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1 **Laboratory assessment of the contribution of aggressive to concrete chemical compounds to the**  
2 **degradation of Portland cement-based materials during anaerobic digestion**

3 Marie Giroudon<sup>1, 2, \*</sup>, Matthieu Peyre Lavigne<sup>2</sup>, Cédric Patapy<sup>1</sup>, and Alexandra Bertron<sup>1</sup>

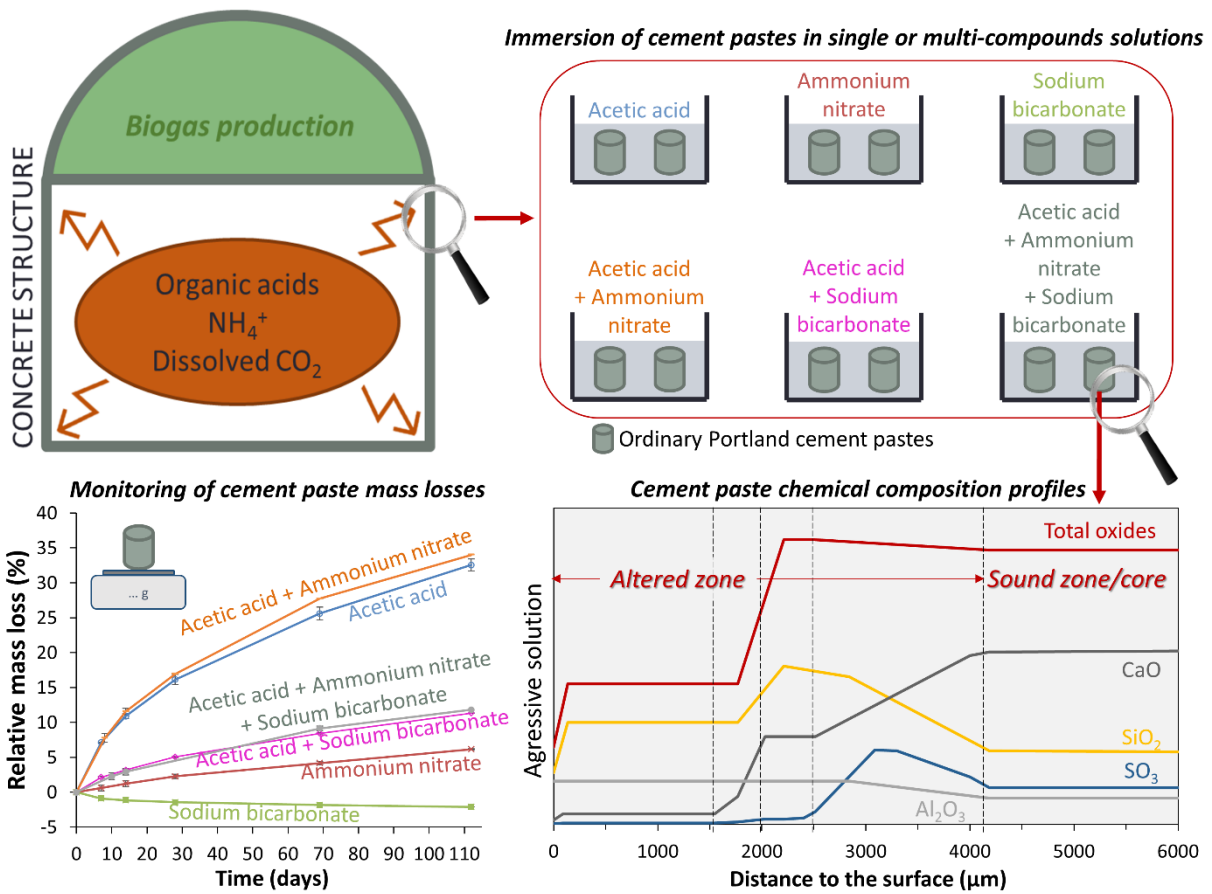
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7 **Graphical abstract**

8



9

10

11 **Abstract**

12 Anaerobic digestion allows renewable energy to be produced through the degradation of bio-waste.  
13 The process, which is of economic and ecological interest, is implemented industrially in concrete  
14 digesters. Bio-waste is a complex medium with a composition that can vary in time and space. It  
15 contains several chemical compounds, including volatile fatty acids, ammonium, and CO<sub>2</sub>, which are  
16 aggressive towards concrete and compromise its durability. The individual effects of the different  
17 compounds on concrete are significantly different. To move toward a better design of concrete  
18 intended for the building of biogas digesters, this paper aims to understand the mechanisms and  
19 intensity of alteration associated with the different components of biowaste and their contribution to  
20 the total deterioration. Ordinary Portland cement pastes were immersed for 16 weeks in six synthetic

21 solutions made of the three metabolites, taken alone or in mixes. The mass variations of the  
22 specimens, the pH, and the concentration of the chemical elements in solution were monitored over  
23 time. The microstructural, chemical and mineralogical changes of the samples were analysed by  
24 scanning electron microscopy, electron probe micro-analysis and X-Ray diffraction analyses and  
25 showed phenomena of dissolution, leaching and carbonation. The results show that the acetic acid  
26 solution was the most aggressive, in accordance with its pH value, and had a predominant effect in  
27 mixed solutions, whereas sodium bicarbonate solution induced carbonation and showed a protective  
28 effect. Interestingly, despite its reputed high aggressiveness, ammonium nitrate did not have a major  
29 impact in mixed solutions.

30 Keywords: cement, anaerobic digestion, leaching, acetic acid, ammonium nitrate, sodium bicarbonate

## 31 **1 Introduction**

32 Anaerobic digestion is a biological process allowing the degradation of organic matter into biogas and  
33 digestate by the action of microorganisms. The biogas, mainly composed of methane (CH<sub>4</sub>) and carbon  
34 dioxide (CO<sub>2</sub>) [1–3], can be used in many ways, the most common being cogeneration (75 % of current  
35 French installations [4]), which consists of the combined production of heat and electricity. However,  
36 France is now turning towards injection into the natural gas network, which allows higher yields [5].  
37 As one of the most environmentally friendly technologies for bioenergy production [6,7], biogas  
38 production is supported by the European Union and more than 300 anaerobic digestion plants are  
39 being built each year in Europe [8].

40 Most anaerobic digestion structures are built with concrete because this material is economic, air- and  
41 watertight and thermally insulating. The digesters contain two parts: (i) the lower zone (liquid/solid  
42 phase) where the successive degradation reactions of hydrolysis, acidogenesis, acetogenesis and  
43 methanogenesis [9,10] degrade the biowaste into smaller molecules and (ii) the upper zone containing  
44 the biogas produced, and where the walls are generally protected by polymeric liners [11]. In the liquid  
45 phase, the digestion of biowaste generates complex and multicomponent environments and  
46 deterioration of cementitious materials has been observed in pilot plants and in laboratory tests, in  
47 the relatively short term [12–16]. This aggressiveness towards concrete is mainly due to the presence  
48 of three chemical compounds, associated with the presence of microorganisms in the form of biofilm:  
49 volatile fatty acids (VFA), ammonium cation and dissolved CO<sub>2</sub> are considered to be very aggressive to  
50 concrete and their concentrations can vary greatly with time and according to the inoculum and  
51 substrate [17,18].

52 Studies considering the deterioration of cement matrices in fermenting biowaste [13–16] have shown  
53 that, for different biowaste/inoculum pairs - and therefore different liquid medium compositions - the  
54 intensity and the alteration kinetics are variable, and the degradation is not always a result of the  
55 predominant effect of the same metabolite. Although the deterioration induced by each chemical  
56 metabolites has been investigated in the literature [19–24], experiments were not necessarily carried  
57 out with parameters corresponding to those encountered in the liquid medium of anaerobic digestion  
58 (e.g. data is available for very high concentrated ammonium nitrate solutions and atmospheric  
59 carbonation). Finally, the individual effects of each aggressive component, and especially their  
60 combined effects in the degradation of concrete by the complete medium, are poorly understood.

61 In this context, this study aims to understand the mechanisms and intensity of alteration associated  
62 with the different components of biowaste and their contributions to the total deterioration. It is thus  
63 a question of better understanding the deterioration mechanisms in anaerobic digestion structures  
64 and reviewing the normative context.

## 65 2 Materials and methods

66 Cement paste specimens made of ordinary Portland cement (OPC) were immersed in six chemically  
67 aggressive solutions for 16 weeks. The pH, the mass losses and the concentration of elements in  
68 solution were monitored over time. Scanning electron microscopy observations coupled with electron  
69 probe micro-analysis, and X-Ray diffraction analyses were used to characterize the chemical and  
70 mineralogical changes occurring in the samples.

### 71 2.1 OPC paste

72 There are no precise recommendations on the choice of cement for anaerobic digestion facilities in  
73 the normative texts. In agricultural construction in general, other documents issue recommendations  
74 to cement such as CEM II or CEM III [25–28]. The choice of cements varies according to the country,  
75 without a single, consensual practice being implemented.

76 Therefore, CEM I-based matrix was used in order to carry out a generic study on the comparative  
77 mechanisms and kinetics of attack of different chemical compounds. It should be noted that binders  
78 substituted with supplementary cementing materials, containing less portlandite, are more sensitive  
79 to carbonation [29–31] whereas OPC are more sensitive to leaching in acidic environments [14,32–34].  
80 This work can be used as a basis for the study of all Portland cement-based matrices such as materials  
81 based on CEM II, CEM III, CEM IV and CEM V cements, the use of which is recommended for agricultural  
82 constructions [25–28].

83 CEM I 52.5R (OPC) pastes were made with a water/cement ratio of 0.30 and mixed according to a  
84 procedure adapted from the French Standard NF EN 196-1 [35] without adding sand: low speed ( $140$   
85  $\pm 5$  rpm) for 60 seconds and high speed ( $285 \pm 10$  rpm) for 90 seconds. This low water/cement ratio  
86 was chosen to minimize the porosity and the penetration of aggressive agents into the material. The  
87 specimens were cast in cylindrical plastic moulds 70 mm high and 35 mm in diameter, which were  
88 closed with plastic caps. After a 28-day endothermic cure and just before the experiment, each cylinder  
89 was sawn at half height in order to obtain two cylinders about 35 mm high and 35 mm in diameter.  
90 The water porosity of the OPC paste was measured according to the NF P18-459 standard [36] and was  
91 32.0 %.

