a rise in pH from 8, before leaching, to a value
370 higher than 10.

371



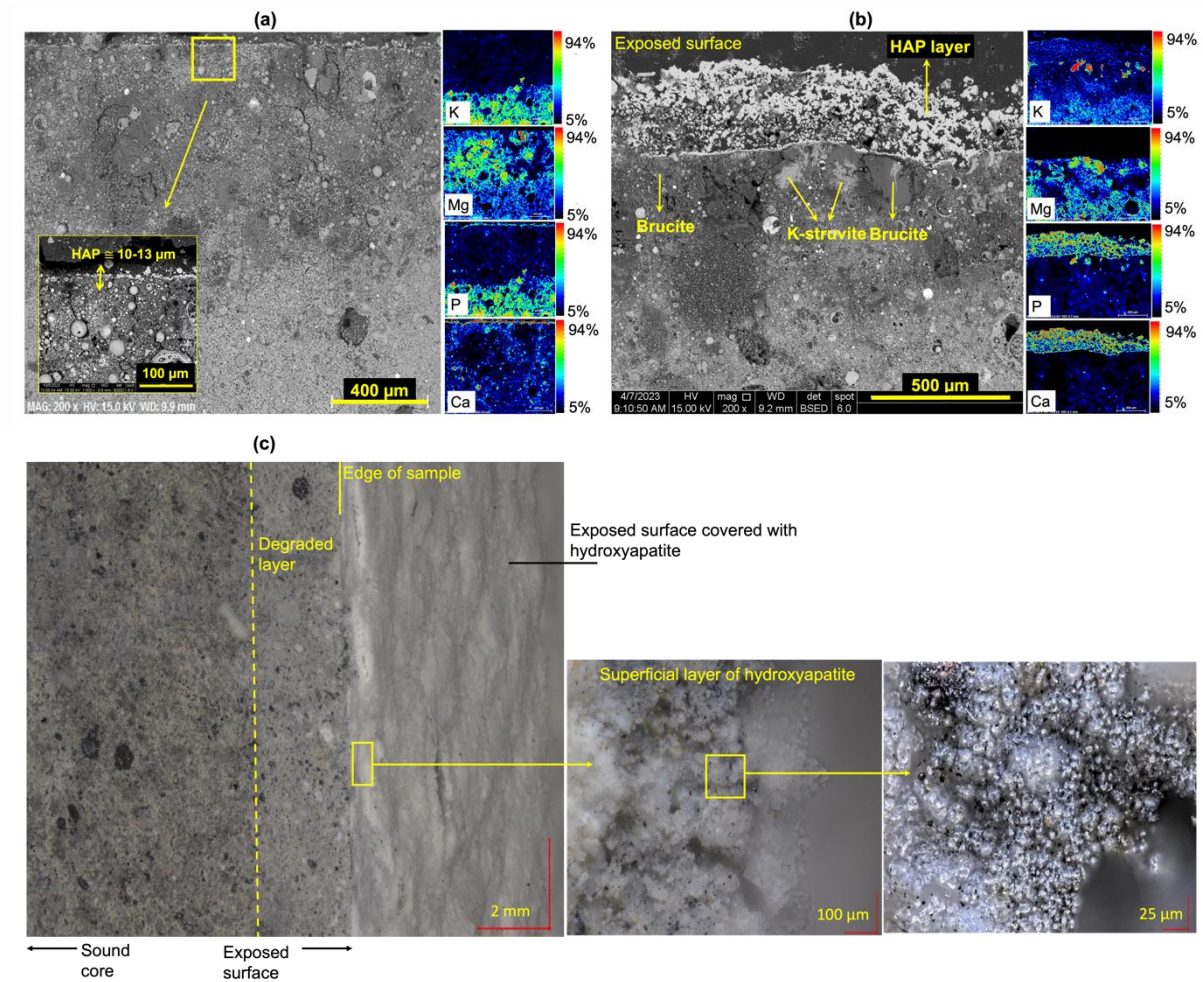
372

373 **Figure 6** – Leached solids and estimation of pH using the Rainbow indicator (a) MKP-14d, and (b) MKP-170d.

374 3.2.3.1. SEM/EDS analyses and optical microscopy

375 The white layer observed on the exposed surfaces of the leached samples was enriched in Ca and P,
376 suggesting the precipitation of a calcium phosphate phase such as hydroxyapatite (HAP). It measured
377 approximately $12 \pm 2 \mu\text{m}$ and $309 \pm 38 \mu\text{m}$ in MKP-14d and MKP-170d, respectively (Figure 7-a and
378 b) and seemed very porous (Figure 7-c). Under this superficial layer, a degraded zone was evidenced
379 by a darker grey color on the SEM/BSE images and a lighter gray by optical microscopy observations,
380 indicating a smaller density than that of the sound material. EDS elemental mapping showed some
381 areas enriched in magnesium, suggesting the precipitation of a Mg-containing phase which could

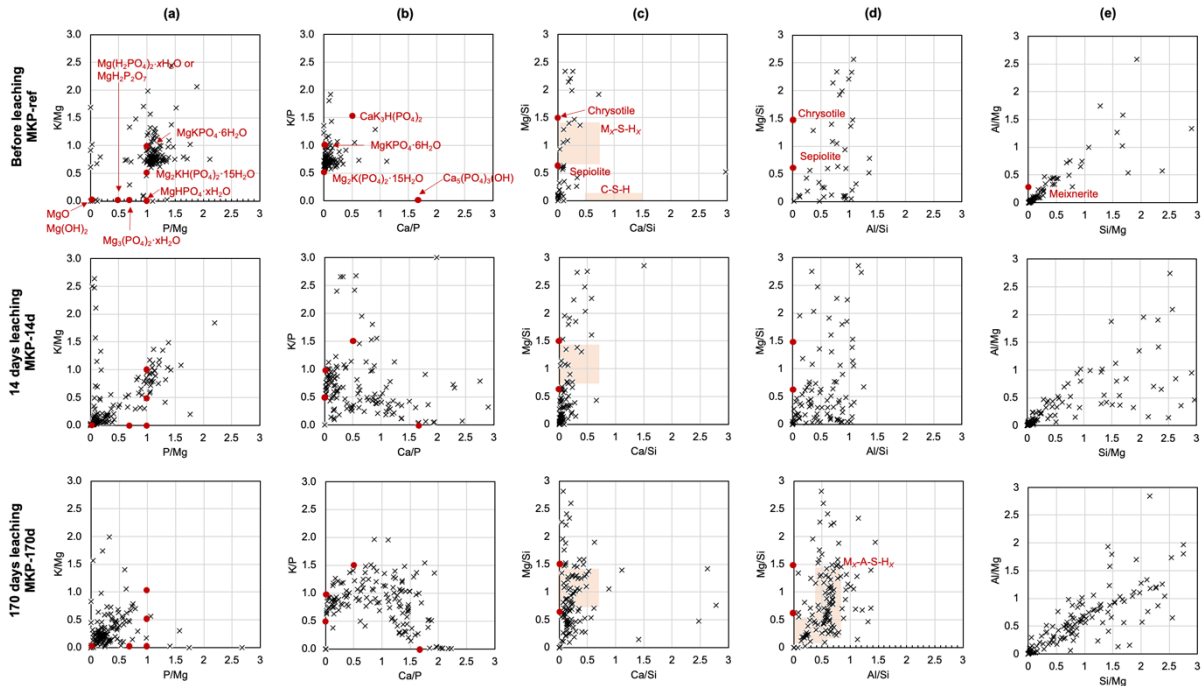
382 explain why Mg was not leached out of the sample (Figure 5 and Table 5). The elemental maps also
 383 showed a decrease in the P and K concentrations, which was consistent with the observed release of
 384 these species in the leachates.



385
 386 **Figure 7** – Characterization of leached solids: SEM/EDS of (a) MKP-14d, and (b) MKP-170d. (c) Optical
 387 microscopy of MKP-170d.

388 Figure 8 presents the mixing diagrams of atomic ratios based on EDS analyses. The figure illustrates
 389 regions corresponding to various phases potentially present in the solids, including residual KH_2PO_4 ,
 390 K-struvite, $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, bobierite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), cattite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$),
 391 phosphorösslerite ($\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$), newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), brucite ($\text{Mg}(\text{OH})_2$), hydroxyapatite
 392 ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), and $\text{CaK}_3\text{H}(\text{PO}_4)_2$ (Lahalle et al., 2018; Lothenbach et al., 2019). Note that Ca-poor
 393 hydroxyapatite (CDHA) was not added in this figure as atomic ratios of Ca/P may vary, as shown in

394 Figure 4. Some additional phases were also included, such as magnesium hydrogen phosphate
 395 ($\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ or $\text{MgH}_2\text{P}_2\text{O}_7$), calcium silicate hydrate (C-S-H), and magnesium silicate hydrate
 396 (M-S-H) (Lahalle et al., 2018; Lothenbach et al., 2019; Xu et al., 2021, 2020). After leaching, EDS
 397 point analyses were primarily carried out from the surface to a depth of 2 mm.



