



# **Cementitious materials in biogas systems: Biodeterioration mechanisms and kinetics in CEM I and CAC based materials**

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1    **Cementitious materials in biogas systems: biodeterioration mechanisms**  
2    **and kinetics in CEM I and CAC based materials**

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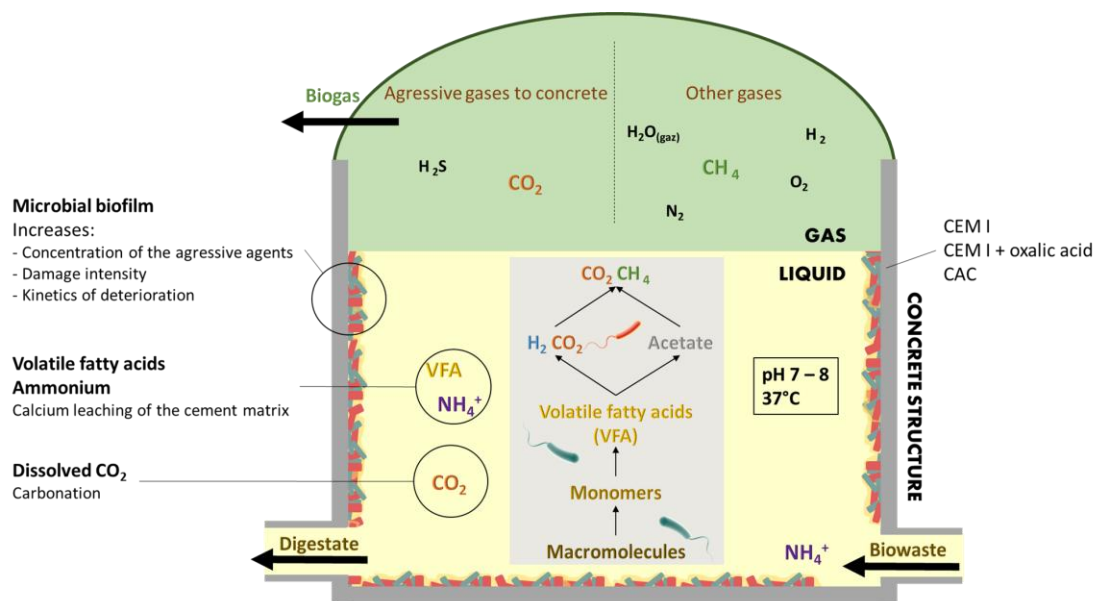
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13    **ABSTRACT**

14    In anaerobic digestion plants, biological activities transform biowaste into a  
15    renewable energy: the biogas. This process produces aggressive and complex  
16    media in direct contact with the structure. Few studies have focused on the  
17    deterioration of concrete in such environments. In order to support the  
18    sustainable development of biogas production growing sector, this study intends  
19    to provide thorough information on the biowaste chemical composition and on  
20    materials biodeterioration mechanisms occurring in biogas plants. Cementitious  
21    materials with various surface compositions (pastes of CEM I, CAC and CEM I  
22    treated with oxalic acid) were immersed in the liquid phase of laboratory  
23    bioreactors reproducing anaerobic digestion conditions. Altered depths  
24    measurements in time highlighted the better resistance of the CAC material. The

25 microbial biofilm coverage on the material's surface was delayed by the surface  
 26 pretreatment with oxalic acid and was less dense for the CAC paste. Chemical  
 27 and mineralogical analyses mainly showed leaching and carbonation  
 28 phenomena.

29 Keywords: degradation, cement paste, durability, SEM, calcium aluminate  
 30 cement



## 32 1. INTRODUCTION

33 The microbial fermentation of organic matter in the absence of oxygen, called  
 34 anaerobic digestion, leads to the production of biogas, a sustainable fuel gas  
 35 energy mostly composed of methane (65% CH<sub>4</sub>) but also containing a significant  
 36 amount of carbon dioxide (35% CO<sub>2</sub>), and leaves a solid residue, the digestate.

37 Anaerobic digestion ensures the treatment of biowaste directly at the production  
 38 source (thus reducing the final quantity of waste). Biogas can be used to produce  
 39 heat with a good energy efficiency and can also be used as a fuel to produce  
 40 electricity, with a lower yield. The most common energy recovery method for

41 biogas is cogeneration, which consists of combining the production of heat and of  
42 electricity by recovering the heat of combustion to transform it into electricity [1].  
43 The digestate, made up of non-biodegradable organic matter (mostly lignin is the  
44 case of vegetal waste), mineral matter and water, is used as a soil fertilizer and  
45 can be a source of additional revenue [2]. In addition, anaerobic digestion permits  
46 greenhouse gas emissions to be reduced and helps to increase the incomes of  
47 the biogas plants operators. This technology of sustainable energy production  
48 has been evaluated as one of the most energy-efficient and environmentally  
49 friendly [3].

50 In view of these multiple advantages, biogas production by anaerobic digestion is  
51 strongly encouraged by European policies and its development has become  
52 global, using many sources of organic waste. Since 2009, the number of biogas  
53 plants in Europe has steadily increased from 6227 to 17662 anaerobic digestion  
54 structures in 2016 [4].