### 92 2.2 Synthetized aggressive solutions

93 Three single compound-based solutions were prepared: an acetic acid solution representing attack by  
94 VFAs (called AA solution), an ammonium nitrate solution representing the attack by ammonium cation  
95 (called AN solution) and a sodium bicarbonate solution representing the attack of dissolved CO<sub>2</sub> (called  
96 SB solution). An acetic acid solution was chosen to represent the VFA attack since all VFAs (carboxylic  
97 acids with less than 5 carbon atoms) have equivalent effects on the cement matrix because their  
98 chemical characteristics are similar (pKa and high solubility of their calcium salts) [34,37]. The acid  
99 concentration was set to 300 mmol.L<sup>-1</sup>, slightly higher than the value of 280 mmol.L<sup>-1</sup> used by Bertron  
100 et al. [34] and representative of the higher ranges of VFA concentration found in agricultural effluents  
101 [38]. For a functional digester, the VFA concentrations can vary from 40 to 250 mmol.L<sup>-1</sup> [39–41] and  
102 these concentrations can exceed 500 mmol.L<sup>-1</sup> in the case of acidosis [42]. The concentration of the  
103 ammonium nitrate solution was chosen according to a previous study of anaerobic digestion in a  
104 laboratory set-up [13], where the authors found an ammonium concentration of about 800 mg.L<sup>-1</sup> and  
105 also correspond to the values conventionally encountered in industrial digesters since the  
106 concentrations of ammonium ions range between a few hundred mg.L<sup>-1</sup> and several g.L<sup>-1</sup> [43,44]. The  
107 sodium bicarbonate concentration was chosen in order to represent a gas phase with 50 % of CO<sub>2</sub>  
108 (calculated using Henry's law at 35 °C, at atmospheric pressure and for a pH of 7.5), which is slightly  
109 higher than the proportion of CO<sub>2</sub> in optimal condition for biogas production [45–47] but which is a

110 coherent portion with non-optimal conditions for biogas production. Thus, conditions in the high range  
111 of aggressiveness were chosen to accentuate the degradation. The solutions were prepared with  
112 demineralized water as follows:

- 113 • AA solution was a 300 mmol.L<sup>-1</sup> acetic acid solution (glacial acetic acid 99.8-100.5 %, AnalaR®  
114 NORMAPUR – VWR)
- 115 • AN solution was a 44.4 mmol.L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> solution (industrial ammonium nitrates, 99.0 %  
116 minimum of NH<sub>4</sub>NO<sub>3</sub>, Orange Label Ammonium Nitrate, MAXAM Tan)
- 117 • SB solution was a 243 mmol.L<sup>-1</sup> NaHCO<sub>3</sub> solution (food grade sodium bicarbonate, 99.0-100.5  
118 % NaHCO<sub>3</sub>, NOVACARB)

119 Furthermore, solutions combining several chemical compounds together in the same concentrations  
120 as above were also studied in order to highlight the contribution of each chemical compound in terms  
121 of degradation and aggressiveness mechanisms and to identify combined mechanisms. These solutions  
122 were as follows:

- 123 • AA+AN solution was a 300 mmol.L<sup>-1</sup> acetic acid and 44.4 mmol.L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> solution
- 124 • AA+SB solution was a 300 mmol.L<sup>-1</sup> acetic acid and 243 mmol.L<sup>-1</sup> NaHCO<sub>3</sub> solution
- 125 • AA+SB+AN solution was a 300 mmol.L<sup>-1</sup> acetic acid, 243 mmol.L<sup>-1</sup> NaHCO<sub>3</sub> and 44.4 mmol.L<sup>-1</sup>  
126 NH<sub>4</sub>NO<sub>3</sub> solution

127 As the volume of buffer solution to be added was significant (especially in the case of the AA solution),  
128 it was chosen not to buffer the solutions, in order to avoid addition of chemical compounds that could  
129 possibly interact with the OPC paste.

### 130 **2.3 Test methods**

131 For each type of solution, four samples were added to 2.5 L which corresponds to a liquid/solid ratio  
132 of about 1/17 and a surface area/volume ratio of about 97 cm<sup>2</sup>.L<sup>-1</sup>. These values were chosen in  
133 accordance with previous studies [34,38,48] to allow comparison. The solutions were kept at 20 °C in  
134 closed plastic containers. The pH was measured regularly once the solution was homogenized (daily at  
135 the start of the experiment and several times a week thereafter). As soon as the pH of one of the  
136 solution exceeded 8.6 (upper limit of anaerobic digestion conditions), a few mL of each solution was  
137 sampled for further analyses and all containers were emptied to receive fresh solution. The  
138 experiments lasted 16 weeks (112 days). On average, the solutions were renewed every 2.5 (± 1.4)  
139 days.

140 Two of the four samples from the container were dedicated to mass change monitoring and the other  
141 two to the microstructural analyses of the materials.

142 The compositions of the liquid samples were analysed by inductively coupled plasma/optical emission  
143 spectroscopy (ICP/OES) (Optima 7000DV ICP/OES Perkin Elmer) (Si, Na, K, Ca, Al, Fe) and high  
144 performance ion chromatography HPIC (Dionex ICS-300) (SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>).

145 Mass variations were monitored over time: the samples were removed from the solutions, the excess  
146 liquid was quickly removed with absorbent paper and, after 5 minutes in the open air, the samples  
147 were weighed. After 4 weeks, 10 weeks, and at the end of the experiment, the upper edge of one  
148 sample was carefully sawn with a diamond saw and then split in half. One part was used for X-Ray  
149 diffraction analysis (XRD) (Bruker D8 Advance, Cu anti-cathode, 40 kV, 40 nA) and the other part was  
150 embedded in epoxy resin (Mecaprex Ma2+, Presi) and dry polished using silicon carbide polishing disks  
151 (Presi) (polishing disc references and grain sizes: ESCIL, P800–22 µm, P1200–15 µm and P4000–5 µm).  
152 The flat polished sections were then coated with carbon and analysed by Electron Probe Micro-Analysis

153 (EPMA) (Cameca SXFAA+SBe, 15 kV, 20 nA). The chemical composition changes were characterized  
154 using chemical profiles, from the surface to the core according to the distance to the surface. Each  
155 plotted graph contains values from two experimental profiles in the same specimen. Particular care  
156 was taken to analyse hydrated paste and not residual anhydrous grains. The following elements were  
157 taken into account in the selection of microprobe: Ca, Si, Al, Fe, S, Mg, Na and K.

158 To assess mineralogical changes, the plane side of the slice was first analysed, and the sample was then  
159 successively abraded and analysed in order to characterize deeper zones, until the sound paste was  
160 reached [48].

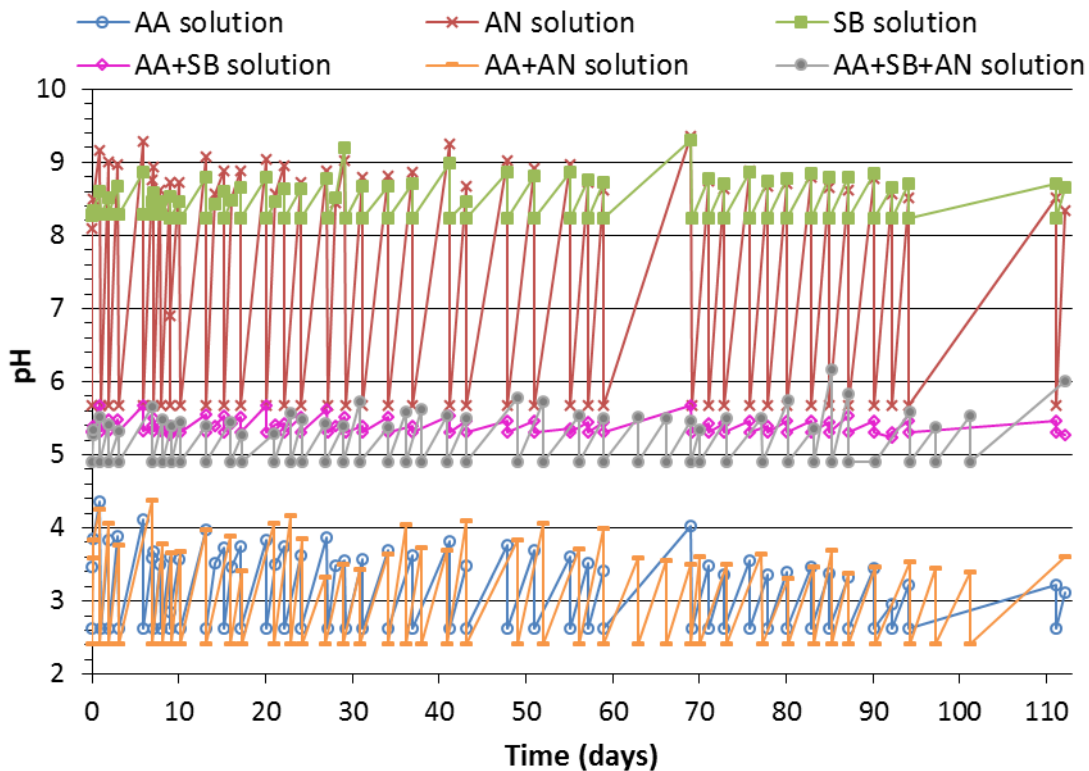
### 161 3 Results

#### 162 3.1 pH evolution

163 Figure 1 shows the evolution of the pH of the solutions over time. Each drop in pH corresponds to a  
164 renewal of the solutions.

165 The pH ranges differ quite significantly depending on the nature of the aggressive solution (Figure 1):

- 166 - AA and AA+AN solutions have the lowest pH, with fairly strong variations of between 2.4 and  
167 4;
- 168 - the AA+SB+AN solution has an intermediate pH range with slight variations (between 4.9 and  
169 5.5);
- 170 - the AA+SB solution is the solution showing the smallest variations in pH, since the values are  
171 between 5.3 and 5.5, which reflects a strong buffering capacity of the solution;
- 172 - unlike the other solutions, the AN solution exhibits strong variations in pH, between 5.6 and  
173 9, reflecting the low buffering capacity of this solution;
- 174 - the SB solution has the highest initial pH and the pH variations are between 8.2 and 9.



175

176 Figure 1: pH evolution of the solutions according to time of immersion (AA: acetic acid, AN: ammonium nitrate, SB: sodium  
177 bicarbonate)

### 178 3.2 Total leaching of chemical elements in the solutions

179 Table 1 brings together the cumulative mass of elements leached in solution, per sample, at the end  
180 of the experiment. The cumulated concentrations and leaching kinetics are given as supplementary  
181 data (Appendix A).

182 Table 1: Cumulative leached ions per cement paste sample in the solutions during the experiment (AA: acetic acid, AN:  
183 ammonium nitrate, SB: sodium bicarbonate). \*concentrations cannot be provided with sufficient precision, see text.

	Cumulative leached ion from the specimens (mmol)						
	Calcium	Silicon	Aluminium	Sulfate	Iron	Potassium	Sodium
AA solution	423 ± 46	15.6 ± 1.7	9.1 ± 1	2.2 ± 0.2	3.5 ± 0.4	7.1 ± 0.8	2.9 ± 0.3
AN solution	166 ± 18	5.1 ± 0.6	0.0 ± 0	0.5 ± 0.1	0.0 ± 0	5.3 ± 0.6	2.1 ± 0.2
SB solution	0.0 ± 0	1.2 ± 0.1	0.0 ± 0	0.0 ± 0	0.0 ± 0	4.1 ± 0.4	-*
AA+AN solution	415 ± 46	17.8 ± 2	9.0 ± 1	0.8 ± 0.1	3.1 ± 0.3	7.8 ± 0.9	7.8 ± 0.9
AA+SB solution	137 ± 15	3.2 ± 0.3	0.0 ± 0	1.7 ± 0.2	0.0	5.0 ± 0.6	-*
AA+SB+AN solution	185 ± 20	5.4 ± 0.6	0.0 ± 0	0.6 ± 0.1	0.0	6.9 ± 0.8	-*

184

185 It was not possible to precisely quantify the variations of sodium concentration in SB, AA+SB and  
186 AA+SB+AN solutions since the concentrations of sodium were originally very high in solution, and the  
187 variations in the measured concentrations were not large enough to be significant.

188 Solutions containing acetic acid and no sodium bicarbonate, i.e. AA and AA+AN, were the most  
189 aggressive in terms of leaching, with slightly lower amounts measured for the AA+AN solution  
190 compared to the AA one: in both solutions, greater amounts of calcium (mean value of the two samples  
191 of about 419 ± 5.1 mmol), silicon (17 ± 1.6 mmol) and sulfates (2 ± 0.3 mmol) were found. Moreover,  
192 these solutions were the only ones to generate aluminium (9 ± 0.1 mmol) and iron (3 ± 0.3 mmol)  
193 leaching, which might be related to their low pH. The decreasing order of ion release in both solutions  
194 was as follows:  $Ca^{2+} > Si^{4+} > Al^{3+} > K^+ > Fe^{3+} > SO_4^{2-}$ .

195 Solutions of ammonium nitrate AN, and acetic acid containing bicarbonate with or without ammonium  
196 nitrate, AA+SB and AA+SB+AN, were less aggressive and showed intermediate leaching values for  
197 calcium (163 ± 25 mmol), silicon (5 ± 1.2 mmol), sulfates (1 ± 0.1 mmol), and potassium (1 ± 1.2 mmol).  
198 These solutions did not lead to iron and aluminium leaching within the duration of the experiment.  
199 The decreasing order of ion release in both solutions was as follows:  $Ca^{2+} > Si^{4+} > SO_4^{2-}$  and  $K^+$ .

200 Sodium bicarbonate solution SB was the least aggressive and only small amounts of potassium (4.1  
201 mmol) and silicon (1.2 mmol) were released. There is therefore a relative release of the ions as follows:  
202  $K^+ > Si^{4+}$ .