398
 399 **Figure 8** – EDS mixing diagrams of atomic ratios obtained from the MKPC paste samples before and after
 400 leaching (2 mm deep from the interface). (a) K/Mg vs. P/Mg, (b) K/P vs. Ca/P, (c) Mg/Si vs. Ca/Si, (d) Mg/Si vs.
 401 Al/Si, and (e) Al/Mg vs. Si/Mg.

402 The P/Mg and K/Mg ratios measured in the leached samples tended to decrease as compared to the
 403 pristine material, suggesting the dissolution of K struvite, and the possible precipitation of brucite. In
 404 MKP-14d sample, the P/Mg and K/Mg ratios were still comprised between those of K-struvite and
 405 $\text{Mg}_2\text{KH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$ for a number of point analyses, indicating the persistence of K-struvite after
 406 leaching (Figure 8-a). In MKP-170d sample, the scatter plot was shifted towards origin, suggesting
 407 advanced dissolution of K-struvite and higher precipitation of brucite. The mixing diagrams plotting
 408 the K/P vs. Ca/P ratios (Figure 8-b) showed the precipitation of a Ca-phosphate phase, probably
 409 CDHA with a Ca/P ratio close to 1.5, or HAP possibly intermixed, at the submicronic level, with other
 410 phases having lower Ca/P ratio, such as $\text{CaK}_3\text{H}(\text{PO}_4)_2$. Additionally, both leached solids presented

411 EDS points with Mg/Si atomic ratios ranging from 0.7 to 1.4, which may correspond to the formation
412 of Mg-silicates phases such as M_x-S-H_y , sepiolite ($Mg_4Si_6O_{15}(OH)_{12}\cdot 6H_2O$), or chrysotile
413 ($Mg_3(Si_2O_5)(OH)_4$) (Figure 8-c). No EDS points were related to the formation of C-S-H.

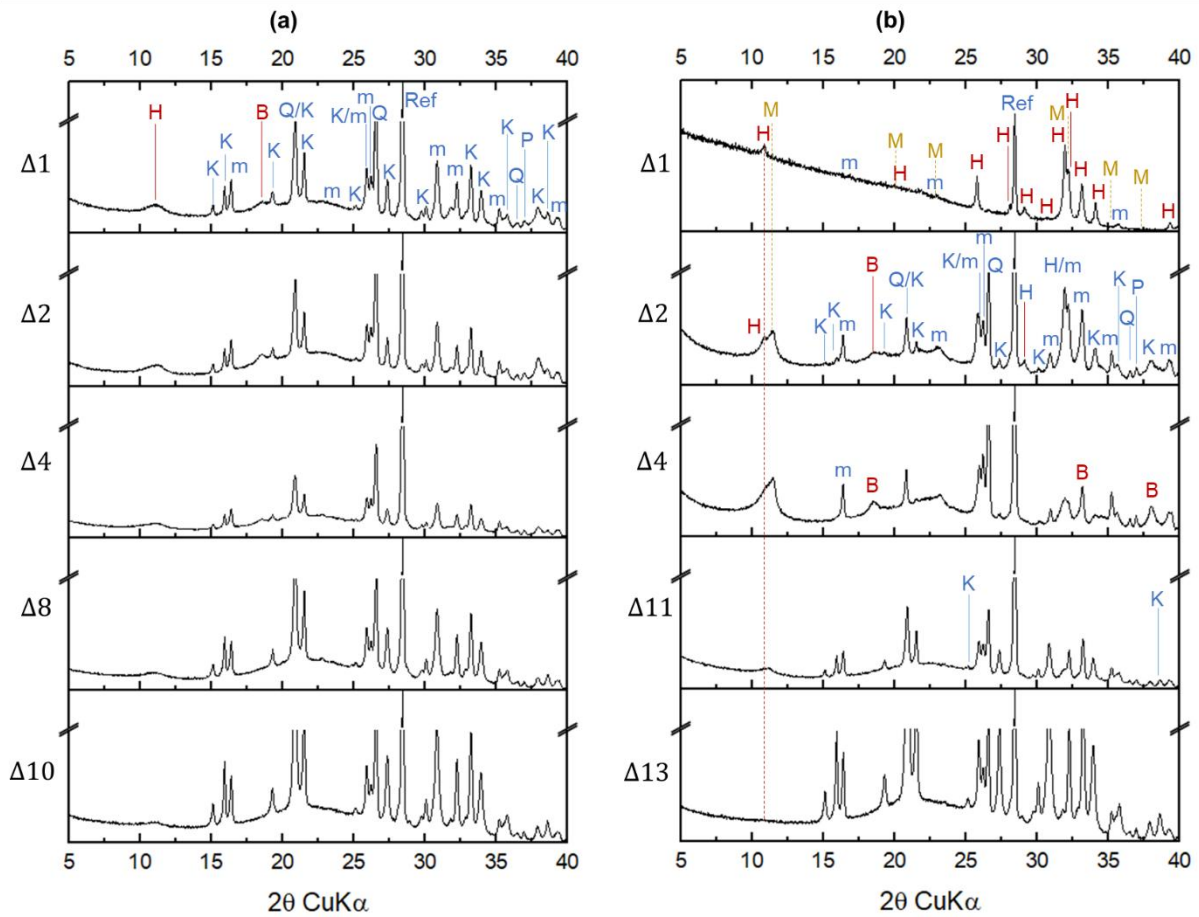
414 In MKP-170d, some EDS point analyses indicated the formation of a compound with Al/Si atomic
415 ratios varying from 0.2 to 0.6, suggesting the formation of Mg-silicate phases containing Al such as
416 $M_x-A_y-S-H_z$ (Figure 8-d). The incorporation of aluminum in both tetrahedral and octahedral sites of
417 M-S-H phases having a Mg/Si ratio of 1.1 or 1.7 has been evidenced by Bernard et al., 2020.
418 Nevertheless, the Al/Si ratio was limited to 0.15–0.18. Another possible explanation would be the
419 intermixing of magnesium silicate phases with hydrotalcite-like phases, Al-phosphates (such as
420 minyulite ($KAl_2(PO_4)_2OH\cdot 4H_2O$) or amorphous Al-phosphates) which have been predicted to form
421 during hydration of MPC materials containing aluminates (Xu et al., 2022), or mullite ($Al_{4+2x}Si_{2-2x}O_{10-}$
422 x , possibly containing up to 0.5 wt% MgO (Schneider et al., 2008)) supplied by the fly ash.

423 Finally, the Al/Mg vs Si/Mg mixing diagram evidenced a correlation between the Al and Si contents
424 for a number of analysis points (Figure 8-e), likely corresponding to the glassy fraction of fly ash
425 (Aughenbaugh et al., 2016). The Al/Si ratios in the pristine material and in the paste leached for
426 14 days were close to 1. Interestingly, this value decreased to about 0.67 in the sample leached for 170
427 days, suggesting that non-congruent dissolution of the glassy phase(s) occurred during the longer
428 leaching test, with preferential release of Al compared to Si. It has already been reported that when fly
429 ash is exposed to a strongly alkaline solution, Al is more prone to dissolve than Si due to weaker Al-O
430 bonds than Si-O bonds (Li et al., 2011).

431 3.2.3.2. XRD analyses

432 Figure 9 displays some XRD patterns of powders obtained at different depths (denoted as “delta” on
433 the y-axis) in MKP-14d and MKP-170d samples. The selected patterns are presented in the 5° - 40° 2θ
434 range to highlight the main differences. The crystalline phases and amorphous fraction in MKP-14d
435 and MKP-170d samples were also quantified by Rietveld refinement (Table 6). Note that
436 polycrystalline or low crystallinity nature of CDHA or HAP phases unable their quantification by

437 Rietveld refinement in the MKP-14d leached sample. Several minerals containing Mg, Al and/or Si
 438 were tested in the refinement of the XRD patterns of MKP-170d. Only meixnerite
 439 ($\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 4\text{H}_2\text{O}$), a Mg-Al layered double hydroxide (LDH) phase with a structure close to
 440 hydrotalcite (Koritnig and Süssé, 1975), matched well the patterns.
 441



442 **B:** Brucite, **H:** Hydroxyapatite, **K:** K-struvite, **m:** Mullite, **M:** meixnerite, **P:** Periclase, **Q:** Quartz, **Ref:** Silicon

443 **Figure 9** –XRD patterns obtained at different depths of (a) MKP-14d, and (b) MKP-170d. Patterns are
 444 presented in the 5°-40° 2θ range to highlight the main differences. “Delta Δ” on the y-axis denotes the
 445 different depths where the samples were taken (cf. Table 6).

