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Understanding the setting and hardening process of wollastonite-based brushite cement. Part 1: Influence of the Ca/P ratio and H₃PO₄ concentration of the mixing solution

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1 **Understanding the setting and hardening process of wollastonite-based**
2 **brushite cement. Part 1: influence of the Ca/P ratio and H₃PO₄**
3 **concentration of the mixing solution**

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16 **Abstract (≤ 150 words)**

17

18 Wollastonite-based brushite cement are prepared by mixing wollastonite with a phosphoric
19 acid solution containing metallic cations and boric acid. This work investigates simplified
20 systems comprising wollastonite and H₃PO₄ solutions only, in order to clarify the influence of
21 the H₃PO₄ concentration, Ca/P and l/s ratios (this latter parameter being correlated to the two
22 others) on the setting and hardening process.

23 At constant H₃PO₄ concentration, increasing the Ca/P ratio, and decreasing the l/s ratio,
24 accelerates the early stages of hydration but limits its progress at 7 d. At high Ca/P ratio, more
25 basic calcium orthophosphates form in addition to dicalcium phosphate.

26 At constant l/s ratio, increasing the H₃PO₄ concentration in the range 7-10 mol.L⁻¹ retards
27 cement hydration, and inhibits the setting at concentrations ≥ 12 mol.L⁻¹. A good compromise
28 is obtained for H₃PO₄ concentrations between 9 and 10 mol.L⁻¹: hydration is not too fast and
29 yields the maximum amount of dicalcium phosphate.

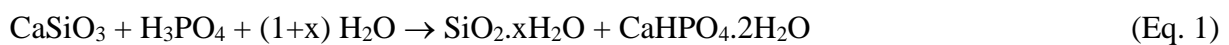
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31 **Keywords:** hydration (A), hydration products (B), chemically bonded ceramics (D),
32 Thermodynamic calculations (B)

1. Introduction

Phosphate binders are often referred as “chemically bonded phosphate ceramics” because they can produce materials with low porosity and high mechanical strength [1, 2]. However, their setting and hardening process results from a dissolution / precipitation process, yielding to crystallized hydrates of low solubility, often associated with poorly characterized amorphous phases. This work is focused on brushite cements prepared from wollastonite (CaSiO_3), a natural calcium meta-silicate, and phosphoric acid (H_3PO_4) mixing solution, as firstly described by Semler [3, 4]. These binders can exhibit very good thermal resistance after hydrothermal post-treatment and are thus mainly used for refractory applications [5, 6]. They are also of interest for sealing and bonding due to their good adhesion properties with wood, ceramics and concrete [7]. Their potential for radioactive waste management has been pointed out more recently. Composite materials incorporating up to 50% of lead oxide by weight of cement may be used for radiation shielding [8]. Besides, Lanieste *et al.* [9] have shown that wollastonite-based brushite cements may show a better chemical compatibility with acidic radwaste than conventional calcium silicate cements and can improve the confinement of strontium [10].

In contrast with Portland cement, the setting and hardening process occurs under acidic conditions [5]: the reaction starts in very acidic medium ($\text{pH} < 1$), but the pH increases rapidly to reach an equilibrium which depends on the Ca/P ratio of the material. Mosselmans *et al.* [11] investigated model systems comprising wollastonite and a 13 mol% phosphoric acid (corresponding to a concentration close to 3.8 mol/L) with Ca/P molar ratios varying between 0.34 and 2.56. At Ca/P ratios higher than 1, brushite and amorphous silica were the two main products formed according to mass balance equation (Eq. 1):



57 At lower Ca/P ratios (between 1 and 0.34), monetite (CaHPO_4) and calcium
58 dihydrogenophosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ –MCPM) additionally precipitated.
59 When the Ca/P ratio is less than 0.71, brushite was not observed anymore.

60 In practice, wollastonite-based binders are prepared with more concentrated phosphoric acid
61 solutions (typical concentrations of 9-10 mol.L⁻¹). To avoid flash setting as well as excessive
62 heat output, retarders, such as boric acid or borax, are added, as well as metallic cations
63 (typically Al³⁺, Zn²⁺, Mg²⁺) [3, 6, 12, 13]. A recent paper [14] reports a thorough investigation
64 of the hydration of a commercial binder prepared by mixing wollastonite with a phosphoric
65 acid solution ($[\text{P}]_{\text{tot}} = 9.3 \text{ mol.L}^{-1}$) comprising Al³⁺ and Zn²⁺ cations (at concentrations of 1.3
66 mol.L⁻¹) and borax ($[\text{Na}_2\text{B}_4\text{O}_7] = 0.15 \text{ mol.L}^{-1}$) at a liquid/solid ratio of 1.25 (resulting in a
67 molar Ca/P ratio of 1.2). A multi-step process was evidenced:

- 68 - monocalcium phosphate monohydrate (MCPM - $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) formed transiently,
- 69 - an amorphous phase containing Al, Zn and Ca massively precipitated during the first
70 minutes after mixing, and progressively became richer in calcium as hydration progressed,
- 71 - brushite ($\text{Ca}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$) formed once MCPM started to destabilize.

72 There is however a lack of data about the influence of a variation in the composition of the
73 mixing solution on the cement hydration process and properties of the resulting material. In this
74 work, the focus is placed on the effect of the phosphoric acid concentration, Ca/P molar ratio
75 and liquid-to-solid (l/s) weight ratio, with investigated domains relevant for wollastonite-based
76 brushite cement pastes. A second paper will be more specifically dedicated to the role of
77 metallic cations.

78

79

80 **2. Experimental**

81

82 *2.1 Materials and specimen preparation*

83 The wollastonite powder was provided by Sulitec. It also contained small amounts of calcite
84 and quartz which were evidenced by X-ray diffraction and thermogravimetric analysis (TGA
85 and XRD diagrams are given in [14]). The proportion of calcite was assessed to be 1.6 ± 0.1
86 wt.% (weight loss due to CaCO_3 decarbonation recorded by TGA at 654°C). The particle size
87 distribution of the powder, determined by laser granulometry, ranged between $0.5 \mu\text{m}$ and
88 $135 \mu\text{m}$ ($d_{10} = 2.8 \mu\text{m}$, $d_{50} = 15.2 \mu\text{m}$, $d_{90} = 48.3 \mu\text{m}$). The wollastonite particles had a needle
89 shape. Their mean aspect ratio (ratio of the length-to-diameter), which was determined using
90 SEM images of c.a. 100 particles, was close to 4:1.

91 The mixing solution was a phosphoric acid solution, prepared from a 85% wt. H_3PO_4 (14.6
92 mol.L^{-1}) analytical grade commercial solution provided by VWR. As the solution was initially
93 very acidic, its pH could not be measured directly with a pH electrode. Therefore, its acidity
94 function H_0 was determined. This function was first developed by Hammett [15] and provides
95 a quantitative measure of acidity derived from ionization equilibria of an indicator behaving in
96 the Brönsted-Lowry sense.



98 The acidity function (a unitless parameter) is defined by (Eq.3).

99 $H_0 = \text{p}K_{\text{BH}} + \log (C_{\text{B}}/C_{\text{BH}})$ (Eq. 3)

100 It was determined using UV-visible spectroscopy with 4-chloro-2-nitroaniline as the acidity
101 indicator since its $\text{p}K_{\text{BH}}$ value (-0.89 at 19°C) falls within the range of interest. More details
102 about the experimental procedure can be found in [14]. The pore solution pH of hardened
103 materials was less acidic and could be measured using conventional pH-metry.

104 Mixing was performed using a laboratory mixer equipped with an anchor stirrer and rotating
 105 at 250 rpm for 5 min. Paste samples were then cast into airtight polypropylene boxes (20 mL
 106 of paste per box) and cured at $25 \pm 1^\circ\text{C}$.