55 As for agricultural and agro-industrial buildings, concrete is the material the most  
56 commonly used for the construction of biogas plants. This is related not only to its  
57 low cost and ease of implementation but also to its air- and water-tightness and  
58 its good thermal inertia [5,6]. However, in digesters, structural concrete is directly  
59 in contact with both the liquid and gas phases of the digesting biowaste, which  
60 are aggressive to concrete [7,8].

61 Biogas is the final product of four consecutive degradation reactions that make up  
62 the anaerobic process: hydrolysis, acidogenesis, acetogenesis and  
63 methanogenesis [9,10]. In most plants, the digestion process is performed under  
64 mesophilic conditions, with an optimal operating temperature of around 37°C  
65 which requires low self-consumption of energy for the heating [11]. In the first

66 step of the process, hydrolysis decomposes complex organic polymers (proteins,  
67 lipids and carbohydrates) into simple soluble molecules: amino acids, long-chain  
68 fatty acids and sugars. These compounds are then reduced into short chain  
69 volatile fatty acids (VFA) during the acidogenesis step. Acetogenic bacteria  
70 degrade the organic acids into acetate, hydrogen and carbon dioxide. These  
71 three compounds are finally consumed by the methanogenic archaea to produce  
72 methane, and also  $\text{CO}_2$  [12–14]. The degradation of nitrogenous compounds  
73 such as proteins and urea leads to the production of ammonia, mainly present in  
74 the form of ammonium ions under the pH conditions of the anaerobic digestion  
75 [15,16].

76 Consequently, by being in contact with the biowaste at every step of the  
77 anaerobic digestion, concrete may undergo deterioration due to both the  
78 chemical and biological agents. Several compounds in the medium [6,7] are  
79 aggressive to concrete: volatile fatty acids, excreted by the acidogenic bacteria,  
80 ammonium and dissolved  $\text{CO}_2$ :

- 81 • Volatile fatty acids metabolized during anaerobic digestion are organic  
82 acids whose calcium salts are soluble in water. Even if the acidity of  
83 organic acids is lower than mineral acids, the buffer effects and the  
84 solubility of the organic salts make them not less aggressive to concrete.  
85 Their attack results in a progressive dissolution of all the initial hydrated  
86 phases of the cement paste [17–19].
- 87 • The ammonium cation  $\text{NH}_4^+$  is the conjugated acid of ammonia  $\text{NH}_3$ ,  
88 produced during the anaerobic digestion. The ammonium ion react with  
89 the cementitious matrix supposedly according to an exchange mechanism  
90  $2 \text{NH}_4^+ \rightarrow \text{Ca}^{2+}$  [20,21]. This leads to the dissolution of portlandite and C-  
91 S-H and the decalcification of the cementitious matrix [22,23].

92       • The presence of carbon dioxide in the medium leads to the carbonation of  
93       the cement paste: portlandite and C-S-H are dissolved and calcium  
94       carbonates are formed [24–26]. Even if most of the time, carbonation can  
95       be beneficial for the concrete durability by clogging the porosity [24,25], in  
96       submerged systems such as anaerobic digestion medium, dissolved CO<sub>2</sub>  
97       can lead to the dissolution of calcium bearing phases, including the  
98       calcium carbonates [21].

99       The microorganisms involved may organize themselves as a biofilm on the  
100       surface of the material [27] and induce very high local concentrations of  
101       aggressive agents, accentuating the deterioration [7,28]. In this context, the  
102       concrete undergoes deterioration resulting in increased porosity and reduced  
103       impermeability, leading to a greater risk of reinforcement corrosion [6,29].  
104       Damage to the structures could lead to both important economic and  
105       environmental impacts such recovery of a smaller amount of biogas, pollutant  
106       flows nearby the plant, and the need for repairs.

107       The European standard EN 206 [30] and the French information document FD P  
108       18-011 [31] classify environments that are chemically aggressive for concrete by  
109       defining three classes of increasing aggressiveness, XA1 to XA3. Among the  
110       aggressive species present in the liquid phase of fermenting biowaste, the texts  
111       consider the presence and the concentration of carbon dioxide (aggressive CO<sub>2</sub>),  
112       sulphate (SO<sub>4</sub><sup>2-</sup>), magnesium (Mg<sup>2+</sup>), and ammonium (NH<sub>4</sub><sup>+</sup>), together with the pH  
113       and the water hardness. However, neither document considers the action of  
114       organic acids or of microorganisms [17,29], nor the temperature effect, which  
115       could accelerate the degradation reactions [32]. Moreover, the pH is not suitable  
116       to characterize the aggressiveness of some liquid media, including those  
117       containing organic acids [5,33]. It therefore appears that the normative texts are

118 incomplete as far classifying the aggressiveness of agricultural environments,  
119 and especially the anaerobic digestion environment, is concerned. In order to  
120 facilitate their classification in the standards, better knowledge of these complex  
121 environments, in terms of composition and aggressiveness toward concrete, is  
122 needed.

123 This study aims to (i) widely characterize the medium in terms of chemical  
124 composition; (ii) identify and understand the biodeterioration mechanisms and (iii)  
125 compare the performances of different cementitious materials (CEM I, CAC and  
126 CEM I surface-treated with oxalic acid). The influence of the oxalic acid  
127 treatment, the type of binder and the biofilm coverage on the material durability  
128 are discussed.