446
 447 **Table 6** – Quantification of mineralogical phases in the leached solids using Rietveld refinement (results given
 448 in wt%).

Depth (μm)	K-struvite	HAP ^a	Brucite	Mg-Al phase ^b	Amorphous	MgO	Quartz	Mullite
------------	------------	------------------	---------	--------------------------	-----------	-----	--------	---------

	Depth (μm)	K-struvite	HAP ^a	Brucite	Mg-Al phase ^b	Amorphous	MgO	Quartz	Mullite	
MKP-ref	-	53.8	-	-	-	33.6	1.8	2.6	8.2	
MKP-14d	$\Delta 1$	0 - 137	22.8	-	6.3	-	51.8	1.5	5.9	11.7
	$\Delta 2$	137 - 238	19.5	-	4.1	-	57.2	2.1	6.0	11.0
	$\Delta 3$	238 - 470	13.6	-	1.3	-	70.2	1.9	4.7	8.3
	$\Delta 4$	470 - 677	10.7	-	1.3	-	75.3	1.5	4.0	7.1
	$\Delta 5$	677 - 1009	10.3	-	0.6	-	81.0	1.0	2.6	4.6
	$\Delta 6$	1009 - 1387	16.9	-	0.0	-	72.3	1.4	3.4	6.1
	$\Delta 7$	1387 - 1878	31.2	-	0.0	-	52.5	2.3	4.7	9.2
	$\Delta 8$	1878 - 2439	39.0	-	0.0	-	42.2	2.2	5.8	10.7
	$\Delta 9$	2439 - 3000	32.3	-	0.0	-	54.0	1.3	4.2	8.2
	$\Delta 10$	3000 - 3648	48.5	-	0.0	-	33.8	2.5	5.5	9.6
MKP-170d	$\Delta 1$	0 - 579	0.0	51.0	0.0	0.0	49.0	0.0	0.0	0.0
	$\Delta 2$	579 - 854	7.6	26.1	10.7	9.4	27.6	2.7	4.8	11.1
	$\Delta 3$	854 - 1075	3.7	10.0	5.6	10.6	42.1	2.7	6.7	18.7
	$\Delta 4$	1075 - 1607	3.2	4.8	3.3	9.1	61.9	2.1	4.1	11.4
	$\Delta 5$	1607 - 1919	2.3	3.1	1.9	13.1	58.0	2.4	5.3	13.8
	$\Delta 6$	1919 - 2084	5.6	4.2	1.7	7.1	58.5	2.8	5.6	14.5
	$\Delta 7$	2084 - 2268	7.9	3.9	0.3	12.4	58.4	1.9	4.2	10.9
	$\Delta 8$	2268 - 2626	11.7	5.3	0.1	5.3	61.8	1.5	4.1	10.2
	$\Delta 9$	2626 - 3019	18.0	3.7	0.0	7.0	55.0	1.7	3.9	10.6
	$\Delta 10$	3019 - 3473	15.7	3.0	0.0	5.1	63.7	1.3	3.0	8.3
	$\Delta 11$	3473 - 3964	20.9	2.7	0.0	1.8	56.9	1.8	3.9	11.9
	$\Delta 12$	3964 - 4507	26.6	3.2	0.0	1.4	50.4	2.3	4.2	12.0
	$\Delta 13$	4507 - 8240	72.8	0.0	0.0	0.0	7.5	2.0	4.8	13.0

449 ^aIn the MKP-14d powders, quantification by Rietveld refinement of CDHA or HAP phases was not possible due
450 to their polycrystalline or low crystallinity nature.

451 ^bMg-Al layered double hydroxide (LDH) phase with a structure close to hydrotalcite.

452

453 K-struvite was detected in all the patterns of MKP-14d but was absent from the first layer ($\Delta 1$: 0-
454 579 μm) of MKP-170d (Figure 9-b). Its content in the deepest investigated layer of MKP-14 d was
455 close to that of the pristine material. In MKP-170d, however, it was significantly higher (72.8 wt% vs
456 53.8 wt% in MKP-ref), indicating a progress of cement hydration during the leaching test, with the
457 conversion of amorphous precursors into more crystalline K-struvite. The periclase/mullite and
458 periclase/quartz weight ratios remained approximatively constant (Table 6), except in the first layer.
459 Since mullite and quartz are non-reactive phases, this result shows that the consumption of MgO was
460 almost negligible during the leaching tests. The residual MgO likely corresponded to large particles
461 having very low reactivity.

462 Leaching caused the precipitation of novel crystalline phases. XRD confirmed the precipitation of
 463 hydroxyapatite (Figure 9-a) with low crystallinity (broad peak at 10°-12° 2θ) near the exposed surface
 464 of the leached cement pastes, but also deeper in the materials. In MKP-170d, this peak seemed to shift
 465 towards higher angles, possibly due to the presence of meixnerite (Mg₆Al₂(OH)₁₈·4H₂O), which was
 466 identified up to a depth of 4.5 mm. Its amount varied between 1.4 wt% (Δ1) to 13.1 w% (Δ5).
 467 Moreover, brucite (Mg(OH)₂) precipitated in both leached solids, up to a depth of about 1 mm in
 468 MKP-14d, and 2.6 mm in MKP-1710d. Finally, precipitation of low Ca/P calcium phosphates such as
 469 CaK₃H(PO₄)₂, hydrated magnesium silicate phases or phospho-aluminate phases such as OH-
 470 minyulite (KAl₂(PO₄)₂OH·4H₂O) was not evidenced by XRD.

471

472 3.2.3.3. ³¹P MAS-NMR analyses

473 The precipitate recovered from the leachates (section 3.2.1) and some samples collected at various
 474 depths in the leached cement pastes were analyzed by ³¹P MAS-NMR, meaning that only the fraction
 475 of ³¹P was quantified (Figure 3 and Table 7).

476 **Table 7** - ³¹P site fractions (mol. %) assessed from decomposition of ³¹P MAS-NMR spectra after leaching.

		Depth (μm)	Phase ^a	Chemical shift (ppm)	FWHM (ppm)	³¹ P fraction (%)
14-day leached solid	Δ1	0 - 137	K-struvite	+6.3	1.6	69
			HAP	+2.6	2.7	31
	Δ2	137 - 238	K-struvite	+6.2	1.6	60
			HAP	+2.6	2.7	40
	Δ8	1387 - 1878	K-struvite	+6.3	1.7	91
			HAP	+2.5	3.6	9
170-day leached solid	Δ1	0 - 579	K-struvite ^b	+5.3	2.3	12
			HAP	+2.7	2.3	88
	Δ2	579 - 854	K-struvite ^b	+6.0	2.1	15
			HAP	+2.6	2.6	85
	Δ3	854 - 1075	K-struvite ^b	+5.9	2.1	12
			HAP	+2.5	2.8	88
	Δ4	1075 - 1607	K-struvite ^b	+6.0	2.4	15
			HAP	+2.6	3.0	85
	Δ5	1607 - 1919	K-struvite	+6.2	2.5	24
			HAP	+2.6	3.2	76
	Δ6	1919 - 2084	K-struvite	+6.2	2.1	31
			HAP	+2.6	3.2	70

477 ^aThe fraction of ³¹P was estimated to be present in either K-struvite or HAP (±0.2%).

478 ^bK-struvite probably disordered or presenting structural defaults.

479

480 The precipitate formed in the leachates showed a single ^{31}P resonance at $\delta = +3.0$ ppm (Figure 3),
481 which was consistent with the chemical shift reported for stoichiometric HAP (Ca/P of 1.67) and for
482 CDHA (Elliot, 1994). The spectra from the leached samples showed two main resonances at $\delta \approx$
483 $+6.2$ ppm and $\delta \approx +2.6$ ppm, which could be assigned to K-struvite and HAP/CDHA respectively.
484 There was no evidence for the presence of OH-minyulite ($\text{KAl}_2(\text{PO}_4)_2(\text{OH})\cdot 4\text{H}_2\text{O}$) and $\text{CaK}_3\text{H}(\text{PO}_4)_2$,
485 whose signals are expected at $\delta = -9.6$ ppm and $\delta = 0$ ppm, respectively (Dick et al., 1998; Xu et al.,
486 2020). In sample MKP-170d, the spectrum of the powder collected in the first layer close to the
487 exposed surface (Δ_1), presented a peak centered at $\delta = 5.3$ ppm, significantly shifted as compared to
488 that of crystalline K-struvite ($\delta \approx +6.2$ ppm). This shift of position indicated a change in the P
489 environment, possibly resulting from the amorphization of K-struvite (this mineral was not detected by
490 XRD in Δ_1 sample), or its transformation into another amorphous or poorly crystallized phase (e.g.,
491 hazenite $\text{Mg}_2\text{NaK}(\text{PO}_4)_2\cdot 14\text{H}_2\text{O}$).