107 A first series of cement pastes was prepared by varying the Ca/P molar ratio from 0.96 to
 108 1.92, while keeping constant the initial orthophosphoric acid concentration (9 mol.L^{-1}) in the
 109 mixing solution (Table 1). The l/s ratio, which is correlated to these two parameters, varied
 110 from 1 to 0.5 in these experiments. In a second series of experiments, the l/s ratio was fixed at
 111 0.76 mL.g^{-1} whereas the initial phosphoric acid concentration was increased from 7 to 16.6
 112 mol.L^{-1} . As a consequence, the Ca/P molar ratio decreased from 1.63 to 1.78.

113

114 Table 1: Composition of the cement pastes (H_0 stands for the acidity function, the pastes are
 115 labelled $P_{X/Y/Z}$ where X, Y and Z stand for the Ca/P ratio, initial H_3PO_4 concentration and l/s
 116 ratio respectively).

	Paste reference	Ca/P (mol/mol)	$[\text{H}_3\text{PO}_4]_{\text{tot}}$ (mol.L^{-1})	l/s (mL/g)	H_0	V_{mixing} solution (mL)	$M_{\text{wollastonite}}$ (g)
Series 1	$P_{0.96/9/1}$	0.96	9	1.00	-1.85	50	50
	$P_{1.24/9/0.76}$	1.24	9	0.76	-1.85	38	50
	$P_{1.92/9/0.5}$	1.92	9	0.50	-1.85	25	50
Series 2	$P_{1.63/7/0.76}$	1.63	7	0.76	-1.28	38	50
	$P_{1.52/7.5/0.76}$	1.52	7.5	0.76	-1.40	38	50
	$P_{1.42/8/0.76}$	1.42	8	0.76	-1.56	38	50
	$P_{1.35/8.5/0.76}$	1.35	8.5	0.76	-1.70	38	50
	$P_{1.24/9.5/0.76}$	1.24	9.5	0.76	-1.99	38	50
	$P_{1.14/10/0.76}$	1.14	10	0.76	-2.13	38	50
	$P_{0.95/12/0.76}$	0.95	12	0.76	-2.89	38	50
	$P_{1.24/12/0.57}$	1.24	12	0.57	-2.89	28	50
	$P_{0.78/14.6/0.76}$	0.78	14.6	0.76	-3.61	38	50

117

118 2.2 Characterization techniques

119 A TAM AIR isothermal conduction microcalorimeter was used to investigate the hydration
 120 rate of cement pastes at 25°C . Experiments were performed on 2-g samples prepared outside of
 121 the calorimeter (see [14] for more details).

122 To stop cement hydration, pastes were first immersed into isopropanol, crushed by hand,
123 filtrated and dried in an oven at 38°C for 24 h. Preliminary tests showed that this drying
124 procedure did not change the phase assemblage as compared with drying at room temperature
125 for several days.

126 The powder obtain after stopping the hydration was further ground by hand to a particle size
127 below 100 µm and characterized by TGA and XRD, as described in a previous work [14].
128 Rietveld analysis was performed with the internal standard method, using silicon as the
129 standard. Table 2 gives the ICDS number of the phases used for the refinement.

130

131 Table 2: ICDS files associated to crystalline phase

Crystalline phase	ICDS file
Brushite	72-0713
Monetite	70-0359
Wollastonite	84-0654
OCP	74-1301
Quartz	70-7344
Silicon	27-1402
CDHA	46-0905
MCPM	09-0347

132

133 The mechanical strength of 4×4×4 cm paste specimens was characterized after 28 d of curing
134 at ambient temperature in a sealed bag to prevent desiccation. The compressive strength was
135 measured following EN 196-1 European standard (loading rate: 2.4 kN.s⁻¹) with a mechanical
136 compression testing machine (3R RP 40/400FC).

137 The pore solution of a 3 month-old hardened paste was extracted by compaction of about
138 140 g crushed sample using the device described by Cyr *et al.* [16] with a 3R RP-3000 QC
139 mechanical press at a pressure up to 300 MPa. The pH of the recovered liquid was immediately
140 measured with a pH electrode (Mettler Toledo InLab Expert Pt1000 pH 0–14 T 0–100 °C)
141 calibrated using two pH buffers at 1.09 (25 °C) and 4.01 (25 °C).

142

143 *2.3 Thermodynamic modelling*

144 Experiments were supported by thermodynamic equilibrium modelling in order to predict
145 phase assemblages in the cement pastes as a function of their hydration degree. Thermodynamic
146 calculations were carried out using CHESS software which works by minimizing the free
147 energy of a pre-defined system [17]. The Chess database was enriched by adding new calcium
148 phosphate species relevant to the investigated system, as detailed in [14]. The activity
149 coefficients of the aqueous species were calculated using the B-dot model which is considered
150 to be reasonably accurate in predicting the activities of Na⁺ and Cl⁻ ions to concentrations as
151 large as several mol.kg⁻¹, and of other species to ionic strengths up to 0.3 to 1 mol.kg⁻¹ [18].
152 Note that the ionic strength of the mixing solution was initially extremely high but rapidly
153 dropped below 0.75 mol.L⁻¹ when the products started to precipitate.

154

155 **3. Results and discussion**

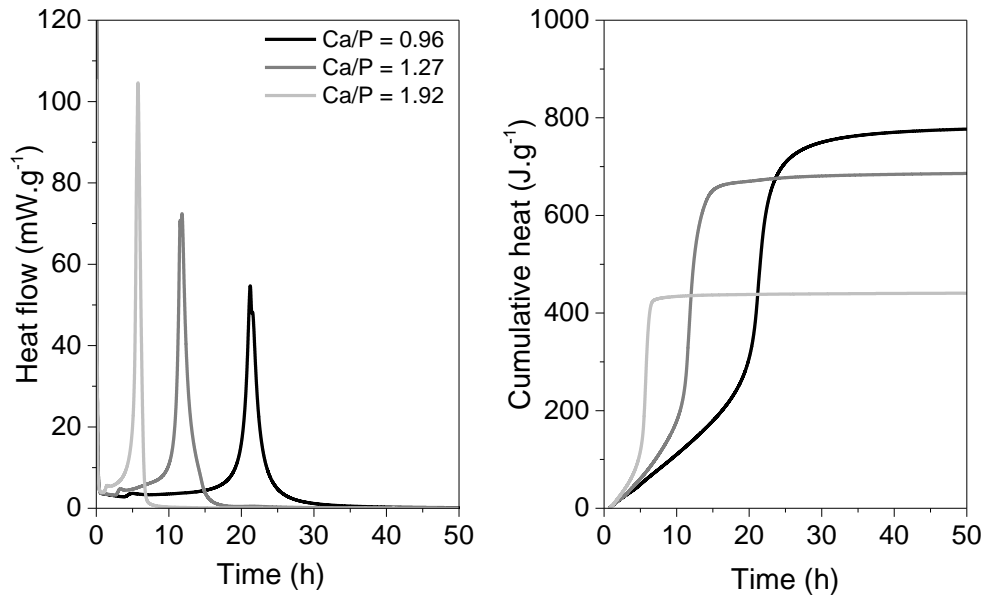
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157 *3.1 Influence of the Ca/P and l/s ratios*

158 3.1.1. Hydration rate

159 Hydration of pastes P_{0.96/9/1}, P_{1.27/9/0.76} and P_{1.92/9/0.5}, prepared with a 9 mol.L⁻¹ H₃PO₄ solution,
160 but having different Ca/P and l/s ratios, was monitored using isothermal microcalorimetry
161 (Figure 1). An increase in the Ca/P ratio, correlated with a decrease in the l/s ratio, accelerated
162 the hydration process: the duration of the period of low thermal activity decreased, as well as
163 the time at which the heat flow reached its maximum. The cumulative heat produced at 50 h
164 (normalized with respect to the mass of wollastonite) also diminished.