## 129 2. MATERIALS AND METHODS

### 130 2.1 Materials

#### 131 2.1.1 *Cement paste manufacturing*

132 Three types of materials were used for this study: (i) cement pastes of ordinary  
133 Portland cement, CEM I 52.5 R (denominated CEM I); (ii) cement pastes made of  
134 calcium aluminate cement, Secar 51 RG (CAC) (chemical oxide composition and  
135 Blaine specific surface of both the previous cements are given in Table 1) and (iii)  
136 CEM I pastes the surface of which had been treated with a 0.28M oxalic acid  
137 solution (denominated CEM I-Ox) [34]. CEM I paste was considered as the  
138 reference material and CAC and CEM I-Ox cements were chosen because of  
139 their already proven higher durability in an acid environment [33–36].

140 **Table 1. Oxide compositions of the cements in mass percentages and**  
141 **Blaine's specific surface area**

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Blaine's specific surface (cm <sup>2</sup> /g)
CEM I	64.5	20.1	4.83	2.47	1	3.49	0.14	0.17	4970
CAC	44	5.6	52.9	1.47	0.2	<0.2	0.23	0.37	3870

142

143 According to several authors [33,35,36], calcium aluminate cements show high  
144 durability in acidic media, with a good chemical stability. This could be explained  
145 by the alkalinity and the stability of the initial (e.g. katoite C<sub>3</sub>AH<sub>6</sub>, aluminium  
146 hydroxide AH<sub>3</sub>) phases and that newly formed through acidic attack, aluminium  
147 hydroxide AH<sub>3</sub>, which has a high thermodynamic stability [37,38]. Moreover, the  
148 alkalinity of CAC binders vs. OPC ones is detailed in the study of Buvignier et al.  
149 [39] by comparing the neutralization capacity of an OPC with the one of CAC-  
150 based materials on the basis of the calculation by Letourneux and Scrivener [40].  
151 The higher neutralization capacity of the CAC was highlighted and it was  
152 assumed that it could contribute to the higher resistance of CAC materials to  
153 microorganisms-bearing environments by hindering or inhibiting microbial activity  
154 on their surface [39].

155 Chemical action of the oxalate anion has already been studied and used to  
156 provide a surface protection for marble [41,42]; electron microscope observations  
157 showed a structural correspondence between the calcium oxalate and the calcite  
158 crystals of the marble [43]. The chemical reaction is thought to be based on the  
159 transformation of calcium carbonate from the marble into calcium oxalate [44].  
160 This surface layer protects the marble without clogging the pores of the stone  
161 [42]. This type of treatment has also been explored on cementitious materials in



laboratory studies, which have shown that, despite the very low pH of the oxalic solution used (pH=1), ordinary Portland paste does not lose mass and is not degraded in depth [33,34]. Calcium oxalate forms a layer on the surface of the material, filling the peripheral porosity. The salt formation is believed to be due to the reaction of the oxalate solution with the Portland cement matrix [17], where the sacrificial dissolution of the portlandite allows the formation of calcium oxalate in the outer layer of the paste specimen. According to Larreur-Cayol et al. [33], the protective effect of the calcium oxalate salt could come from its molar volume which allows the salt to fill the volume released by the dissolution of portlandite and also some of the capillary porosity. Voegel et al. [34] also showed that the oxalic acid treatment on a CEM I paste could delay the paste alteration by an acetic acid solution.

The CEM I and CAC paste specimens were made with a water/binder ratio of 0.4. This ratio optimizes the effects of the acid oxalic treatment and a study by Voegel et al. [34] showed that the water/binder ratio of 0.4 led to a positive mass variation, whereas no mass change was detected for a ratio of 0.27. Thus, the higher porosity of the matrix with a water/binder ratio of 0.4 could have led to the precipitation of a larger amount of calcium oxalate [34]. The pastes were mixed according to the French standard NF EN 196-3 [45] and cast in cylindrical moulds 75 mm high and 25 mm in diameter. The pastes were cast in three consecutive layers, each vibrated for 120 seconds. They were removed from their moulds 24h after pouring. Then, each specimen underwent an exogenous cure in a small amount of water at 20 °C for 27 days, which allowed the hydration to continue while limiting leaching. After the curing period, 5 mm thick slices were sawn from paste cylinder specimen, to be used for the biofilm growth testing. Also, some CEM I paste cylinders and slices were immersed in a 0.28 M oxalic acid solution