### 203 3.3 Macroscopic observations of specimens

204 Figure 2 shows the macroscopic aspects of the samples at the end of the immersion experiments.



205

206 *Figure 2: (A) Visual appearance of the samples' surfaces at the end of the experiment and (B) visual appearance of the slices*  
 207 *of the samples AA+AN and AA+SB+AN at the end of the experiment (AA: acetic acid, AN: ammonium nitrate, SB: sodium*  
 208 *bicarbonate)*

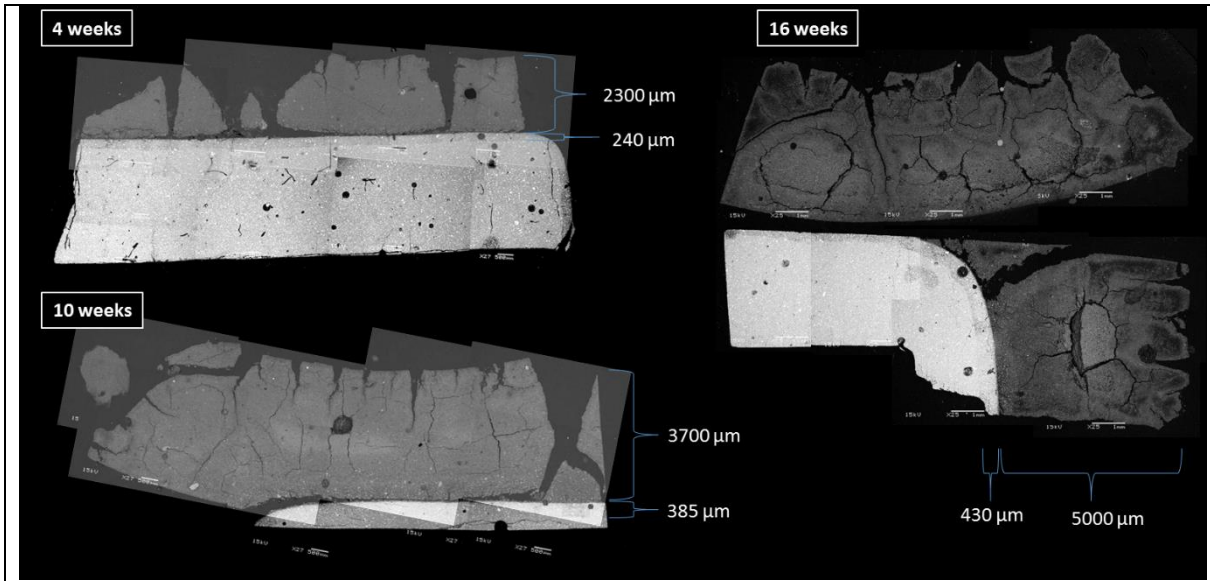
209 Samples immersed in solutions containing acetic acid (AA, AA+SB and AA+SB+AN) showed an orange  
 210 colour because the intense decalcification of the cement matrix allowed the expression of the iron  
 211 oxide colour. For the AA, AA+SB and AA+SB+AN solutions, a dense crack network was observed when  
 212 these samples were taken out of the solutions and left to dry on a bench. This cracking was related to  
 213 chemical shrinkage as a result of calcium being leached from the sample in large quantities. Figure 2  
 214 shows that the coloured zonation is a function of the distance to the exposed surface. Finally, the  
 215 colour is preserved for the cement paste exposed to the sodium bicarbonate (SB) solution, whereas  
 216 the sample immersed in the ammonium nitrate (AN) solution shows a slight orange colouring, without  
 217 cracking.

### 218 3.4 Microstructural observations

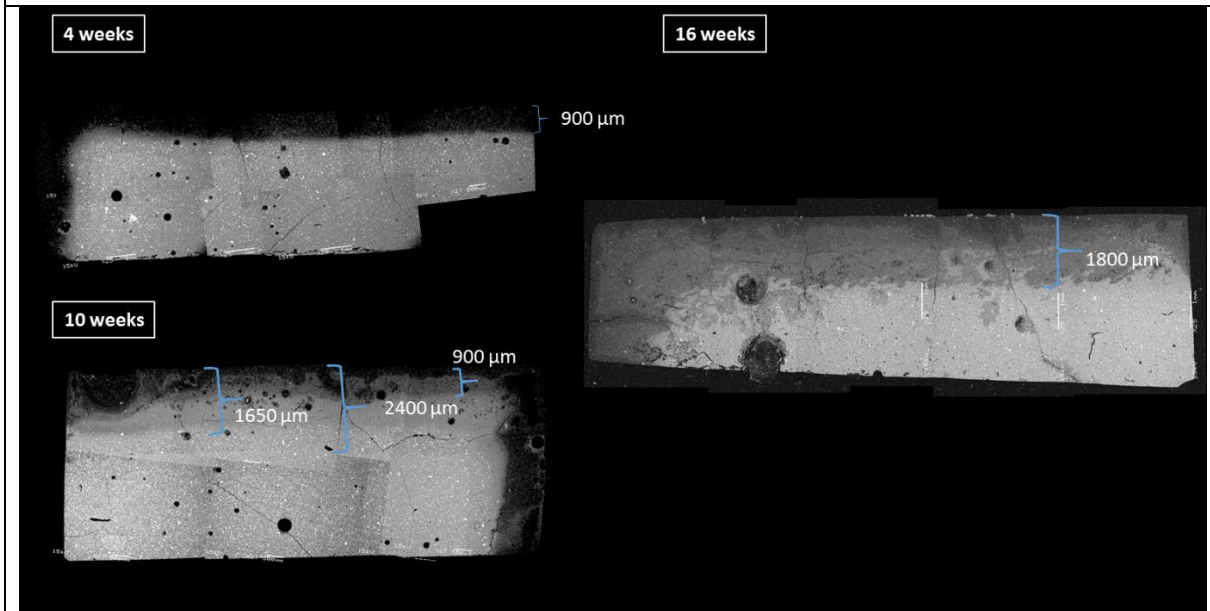
219 Figure 3 shows the SEM images of the OPC samples after 4 weeks or 10 weeks of immersion in the  
 220 aggressive solutions and at the end of the experiment (16 weeks). Since the samples immersed in the  
 221 SB solution did not show any significant changes, the SEM images are only shown for 10 weeks and 16  
 222 weeks. Moreover, it should be noted that, on the same sample, the difference in density between the  
 223 degraded zone and the sound core was sometimes so great that the two zones could not be correctly  
 224 observed with the same contrast. Some of the images presented are therefore an assembly of two  
 225 images with different contrasts.

AA solution

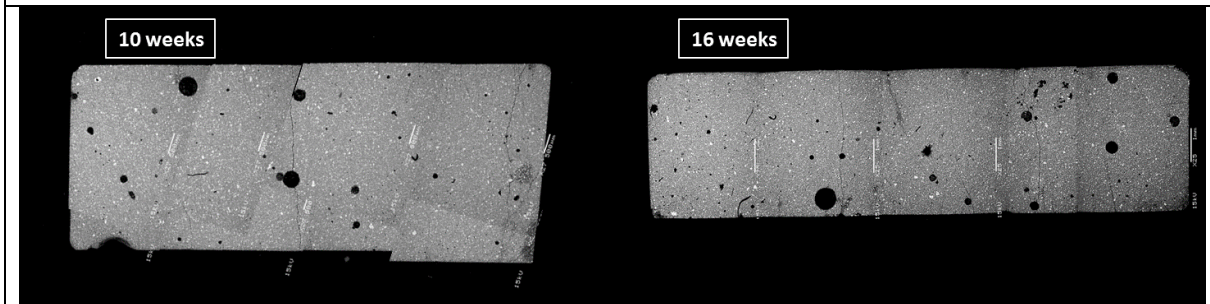




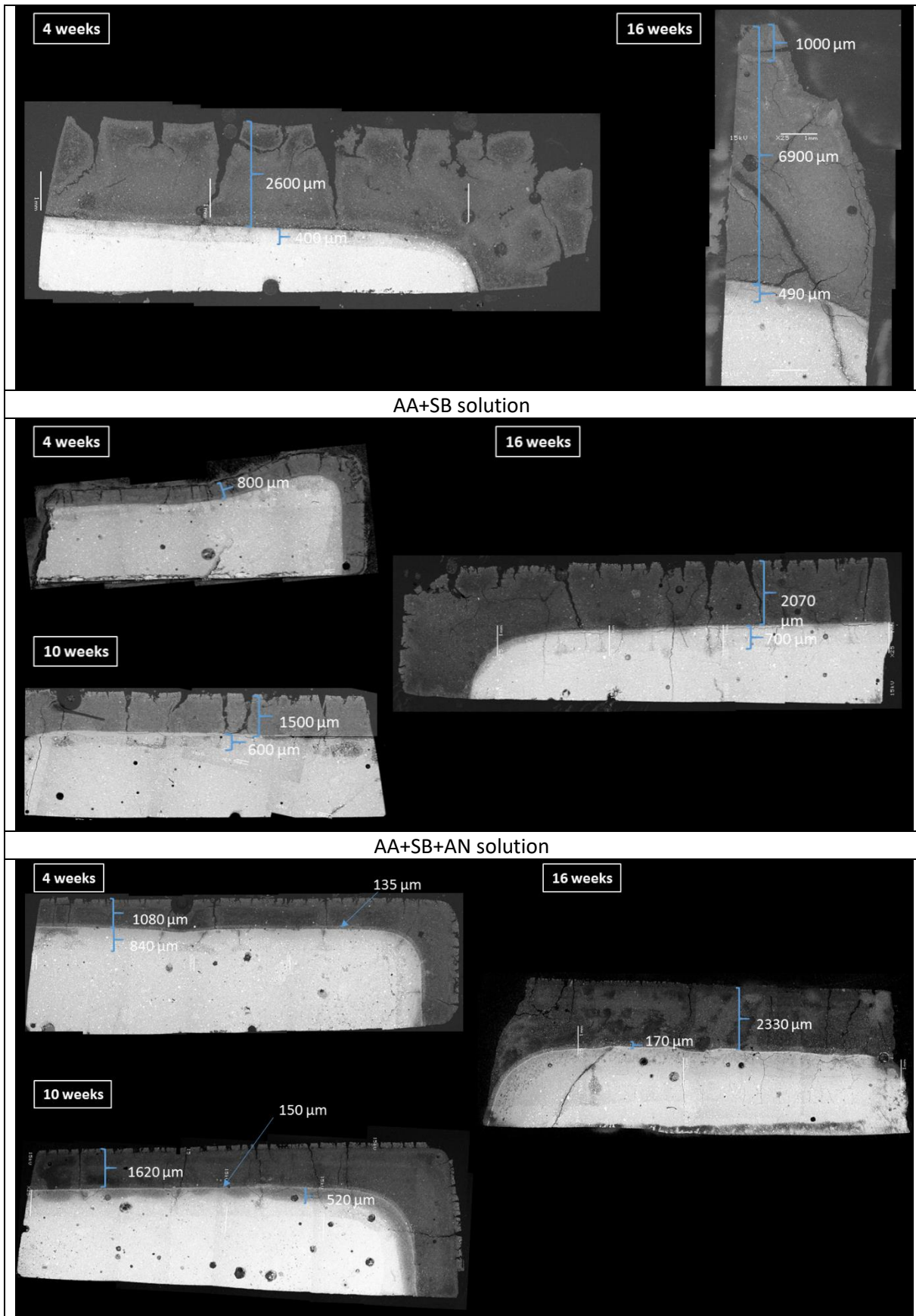
AN solution



SB solution



AA+AN solution



226 Figure 3: SEM images of OPC paste samples immersed in the different aggressive solutions after 4 weeks, 10 weeks and 16  
 227 weeks (AA: acetic acid, AN: ammonium nitrate, SB: sodium bicarbonate). Approximate magnification: x25. Some of the images  
 228 are an assembly of two images with different contrasts.