492 In the 14-day leached solid, quantification presented in Table 7 showed a significant increase in the ^{31}P
493 fraction in HAP in the layer close to the surface. In layer Δ_8 , 91% of ^{31}P was estimated to be present in
494 the form of K-struvite, which can be crystalline or nano-crystalline/amorphous, while 9% of the ^{31}P
495 was estimated to be in HAP. This may indicate less degradation of the sample in deeper layers. It is
496 important to note that this fraction of ^{31}P should not be confused with the total amount of K-struvite
497 present in the sample. As indicated in Table 6, XRD analyses estimated that only 39% of the sample
498 was composed of crystalline K-struvite, an amount lower than that of the original sample (i.e., before
499 leaching). In the 170-day leached solid, the proportion of ^{31}P significantly decreased in K-struvite,
500 while its proportion increased in HAP, indicating a higher level of degradation in this sample.

501 3.3. *Modeling results*

502 3.3.1. *Input data*

503 The composition of MKP-ref was simplified for modeling (Table 3). K-struvite was assumed to be the
504 main hydration product. Its content was inferred from XRD and Rietveld analyses. Therefore, the
505 volume fractions of residual MgO and fly ash were considered, although these components were

506 treated as inert. In addition, traces of hazenite ($\approx 2 \times 10^{-11}$ mmol/L), predicted to be thermodynamically
 507 stable, were also included in the initial matrix composition. The initial porosity of the paste was set at
 508 its experimental value of 15.5% (as determined by total porosity accessible to water) and assumed to
 509 be fully saturated. The pore solution, extracted using pressure from MKP-ref after 6 months of curing,
 510 presented a pH of about 8.0 (at 25 °C) and mainly comprised potassium (1033.8 mmol/L), magnesium
 511 (1.1 mmol/L), phosphate (370 mmol/L), sodium (13.2 mmol/L) and borate (136.4 mmol/L) ions. Note
 512 that this solution was still oversaturated with respect to K-struvite (Saturation Index of 0.87).

513 **Table 8** – Main parameters defining the initial composition of the MKPC paste in the model. Concentrations are
 514 given in mmol/L of interstitial solution.

MgKPO ₄ ·6H ₂ O	KH ₂ PO ₄	B(OH) ₃	K ₂ O	Na ₂ O
20700	565	135	237	50

515 **Na₂O was added to adjust the initial pH at 8.0. Na₂O and K₂O are fictive species which fully dissolve, thus*
 516 *providing Na⁺, K⁺ and OH⁻ ions to the pore solution.*
 517

518 3.3.2. Phase evolution in the leached cement paste

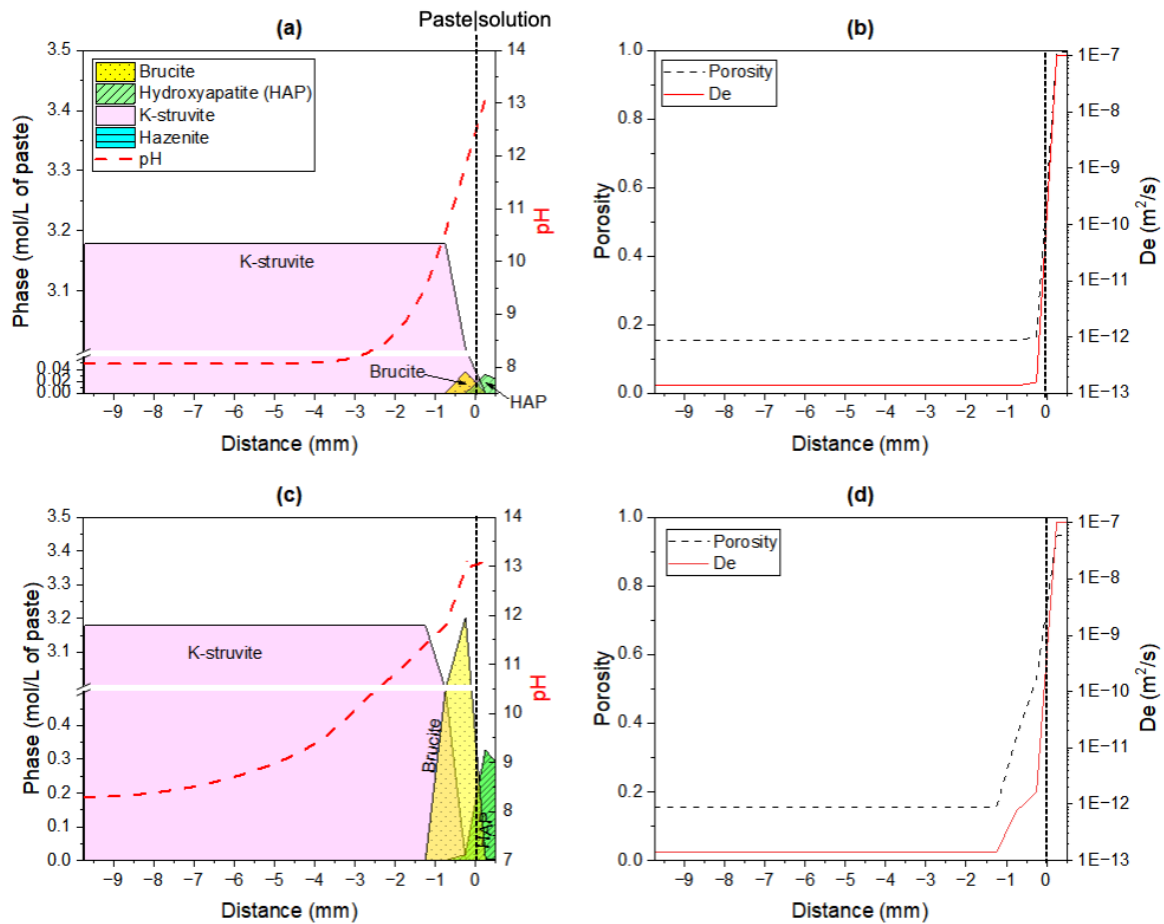
519 Figure 10 displays the phase evolution, predicted by modeling, in the paste after 14 and 170 days of
 520 leaching. The effective diffusion coefficient (D_e) in the cement paste was adjusted at 1.37×10^{-13} m²/s to
 521 reproduce the experimental precipitation front of brucite in the sample leached for 14 d.

522 Modeling showed that dissolution of K-struvite occurred, producing an increase in porosity and
 523 effective diffusion coefficient (Figure 10-b and d). This was accompanied by the precipitation of
 524 brucite and hydroxyapatite (HAP) near the exposed surface, along with traces of hazenite. Note that
 525 the precipitation of HAP was predicted to occur only close to the exposed surface, whereas
 526 experimentally it was observed deeper in the material and coexisted with brucite and K-struvite. The
 527 extent of K-struvite dissolution was predicted in both pastes leached for 14 d and 170 d. Nonetheless,
 528 the thickness of the zone where brucite precipitated was underestimated by the model in MKP-170d.
 529 HAP and brucite were also predicted to precipitate in the leaching solution. HAP precipitation in
 530 solution was in line with experimental results (cf. Figure 4). Nonetheless, brucite was not detected
 531 experimentally possibly due to the low concentrations. Moreover, the model predicted the gradual

532 increase in pH from 8 in the sound core to 13 at the leached surface. Besides, modeling tended to
533 overestimate Ca concentrations and to underestimate P and B concentrations in solution.

534 Several hypotheses could be postulated to explain the differences between the experimental and
535 modeling results: (i) the paste composition was oversimplified in the model due to a lack of
536 thermodynamic data of phosphate phases available in the literature. In this model, only the aqueous
537 fraction of B was taken into account, whereas Lahalle et al., 2018 have shown that boron is also partly
538 precipitated as a boro-phosphate phase. Nevertheless, the composition of this phase is still unknown,
539 as well as its thermodynamical properties, and thus it could not be included in the model.

540 Consequently, the model predicted a too fast depletion of B from the cement paste and underestimated
541 its total concentration released in solution. (ii) The solubility of HAP was overestimated. Thus,
542 precipitation of HAP occurred only very close to the surface. It should be noted that there is a rather
543 wide range of thermodynamic data reported for synthetic HAP (Vieillard and Tardy, 1984), and thus,
544 the extent of precipitation of HAP depends on the selected value. (iii) The model predicted the
545 precipitation of traces of hazenite ($\text{Mg}_2\text{NaK}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$) in the leached solid. Hazenite
546 concentrations were however too low (ranging from 2×10^{-11} to 1×10^{-4} mmol/L of paste) to be detected
547 experimentally. Hazenite has been reported as a degradation product of K-struvite at pH >7 by several
548 authors (Lahalle et al., 2019; Xu et al., 2023), but is very difficult to evidence in cement pastes. Its
549 crystal structure corresponds to a superstructure of K- and Na-struvite (Yang et al., 2014, 2011; Yang
550 and Sun, 2004) and thus possesses many structural features similar to those of K-struvite. Lahalle et
551 al., 2019 observed by SEM/EDS some sodium enrichment, and thus potentially the presence of
552 hazenite, in cement pastes exposed to a synthetic PC pore solution. Xu et al., 2023 succeeded in
553 evidencing by XRD the precipitation of small amounts of hazenite when synthetic K-struvite was
554 exposed to an alkaline solution, but failed to detect this phase when a cement paste was used.