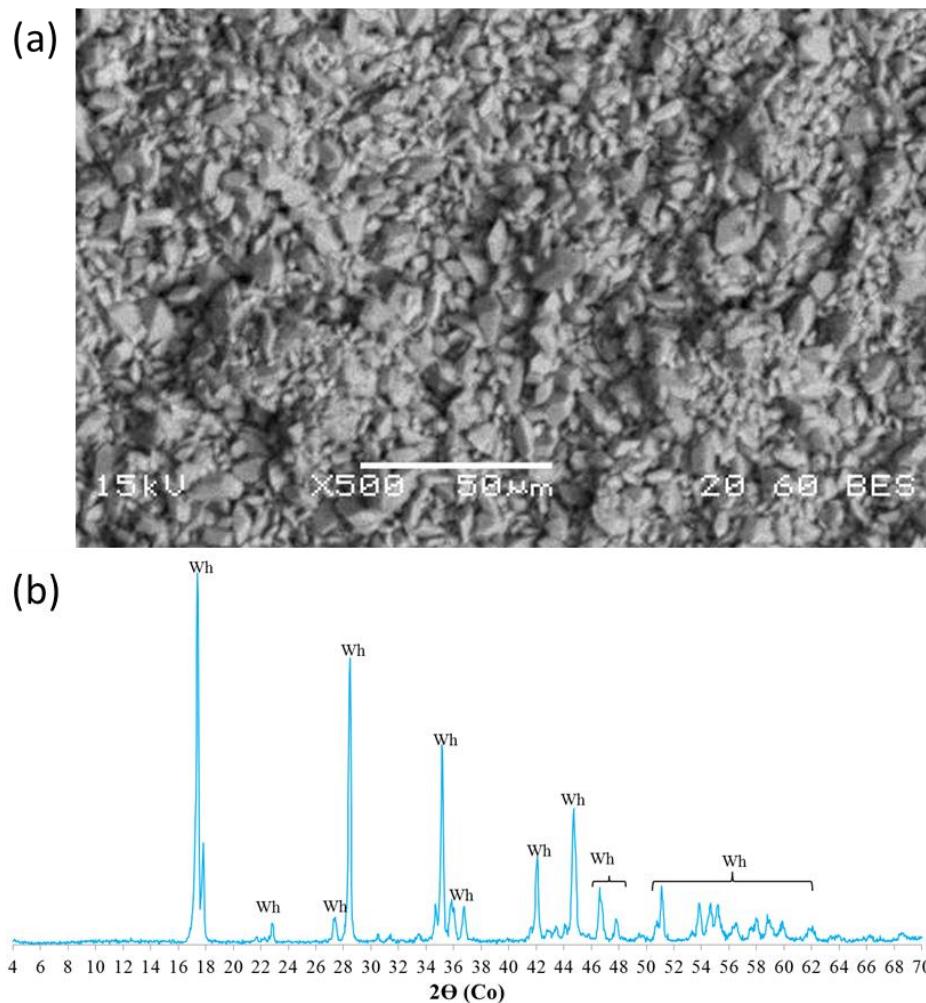
188 (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) (pH=0.76) for 7 days, the other specimens being kept in sealed bags.  
189 The initial porosities of the paste specimens were measured by water intrusion  
190 porosimetry adapting the French standard NF P18-459 [46] for cement pastes  
191 specimens. The results were 40±1 % for CEM I and 27±1 % for CAC.

### 192 2.1.2 Characterization of cement paste surfaces

193 Just before immersion in the biowaste, the surface pH of the specimens was  
194 measured with pH paper: it was between 12 and 13 for the CEM I and CAC  
195 pastes (sound cementitious materials) whereas it was about 1 for the CEM I-Ox  
196 paste (because of the pH 0.76 oxalic acid treatment) [27].

197 The main mineralogical phases of the cement pastes surfaces before the  
198 immersion were determined by X-Ray Diffraction (XRD) analyses. The  
199 diffractograms showed the phases habitually encountered in sound CEM I and  
200 CAC cement pastes. The CEM I paste surface was composed of C-S-H,  
201 portlandite (Ca(OH)<sub>2</sub>), ettringite, C<sub>x</sub>AH<sub>y</sub>, C<sub>3</sub>S and C<sub>2</sub>S. The CAC paste surface  
202 showed C<sub>3</sub>AH<sub>6</sub>, gibbsite (AH<sub>3</sub>), gehlenite (C<sub>2</sub>AS), mayenite (C<sub>12</sub>A<sub>7</sub>), C<sub>2</sub>AH<sub>8</sub>,  
203 brownmillerite (C<sub>4</sub>AF) and calcium aluminate oxide (CA). Microscopic  
204 observations (performed with a Scanning Electron Microscope (SEM) in back  
205 scattered electron mode (BSE)) and mineralogical analysis (by XRD) were made  
206 on the surface of the CEM I specimens treated with oxalic acid. They showed an  
207 adherent, continuous layer of precipitate of whewellite (calcium oxalate  
208 monohydrate) covering the whole specimen (Figure 1). This layer was formed  
209 over a thickness of 100 to 200 µm and clogged the porosity locally [33,34]. More  
210 details about the method are given in §2.5.

211



**Figure 1. (a) SEM observation and (b) mineralogical analysis of the CEM I-Ox paste surface after the 7 days oxalic acid treatment (Wh: whewellite (calcium oxalate monohydrate))**

## 2.2 Immersion of cement pastes in the synthetic biowaste

The substrate for biogas production by anaerobic digestion used in this study was a laboratory synthetic biowaste representative of the organic domestic waste currently produced in France according to the CIRSEE (International Research Center On Water and Environment). Its composition was provided by IRSTEA of Antony (France): a mix of different food products. All the details on composition and production are given in Voegel et al. [7]. Bacterial inoculation was made from a sludge sampled in a municipal wastewater treatment in Toulouse (France) in