165



166
 167 Figure 1: Heat flow (left) and cumulative heat (right) of pastes P_{0.96/9/1}, P_{1.27/9/0.76} and P_{1.92/9/0.5}
 168 (standardized with respect to the mass of wollastonite).

169

170 The heat measured in microcalorimetry results from the heat produced or absorbed by the
 171 reactions taking place during setting. Table 2, summarizing the enthalpies of the main possible
 172 reactions, shows that dissolution of wollastonite is strongly exothermic, whereas precipitation
 173 of hydroxyapatite (HA) or calcium-deficient hydroxyapatite (CDHA) is strongly endothermic.
 174 In comparison, precipitation of brushite, monocalcium phosphate monohydrate and monetite
 175 should have a much more limited effect on heat. The decrease in the cumulative heat observed
 176 in our study when the Ca/P ratio of the paste increased could thus result from a decrease in the
 177 fraction of dissolved wollastonite, but also from a change in the phase assemblage. Indeed, if
 178 precipitation of HA or CDHA is promoted at the expense of brushite at high Ca/P ratio, the heat
 179 released by the dissolution of wollastonite might be partly balanced by the heat absorbed by the
 180 precipitation of hydrates. To check these two hypotheses, it was necessary to determine the
 181 mineralogy of the hydrated cement pastes.

182

183 Table 2: Enthalpy of reactions that may occur during the hydration of wollastonite with an
 184 orthophosphoric solution [19, 20].

Reaction	Balance equation	Enthalpy of reaction (kJ/mol)
Dissolution of wollastonite	$\text{CaSiO}_3 + 2 \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{Si}(\text{OH})_4$	-88.20
Precipitation of MCPM	$\text{Ca}^{2+} + 2 \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 2\text{H}^+$	-4.36
Precipitation of brushite	$\text{Ca}^{2+} + \text{H}_3\text{PO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+$	-0.77
Precipitation of monetite	$\text{Ca}^{2+} + \text{H}_3\text{PO}_4 \rightarrow \text{CaHPO}_4 + 2\text{H}^+$	16.77
Precipitation of OCP	$8 \text{Ca}^{2+} + 6 \text{H}_2\text{PO}_4^- + 5 \text{H}_2\text{O} \rightarrow \text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O} + 10 \text{H}^+$	Not available
Precipitation of HA	$5 \text{Ca}^{2+} + 3 \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 7 \text{H}^+$	178.4
Precipitation of CDHA	$9 \text{Ca}^{2+} + 6 \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) + 12 \text{H}^+$	228.9
Conversion MCPM → Monetite	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} \rightarrow \text{CaHPO}_4 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O}$	21.43
Conversion MCPM → Brushite	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_3\text{PO}_4$	3.59

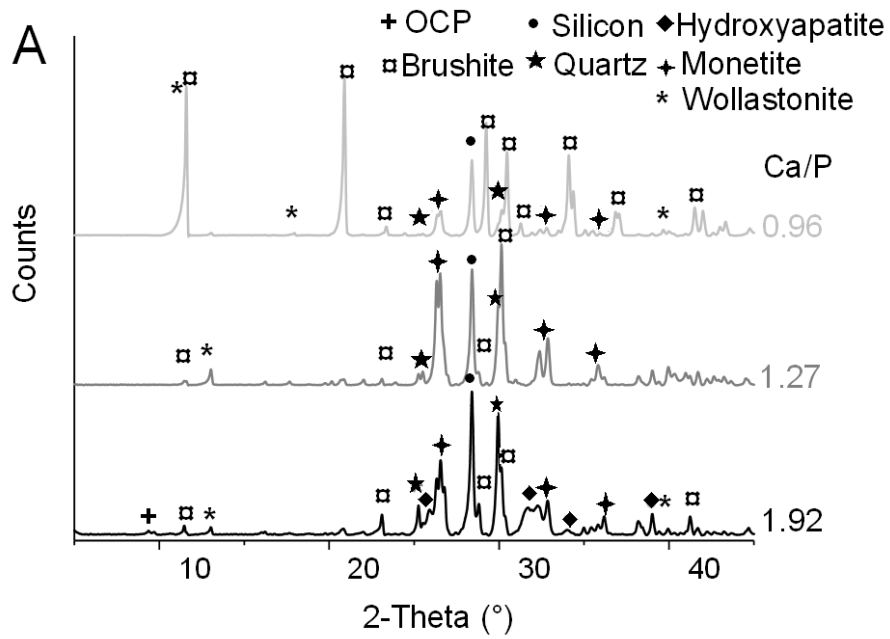
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186 3.1.2. Phase assemblage

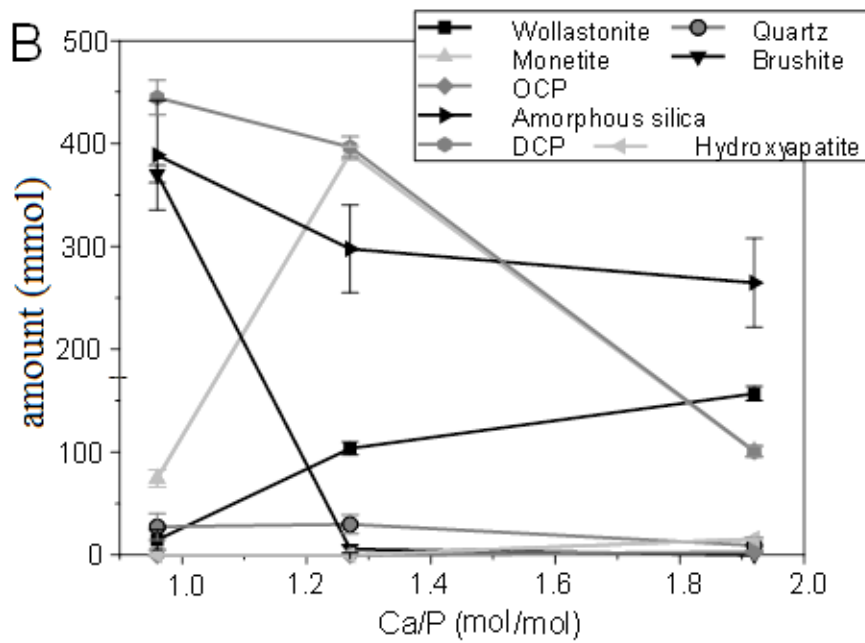
187 The X-ray diffraction patterns of the 7-d old cement pastes are compared in Figure 2A.
 188 Wollastonite, brushite, quartz and monetite were evidenced whatever the sample. In addition,
 189 the paste with the highest Ca/P ratio contained small amounts of hydroxyapatite (HA or CDHA)
 190 and octacalcium phosphate (OCP). The Rietveld quantification (Figure 2B) showed the
 191 presence of an amorphous phase which was likely amorphous silica. Its amount was indeed in
 192 good agreement with that calculated for silica using equation (Eq. 5) and the amount of
 193 consumed wollastonite (Figure 3).