555

556 **Figure 10** – Predicted evolution of the cement pastes: mineral phases and pH evolution, porosity, and effective
 557 diffusion coefficient (De) at (a), (b) 14 days, and (c), (d) at 170 days of leaching. *Traces of hazenite precipitated*
 558 *all along the paste (ranging from $\approx 2 \times 10^{-11}$ to $\approx 1 \times 10^{-4}$ mmol/L). Black dotted line indicates the paste-solution*
 559 *interface.*

560 4. Discussion

561 The findings of this study highlight the complex degradation process of MKPC paste samples under
 562 aggressive alkaline conditions. A phase evolution was observed near the leached surface, leading to
 563 the dissolution of K-struvite. In these samples, no interface retreat was observed since novel phases
 564 precipitated, which differs from what was observed by Diaz Caselles et al., 2024 on MKPC paste
 565 samples leached by demineralized water. Under alkaline conditions, the formation of calcium-deficient
 566 hydroxyapatite (CDHA) resulted from the reaction between Ca^{2+} ions present in the leaching solution,
 567 and phosphate anions provided by the MKPC paste (initially dissolved in the pore solution or released

568 by the dissolution of phosphate minerals such as K-struvite, residual KH_2PO_4 and/or other amorphous
569 phosphate phases evidenced in the pristine material). A layer formed at the solid/solution interface,
570 and its thickness increased with the leaching time ($\approx 12 \mu\text{m}$ at 14 days, and $\approx 300 \mu\text{m}$ at 170 days).
571 Even though hydroxyapatite (HAP) is a mineral known for its low solubility (Elliot, 1994), its
572 formation was not sufficient to ensure the long-term durability of the MKPC pastes. The superficial
573 layer was rather porous (as evidenced by SEM/EDS in Figure 7) and did not seem to play any
574 protective role, since degradation progressed significantly between 14 days and 170 days of leaching.
575 More diffuse precipitation of poorly crystallized HAP was also evidenced by XRD under this surface
576 layer, up to a depth of $\approx 4 \text{ mm}$ in the sample leached for 170 days. SEM/EDS analyses suggested the
577 precipitation of CDHA, since the Ca/P ratio was inferior to 1.67, the expected value for HAP, for a
578 large number of point analyses. Nevertheless, the additional formation of amorphous calcium
579 phosphate (ACP) cannot be excluded. ACP often occurs as a transient phase during the formation of
580 non-stoichiometric hydroxyapatite in aqueous systems (Boskey and Posner, 1973; Chow, 1999; Elliot,
581 1994; Zhang et al., 2011). When it is prepared by rapid precipitation in the pH range 8.9 – 11.7, its
582 Ca/P molar ratio is close to 1.5 (Combes and Rey, 2010; Heughebaert and Montel, 1977). Chemical
583 shifts ranging from 1.7 to 3.0 ppm have been reported for ACP analyzed by ^{31}P MAS-NMR (Belton et
584 al., 1988; Roufosse et al., 1984; Tropp et al., 1983). These values are close to those obtained for HAP,
585 making the two calcium phosphates difficult to distinguish on the ^{31}P spectra based on this sole
586 parameter. It should be noted that no calcium phosphate phases were detected on MKPC samples
587 leached under neutral conditions, as reported in Diaz Caselles et al., 2024. This can be attributed to the
588 absence of Ca^{2+} ions in the demineralized water.

589 Magnesium dissolved from the cement phases almost entirely reprecipitated in the cement matrix.
590 Two main phases formed, brucite, and an hydrotalcite-like phase, which may be meixnerite
591 ($\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 4\text{H}_2\text{O}$) according to its diffraction pattern (cf. Figure 9). Precipitation of this
592 magnesium aluminate hydrate implied that the glassy fraction of the fly ash partly dissolved, since it
593 was the only source of aluminate in the system. Such reactivity of the fly ash was also indicated by the
594 decrease in its Al/Si content, as highlighted by EDS analyses (Figure 8-e). It was enhanced by the pH
595 increase of the pore solution occurring in the leached sample (Kumar et al., 2020; Wang et al., 2020).

596 Modeling showed indeed a pH gradient from 8 (initial pH of the pore solution) to 13, and experimental
597 observations using a pH indicator confirmed that the pH exceeded 10 in the leached solid (cf. Figure 6
598 and Figure 10). The mixing diagrams, built from the EDS point analyses in the degraded part of the
599 cement paste, also suggested the precipitation of magnesium silicate phases, with Mg/Si atomic ratios
600 ranging from 0.7 to 1.4, and possibly containing aluminate (Figure 8). These phases were not detected
601 by XRD, which means that they were amorphous or poorly crystalline. Previous studies have also
602 reported the presence of M-S-H upon hydration of MKP cement (Xu et al., 2021, 2020). M-S-H have
603 an ill-defined layered structure similar to that of hydrated precursors of 2:1 and 1:1 phyllosilicates
604 (Bernard et al., 2019a; Nied et al., 2016; Roosz et al., 2015). Their stoichiometry may vary, with a
605 Mg/Si molar ratio typically comprised between 0.7 and 1.5 (Nied et al., 2016). At $\text{Mg/Si} \geq 1.3$, M-S-H
606 coexist with brucite. They can also incorporate aluminum in their structure, in both tetrahedral and
607 octahedral sites (Bernard et al., 2020). Some studies have reported that M-S-H are stable at pH values
608 ranging from 9 to 11 (Nied et al., 2016) or from 8 to 14 (Bernard et al., 2019b). Therefore, it would be
609 interesting to estimate the zone of occurrence of M-S-H in the leached samples. The poor crystallinity
610 of M-(A)-S-H makes their characterization by XRD a difficult task (Roosz et al., 2015). It was
611 attempted to highlight their presence by ^{29}Si MAS NMR. However, the collected spectra (not
612 presented here) were complex due to signals overlapping and did not enable to confirm or infirm their
613 formation. It is worth noting that Diaz Caselles et al., 2024 found that leaching MKPC samples (with
614 fly ash as a filler) under neutral conditions did not activate the fly ash, and consequently, no novel
615 phases containing Al or Si were observed after leaching.

616 The phase evolution induced by leaching of MKPC pastes under alkaline condition influenced the
617 mechanical properties of the cement paste. The superficial layer, mainly consisting of HAP was rather
618 porous and brittle. The subsequent layer, containing brucite, was also abraded rather easily whereas, at
619 higher depth, the paste appeared much more resistant. These qualitative observations are consistent
620 with the calculations carried out with the reactive transport model, which show that, going from the
621 sound core to the leached surface, porosity starts to increase when brucite precipitates (Figure 10).
622 This suggests that brucite may be regarded as a good indicator of MKPC paste alteration from a
623 mechanical point of view: its presence would indicate a degraded zone with low mechanical strength.

624 The findings in this investigation may suggest approaches to enhance the durability of MKPC
625 materials, consistent with Diaz Caselles et al., 2024:

- 626 - Increasing the Mg/P molar ratio of the cement. This would result in less depletion of KH_2PO_4
627 and fewer available P ions for precipitation as calcium phosphates.
- 628 - Utilizing a filler other than fly ash. This would enable modification of the paste microstructure
629 and, consequently, its transport properties. A change in filler could ensure a lower diffusion
630 coefficient and reduced porosity.

631

632 5. Conclusion

633 This study aimed to (i) investigate the leaching behavior of MKPC paste samples (with fly ash a filler)
634 under alkaline condition, and (ii) gain insights into their degradation mechanisms. To this end, semi-
635 dynamic leaching tests were conducted on MKPC paste monoliths using an alkaline solution (pH
636 13.2 ± 0.1), which simulated a simplified pore solution of a conventional concrete that may be
637 encountered close to the MKPC-based material. The leaching solution was renewed over time and the
638 leachates were analyzed. The mineralogy and microstructure of the leached cement pastes were also
639 characterized at the end of the leaching tests. The main conclusions drawn from this work are as
640 follows:

- 641 1. Leaching by the alkaline solution modified the phase assemblage in the cement paste near the
642 exposed surface. K-struvite tended to dissolve while Ca-deficient hydroxyapatite (CDHA), brucite
643 and an hydrotalcite-like phase (possibly meixnerite $\text{Mg}_6\text{Al}_2(\text{OH})_{18} \cdot 4\text{H}_2\text{O}$) precipitated. The
644 additional formation of other phases such as M-(A)-S-H, amorphous calcium phosphate (ACP)
645 and hazenite was possible, but still needs to be confirmed.
- 646 2. The leached solids did not exhibit any interface retreat. However, the exposed surfaces of the
647 leached solids were highly brittle, and material was easily removed by scratching.
- 648 3. A layer of CDHA rapidly formed on the exposed surfaces and its thickness increased with the
649 leaching duration. However, it was not sufficient to clog the porosity and protect the samples from
650 further degradation, as the alterations fronts were found to be greater and more detrimental in the

651 170-day leached solid than in the 14-day leached solid. After 170 days of leaching, the altered
652 layer had a thickness of about 4.5 mm.