order to induce the anaerobic digestion process [47]. The inoculation was operated with a  $V_{\text{inoculum}}/V_{\text{substrate}}$  ratio of 2.5, which corresponded to an optimal ratio of 1 g COD<sub>inoculum</sub>/ g COD<sub>substrate</sub>, (with COD the chemical oxygen demand) as already established in previous works [7,48]. Cement pastes were totally immersed in the liquid phase of the biowaste in anaerobic bioreactors for 5 weeks. The surface area/volume ratio (cement paste surface area/inoculated biowaste volume) was 224 cm<sup>2</sup> L<sup>-1</sup> for the cylindrical samples and 34 cm<sup>2</sup> L<sup>-1</sup> for the slices used for biofilm development monitoring. These two ratios are quite high in comparison with real situations of industrial digester (4 cm<sup>2</sup> L<sup>-1</sup> [48]) but allow to amplify the phenomena occurring close to the material. The bioreactors (two reactors per type of material, experiments run in duplicate) were kept in an oven at 37° C throughout the experiment. The reaction medium, with an initial volume of 525 mL, was continuously stirred by a magnetic stirring system. Biowaste was renewed at the end of each 5-week digestion cycle. This period corresponds to the average time required for the complete digestion of a substrate [49] and is commonly used as a typical duration for laboratory tests [50,51]. Two cycles were carried out.

### **2.3 Analysis of the liquid phase of the digesting biowaste**

The liquid phase composition of the digesting biowaste was monitored over time in order to analyse the concentration of organic acids, ammonium and CO<sub>2</sub>, and the pH [7]. Regular sampling of 1.5 mL of the liquid phase was carried out and concentrations of the organic acids were measured using High Performance Liquid Chromatography analyses (Thermo Fisher U3000; column: Aminex HPX-87H BIORAD; eluant: H<sub>2</sub>SO<sub>4</sub>; flow rate: 0.5 mL.min<sup>-1</sup>) [7,48]. Ammonium concentrations were measured using Ionic Chromatography (Thermo Electron ICS 3000, column: CS16; pre-column; cartridge holder; eluant: 30 mM

methanesulfonic acid; flow rate: 1.0 mL.min<sup>-1</sup>). The soluble CO<sub>2</sub> produced from the microbial activity was occasionally determined by analysis of total inorganic carbon (TOC-SCHIMADZU) [7].

## **2.4 Observation of biofilm on cement pastes**

Cement paste slices were sawn carefully in order to preserve the biofilm on their surfaces. Before the observations, the biofilms were first chemically fixed and then dehydrated according to the method of Voegel et al. [7,48]. The biofilm was observed by SEM-FEG (JEOL 7100F TTLS combined with EDX XMax, 5kW) after 5 weeks (CEM I, CEM I-Ox, CAC) and 10 weeks (CEM I-Ox).

## **2.5 Microscopic observations and analysis of chemical and mineralogical changes in cementitious materials**

The cylindrical cement paste specimens were removed from the biowaste after each digestion cycle (i.e. after 5 and 10 weeks of immersion) and 5 mm cement paste slices were collected by sawing the cylindrical specimens perpendicularly to their longitudinal axis with a diamond saw. A part of a slice was then embedded in an epoxy resin (Mecaprex MA2+ by Presi) and dry-polished using silicon carbide polishing disks (Presi) according to the procedure described by Bertron et al. [52]. The polished sections were coated with carbon before being analysed. Microstructural observations of cement pastes were made by Scanning Electron Microscopy (SEM, JEOL JSM 6380LV) using back scattered electron (BSE) mode. Chemical analyses were performed on the same specimens using energy dispersive X-ray spectrometry (EDS, Bruker Xflash 6/30 - SDD) and electron-probe micro-analysis (EPMA, Cameca SXFive, 15 kV, 20 nA, scanning area of the beam 2 x 2 µm<sup>2</sup>). Punctual analyses were carried out by positioning a hundred points manually, carefully avoiding anhydrous grains, from the degraded

275 surface to the sound core [7]. A microstructural and chemical zonation of the  
276 deteriorated specimens according to the distance to the surface was identified  
277 from the correlated results of SEM+EDS and EPMA: the zonation is primarily set  
278 through chemical composition profiles obtained from EPMA and then X-ray  
279 diffraction (XRD) analyses are performed to evaluate the mineralogical  
280 composition in each zone. Mineralogical analyses in the different zones identified  
281 were carried out by XRD (Siemens D5000, Co cathode, 40 kV, 30 nA) using the  
282 procedure presented in Bertron et al. [53].

### 283 3. RESULTS

#### 284 3.1 Composition of the liquid fraction of the digesting biowaste

285 Table 2 summarizes the composition of the liquid fraction of the bioreactors  
286 through several cycles. The values in the table are averages over the six  
287 bioreactors run at the same time (two bioreactors per material type). Figure 2  
288 shows the typical evolutions of the pH and the acid concentrations during a cycle  
289 of anaerobic digestion [7].

290 From Table 2, no major difference in the composition of the liquid fraction is  
291 observed between the two cycles (5 and 10 weeks). The acetic acid  
292 concentration reaches 23 mmol.L<sup>-1</sup> on average, whereas the propionic and  
293 butyric acids concentrations reach 9 mmol.L<sup>-1</sup>. Table 2 and Figure 2 show that  
294 the pH decreases in the first few days, to values around 4.5. Within this period,  
295 hydrolysis and acidogenesis steps correlated with the production of organic  
296 acids. After that, the pH reaches 7.0 on the 10<sup>th</sup> day and stabilizes around 7.8  
297 thereafter due to a progressive and then total consumption of the VFA during the  
298 acetogenesis and methanogenesis steps. Koenig and Dehn [8] found similar pH  
299 values (pH of approximately 7) in the liquid phase of their laboratory fermenter.