195



196



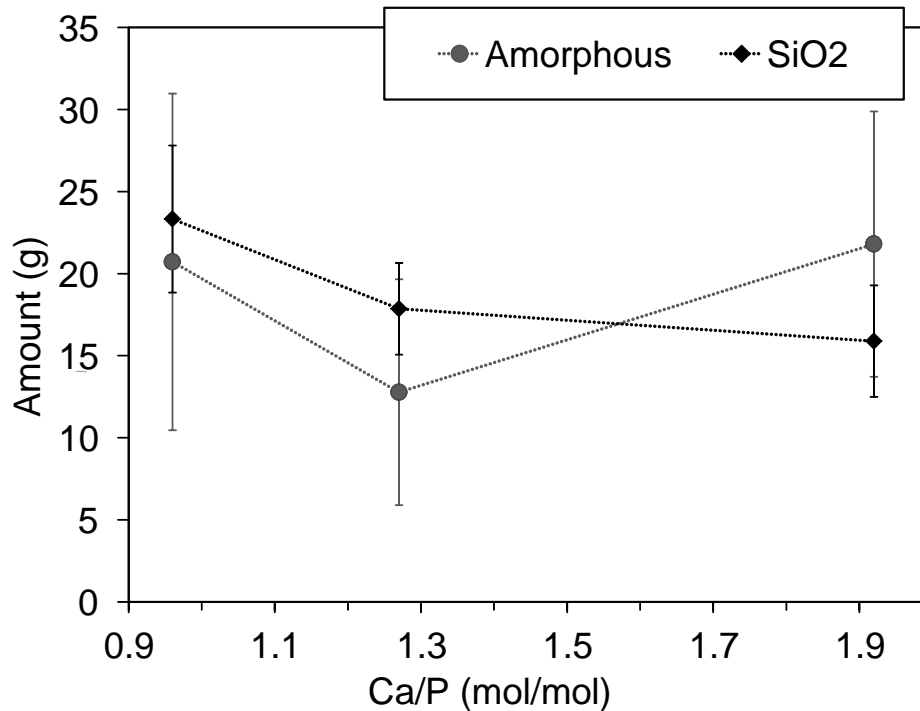
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198 Figure 2: X-ray diffraction patterns of pastes P_{0.96/9/1}, P_{1.27/9/0.76} and P_{1.92/9/0.5} after 7 d of curing

199 (A) and phase evolution as a function of the Ca/P molar ratio at 7 d (B) (OCP: octacalcium

200 phosphate, DCP: dicalcium phosphate (monetite + brushite)).

201



202

203 Figure 3: Comparison of the amounts of silica calculated from consumed wollastonite and of
 204 total amorphous phase in pastes P_{0.96/9/1}, P_{1.27/9/0.76} and P_{1.92/9/0.5} after 7 d of curing.

205

206 The fraction of wollastonite consumed at 7 d was calculated from the Rietveld results: $97 \pm$
 207 8% for paste P_{0.96/9/1}, $76 \pm 6 \%$ for paste P_{1.27/9/0.76} and $64 \pm 7 \%$ for paste P_{1.92/9/0.5}. Increasing
 208 the Ca/P ratio (and decreasing the l/s ratio) thus limited the consumption degree of wollastonite
 209 at 7 d. Several reasons can be postulated:

- 210 - a lack of water at low l/s ratio;
- 211 - a faster decrease in the acidity of the interstitial solution, which slowed down the dissolution
 212 of wollastonite [21];
- 213 - rapid precipitation of dense layers of hydrates around the wollastonite particles, which made
 214 it more difficult for water molecules to react with this mineral.

215 Increasing the Ca/P ratio also modified the mineralogy: OCP and hydroxyapatite were
 216 observed at high Ca/P ratio whereas the amount of dicalcium phosphate strongly decreased.
 217 Therefore, the smaller cumulative heat reported at high Ca/P ratio in the previous section

218 resulted both from a decrease in the degree of hydration (less wollastonite was consumed) and
219 from the precipitation of hydroxyapatite, an endothermic reaction partly compensating for the
220 exothermic dissolution of wollastonite. The type dicalcium phosphate formed also depended on
221 the Ca/P ratio: brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was the main phase at Ca/P 0.96, whereas monetite
222 (CaHPO_4) predominated at higher ratios. This result is closely related to the evolution of the
223 maximum heat flow observed by microcalorimetry. The higher the heat flow, the higher the
224 self-heating of the material during hydration, which favours the precipitation of monetite at the
225 expense of brushite [5]. In fact the thermal evolution of the paste with time has been recorded:
226 a significant temperature rise was observed a few hours after mixing (the temperature of the
227 sample reached 67.7°C at 16 h), which promoted the precipitation of monetite.

228

229 3.1.3. Thermodynamic modelling

230 The reaction of wollastonite with a H_3PO_4 solution was simulated using Chess software at
231 different Ca/P molar ratios. The input data were the amounts of liquid and solid phases and the
232 initial H_3PO_4 concentration used to prepare pastes $\text{P}_{0.96/9/1}$, $\text{P}_{1.27/9/0.76}$ and $\text{P}_{1.92/9/0.5}$. Table 3 shows
233 the calculated phase assemblages for degrees of wollastonite consumption corresponding to
234 those measured experimentally after 7 d of hydration. Two differences were noticed as
235 compared with the experiments:

- 236 - the calculations always predicted the formation of monetite instead of brushite since
237 monetite is the most stable phase at 25°C from a thermodynamic point of view [19],
- 238 - monocalcium phosphate monohydrate (MCPM) was expected to form at the lowest Ca/P
239 ratio of 0.96. The calculated amount was however very small (2.6%), which could explain
240 why this mineral was not evidenced by X-ray diffraction.

241 The calculated amount of monetite decreased when the Ca/P ratio increased, which was in good
242 agreement with the experimental results. The simulation also predicted the formation of

243 hydroxyapatite at a Ca/P ratio of 1.92, which again was consistent with the experimental
244 observations.

245

246 Table 3: Thermodynamic modelling results at 25°C

Ca/P	Progress of wollastonite dissolution (%)	MCPM (mmol)	Monetite (mmol)	HA (mmol)	Silica (mmol)
0.96	97	8.5	398	0	418
1.24	76	0	322	0	308
1.92	64	0	117	36	275

247

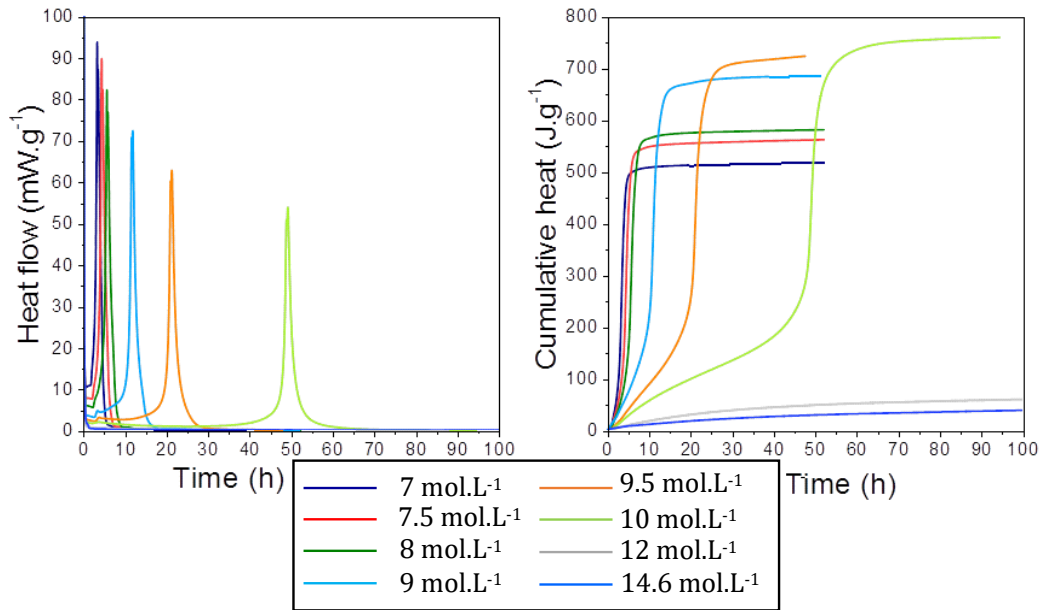
248 3.2 Effect of phosphoric acid concentration and acidity

249 3.2.1. Hydration rate

250 Figure 4 shows the heat flux and cumulative heat produced by the second series of cement
251 pastes, prepared at constant l/s ratio, but with a variable H₃PO₄ concentration in the mixing
252 solution, and thus a variable Ca/P ratio. The initial H₃PO₄ concentration strongly influenced the
253 rate of hydration. Its increase within the range 7 - 10 mol.L⁻¹ increased the duration of the low
254 thermal activity period and the cumulative heat produced at the end of the experiment, but
255 decreased the maximal heat flow.