653 4. The glassy fraction of the fly ash used as a filler in the paste formulation was shown to partly react
654 due to the pH increase occurring close to the leached surface.

655 5. A reactive transport model was used to simulate the leaching experiments. Despite the simplified
656 composition of the paste used for the calculations, the main phase evolutions (dissolution of K-
657 struvite, and precipitation of both brucite and hydroxyapatite) were well predicted by the model.

658 6. To improve modeling, future work should consider the determination of solubility products of
659 boro-phosphate phases lacking in the literature to use a more realistic paste composition. The
660 glassy fraction of fly ash should be considered as reactive to enable the formation of phases
661 containing aluminates and/or silicates. Finally, it would be necessary to measure experimentally
662 the diffusion coefficient D_e in pristine and altered MKPC pastes to avoid adjusting this parameter
663 in the model.

664

665 **Credit authorship statement**

666 **Laura Diaz Caselles:** Investigation, Methodology, Software, Writing – Original Draft, Project
667 administration. **Céline Cau Dit Coumes:** Conceptualization, Validation, Writing – review and editing,
668 Supervision, Funding acquisition, Project administration. **Pascal Antonucci:** Sample fabrication,
669 Experimental setup. **Angélique Rousselet:** Conceptualization, Validation, Writing – review and
670 editing. **Adel Mesbah:** Conceptualization, Data analysis, Writing – review and editing. **Valérie**
671 **Montouillout:** Conceptualization, Data analysis, Writing – review and editing.

672 **Declaration of competing interest**

673 The authors declare no conflict of interest.

674 **Data availability**

675 Data will be made available on request.

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681 **References**

682 Adenot, F., Buil, M., 1992. Modelling of the corrosion of the cement paste by deionized water.

683 *Cement and Concrete research* 22, 489–496.

684 Arora, A., Singh, B., Kaur, P., 2019. Novel material i.e. Magnesium phosphate cement (MPC) as
685 repairing material in roads and buildings. *Materials Today: Proceedings* 17, 70–76.

686 <https://doi.org/10.1016/j.matpr.2019.06.402>

687 Aughenbaugh, K.L., Stutzman, P., Juenger, M.C.G., 2016. Identifying Glass Compositions in Fly Ash.

688 *Frontiers in Materials* 3. <https://doi.org/10.3389/fmats.2016.00001>

689 Belton, P.S., Harris, R.K., Wilkes, P.J., 1988. Solid-state phosphorus-31 NMR studies of synthetic
690 inorganic calcium phosphates. *Journal of Physics and Chemistry of Solids* 49, 21–27.

691 [https://doi.org/10.1016/0022-3697\(88\)90129-1](https://doi.org/10.1016/0022-3697(88)90129-1)

692 Bernard, E., Lothenbach, B., Cau-Dit-Coumes, C., Pochard, I., Rentsch, D., 2020. Aluminum

693 incorporation into magnesium silicate hydrate (M-S-H). *Cement and Concrete Research* 128,

694 105931. <https://doi.org/10.1016/j.cemconres.2019.105931>

695 Bernard, E., Lothenbach, B., Chlique, C., Wyrzykowski, M., Dauzères, A., Pochard, I., Cau-Dit-

696 Coumes, C., 2019a. Characterization of magnesium silicate hydrate (M-S-H). *Cement and*

697 *Concrete Research* 116, 309–330. <https://doi.org/10.1016/j.cemconres.2018.09.007>

698 Bernard, E., Lothenbach, B., Pochard, I., Cau- Dit- Coumes, C., 2019b. Alkali binding by magnesium

699 silicate hydrates. *Journal of the American Ceramic Society* 102, 6322–6336.
700 <https://doi.org/10.1111/jace.16494>

701 Boskey, A.L., Posner, A.S., 1973. Conversion of amorphous calcium phosphate to microcrystalline
702 hydroxyapatite. A pH-dependent, solution-mediated, solid-solid conversion. *The Journal of*
703 *Physical Chemistry* 77, 2313–2317. <https://doi.org/10.1021/j100638a011>

704 Braney, M.C., Haworth, A., Jefferies, N.L., Smith, A.C., 1993. A study of the effects of an alkaline
705 plume from a cementitious repository on geological materials. *Journal of Contaminant*
706 *Hydrology* 13, 379–402. [https://doi.org/10.1016/0169-7722\(93\)90072-Z](https://doi.org/10.1016/0169-7722(93)90072-Z)

707 Buj, I., Torras, J., Rovira, M., de Pablo, J., 2010. Leaching behaviour of magnesium phosphate
708 cements containing high quantities of heavy metals. *Journal of Hazardous Materials* 175, 789–
709 794. <https://doi.org/10.1016/j.jhazmat.2009.10.077>

710 Cau Dit Coumes, C., Lambertin, D., Lahalle, H., Antonucci, P., Cannes, C., Delpech, S., 2014.
711 Selection of a mineral binder with potentialities for the stabilization/solidification of aluminum
712 metal. *Journal of Nuclear Materials* 453, 31–40. <https://doi.org/10.1016/j.jnucmat.2014.06.032>

713 Chau, C.K., Qiao, F., Li, Z., 2012. Potentiometric Study of the Formation of Magnesium Potassium
714 Phosphate Hexahydrate. *Journal of Materials in Civil Engineering* 24, 586–591.
715 [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000410](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000410)

716 Chow, L.C., 1999. Calcium Phosphate Cements: Chemistry, Properties, and Applications. *MRS*
717 *Proceedings* 599, 27. <https://doi.org/10.1557/PROC-599-27>

718 Combes, C., Rey, C., 2010. Amorphous calcium phosphates: Synthesis, properties and uses in
719 biomaterials. *Acta Biomaterialia* 6, 3362–3378. <https://doi.org/10.1016/j.actbio.2010.02.017>

720 De Windt, L., Badreddine, R., 2007. Modelling of long-term dynamic leaching tests applied to
721 solidified/stabilised waste. *Waste Management* 27, 1638–1647.
722 <https://doi.org/10.1016/j.wasman.2006.07.019>

- 723 De Windt, L., Devillers, P., 2010. Modeling the degradation of Portland cement pastes by biogenic
724 organic acids. *Cement and Concrete Research* 40, 1165–1174.
725 <https://doi.org/10.1016/j.cemconres.2010.03.005>
- 726 Diaz Caselles, L., Cau Dit Coumes, C., Antonucci, P., Rousselet, A., Mesbah, A., Montouillout, V.,
727 2024. Chemical degradation of magnesium potassium phosphate cement pastes during leaching
728 by demineralized water: Experimental investigation and modeling. *Cement and Concrete*
729 *Research* 178, 107456. <https://doi.org/10.1016/j.cemconres.2024.107456>
- 730 Dick, S., Grossmann, G., Ohms, G., Zeiske, T., 1998. ChemInform Abstract: Aluminum Phosphates
731 with Non- Centrosymmetric Layer- and Framework- Structures of Topologically Related
732 Motifs. Part 1. $KAl_2(PO_4)_2(OH) \times 4H_2O$. *ChemInform* 29.
733 <https://doi.org/10.1002/chin.199814010>
- 734 Ding, Z., Dong, B., Xing, F., Han, N., Li, Z., 2012. Cementing mechanism of potassium phosphate
735 based magnesium phosphate cement. *Ceramics International* 38, 6281–6288.
736 <https://doi.org/10.1016/j.ceramint.2012.04.083>
- 737 Elliot, J.C., 1994. *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*,
738 Department of Child Dental Health The London Hospital Medical College Turner Street London
739 El 2AD, U.K. Elsevier, Amsterdam. <https://doi.org/10.1021/ja945007t>
- 740 Frontera, C., Rodríguez-Carvajal, J., 2003. FullProf as a new tool for flipping ratio analysis. *Physica*
741 *B: Condensed Matter* 335, 219–222. [https://doi.org/10.1016/S0921-4526\(03\)00241-2](https://doi.org/10.1016/S0921-4526(03)00241-2)
- 742 Gardner, L.J., Bernal, S.A., Walling, S.A., Corkhill, C.L., Provis, J.L., Hyatt, N.C., 2015.
743 Characterisation of magnesium potassium phosphate cements blended with fly ash and ground
744 granulated blast furnace slag. *Cement and Concrete Research* 74, 78–87.
745 <https://doi.org/10.1016/j.cemconres.2015.01.015>
- 746 Heughebaert, J.-C., Montel, G., 1977. Étude de l'évolution de l'orthophosphate tricalcique non

747 cristallin en phosphate apatitique à la faveur d'une réaction chimique, à température ordinaire.
748 Revue de Physique Appliquée 12, 691–694.
749 <https://doi.org/10.1051/rphysap:01977001205069100>

750 Ionascu, L., Nicu, M., Turcanu, C., Dragolici, F., Rotarescu, G.H., 2014. Study of the conditioning
751 matrices for aluminium radioactive wastes. Romanian Journal of Physics 59, 360–368.