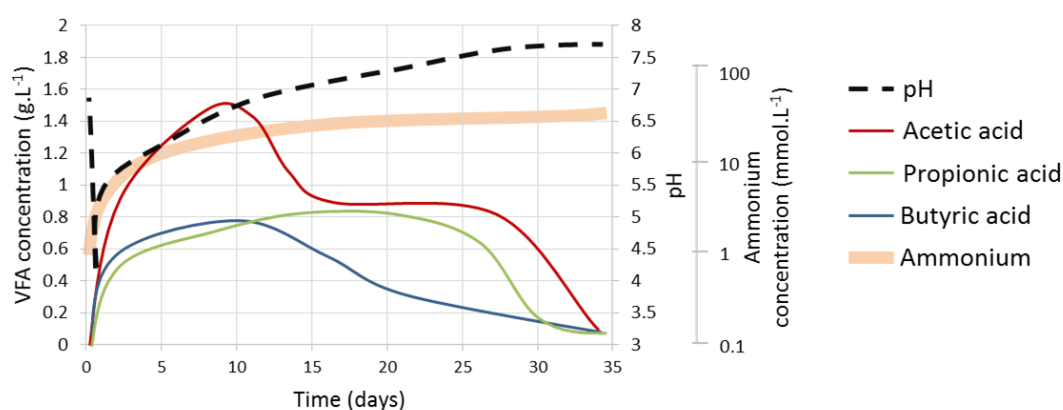
300 The average ammonium concentrations reach  $55 \text{ mmol.L}^{-1}$ . This value is  
301 consistent with the studies by Voegel et al. [7] and Giroudon et al. [54], where the  
302 evolutions of the ammonium concentration were similar and reached about 800  
303  $\text{mg.L}^{-1}$  ( $40 \text{ mmol.L}^{-1}$ ) and with McCarty [49] who states that ammonium  
304 concentrations can reach  $1000 \text{ mg.L}^{-1}$  for a digester in good function.

305 Punctual analyses of dissolved  $\text{CO}_2$  concentrations showed that, after 3 weeks of  
306 biowaste anaerobic digestion, the  $\text{CO}_2$  concentration was  $2.3 \text{ mmol L}^{-1} \pm 0.2$   
307  $\text{mg.L}^{-1}$ . The digesting biowaste contained little or no sulfur bearing compounds.

308 **Table 2. Composition of the liquid fraction of the digesting biowaste in**  
309 **terms of VFA concentration, ammonium concentration and pH: minimum**  
310 **value–maximum value (standard deviations).**

	VFA concentration ( $\text{mmol.L}^{-1}$ )			Ammonium concentration ( $\text{mmol.L}^{-1}$ )	pH
	Acetic acid	Propionic acid	Butyric acid		
1 <sup>st</sup> cycle (week 1 to 5)	0.14-22.99 (0.22-2.14)	0.26-10.79 (0.12-2.54)	0.00-8.31 (0-1.17)	0.85-54.90 (0.11-1.00)	4.33-7.81 (0.31-0.18)
2 <sup>nd</sup> cycle (week 6 to 10)	1.14-24.42 (0.10-2.87)	0.14-9.84 (0.09-2.55)	0.00-9.83 (0-2.32)	0.83-52.24 (0.09-2.11)	4.47-7.52 (0.23-0.15)

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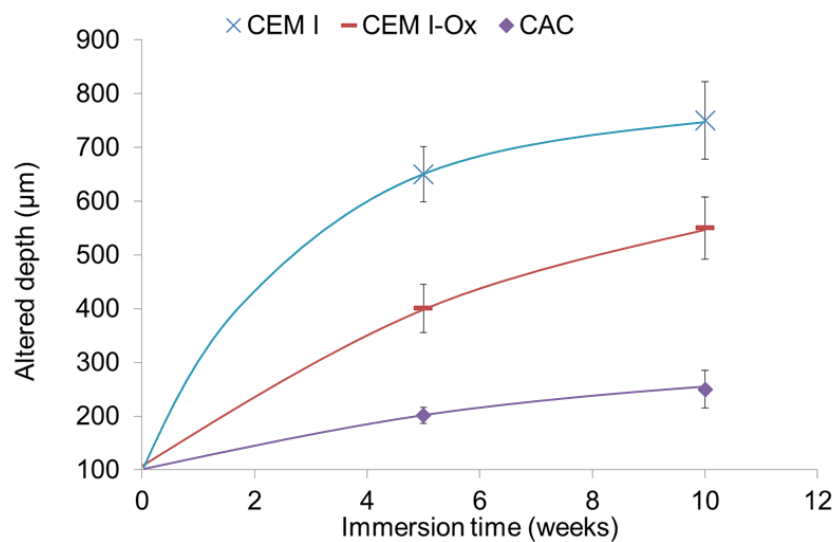


312

313 **Figure 2. Typical evolution of pH, VFA concentrations and ammonium**  
314 **concentration for a single anaerobic digestion cycle, adapted from Voegel**  
315 **et al. [7]**

### 3.2 Altered depths of the cement pastes

Figure 3 shows the altered depths of the cement pastes after 5 weeks (one digestion cycle) and 10 weeks (two digestion cycles) of immersion in the digesting biowaste. Altered depths were obtained by analyses of flat polished sections using BSE-mode SEM coupled to EDS and EPMA. Altered depths correspond to limits between the sound zone (zone 1) and the beginning of the altered zone (zone 2) on Figures 5, 7 and 9.