229 From the macroscopic and microscopic observations, three types of microstructural patterns can be  
230 observed:

- 231 • In the presence of acetic acid, the samples show an outer degraded zone (hereafter called the  
232 degraded zone) of very low density, yellowish to brownish in colour (Figure 2), friable and  
233 subject to desiccation shrinkage for the samples removed from the bins and dried before  
234 observation (very porous zone) (see Figure 2, samples AA, AA+SB, AA+AN and AA+SB+AN). The  
235 cracking observed on wet samples is related to the chemical shrinkage associated with the  
236 departure of the ions. This area has a completely different structure from the sound paste: the  
237 anhydrous grains are no longer visible and it has very low mechanical strength, as pointed out  
238 by several authors in studies on acetic, lactic or succinic acids [33,34,49]. Below the degraded  
239 zone, a thinner area appears, slightly darker than the sound core, and therefore slightly less  
240 dense. In this area, anhydrous cement grains can still be observed. The limits between the  
241 different zones are clear and the fronts are parallel to the surface. The degraded zone tends  
242 to detach from the rest of the sample when dry.
- 243 • Samples exposed to the AN solution show an outer zone of lower density, with a non-  
244 rectilinear limit between the sound core and the zone of lower density. The attack by AN being  
245 much less aggressive than that of acetic acid, the diffusive phenomena might take a higher  
246 part in the deterioration pattern compared to acid attack that creates a sharp front of  
247 cementitious matrix dissolution. The heterogeneous microstructure of the cement matrix in  
248 terms of pores, air voids and microcracks provides preferential routes for the ingress of the AN  
249 solution, leading to this irregular deterioration front.
- 250 • For samples exposed to the SB solution, no change is clearly visible on the SEM images,  
251 whether after 4, 10 or 16 weeks. However, an intensification of the calcium signal could be  
252 seen on the surface on the EDS maps (not shown here).

253 On samples exposed to both acetic acid and sodium bicarbonate (AA+SB and AA+SB+AN), there is a  
254 thin cracked outer layer with a slightly higher density than that of the degraded part just below.

### 255 **3.5 Mass variations and degraded layer depths**

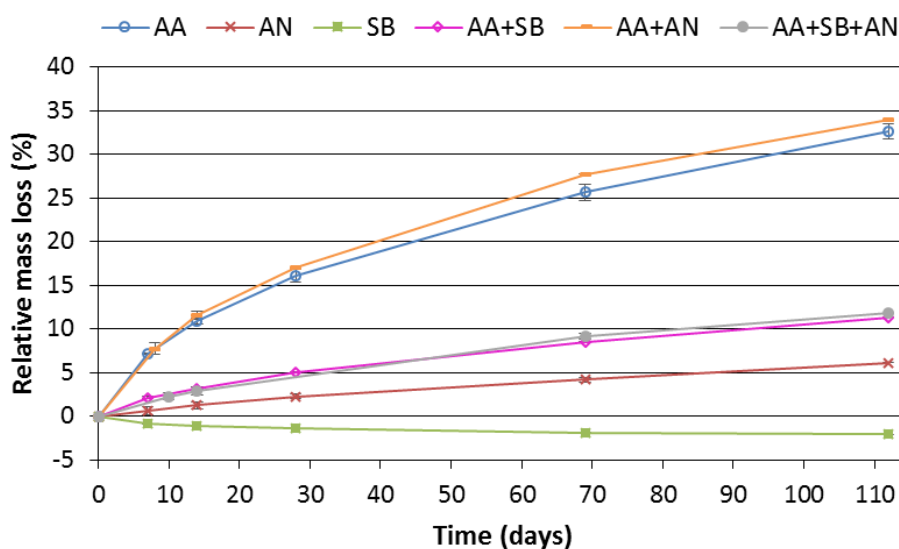
256 Figure 4 shows the evolution of the mass variations of the OPC paste in the different solutions and  
257 Figure 5 the degraded layer depths, obtained from the SEM observations presented in Figure 3. After  
258 112 days of immersion, the OPC paste is seen to have undergone a significant mass loss of about 33 %  
259 for the AA and AA+AN solutions, with a slightly more severe attack for the AA+AN solution. Conversely,  
260 a mass gain of 2.1 % is observed when the OPC paste is immersed in the bicarbonate sodium solution.  
261 The other solutions have an intermediate aggressiveness. The lowest mass losses (6.1 %) are observed  
262 for the AN solution (ammonium nitrate only) whereas the immersion in the AA+SB and AA+SB+AN  
263 solutions leads to similar higher mass losses of about 11.5 % at the end of the experiment. Based on  
264 these results, it is observed that ammonium nitrate is much less aggressive to the cement matrix than  
265 acetic acid is, and sodium bicarbonate appears to provide a protective effect when it is present in  
266 solution with acetic and/or ammonium nitrate. In mixtures, the additional effect of ammonium nitrate  
267 in terms of aggressiveness appears almost negligible. It can be noted that the mass variation  
268 classification is unsurprisingly consistent with the pH of the solutions (Figure 1): the AA and AA+AN  
269 solutions have identical pH values and mass losses and the same is true for the AA+SB and AA+SB+AN  
270 solutions. The AN and SB solutions are those exhibiting the highest pH and the lowest mass losses.  
271 Beyond the aggressiveness of the metabolites, there is therefore also an effect of acidity on  
272 degradation.

273 In all the solutions, the mass loss kinetics are higher in the first weeks, and tend to slow over time. This  
274 could be due to the slowing down of the penetration of aggressive agents into the cement matrix

275 because of the greater depth of paste to cross (diffusion). It can also be noted that, in view of the  
276 cylindrical geometry of the samples, a smaller and smaller volume of paste is degraded as the  
277 aggressive agents penetrate.

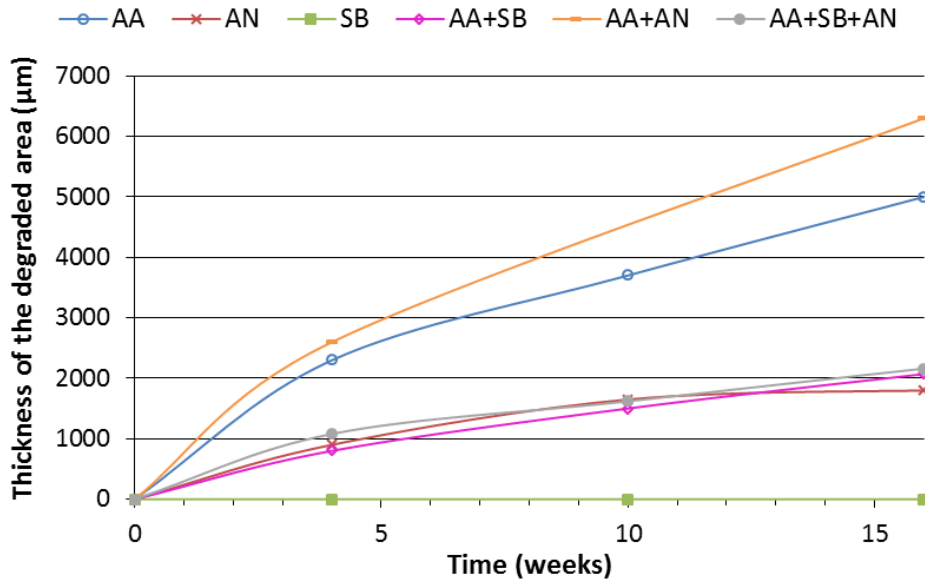
278 Except for the AN solution, for which it is difficult to precisely identify the different areas of degradation  
279 and their evolution (see Table 1), there is a clear increase in the thickness of the degraded area over  
280 time, with a similar evolution for the AA and AA+AN solutions and for the AA+SB and AA+SB+AN  
281 solutions. This evolution is correlated with the mass losses shown in Figure 4, and with the pH. The  
282 aggressive trend shown by the mass losses is confirmed since, at the end of the experiment, the  
283 degraded depths (measured with SEM images) reached thicknesses of 0  $\mu\text{m}$ , 1800  $\mu\text{m}$ , 2070  $\mu\text{m}$ , 2330  
284  $\mu\text{m}$ , 5000  $\mu\text{m}$  and 6900  $\mu\text{m}$  respectively for the SB, AN, AA+SB, AA+SB+AN, AA and AA+AN solutions. It  
285 is interesting to note that the deteriorated layer thicknesses of cement pastes exposed to solutions  
286 containing AN, AA + AN and AN, are relatively larger than those observed in other solutions when their  
287 relative aggressiveness in terms of mass losses is considered.

288



289

290 *Figure 4: Mass losses of the OPC paste according to the time of immersion in the aggressive solutions (AA: acetic acid, AN:*  
291 *ammonium nitrate, SB: sodium bicarbonate)*



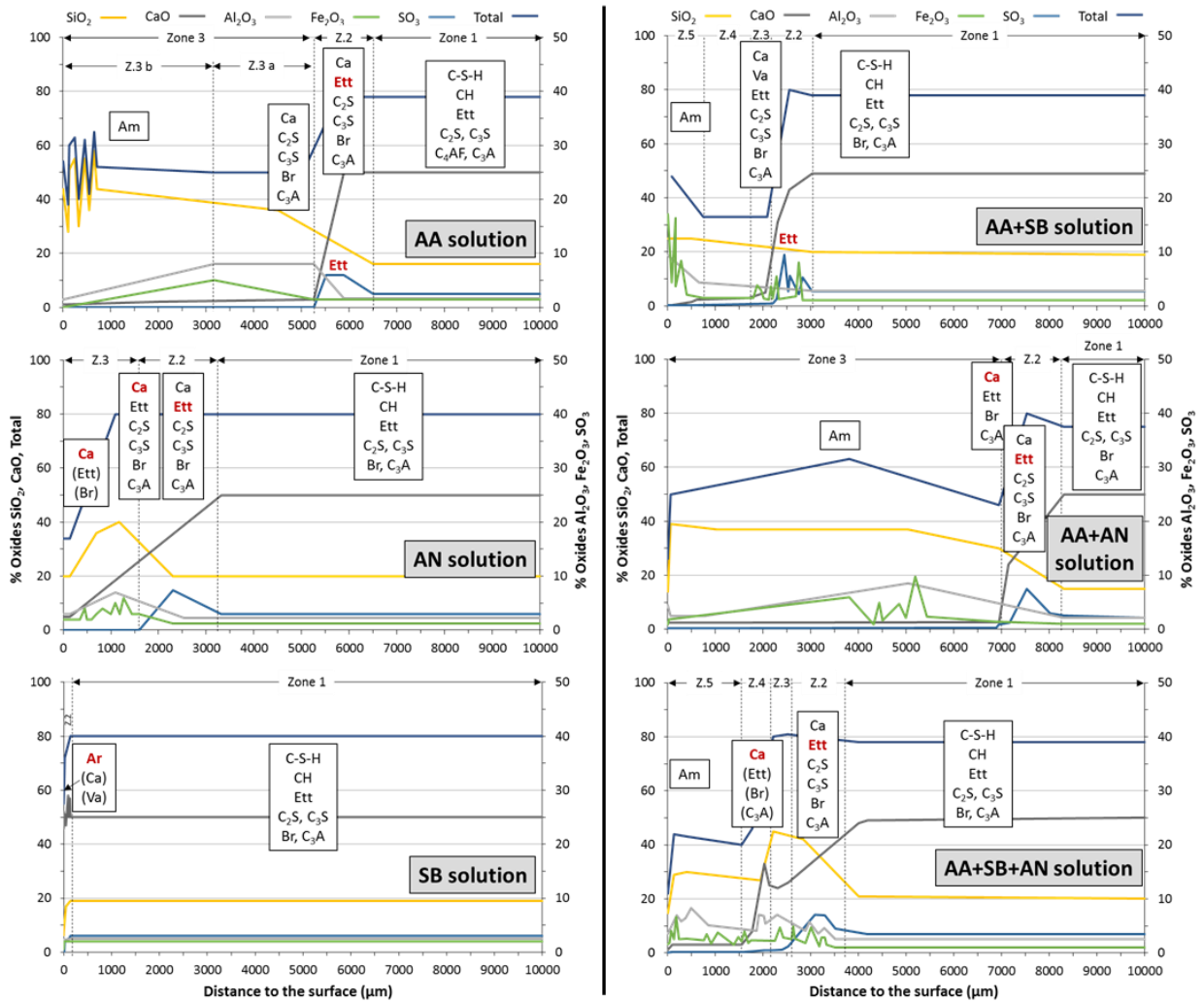
292

293 *Figure 5: Evolution of the degraded depth of the samples (from SEM observations) over time according to the aggressive*  
 294 *solution (AA: acetic acid, AN: ammonium nitrate, SB: sodium bicarbonate)*

295 **3.6 Chemical and mineralogical changes**

296 Figure 6 shows the major chemical and mineralogical changes in the OPC pastes immersed in the  
 297 synthetic solutions for 16 weeks. The data are given in amounts of oxides according to the distance to  
 298 the surface. Thus, the sum of all the oxide amounts (Total) gives indications about the deterioration of  
 299 the cement paste. For greater clarity, the profiles of chemical compositions were modelled and only  
 300 the main trends are represented. The original plots are given as supplementary data (Appendix B). The  
 301 main patterns of the mineralogical analysis by XRD obtained at different depths by successive abrasion  
 302 of the degraded surface have been added on the same figure. The original diffractograms of the  
 303 samples immersed in the AA, AN and SB solutions are given as supplementary data (Appendix C,  
 304 Appendix D and Appendix E). The chemical and mineralogical zonation is represented on the graphs.  
 305 The core of the specimens with the same composition as the unexposed control specimens is noted  
 306 zone 1 for all the materials.