256 As previously, two processes could contribute to increase the cumulative heat flow: a higher
257 dissolution degree of wollastonite, and a decrease in the progress of endothermic reactions
258 (mainly hydroxyapatite precipitation). For H₃PO₄ concentrations above 12 mol.L⁻¹, no heat
259 flow peak was observed, even after 7 days, and the cumulative heat remained of small
260 magnitude. The pastes prepared with these solutions exhibited a stiffening but no setting was
261 observed after 3 months.

262



263

264 Figure 4: Heat flow (left) and cumulative heat (right) of cement pastes P_{1.63/7/0.76}, P_{1.52/7.5/0.76},

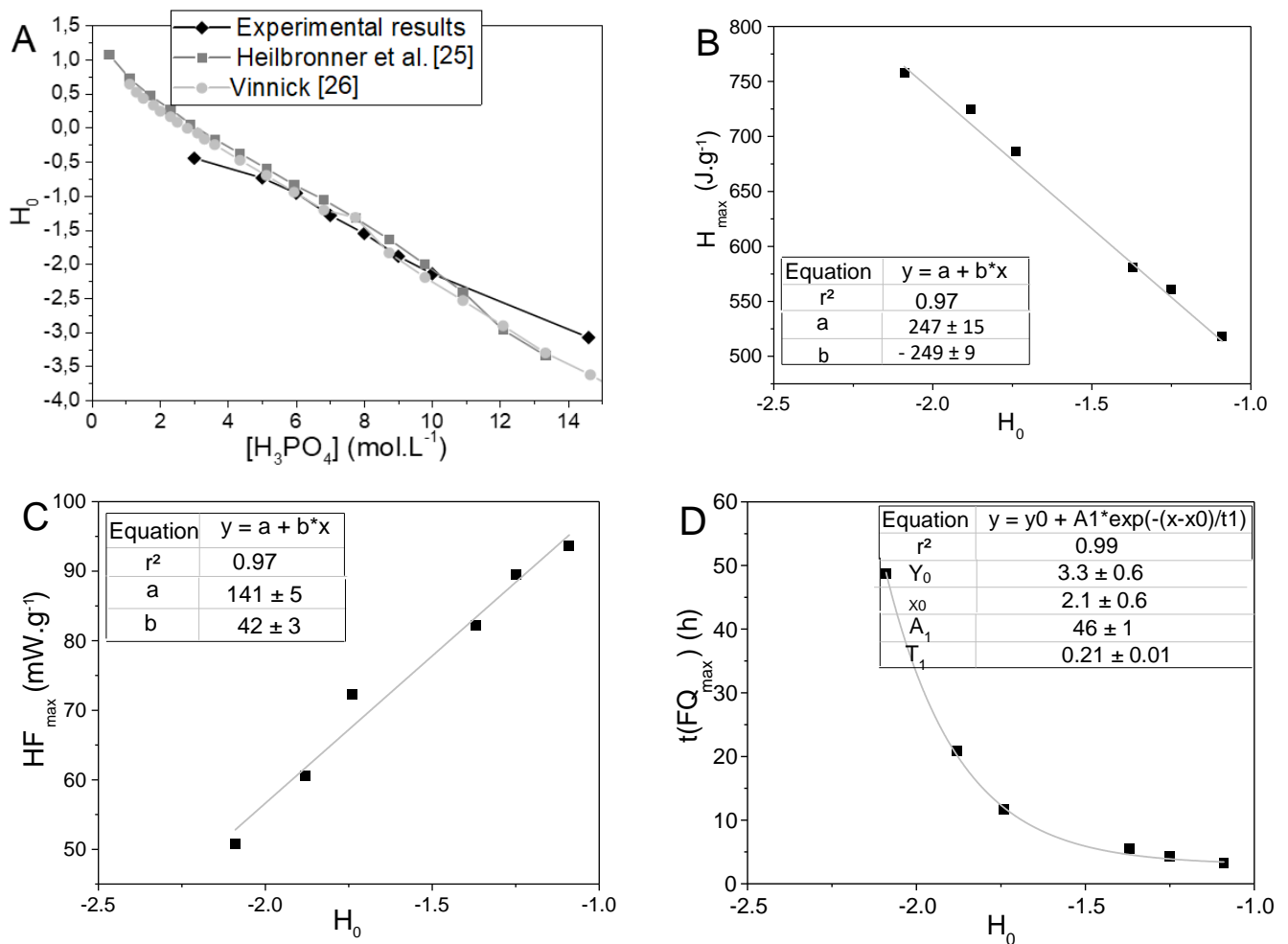
265 P_{1.42/8/0.76}, P_{1.35/8.5/0.76}, P_{1.24/9/0.76}, P_{1.20/9.5/0.76}, P_{1.14/10/0.76}, P_{0.95/12/0.76} and P_{0.78/14.6/0.76}

266 (standardization with respect to the mass of wollastonite).

267

268 Raising the H₃PO₄ concentration not only decreased the Ca/P molar ratio of the cement paste,
 269 but also increased the acidity of the mixing solution. The acidity function value H₀ was
 270 measured for each investigated H₃PO₄ concentration (Figure 5-A). The results were consistent
 271 with those of previous studies [26, 27]. The maximal heat flow, the corresponding ageing time
 272 (t(FQ_{max})) and the maximal cumulative heat were then plotted as a function of the acidity
 273 function of the mixing solution (Figure 5-B, C, D). The maximal heat flow and cumulative heat
 274 varied linearly with the acidity function. The smaller the acidity function (i.e. the higher the
 275 acidity), the smaller the maximal heat flow, but the higher the cumulative heat released at the
 276 end of the experiment. As for time t(FQ_{max}), it decreased exponentially when the acidity
 277 function increased.

278



279 Figure 5: Evolution of the acidity function (H_0) with the phosphoric acid concentration (A),
 280 Evolution of the maximal cumulative heat (B), maximal heat flow (C) and corresponding ageing
 281 time (D) as a function of the acidity function.

282

283 The absence of any setting or heat flow peak for the pastes prepared with a H_3PO_4 solution
 284 at a concentration ≥ 12 mol.L⁻¹ raised several questions. Did wollastonite react under these
 285 conditions? What was the limiting factor, a lack of water, a too low Ca/P ratio (below 1) to
 286 make it possible to precipitate brushite or monetite (Ca/P = 1), a too strong acidity as compared
 287 with the stability domain of brushite or monetite (c.a. $2 \leq pH \leq 6$ [22]) ? To investigate the
 288 influence of the Ca/P ratio, a supplementary paste sample was prepared with a 12 mol.L⁻¹ H_3PO_4
 289 solution, but with a smaller l/s ratio (0.57 mL.g⁻¹ instead of 0.76 mL.g⁻¹) in order to get a Ca/P
 290 ratio of 1.24, as for paste P_{1.24/9/0.76} prepared with a 9 mol.L⁻¹ H_3PO_4 solution. Hydration was

291 monitored by microcalorimetry: no heat flow peak could be detected despite the higher Ca/P
292 ratio. This rules out the hypothesis of a limitation due to a deficit in calcium. Mineralogical
293 characterizations were thus required to get a better understanding of the cement reactivity.