**Figure 3. Altered depths of the cement pastes immersed in the digesting biowaste**

After 5 weeks of exposure to the digesting biowaste, the CAC samples had the smallest altered depth (200 μm) whereas CEM I-Ox and CEM I pastes had altered depths of 400 and 650 μm respectively. After 10 weeks, the degraded depth of the CAC pastes had increased slightly, reaching a value of 250 μm, whereas CEM I-Ox and CEM I reached degraded depths of 550 and 750 μm.

During the first cycle (< 5 weeks), the protective properties of the calcium oxalate seemed to be efficient as the CEM I-Ox degraded depth was 1.6 times less than that of CEM I pastes. During the second cycle (between 5 and 10 weeks), the



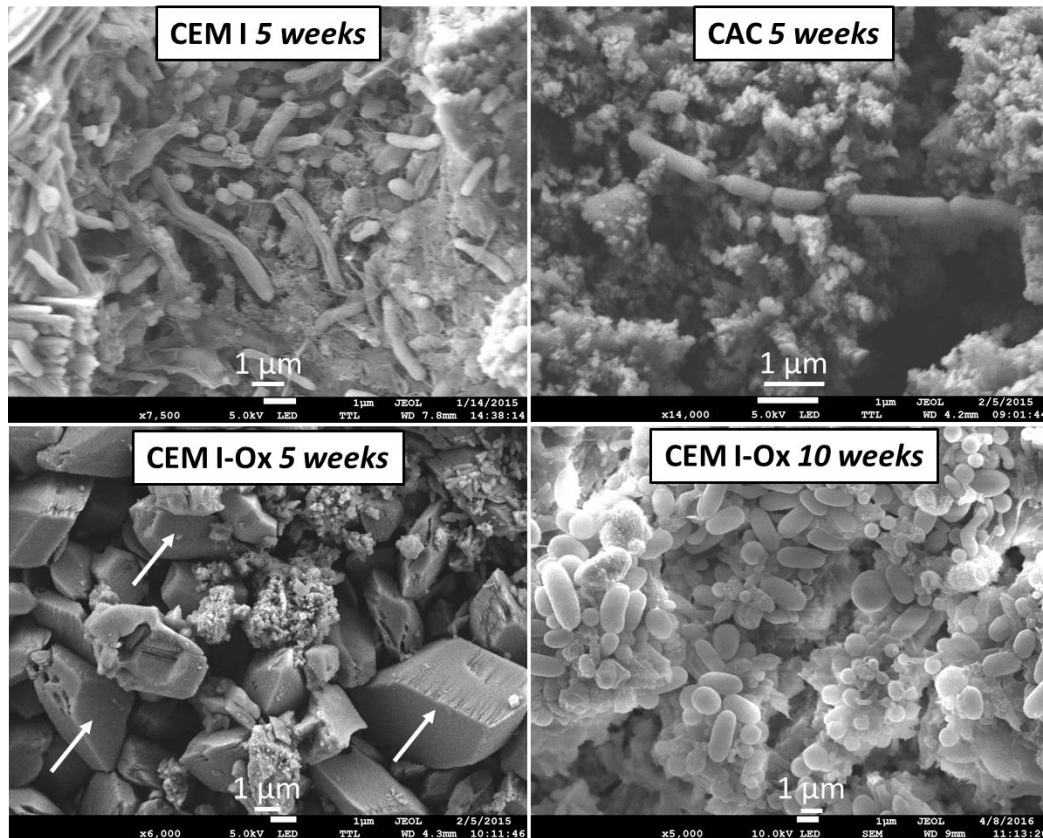
334 increase of the degraded depth of the CEM I-Ox paste was 150  $\mu\text{m}$  which was  
335 greater than the increase of the degraded depth of the non-treated CEM I paste  
336 (of 100  $\mu\text{m}$ ). Thus, it seems that the calcium oxalate treatment was no longer  
337 effective at this point.

338 The CAC pastes showed positive achievement throughout the experiment as  
339 their degraded depths after 10 weeks were only 250  $\mu\text{m}$  which was 2 or 3 times  
340 less than the CEM I-Ox and CEM I degraded depths after 5 weeks.

### 341 **3.3 Microscopic observation of biofilms**

342 Figure 4 presents the SEM observation of the surface of CEM I, CAC and CEM I-  
343 Ox pastes after 5 weeks of immersion and 10 weeks of immersion for the CEM I-  
344 Ox sample. At both sampling dates (i.e. 5 and 10 weeks), the CEM I pastes  
345 surfaces showed a uniform, dense biofilm whereas the biofilm observed on the  
346 surface of the CAC was less dense, with few microorganisms. In contrast,  
347 microbial colonization was not observed on the surface of the CEM I-Ox slice  
348 after 5 weeks of anaerobic digestion and calcium oxalate precipitates, similar to  
349 those observed on the cement paste immediately after the oxalic acid treatment  
350 (Figure 1), covered the surface. After 10 weeks of immersion, the entire surface  
351 of the CEM I-Ox paste was covered by a dense biofilm and calcium oxalate  
352 precipitates were no longer observed. It can be assumed that between 5 and 10  
353 weeks of exposure the surface conditions enabled a biofilm to form on the  
354 surface. The biofilm may have produced local conditions that finally dissolved the  
355 oxalate salt.