307

308 *Figure 6: Schematic representations of chemical composition of oxides and mineralogical composition (analysed by EPMA and*  
 309 *XRD, respectively) of the OPC pastes after 16 weeks of immersion in the aggressive chemical solutions (AA: acetic acid, AN:*  
 310 *ammonium nitrate, SB: sodium bicarbonate) – Ett: ettringite; Ca: calcite; Va: vaterite; Br: brownmillerite; Am: mainly*  
 311 *amorphous pattern – Red bold characters = intensification of the XRD signal in comparison with the deeper zone; Parentheses*  
 312 *= significantly lower intensity of the XRD signal in comparison with the main phase*

### 313 3.6.1 AA solution

314 Zone 1 (the sound zone) contains typical phases of a Portland paste (portlandite, ettringite,  
 315 brownmillerite,  $C_3A^1$ ,  $C_3S$  and  $C_2S$ ). The EPMA chemical analysis shows a thick degraded zone of 6400  
 316  $\mu\text{m}$  (zone 2 + zone 3) with a total and sharp decalcification of the paste occurring in zone 2. From a  
 317 mineralogical point of view, this zone shows the dissolution of the portlandite and the precipitation of  
 318 calcite. A slight enrichment in ettringite may be associated with the increase of the sulfur content.  
 319 Zone 3 shows an amorphization of the paste, with a predominantly amorphous outer zone more than  
 320 4 mm thick. It consists of an amorphous aluminium-silicate skeleton containing iron: in zone 3.a, the  
 321 aluminium, iron and silicon contents show a relative increase due to the significant decrease in the  
 322 calcium content and there is then a gradual decrease in aluminium and iron in zone 3.b. The outer  
 323 surface is made of silica gel only.

<sup>1</sup> Cement chemistry shorthand notations: A =  $Al_2O_3$ , C = CaO, F =  $Fe_2O_3$ , H =  $H_2O$ , M = MgO, S =  $SiO_2$

324 3.6.2 AN solution

325 Beyond 3100  $\mu\text{m}$  (zone 1), the paste seems unaltered, with a chemical composition corresponding to  
326 a sound OPC paste. The EPMA chemical analysis shows a very gradual decalcification from 3100  $\mu\text{m}$   
327 depth (start of zone 2) with no sharp drop in the calcium content, reflecting a less aggressive attack  
328 than for the AA solution. Zone 2 is characterized by the dissolution of portlandite and an enrichment  
329 in sulfur content, associated with the intensification of the ettringite peaks. Calcite precipitation is  
330 detected. From 2500  $\mu\text{m}$ , the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents increase whereas the sulfur content  
331 decreases. The  $\text{SO}_3$  content reaches 0 % in zone 3 and the  $\text{SiO}_2$  content and the total oxides content  
332 decrease from 1150  $\mu\text{m}$  onwards. The paste chemical composition is stable over the last 100  $\mu\text{m}$ ,  
333 where only the brownmillerite phase and some ettringite remain from the initial composition of the  
334 OPC paste, and calcite is the main phase (zone 3).

335 3.6.3 SB solution

336 The chemical composition of the OPC paste immersed in SB solution changed very little after 16 weeks  
337 of immersion. Only a thin external layer about 50  $\mu\text{m}$  thick (zone 2) shows changes, with a decrease in  
338 the total oxides content (from 80 % to 55 %) as well as a decrease in each oxide content except for  
339 calcium oxide, which remains around 50 %. The stable calcium content is might be due to the  
340 phenomena of dissolution and precipitation of calcium carbonates, since the only detected phases of  
341 the outer layer are carbonation products: mainly aragonite, but also calcite and vaterite

342 3.6.4 AA+AN solution

343 The specimen in the AA+AN solutions shows the greatest degraded depth, significantly greater than in  
344 AA, contrary to what the mass loss suggested. The chemical changes are similar to those of the  
345 specimen in the AA solution but with a greater degraded depth. Decalcification occurs in zone 2: it  
346 starts from 8100  $\mu\text{m}$  depth and is complete at 7000  $\mu\text{m}$  depth. This decalcification is less sharp than in  
347 AA solution and extends over more than a millimetre, as for the immersion in AN solution, while the  
348 drop in the total oxide content occurs suddenly at a depth of about 7000  $\mu\text{m}$ . As for other solutions  
349 containing acetic acid, a sulfur enrichment associated with the intensification of the ettringite X-ray  
350 diffraction peaks is observed in zone 2, just before this element is completely leached out. The total  
351 oxides content drops from 80 % to 40 % between 7200 and 6800  $\mu\text{m}$ . Then, zone 3 is made of  $\text{Al}_2\text{O}_3$ ,  
352  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  up to 1000  $\mu\text{m}$  deep but only  $\text{SiO}_2$  remains on the surface.

353 3.6.5 AA+SB solution

354 The EPMA analysis of the OPC paste immersed in AA+SB solution shows a chemical composition similar  
355 to that resulting from the acetic acid attack, with a smaller degraded depth than for the AA solution.  
356 Zone 2 shows a sudden drop in calcium oxide as well as total oxides and sulfur enrichment. It is marked  
357 by the dissolution of portlandite and the intensification of the ettringite peaks. Calcium carbonates,  
358 calcite and vaterite, are detected. There is no longer any  $\text{SO}_3$  in zone 3 but the paste is not completely  
359 decalcified, which could be linked to the precipitation of calcium-rich phases in this zone. The  
360 mineralogical analysis shows the dissolution of the initial phases of the paste in favour of calcium  
361 carbonate, calcite and vaterite, for which intensity of the peaks increases. In zone 4, the cement matrix  
362 is decalcified, with a total oxide content of less than 40 %. In this solution, compared with the AA  
363 solution, the aluminium and iron oxides are better preserved in the outer layer, resulting in a smaller  
364 relative increase in the silica content. As for the AA solution, the outer zone (zone 4) is completely  
365 amorphous and the surface is composed of a Si-Fe-Al gel. The increase in the total oxide content is  
366 observed in the outer 400  $\mu\text{m}$  due to the increase in the  $\text{Fe}_2\text{O}_3$  content.

367 3.6.6 AA+SB+AN solution

368 The EPMA chemical analyses of the OPC paste immersed in AA+SB+AN solution show a progressive  
369 decalcification (as for AN solution) from 3500 to 2100  $\mu\text{m}$  (zones 2 and 3) and a sharper decalcification

370 (as for AA solution) from 2000  $\mu\text{m}$  to 1750  $\mu\text{m}$ . Zone 2 shows an enrichment in the  $\text{SO}_3$  content  
371 associated with more intense ettringite peaks in the XRD analysis. Zone 3 is marked by the stabilization  
372 of the calcium content, probably due to the precipitation of calcium carbonates (main phases detected  
373 by DRX analyses). This induces a high total oxides content, an effect that is much more significant in  
374 this solution, in the presence of AN, than for the AA+SB solution. Zone 4 shows the decrease of the  
375  $\text{SiO}_2$  and CaO contents, associated with the drop of the total oxides content. The external layer (zone  
376 5) is made of an Si-Al gel. The external layer of this specimen is mainly amorphous but weak peaks of  
377 brownmillerite are detected.

## 378 **4 Discussion**

### 379 **4.1 Phenomenology**

380 According to the mass losses and the degraded depths identified in the EPMA analyses, the solutions  
381 studied in these conditions can be classified in increasing order of aggressiveness (considering the  
382 modified depth): SB solution < AN solution < AA+SB solution < AA+SB+AN solution < AA solution <  
383 AA+AN.

#### 384 *4.1.1 Degradation by acetic acid alone*

385 The degradation mechanisms of the OPC paste immersed in AA solution were those classically  
386 encountered in acid attacks for acids whose calcium salts are soluble in water [37]:

- 387 • A progressive dissolution of all the initial phases of the cement paste
- 388 • Significant mass losses
- 389 • A degraded area almost totally decalcified and made of aluminium, silicon and iron. This  
390 completely amorphous structure was similar to that of a silica gel and / or a silico-aluminous  
391 gel.

392 Moreover, as in the study by Bertron et al. [48], a slight sulfur enrichment was observed just in the  
393 transition zone between the amorphous outer zone and the sound zone, corresponding to the  
394 intensification of the ettringite peaks.

395 Calcium and sulfates were the most leached elements (Table 1), and were not found in the amorphous  
396 outer layer (Figure 6).

397 As in the study by Bertron et al. [48], the altered zone had weaker mechanical strength but was not  
398 dissolved and could have slowed down the ingress of aggressive agents into the core of the sample.

399

#### 400 *4.1.2 Degradation by ammonium nitrate alone*

401 According to the literature [22,50], ammonium salts are aggressive for the cement matrix and react  
402 according to an exchange mechanisms  $2 \text{NH}_4^+ \rightarrow \text{Ca}^{2+}$ , leading to the leaching and decalcification of the  
403 cementitious matrix [24], the degradation being governed by diffusion [23]. Highly concentrated  
404 ammonium nitrate solutions (6 mol.L<sup>-1</sup> or more) are thus used to provide accelerated tests of pure  
405 water leaching [21,51–53]. Both pure water and ammonium nitrate solution lead to the total  
406 dissolution of portlandite and the decalcification of C-S-H, and to a sulfur enrichment in the degraded  
407 area, the difference being that the kinetics of the degradation in the ammonium nitrate solution are  
408 60 to 300 times higher than in deionized water [51,54–56]. The ammonium nitrate solution attack  
409 creates an external degraded zone [21,52,53] and induces a significant increase in the porosity [23,52].  
410 Moreover, the C/S of the C–S–H decreases and the porosity and the diffusivity increase when the  
411  $\text{NH}_4\text{NO}_3$  concentration in the immersion solution is increased [57,58].



412 In this study, a low concentration of ammonium nitrate solution was used ( $4.44 \text{ mmol.L}^{-1}$ ) in order to  
413 reproduce the anaerobic digestion conditions. In this context, the ammonium nitrate attack resulted  
414 in the progressive decalcification of the paste with the dissolution of the Ca-bearing phases (CH and C-  
415 S-H) and led to surface carbonation. The carbonation might be due to the presence of dissolved  $\text{CO}_2$   
416 (from the air) in solution. It probably slowed down the progression of the attack by clogging the  
417 porosity [59,60]. As for AA solution, sulfates and calcium were the most leached elements but they  
418 were in lower concentrations. However, the amount leached out was lower than for the AA solution,  
419 which is consistent with the smaller degraded depths and mass losses of these samples, as well as the  
420 decalcification - which was only progressive in the degraded zone, whereas it was total over the entire  
421 area for the AA solution. Unlike during the acid attack, the iron remained in the outer layer.