752 Janot, C., Ilschner, B., 2001. Biocéramiques et biociments résorbables pour le comblement osseux, in:
753 PPUR (Ed.), Traité Des Matériaux. p. 415.

754 Kongshaug, K.O., Fjellvåg, H., Lillerud, K.P., 2001. The synthesis and crystal structure of a hydrated
755 magnesium phosphate $Mg_3(PO_4)_2 \cdot 4H_2O$. Solid State Sciences 3, 353–359.
756 [https://doi.org/10.1016/S1293-2558\(00\)01109-2](https://doi.org/10.1016/S1293-2558(00)01109-2)

757 Koritnig, S., Süsse, P., 1975. Meixnerit, $Mg_6Al_2(OH)_{18} \cdot 4H_2O$, ein neues Magnesium-Aluminium-
758 Hydroxid-Mineral. Tschermaks Mineralogische und Petrographische Mitteilungen 22,
759 79–87. <https://doi.org/10.1007/BF01081303>

760 Kumar, S., Sonat, C., Yang, E.-H., Unluer, C., 2020. Performance of reactive magnesia cement
761 formulations containing fly ash and ground granulated blast-furnace slag. Construction and
762 Building Materials 232, 117275. <https://doi.org/10.1016/j.conbuildmat.2019.117275>

763 Lahalle, H., 2016. Conditionnement de l'aluminium métallique dans les ciments phospho-magnésiens,
764 Thèse en Chimie-Physique, Université de Bourgogne Franche - Comté.

765 Lahalle, H., Cau Dit Coumes, C., Mercier, C., Lambertin, D., Cannes, C., Delpech, S., Gauffinet, S.,
766 2018. Influence of the w/c ratio on the hydration process of a magnesium phosphate cement and
767 on its retardation by boric acid. Cement and Concrete Research 109, 159–174.
768 <https://doi.org/10.1016/j.cemconres.2018.04.010>

769 Lahalle, H., Patapy, C., Glid, M., Renaudin, G., Cyr, M., 2019. Microstructural evolution/durability of
770 magnesium phosphate cement paste over time in neutral and basic environments. Cement and

771 Concrete Research 122, 42–58. <https://doi.org/10.1016/j.cemconres.2019.04.011>

772 Langton, C., Stefanko, D., 2011. Magnesium Mono Potassium Phosphate Grout For P-reactor Vessel
773 In-Situ Decommissioning. Aiken, SC (United States). <https://doi.org/10.2172/1011325>

774 Le Rouzic, M., Chaussadent, T., Stefan, L., Saillio, M., 2017. On the influence of Mg/P ratio on the
775 properties and durability of magnesium potassium phosphate cement pastes. Cement and
776 Concrete Research 96, 27–41. <https://doi.org/10.1016/j.cemconres.2017.02.033>

777 Li, C., Li, Y., Sun, H., Li, L., 2011. The Composition of Fly Ash Glass Phase and Its Dissolution
778 Properties Applying to Geopolymeric Materials. Journal of the American Ceramic Society 94,
779 1773–1778. <https://doi.org/10.1111/j.1551-2916.2010.04337.x>

780 Li, J., Zhang, W., Cao, Y., 2014. Laboratory evaluation of magnesium phosphate cement paste and
781 mortar for rapid repair of cement concrete pavement. Construction and Building Materials 58,
782 122–128. <https://doi.org/10.1016/j.conbuildmat.2014.02.015>

783 Lothenbach, B., Xu, B., Winnefeld, F., 2019. Thermodynamic data for magnesium (potassium)
784 phosphates. Applied Geochemistry 111, 104450.
785 <https://doi.org/10.1016/j.apgeochem.2019.104450>

786 Massiot, D., Fayon, F., Capron, M., King, I., Le Calvé, S., Alonso, B., Durand, J.-O., Bujoli, B., Gan,
787 Z., Hoatson, G., 2002. Modelling one- and two-dimensional solid-state NMR spectra. Magnetic
788 Resonance in Chemistry 40, 70–76. <https://doi.org/10.1002/mrc.984>

789 Neithalath, N., Weiss, J., Olek, J., 2006. Characterizing Enhanced Porosity Concrete using electrical
790 impedance to predict acoustic and hydraulic performance. Cement and Concrete Research 36,
791 2074–2085. <https://doi.org/10.1016/j.cemconres.2006.09.001>

792 Nied, D., Enemark-Rasmussen, K., L'Hopital, E., Skibsted, J., Lothenbach, B., 2016. Properties of
793 magnesium silicate hydrates (M-S-H). Cement and Concrete Research 79, 323–332.
794 <https://doi.org/10.1016/j.cemconres.2015.10.003>

- 795 Penel, G., Leroy, G., Rey, C., Bres, E., 1998. MicroRaman spectral study of the PO₄ and CO₃
796 vibrational modes in synthetic and biological apatites. *Calcified Tissue International* 63, 475–
797 481. <https://doi.org/10.1007/s002239900561>
- 798 Perona, R., Fernández-García, C., García-Lodeiro, I., Criado, M., Bastidas, J.M., Alonso, M.C., 2023.
799 Corrosion behavior and immobilization of pure aluminum and Al–Mg alloy LLRW in
800 magnesium potassium phosphate cements. *Journal of Nuclear Materials* 582, 154501.
801 <https://doi.org/10.1016/j.jnucmat.2023.154501>
- 802 Poras, G., Cau Dit Coumes, C., Antonucci, P., Cannes, C., Delpech, S., Perrin, S., 2023.
803 Electrochemical Behavior of Al/Mg Alloys Immobilized in a Magnesium Potassium Phosphate
804 Cement-Based Mortar. *Materials* 16. <https://doi.org/10.3390/ma16155415>
- 805 Pyo, J.Y., Um, W., Heo, J., 2021. Magnesium potassium phosphate cements to immobilize radioactive
806 concrete wastes generated by decommissioning of nuclear power plants. *Nuclear Engineering
807 and Technology* 53, 2261–2267. <https://doi.org/10.1016/j.net.2021.01.005>
- 808 Roosz, C., Grangeon, S., Blanc, P., Montouillout, V., Lothenbach, B., Henocq, P., Giffaut, E.,
809 Vieillard, P., Gaboreau, S., 2015. Crystal structure of magnesium silicate hydrates (M-S-H): The
810 relation with 2:1 Mg–Si phyllosilicates. *Cement and Concrete Research* 73, 228–237.
811 <https://doi.org/10.1016/j.cemconres.2015.03.014>
- 812 Roufosse, A.H., Aue, W.P., Roberts, J.E., Glimcher, M.J., Griffin, R.G., 1984. Investigation of
813 mineral phases of bone by solid-state phosphorus-31 magic-angle sample-spinning nuclear
814 magnetic resonance. *Biochemistry* 23, 6115–6120. <https://doi.org/10.1021/bi00320a033>
- 815 Schneider, H., Schreuer, J., Hildmann, B., 2008. Structure and properties of mullite—A review.
816 *Journal of the European Ceramic Society* 28, 329–344.
817 <https://doi.org/10.1016/j.jeurceramsoc.2007.03.017>
- 818 Seehra, S.S., Gupta, S., Kumar, S., 1993. Rapid setting magnesium phosphate cement for quick repair

819 of concrete pavements - characterisation and durability aspects. *Cement and Concrete Research*
820 23, 254–266. [https://doi.org/10.1016/0008-8846\(93\)90090-V](https://doi.org/10.1016/0008-8846(93)90090-V)

821 Snellings, R., Chwast, J., Cizer, Ö., De Belie, N., Dhandapani, Y., Durdzinski, P., Elsen, J., Haufe, J.,
822 Hooton, D., Patapy, C., Santhanam, M., Scrivener, K., Snoeck, D., Steger, L., Tongbo, S.,
823 Vollpracht, A., Winnefeld, F., Lothenbach, B., 2018. RILEM TC-238 SCM recommendation on
824 hydration stoppage by solvent exchange for the study of hydrate assemblages. *Materials and*
825 *Structures/Materiaux et Constructions* 51. <https://doi.org/10.1617/s11527-018-1298-5>