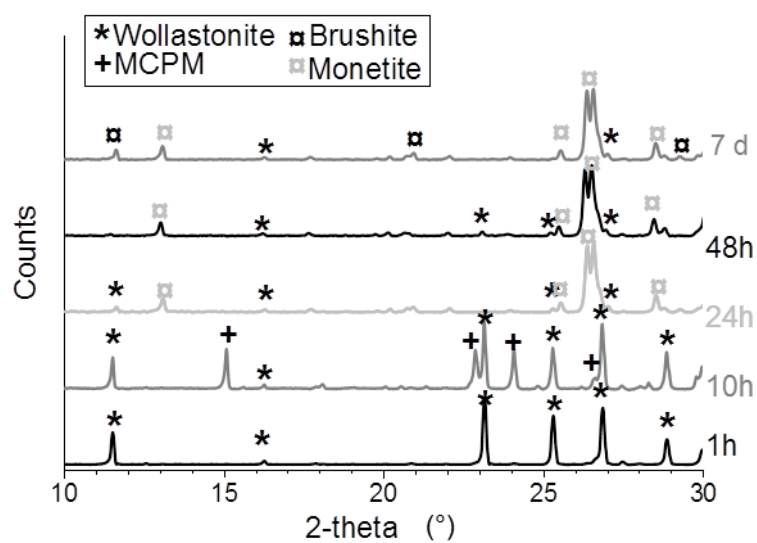
294

295 3.2.2. Phase assemblage

296 The phase evolution of paste P_{1.20/9.5/0.76} with ongoing hydration was first investigated by X-
297 ray diffraction (Figure 6). Wollastonite was almost fully consumed after 48 h. MCPM
298 precipitated transiently at 10 h, and dissolved afterwards. Monetite was the main product, but
299 small amounts of brushite were evidenced at 7 days. Brushite formed afterwards, when the
300 sample cooled back to room temperature.

301 Comparing the mineralogical evolution and calorimetric data (Figure 6) shows that the heat
302 flow peak seemed to occur simultaneously with the conversion of MCPM into monetite. Note
303 that this reaction, which is slightly endothermic (Table 3) could not explain by itself the heat
304 release, but it was associated with an accelerated dissolution of wollastonite, which is a strongly
305 exothermic process, and its precipitation into monetite.

306

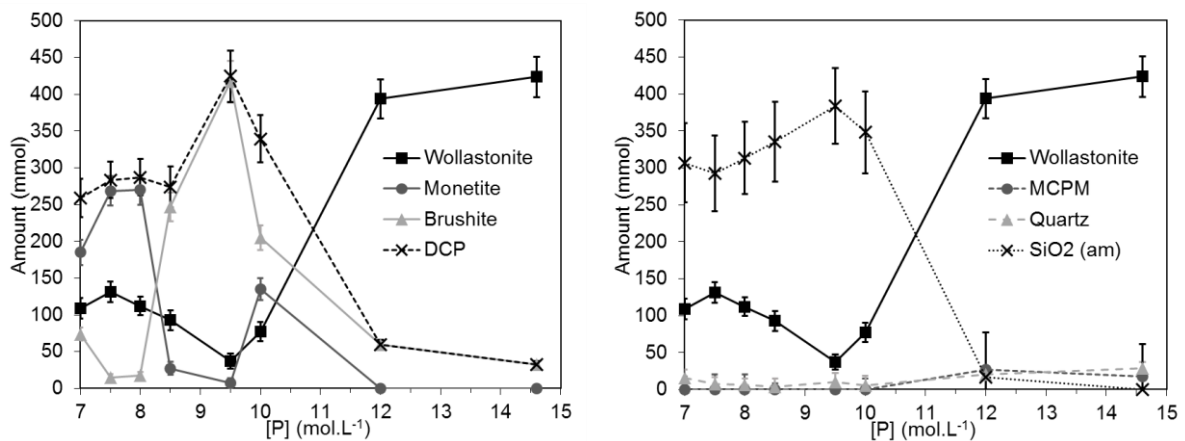


307

308 Figure 6: X-ray diffraction patterns of paste P_{1.20/9.5/0.76} aged from 1 h to 7 d

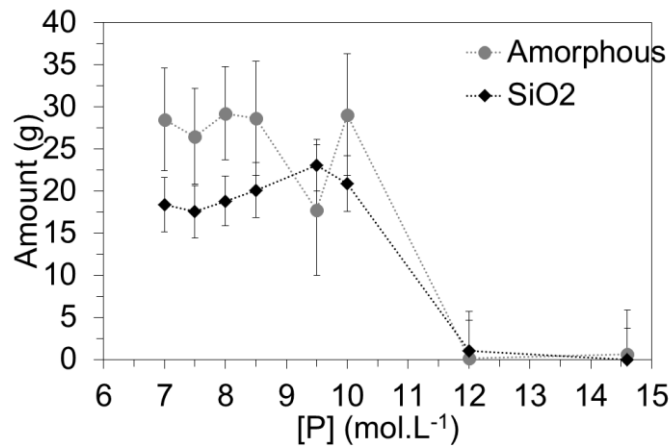
309

310 The X-ray diffraction patterns of the 7 d-old samples prepared with H_3PO_4 solutions of
311 increasing concentrations (from 7 to 14.6 mol.L^{-1}) were refined using Rietveld analysis. Figure
312 7 plots the evolution of the amounts of crystalline and amorphous phases as a function of the
313 initial H_3PO_4 concentration. As previously, the amount of amorphous phase fitted rather well
314 with that calculated for silica using (Eq. 2) and the amount of residual wollastonite (Figure 8).
315 This latter exhibited a non-monotonous evolution: it started to decrease when the H_3PO_4
316 concentration was raised from 7 to 9.5 mol.L^{-1} , and increased at higher concentrations. The
317 amount of precipitated calcium diposphate (monetite + brushite) showed opposite variations.
318



319 Figure 7: Phase evolution as a function of the Ca/P molar ratio of pastes $P_{1.63/7/0.76}$, $P_{1.52/7.5/0.76}$,
320 $P_{1.42/8/0.76}$, $P_{1.35/8.5/0.76}$, $P_{1.24/9/0.76}$, $P_{1.20/9.5/0.76}$, $P_{1.14/10/0.76}$, $P_{0.95/12/0.76}$ and $P_{0.78/14.6/0.76}$ after 7 d of
321 curing (DCP: dicalcium phosphate (monetite + brushite)).

322



323

324 Figure 8: Comparison of the amount of calculated silica from reacted wollastonite and total
 325 amorphous phase in P_{1.63/7/0.76}, P_{1.52/7.5/0.76}, P_{1.42/8/0.76}, P_{1.35/8.5/0.76}, P_{1.24/9/0.76}, P_{1.20/9.5/0.76}, P_{1.14/10/0.76},
 326 P_{0.95/12/0.76} and P_{0.78/14.6/0.76} after 7 d of curing

327

328 At elevated H₃PO₄ concentrations (12 and 14.6 mol.L⁻¹), only a small fraction of wollastonite
 329 had reacted at 7 d (9% and 2% respectively) (Table 4) to form MCPM and brushite, which could
 330 explain the absence of setting. MCPM was still observed after a few months of curing under
 331 sealed bag (results not shown here). The persistence of MCPM could result from several factors:
 332 a lack of water which blocked the reactions, or a too low pH for dicalcium phosphate to
 333 precipitate. To check the first assumption, 7 d-old P_{0.95/12/0.76} and P_{0.78/14.6/0.76} samples were
 334 characterized using thermogravimetry analysis in order to determine the amount of water bound
 335 in the solid phase. This latter represented 45% (paste P_{0.95/12/0.76}) or 71 % (P_{0.78/14.6/0.76}) of the
 336 total water (Table 5). There was thus some residual free water in these samples at 7 d, making
 337 the assumption of a lack of water rather unlikely. The interstitial solution of paste P_{0.95/12/0.76}
 338 and P_{0.78/14.4/0.76} was extracted using pressure after 3 months of curing. Its pH was found to be
 339 close to 1, i.e. within the stability domain of MCPM [22].