#### 422 4.1.3 Degradation by the sodium bicarbonate alone

423 After 16 weeks, the OPC paste immersed in sodium bicarbonate solution remained intact except in a  
424 thin outer layer composed only of carbonation products: calcite, vaterite and aragonite. These samples  
425 were the only ones to show mass gains, linked to the carbonation layer deposited on the surface.  
426 Above a pH of 8, when the pH increases, the equilibrium of bicarbonate to carbonate ions is shifted  
427 towards carbonate ( $\text{pKa}_1 (\text{H}_2\text{CO}_3/\text{HCO}_3^-) = 6.30$ ;  $\text{pKa}_2 (\text{HCO}_3^-/\text{CO}_3^{2-}) = 10.33$ ). In the sodium bicarbonate  
428 solution, the pH was between 8 and 9 during the experiment (Figure 1) and was certainly higher in  
429 contact with the OPC paste. Thus, the carbonate ions in contact with  $\text{Ca}(\text{OH})_2$  led to calcium carbonates  
430 precipitation. Among the elements analysed, only silicon and potassium were leached in small amount.  
431 It can be noted that the amount of leached potassium was lower than in the other solutions, whereas  
432 in the other solutions this element was leached in similar quantities, whatever the solution  
433 aggressiveness. Thus, it seems that the sodium bicarbonate solution limits the leaching by clogging the  
434 porosity with calcium carbonates [59,60]. Whereas calcite is known to be the most stable polymorph  
435 of calcium carbonates under ambient atmospheric conditions [61], the external layer of the paste was  
436 mainly made of aragonite (metastable phase) and also contained vaterite (unstable phase) in small  
437 amounts (solubility product at  $25^\circ\text{C}$ :  $\log K_{sp} = -8.48, -8.34$  and  $-7.91$ ; molar volume:  $35 \text{ cm}^3.\text{mol}^{-1}$ ,  $34$   
438  $\text{cm}^3.\text{mol}^{-1}$  and  $38 \text{ cm}^3.\text{mol}^{-1}$  for calcite, aragonite and vaterite, respectively [62,63]). According to  
439 several authors [64–66], the  $\text{Na}^+$  ion has no effect on the polymorph formed. However, pure aragonite  
440 phases can be synthesized by adding sodium carbonate  $\text{Na}_2\text{CO}_3$  to a  $\text{Ca}(\text{OH})_2$  solution in controlled  
441 conditions [67,68]. According to Kitamura et al. [68], the aragonite content increases when the  
442 addition rate of sodium carbonate decreases, and for a high addition rate, calcite preferably  
443 precipitates. The authors specify that, if the concentration of calcium ions is at or near the solubility of  
444  $\text{Ca}(\text{OH})_2$ , the low local supersaturation of carbonate ion is advantageous for the crystallization of  
445 aragonite. This phenomenon could explain the presence of aragonite in the external layer of the paste.  
446 Furthermore, the presence of vaterite may be related to the lower pH of the external layer, since, at  
447 ambient temperature, vaterite precipitates for  $\text{pH} < 10$  [69,70].

448 The formation of calcium carbonates, reflecting the carbonation phenomenon, is known to be a major  
449 risk of corrosion in reinforced concrete, by depassivation of reinforcements [71]. Moreover, the  
450 carbonation phenomenon could be even more detrimental for concrete with blended cement: the use  
451 of supplementary materials leads to a decrease in the portlandite content for the benefit of C-S-H,  
452 whereas the carbonation of C-S-H results in significant shrinkage, loss of cohesion, increase in the  
453 number of pores and increased porosity [72–75].

454

#### 455 4.1.4 Degradation by the combined solutions

#### 456 **Acetic acid combined with the other aggressive compounds**

457 The degradation mechanisms of the cement paste immersed in the AA+AN, AA+SB and AA+AN+SB  
458 solutions can be explained by the combination of the degradation phenomena caused by the  
459 aggressive agents in solution but the intensity and kinetics of the attack are mainly related to the AA  
460 attack. The structural degradations and the chemical composition profile of these cement pastes are  
461 similar to those of the cement paste immersed in the AA solution, although differences can be noted:  
462 acetic acid leads to the leaching of all the elements, significant mass losses and degraded depths.

#### 463 **Ammonium nitrate combined with the other aggressive compounds**

464 In the AA+AN and AA+SB+AN solutions, the presence of ammonium nitrate increased the degraded  
465 depths and intensified the degradations, but in a moderate way with a relative increase in mass loss  
466 of 4% and of 24 % in degraded depth for the AA+AN solution compared to the AA solution. In the  
467 AA+AN solution, a sudden decalcification was observed as for an acid attack, combined with a more  
468 gradual decalcification in depth, probably linked to the presence of ammonium nitrate. The quantities  
469 of elements released in this solution were similar to those in AA solution, except for sodium and  
470 sulfates: it appears that the presence of ammonium nitrate accentuates the sodium leaching and the  
471 global degradation, while limiting the sulfates leaching.

472 For the AA+SB+AN solution, despite the periodic renewals of the solution, which is the most influential  
473 factor for the aggressiveness of an ammonium nitrate solution of given concentration [76], the  
474 presence of ammonium nitrate in such concentration did not seem to significantly increase the  
475 degradation. If we compare the degradation of the cement paste immersed in the AA+SB solution and  
476 that immersed in the AA+SB+AN solution, it can be observed that the presence of ammonium nitrate  
477 increased the mass loss of the sample only slightly: in the presence of ammonium nitrate, some  
478 elements were more leached (calcium, potassium and silicon) and it was again observed that the  
479 leaching of sulfates was limited. The degraded depth was still greater for the AA+SB+AN solution, and  
480 is linked to the greater leaching of calcium and silicon, major compounds of the cement matrix.

481 No exchange mechanism  $2 \text{NH}_4^+ \rightarrow \text{Ca}^{2+}$  was highlighted since the  $\text{NH}_4^+$  concentration was measured  
482 and remained constant at about  $800 \text{ mg.L}^{-1}$  throughout the experiment.

#### 483 **Sodium bicarbonate combined with the other aggressive compounds**

484 In the AA+SB solution, the presence of sodium bicarbonate seems to protect the cement matrix since  
485 the amount of leached elements is much smaller and iron and aluminium remain on the surface. The  
486 effect of the SB solution is probably associated, at least partially, with an effect on the pH of the AA+SB  
487 solution (initial pH of 5.3), significantly greater than that of the AA solution alone (initial pH of 2.6). The  
488 mass loss is also lower than for the AA solution but is still significant. Calcium carbonates (calcite and  
489 vaterite) were not found on the surface but in depth (zone 3) where the conditions were favourable  
490 to precipitation while more of the material was completely decalcified in the surface. Once again, the  
491 presence of vaterite in the external carbonated zone was probably linked to a  $\text{pH} < 10$ .

492 In the AA+AN+SB solution, the lower intensity of the degradation compared to AA+AN solution  
493 confirms the protective effect of the sodium bicarbonate. Smaller degraded area and mass loss are  
494 observed. The presence of sodium bicarbonate prevents the leaching of aluminium and iron, elements  
495 leached only in the presence of acetic acid and in the absence of sodium bicarbonate. In addition, the  
496 presence of sodium bicarbonate greatly reduces the amounts of calcium, sulfates and silicon leached  
497 out. In this solution, carbonation occurs in depth (zone 3), just before the transition zone containing  
498 the sulfur enrichment (zone 2). Its effect on the chemical composition is more significant than in the  
499 case of the AA+SB solution. In addition, the presence of sodium bicarbonate in the AA+SB+AN solution  
500 induces an initial pH of the solution which is significantly higher (4.9) than for the AA+AN solution (2.4).

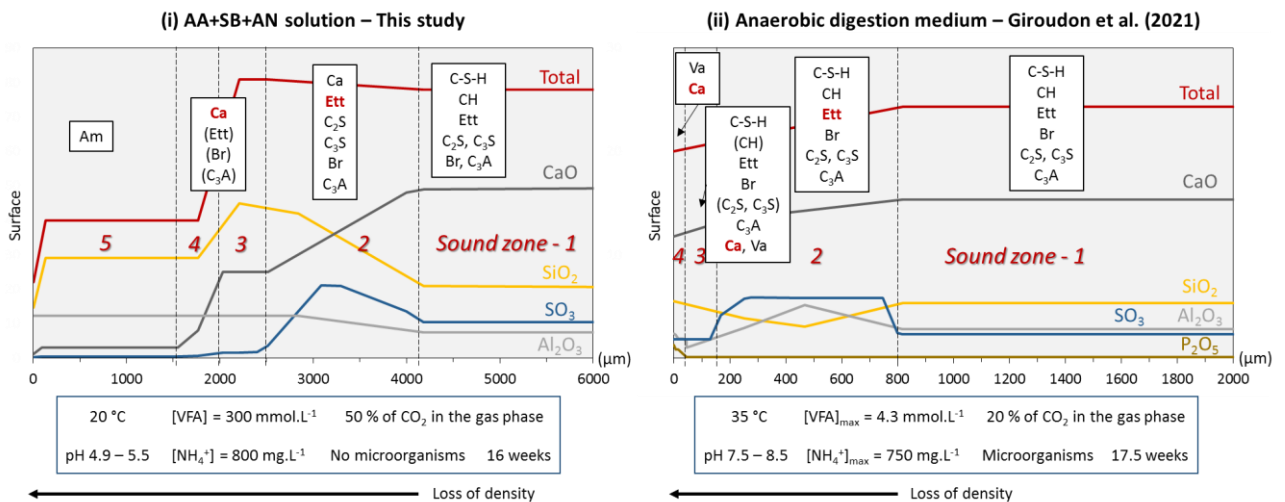
501 **4.2 Comparison with real anaerobic digestion liquid media**

502 The previous results can be compared with the study by Giroudon et al. [13] where OPC pastes  
 503 (water/cement = 0.30) were immersed in the liquid media of anaerobic digestion in bioreactors. In the  
 504 liquid containing the OPC pastes, the maximum concentrations of aggressive agents encountered were  
 505 0.26 g.L<sup>-1</sup> (4.3 mmol.L<sup>-1</sup> if only acetic acid is considered) of VFA, 770 mg.L<sup>-1</sup> of NH<sub>4</sub><sup>+</sup> and about 2000  
 506 mg.L<sup>-1</sup> of inorganic carbon content (or about 20 % of CO<sub>2</sub> in the gas phase). Thus, the materials used  
 507 are comparable with the present study but the concentration ranges are significantly (VFA and CO<sub>2</sub>) or  
 508 slightly (NH<sub>4</sub><sup>+</sup>) higher than the ranges encountered in the study in a real environment. This could be  
 509 expressed by a higher intensity of degradation.

510 Figure 7 summarizes the main chemical and mineralogical changes in the OPC pastes exposed to (i) the  
 511 synthetic AA+SB+AN solution for 16 weeks and (ii) a real anaerobic digestion medium for 17.5 weeks  
 512 [13], together with exposure conditions and degraded depths. In both studies, the total degradation  
 513 was expressed by the dissolution of the initial phases (zones 4 and 5), the decalcification of the  
 514 cementitious matrix associated with a sulfur enrichment and the precipitation of secondary ettringite  
 515 (zone 2). The presence of dissolved CO<sub>2</sub> led to the carbonation of the paste, with the precipitation of  
 516 calcite and vaterite (zones 3 and 4).

517 However, the degradation intensity (altered depth, decalcification, loss of density, mass loss, etc.) was  
 518 much lower in the real environment since the degraded depth in the AA+SB+AN solution (about 4000  
 519 μm from zone 2 to the surface) was about 5 times that in the bioreactors (about 800 μm from zone 2  
 520 to the surface), mostly due to the high concentration of acetic acid in the synthetic solutions, and could  
 521 correspond to real conditions in an industrial digester. Thus, no significant mass loss was detected in  
 522 the experiment of Giroudon et al. [13], neither was any external amorphous structure. An external  
 523 amorphous Si-Al gel was, however, identified in studies by Voegel et al. [15,16], where the authors  
 524 studied the biodeterioration phenomena of cementitious pastes (water/cement = 0.40) in the  
 525 submerged part of a digester using typical food biowaste. Thus, the degradation intensity is strongly  
 526 dependent on the evolution of the medium, the type of substrates used and, especially, how the  
 527 associated process is run. For example, with a rapidly hydrolysable substrate fed continuously using a  
 528 constant charge, there will be no accumulation of VFA and therefore no pH drop.