826 Stoll, W.R., Neuman, W.F., 1956. The Uptake of Sodium and Potassium Ions by Hydrated
827 Hydroxyapatite. *Journal of the American Chemical Society* 78, 1585–1588.
828 <https://doi.org/10.1021/ja01589a022>

829 Torras, J., Buj, I., Rovira, M., de Pablo, J., 2011. Semi-dynamic leaching tests of nickel containing
830 wastes stabilized/solidified with magnesium potassium phosphate cements. *Journal of Hazardous*
831 *Materials* 186, 1954–1960. <https://doi.org/10.1016/j.jhazmat.2010.12.093>

832 Tropp, J., Blumenthal, N.C., Waugh, J.S., 1983. Phosphorus NMR study of solid amorphous calcium
833 phosphate. *Journal of the American Chemical Society* 105, 22–26.
834 <https://doi.org/10.1021/ja00339a006>

835 van der Lee, J., De Windt, L., Lagneau, V., Goblet, P., 2003. Module-oriented modeling of reactive
836 transport with HYTEC. *Computers & Geosciences* 29, 265–275. [https://doi.org/10.1016/S0098-](https://doi.org/10.1016/S0098-3004(03)00004-9)
837 [3004\(03\)00004-9](https://doi.org/10.1016/S0098-3004(03)00004-9)

838 Viani, A., Mácová, P., Sotiriadis, K., 2021. Amorphous-crystalline transformation control on the
839 microstructural evolution of magnesium phosphate cements. *Materials Letters* 292, 129630.
840 <https://doi.org/10.1016/j.matlet.2021.129630>

841 Viani, A., Mali, G., Mácová, P., 2017. Investigation of amorphous and crystalline phosphates in
842 magnesium phosphate ceramics with solid-state ¹H and ³¹P NMR spectroscopy. *Ceramics*

- 843 International 43, 6571–6579. <https://doi.org/10.1016/j.ceramint.2017.02.087>
- 844 Vieillard, P., Tardy, Y., 1984. Thermochemical Properties of Phosphates, in: *Phosphate Minerals*.
845 Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 171–198. [https://doi.org/10.1007/978-3-642-](https://doi.org/10.1007/978-3-642-61736-2_4)
846 [61736-2_4](https://doi.org/10.1007/978-3-642-61736-2_4)
- 847 Wagh, A.S., 2013. Recent Progress in Chemically Bonded Phosphate Ceramics. *ISRN Ceramics 2013*,
848 1–20. <https://doi.org/10.1155/2013/983731>
- 849 Wagh, A.S., Jeong, S.-Y., Singh, D., 1997. High Strength Phosphate Cement Using, in: *Proceedings of*
850 *the 1st International Conference on High Strength Concrete*. pp. 542–553.
- 851 Wang, T., Ishida, T., Gu, R., 2020. A study of the influence of crystal component on the reactivity of
852 low-calcium fly ash in alkaline conditions based on SEM-EDS. *Construction and Building*
853 *Materials* 243, 118227. <https://doi.org/10.1016/j.conbuildmat.2020.118227>
- 854 Weill, B., Bradik, J., 1988. US Patent n°4,756,762 - Magnesium phosphate cement systems.
- 855 Weng, Y., Ruan, S., Li, M., Mo, L., Unluer, C., Tan, M.J., Qian, S., 2019. Feasibility study on
856 sustainable magnesium potassium phosphate cement paste for 3D printing. *Construction and*
857 *Building Materials* 221, 595–603. <https://doi.org/10.1016/j.conbuildmat.2019.05.053>
- 858 Wilson, R.M., Elliott, J.C., Dowker, S.E.P., Rodriguez-Lorenzo, L.M., 2005. Rietveld refinements and
859 spectroscopic studies of the structure of Ca-deficient apatite. *Biomaterials* 26, 1317–1327.
860 <https://doi.org/10.1016/j.biomaterials.2004.04.038>
- 861 Xu, B., Coumes, C.C.D., Lambertin, D., Lothenbach, B., 2023. Compressive strength and hydrate
862 assemblages of wollastonite-blended magnesium potassium phosphate cements exposed to
863 different pH conditions. *Cement and Concrete Composites* 143.
864 <https://doi.org/10.1016/j.cemconcomp.2023.105255>
- 865 Xu, B., Lothenbach, B., Leemann, A., Winnefeld, F., 2018. Reaction mechanism of magnesium

866 potassium phosphate cement with high magnesium-to-phosphate ratio. *Cement and Concrete*
867 *Research* 108, 140–151. <https://doi.org/10.1016/j.cemconres.2018.03.013>

868 Xu, B., Lothenbach, B., Winnefeld, F., 2020. Influence of wollastonite on hydration and properties of
869 magnesium potassium phosphate cements. *Cement and Concrete Research* 131, 106012.
870 <https://doi.org/10.1016/j.cemconres.2020.106012>

871 Xu, B., Winnefeld, F., Kaufmann, J., Lothenbach, B., 2019. Influence of magnesium-to-phosphate
872 ratio and water-to-cement ratio on hydration and properties of magnesium potassium phosphate
873 cements. *Cement and Concrete Research* 123, 105781.
874 <https://doi.org/10.1016/j.cemconres.2019.105781>

875 Xu, B., Winnefeld, F., Lothenbach, B., 2021. Effect of temperature curing on properties and hydration
876 of wollastonite blended magnesium potassium phosphate cements. *Cement and Concrete*
877 *Research* 142, 106370. <https://doi.org/10.1016/j.cemconres.2021.106370>

878 Xu, B., Winnefeld, F., Ma, B., Rentsch, D., Lothenbach, B., 2022. Influence of aluminum sulfate on
879 properties and hydration of magnesium potassium phosphate cements. *Cement and Concrete*
880 *Research* 156, 106788. <https://doi.org/10.1016/j.cemconres.2022.106788>

881 Yang, H., Martinelli, L., Tasso, F., Sprocati, A.R., Pinzari, F., Liu, Z., Downs, R.T., Sun, H.J., 2014.
882 A new biogenic, struvite-related phosphate, the ammonium-analog of hazenite,
883 $(\text{NH}_4)\text{NaMg}_2(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$. *American Mineralogist* 99, 1761–1765.
884 <https://doi.org/10.2138/am.2014.4768>

885 Yang, H., Sun, H.J., 2004. Crystal structure of a new phosphate compound, $\text{Mg}_2\text{KNa}(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$.
886 *Journal of Solid State Chemistry* 177, 2991–2997. <https://doi.org/10.1016/j.jssc.2004.05.008>

887 Yang, H., Sun, H.J., Downs, R.T., 2011. Hazenite, $\text{KNaMg}_2(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$, a new biologically
888 related phosphate mineral, from Mono Lake, California, U.S.A. *American Mineralogist* 96, 675–
889 681. <https://doi.org/10.2138/am.2011.3668>

890 Yang, Q., Zhu, B., Wu, X., 2000. Characteristics and durability test of magnesium phosphate cement-
891 based material for rapid repair of concrete. *Materials and Structures/Materiaux et Constructions*
892 33, 229–234. <https://doi.org/10.1007/bf02479332>

893 Yu, Y., Wang, J., Liu, C., Zhang, B., Chen, H., Guo, H., Zhong, G., Qu, W., Jiang, S., Huang, H.,
894 2010. Evaluation of inherent toxicology and biocompatibility of magnesium phosphate bone
895 cement. *Colloids and Surfaces B: Biointerfaces* 76, 496–504.
896 <https://doi.org/10.1016/j.colsurfb.2009.12.010>

897 Yu, Y., Xu, C., Dai, H., 2016. Preparation and characterization of a degradable magnesium phosphate
898 bone cement. *Regenerative Biomaterials* 3, 231–237. <https://doi.org/10.1093/rb/rbw024>

899 Zhang, X.-J., Lin, D.-Y., Yan, X.-H., Wang, X.-X., 2011. Evolution of the magnesium incorporated
900 amorphous calcium phosphate to nano-crystallized hydroxyapatite in alkaline solution. *Journal of*
901 *Crystal Growth* 336, 60–66. <https://doi.org/10.1016/j.jcrysgr.2011.09.039>

902 Zhang, Z., Yang, Z., Chen, Z., Kang, T., Ding, X., Li, Y., Liao, Y., Chen, C., Yuan, H., Peng, H.,
903 2018. A study on bone cement containing magnesium potassium phosphate for bone repair.
904 *Cogent Biology* 4, 1487255. <https://doi.org/10.1080/23312025.2018.1487255>

905 Zhao, Z., Chen, M., Xu, J., Li, L., Huang, Y., Yang, L., Zhao, P., Lu, L., 2021. Mix design and
906 rheological properties of magnesium potassium phosphate cement composites based on the 3D
907 printing extrusion system. *Construction and Building Materials* 284, 122797.
908 <https://doi.org/10.1016/j.conbuildmat.2021.122797>

909