340

341 Table 4: Fraction of wollastonite depleted at 7 d as a function of the initial H₃PO₄
342 concentration.

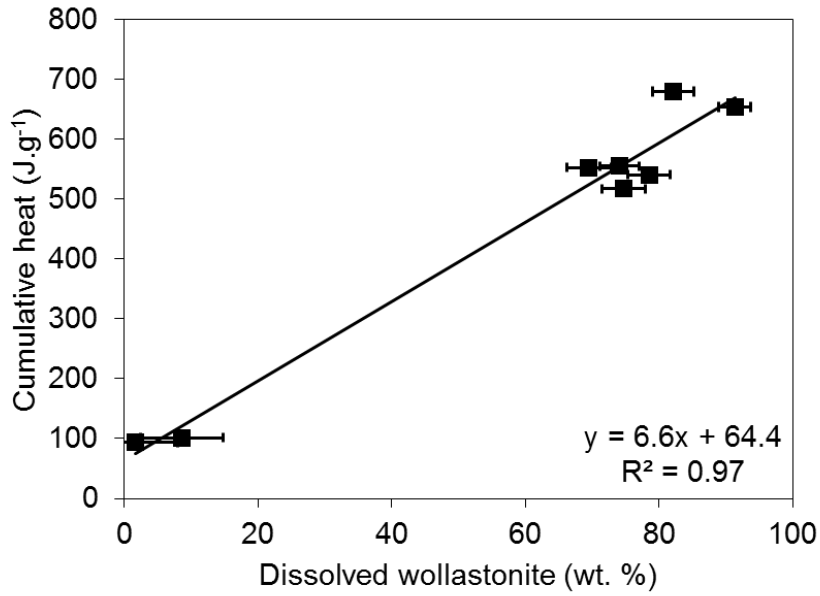
[H ₃ PO ₄] (mol.L ⁻¹)	Depleted wollastonite (%)
7.0	75
7.5	69
8.0	74
9.0	76
9.5	91
10.0	82
12.0	9
14.6	2

343
344 Table 5: Total and bound water contents in 7 d-old pastes P_{0.95/12/0.76} and P_{0.78/14.6/0.76}.

H ₃ PO ₄ concentration	Initial water content (%)	Water content in the solid phase at 7 days (%)
12.0 mol.L ⁻¹	13.1	4.4
14.6 mol.L ⁻¹	8.3	3.3

345
346 The maximal cumulative heat measured by isothermal microcalorimetry was strongly
347 correlated with the consumption degree of wollastonite inferred from Rietveld refinements
348 (Figure 9). Dissolution of wollastonite was thus the main process governing the heat production
349 in the second series of cement pastes: the higher the cumulative heat, the higher the extent of
350 dissolution of wollastonite.

351



352

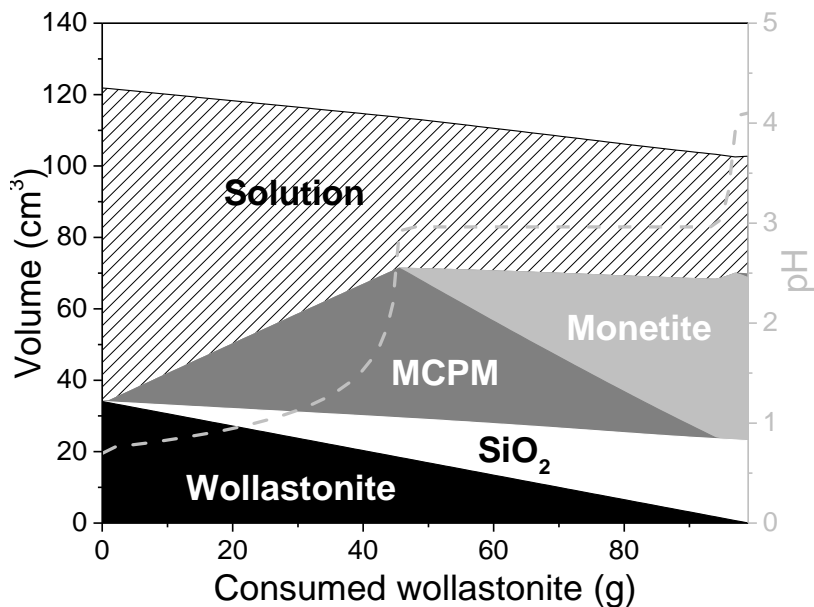
353 Figure 9: Cumulative heat as a function of the fraction of wollastonite depleted at 7 d.

354

355 3.2.3. Thermodynamic modelling

356 The mineralogical evolution of paste P_{1.20/9.5/0.76} with ongoing hydration was simulated using
 357 CHESS software (Figure 10). Thermodynamic modelling well predicted the transient
 358 precipitation of MCPM before that of monetite, which occurred when the pore solution pH
 359 reached a value close to 2.5.

360



361

362 Figure 10: Thermodynamic simulation of the hydration of paste P_{1.20/9.5/0.76} (100 g of
 363 wollastonite + 76 mL of a 9.5 mol.L⁻¹ H₃PO₄ solution)

364
 365 Thermodynamic calculations were also carried out to determine the phase assemblage in
 366 pastes P_{1.63/7/0.76}, P_{1.42/8/0.76}, P_{1.20/9.5/0.76}, P_{1.14/10/0.76}, P_{0.95/12/0.76} and P_{0.78/14.6/0.76} at the same degree
 367 of wollastonite dissolution as in the 7-d old samples. Experimental and calculated results are
 368 compared in Table 6. As previously, thermodynamics predicted the formation of monetite,
 369 which is more stable than brushite at 25°C [23]. Hydroxyapatite was also expected to form in
 370 the pastes prepared with the least acidic solution. This phase was not detected experimentally,
 371 possibly because it was present in rather small amounts (close to the detection limit of X-ray
 372 diffraction), or because the precipitation of hydroxyapatite is often preceded by that of an
 373 amorphous calcium phosphate mineral [24, 25] which could not be evidenced with the
 374 techniques used in this study. In contrast, the formation of MCPM, experimentally observed for
 375 the more concentrated H₃PO₄ solutions and smallest degrees of hydration, was well depicted
 376 by the model.

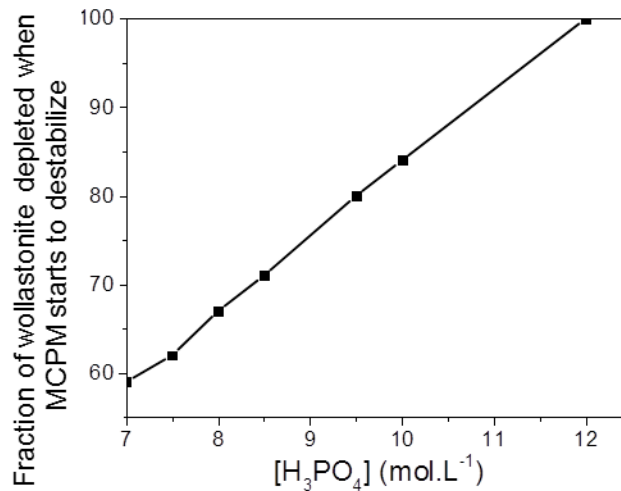
377
 378 Table 6: Experimental and calculated phase assemblages of pastes P_{1.63/7/0.76}, P_{1.42/8/0.76},
 379 P_{1.20/9.5/0.76}, P_{1.14/10/0.76}, P_{0.95/12/0.76} and P_{0.78/14.6/0.76} after 7 d of hydration.