529 In addition, an external phosphorus enrichment has been observed in real media [12,13,15,16], where  
 530 this element was probably brought by the substrate [16].



531  
 532 *Figure 7: Schematic representations of chemical composition of oxides and mineralogical variations (analysed by EPMA and*  
 533 *XRD, respectively) of OPC pastes exposed to (i) a synthetic solution of acetic acid, sodium bicarbonate and ammonium nitrate*

534 for 16 weeks and (ii) a real anaerobic digestion liquid medium for 17.5 weeks [13]. Ett: ettringite; Ca: calcite; Va: vaterite; Br:  
535 brownmillerite; Am: mainly amorphous pattern – Red bold characters = intensification of the XRD signal in comparison with  
536 the deeper zone; Parentheses = significantly lower intensity of the XRD signal in comparison with the main phase.

### 537 **4.3 Normative context**

538 In order to quantify the chemical aggressiveness of an environment toward concrete and to design  
539 durable structures, the European standard EN 206/CN [26] and the French information document FD  
540 P 18-011 [25] classify environments chemically using three classes of increasing aggressiveness: XA1,  
541 XA2 and XA3. For this purpose, the concentration and presence of some aggressive agents are taken  
542 into account: the aggressive carbon dioxide concentration (aggressive CO<sub>2</sub>), the sulfate concentration  
543 (SO<sub>4</sub><sup>2-</sup>), the magnesium ion concentration (Mg<sup>2+</sup>), the ammonium ion concentration (NH<sub>4</sub><sup>+</sup>), the pH, and  
544 the water hardness.

545 According to this study, some inconsistencies can be noted. Whereas both AN and AA solutions are  
546 considered to be highly aggressive ([NH<sub>4</sub><sup>+</sup>] $\gg$ 100 mg.L<sup>-1</sup> and pH $\ll$ 4 for AN and AA solutions  
547 respectively), it appears that the AN solution was much less aggressive than the AA solution. Moreover,  
548 the AA+SB solution is classified XA2 because of its initial pH (5.32), whereas this solution led to a higher  
549 aggressiveness than the AN solution (XA3).

550 Thus, it might be relevant to consider not only the pH but also the concentration of organic acids in  
551 solution, since the pH is not suitable to describe their aggressiveness [38,77]. In addition,  
552 recommended cements (such as blast-furnace slag cements) should also be tested.

## 553 **5 Conclusion**

554 This study assessed the contribution of different aggressive agents to the global degradation of OPC  
555 pastes during anaerobic digestion. In the current experimental conditions:

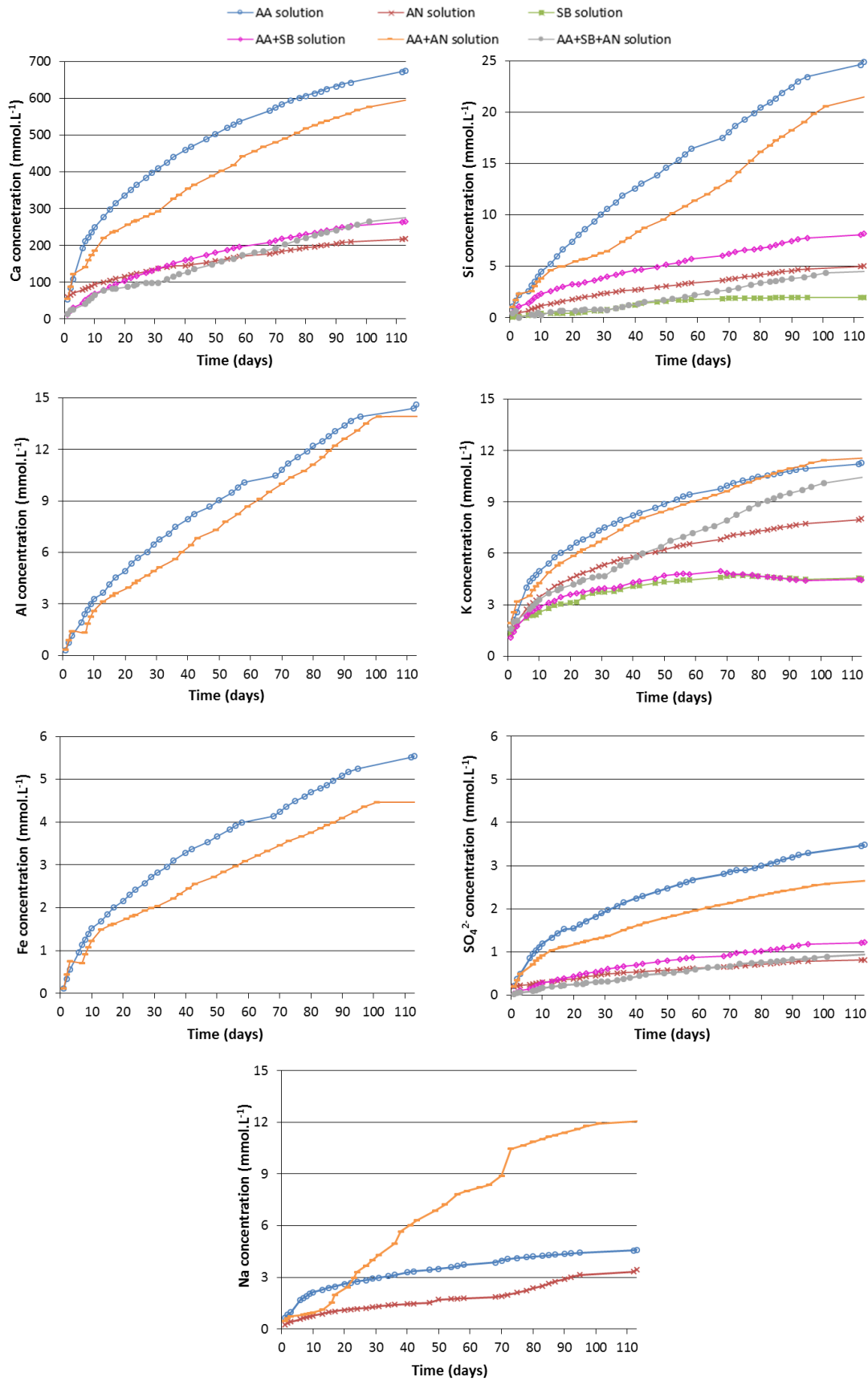
- 556 • Despite the different deterioration mechanisms specific to each aggressive agent, the pH plays  
557 an important role in the aggressiveness of the solutions studied.
- 558 • Immersion in an acetic acid solution led to sharp and total decalcification of the cementitious  
559 matrix, with large mass loss and degraded depth. In mixed solutions, acetic acid had a  
560 preponderant effect, which led to the total decalcification of the degraded zone, with the  
561 appearance of a well-marked structural, mineralogical and chemical zonation.
- 562 • The attack by the ammonium nitrate solution expressed itself by a progressive decalcification,  
563 with significant mass loss and degraded depth. However, in mixed solution, ammonium nitrate  
564 has a negligible effect, even if the concentration used (800 mg.L<sup>-1</sup>) is much higher than the  
565 maximum concentration range considered by standards EN 206 and FD P18-011 for chemically  
566 aggressive environments (XA3 class: 60 to 100 mg.L<sup>-1</sup> of NH<sub>4</sub><sup>+</sup> ion in solution) [25,26].
- 567 • By clogging the porosity through carbonation and increasing the pH of the solution though its  
568 strong buffering capacity, the sodium bicarbonate solution provides a protective effect when  
569 combined with other aggressive agents. However, its effect is not preponderant since the  
570 pastes remain highly degraded when acetic acid is present. The significant carbonation in these  
571 environments induces a risk of corrosion for reinforced concrete structures.
- 572 • While maintaining qualitatively comparable deterioration characteristics, the high  
573 concentrations used for the synthetic chemical solutions led to an intensification of the  
574 degradation compared to the laboratory environment.
- 575 • The normative context does not allow accurate quantification of a solution's aggressiveness  
576 for OPC based material, especially in the presence of organic acids.
- 577 • Modelling work allowing the pH to be adjusted while various concentrations are being studied  
578 would bring new knowledge about the action of each aggressive metabolite on the concrete

579 attack. Finally, this could also be useful for other structures that house complex biological  
580 processes, such as wastewater treatment plants that involve anaerobic digestion, among other  
581 treatments [78].

## 582 **6 Acknowledgements**

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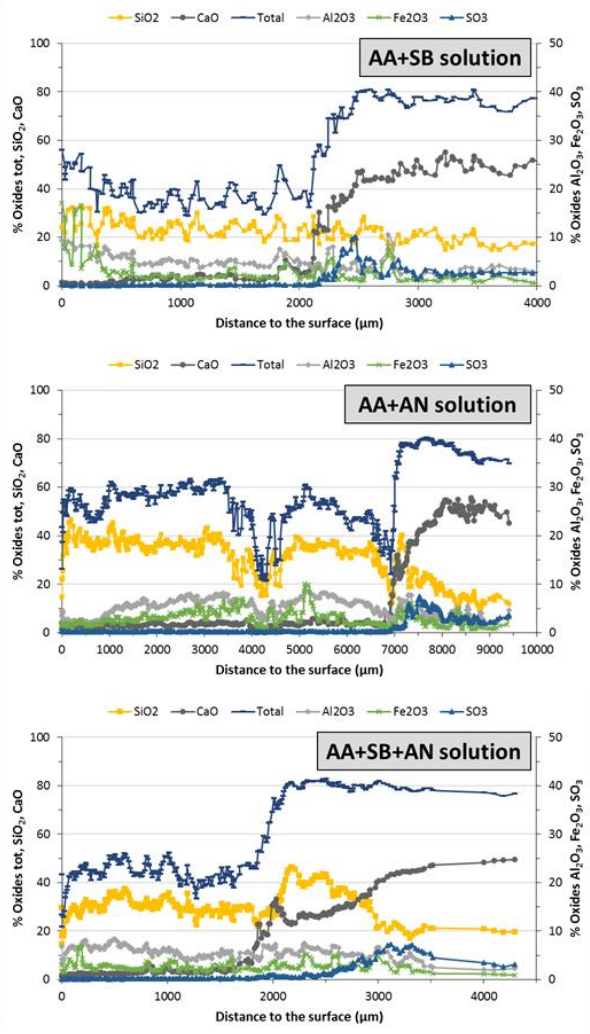
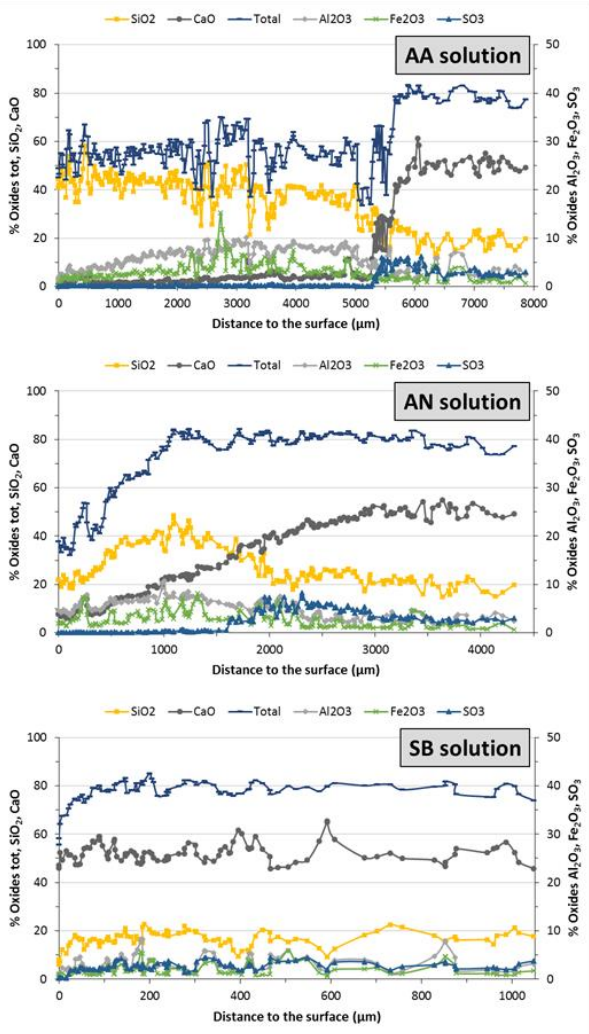
## 586 **7 Supplementary data**



587

588

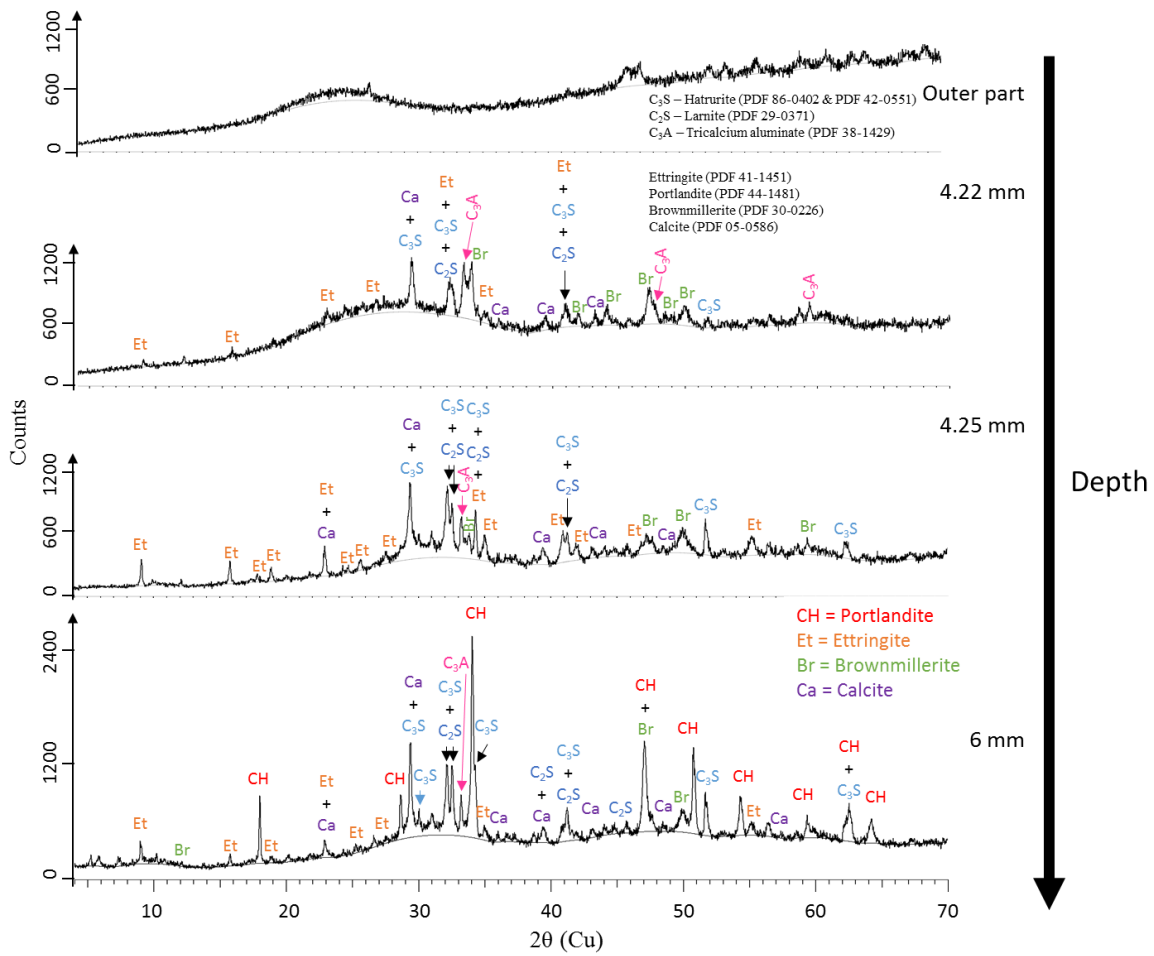
589 *Appendix A : Cumulated concentrations and leaching kinetics of Ca, Si, Fe, SO<sub>4</sub><sup>2-</sup>, Al, K, Na*



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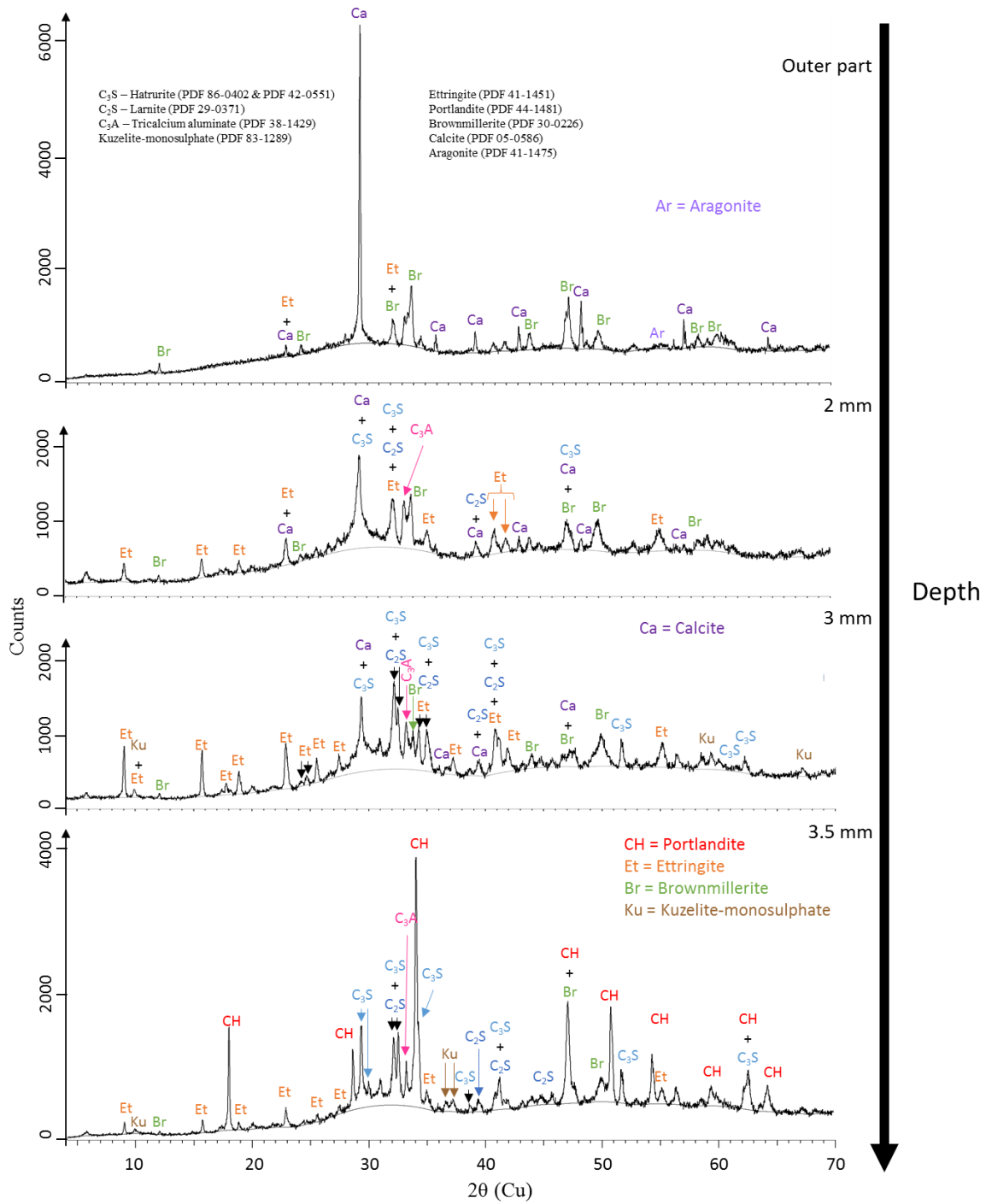
Appendix B: Chemical composition profiles of the OPC pastes after 16 weeks of immersion in the aggressive solutions according to the distance to the surface



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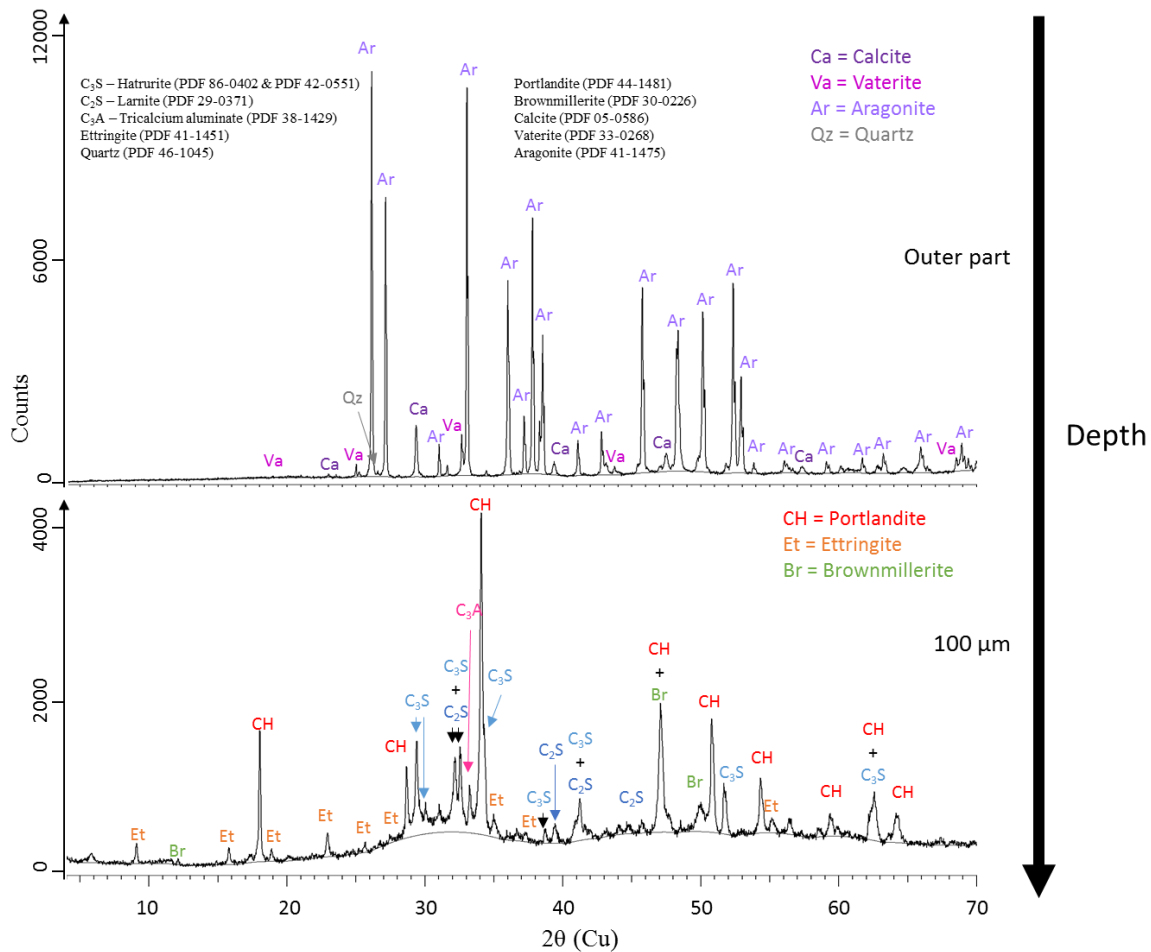
594 Appendix C: X-ray patterns of the OPC specimen immersed in AA solution for 16 weeks according to the depth





595

596 Appendix D: X-ray patterns of the OPC specimen immersed in AN solution for 16 weeks according to the depth



597

598 *Appendix E: X-ray patterns of the OPC specimen immersed in SB solution for 16 weeks according to the depth*

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