380

[H ₃ PO ₄] mol.L ⁻¹	Consumed wollastonite %	MCPM (mmol)		Dicalcium phosphate (mmol)		Hydroxyapatite (mmol)		Silica (mmol)	
		Simulation	Experiment	Simulation	Experiment	Simulation	Experiment	Simulation	Experiment
7.0	75	0	0	332	259	66	0	304	307
8.0	74	0	0	544	287	22	0	299	313
9.5	91	0	0	559	425	52	0	362	384
10.0	82	12	0	676	340	0	0	328	348
12.0	9	64	4	0	60	0	0	33	17
14.6	2	4	2	0	32	0	0	3	0

381

382 Finally, the model was used to calculate the amount of wollastonite needed to be consumed
383 before the destabilization of MCPM. This amount increased with the initial H_3PO_4
384 concentration (Figure 11), which can explain why the heat flow peak, associated with the
385 conversion of MCPM into monetite, was experimentally delayed when the phosphoric acid
386 concentration increased.



387

388 Figure 11: Fraction of wollastonite needed to be dissolved to destabilize MCPM.

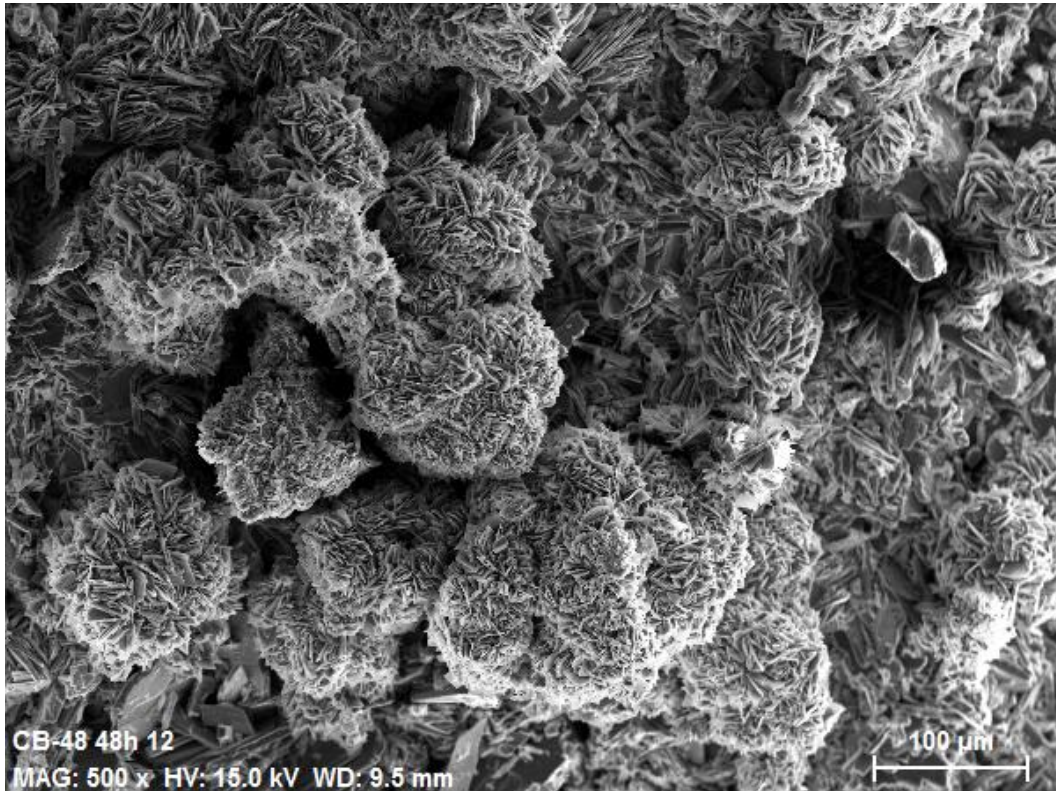
389

390 3.2.4. Mechanical strength

391 After 28 d of curing at room temperature in sealed bag, the paste samples prepared with the
392 the different H_3PO_4 concentrations were still very friable. Several visual aspects indicated a
393 poor mechanical behaviour such as cracks at the surface of samples and swelling. This was
394 confirmed by measuring their compressive strength: all the results were below 1 MPa, which
395 means that the sole presence of phosphoric acid in the mixing solution did not make it possible
396 to get a hardened paste with good mechanical properties (tests were repeated several time to
397 make sure this was not an experimental bias). This poor mechanical behaviour likely resulted
398 from a very porous microstructure. SEM observation of a 2 d-old fracture (the hydration did
399 not progress a lot afterwards) of paste $\text{P}_{1.24/9/0.76}$ showed the presence of platelet crystals,
400 assigned to monetite, and agglomerated into nodules, with large voids between the nodules

401 (Figure 12). Metallic cations, present in the mixing solution of commercial cements, thus play
402 a key role in the consolidation process of the material.

403



404

405 Figure 12: SEM observation of a fracture of paste sample PXXX after 2 d of hydration.

406

407 **3. Conclusion**

408

409 Brushite cements can be prepared by mixing wollastonite with a phosphoric acid solution
410 usually containing boric acid or sodium borate (some retarders) and metallic cations (Zn^{2+} , Al^{3+} ,
411 Mg^{2+} ...). However, the influence of the mixing solution composition on the setting and
412 hardening process still needs to be clarified. In this work, dedicated to simplified systems
413 comprising only wollastonite and phosphoric acid solutions of variable concentrations, three
414 parameters were more particularly investigated: the Ca/P molar ratio, the H_3PO_4 initial

415 concentration, and the l/s weight ratio. Note that these parameters are correlated: setting the
416 Ca/P ratio and H_3PO_4 concentration defines for instance the l/s ratio.

417 At constant H_3PO_4 concentration, the Ca/P ratio, correlated to the l/s ratio, not only
418 influenced the hydration rate, but also the nature of the products formed during hydration. The
419 higher the Ca/P ratio (and the lower the l/s ratio), the faster the start of hydration, but the smaller
420 the fraction of wollastonite reacting, and the smaller the amount of dicalcium phosphate
421 (anhydrous or dihydrate) formed. Moreover, the precipitation of more basic calcium
422 orthophosphates (octacalcium phosphate and hydroxyapatite) occurred at high Ca/P ratio
423 (1.92). The type of dicalcium phosphate precipitating depended on the thermal history of the
424 sample: a high self-heating resulted in the formation of monetite (CaHPO_4) instead of brushite
425 ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).

426 At constant l/s ratio ($0.76 \text{ mL} \cdot \text{g}^{-1}$), increasing the H_3PO_4 concentration in the range 7 to 10
427 $\text{mol} \cdot \text{L}^{-1}$ (and thus decreasing the Ca/P ratio from 1.52 to 1.14) delayed cement hydration. After
428 the transient precipitation of monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), both
429 brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and monetite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) formed. Their total amount, as well as
430 the fraction of depleted wollastonite, reached a maximum for a $9.5 \text{ mol} \cdot \text{L}^{-1}$ H_3PO_4
431 concentration. Setting the H_3PO_4 concentration within the range 9 - 10 $\text{mol} \cdot \text{L}^{-1}$ could thus be
432 recommended: hydration was not too fast and a large amount of dicalcium phosphate was
433 formed under these conditions. At more elevated H_3PO_4 concentrations ($\geq 12 \text{ mol} \cdot \text{L}^{-1}$), setting
434 was inhibited, and the heat production remained very low, indicating limited dissolution of
435 wollastonite. Monocalcium phosphate monohydrate was the only product formed. Its
436 conversion into dicalcium phosphate did not occur because of the too strong acidity of
437 interstitial solution ($\text{pH} \approx 1$).

438 The different phase assemblages obtained experimentally as a function of the H_3PO_4
439 concentration, Ca/P and l/s ratios were rather well reproduced by thermodynamic modelling.

440 Finally, it should be outlined that the consolidation of the pastes after setting remained rather
441 limited: their compressive strength did not exceed 1 MPa after 28 d of curing under sealed bag
442 at room temperature. Metallic cations and borax or boric acid, present in the mixing solution of
443 commercial cements, must thus play a key role in the hardening process of the material. Future
444 work should thus investigate their influence into more details.

445

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448

449 **References**

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