356



**Figure 4. SEM observations of biofilms on cement pastes after 5 weeks (CEM I, CAC, CEM I-Ox) and 10 weeks (CEM I-Ox) of immersion in the digesting biowaste. Calcium oxalate crystals are identified by white arrows.**

### **3.4 Chemical and mineralogical analysis of the cementitious specimens**

#### **3.4.1 CEM I paste**

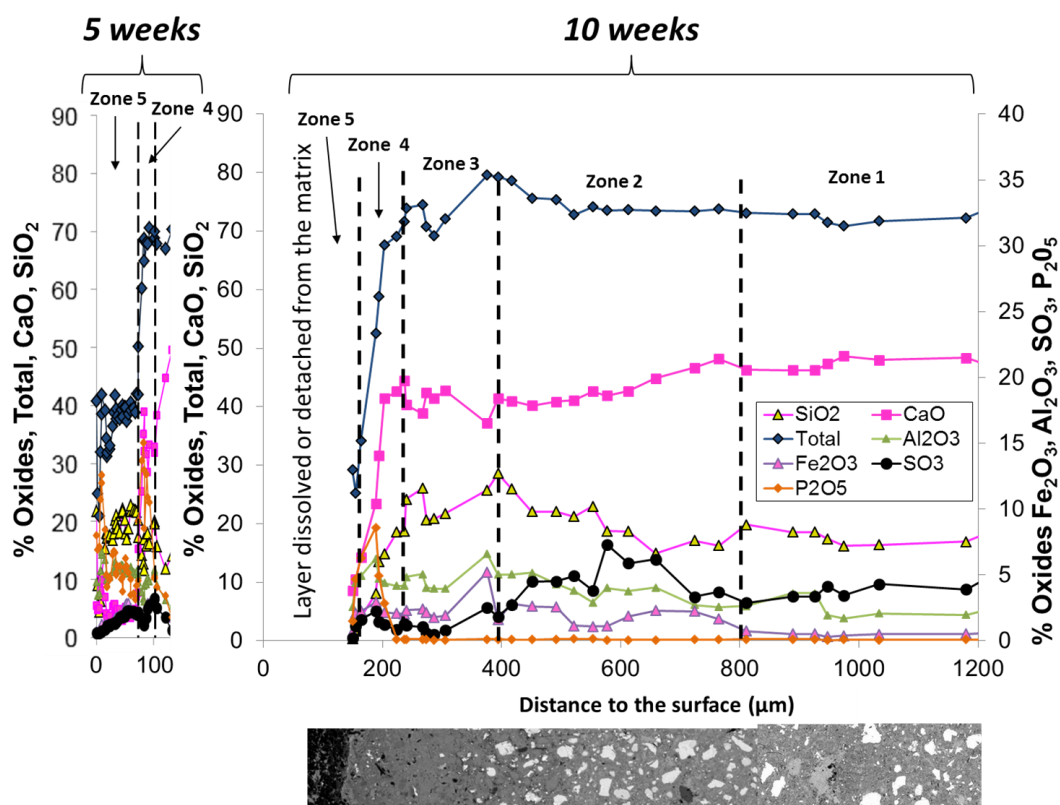
The chemical composition profiles of the CEM I paste sample at 10 weeks of immersion, as a function of the distance to the surface, and the image of the same specimen by SEM in back-scattered electron (BSE) mode are presented on the right side of Figure 5. The outer layer of the specimen was partly dissolved when it was removed from the biowaste. The thickness of the material lost is reported on the figure (about 150  $\mu\text{m}$ ) and was measured by measuring the difference between the initial diameter of the sample and its final dimensions. The left side of Figure 5 gives the chemical composition profile of the outer layers of the CEM I paste immersed for 5 weeks in the fermenting biowaste (adapted from

372 Voegel et al. [7]). A chemical zonation of the specimens was identified and is  
373 represented on the figure, from zone 1, corresponding the intact core, to zone 5,  
374 corresponding to the outer layer in contact with the biofilm and the biowaste. The  
375 mineralogical characterization by XRD in each zone defined in Figure 5 is  
376 presented in Figure 6. From the core to the outer layer, the chemical and  
377 mineralogical evolution of the cementitious matrix is as follows:

- 378 • Zone 1 corresponds to the sound zone. The mineralogical analyses  
379 showed a composition similar to that of an unaltered specimen, mainly  
380 made of hydrated phases (portlandite, ettringite, and C-S-H) and  
381 anhydrous grains ( $C_3S$ ,  $C_2S$ , brownmillerite  $C_4AF$ ). The SEM observations  
382 show the high density of the anhydrous residual cement grains (in lighter  
383 grey on the SEM image).
- 384 • Zone 2 is 350  $\mu m$  thick and shows the same two main phenomena in  
385 each cycle: (i) a slight decalcification corresponding to the dissolution of  
386 portlandite, and (ii) an enrichment in sulfur, which can be correlated with a  
387 slight intensification of the ettringite peaks in the mineralogical pattern  
388 (Figure 6). This secondary ettringite comes from the diffusion of sulfates  
389 from the altered zone, and is classically observed in transition zone of  
390 specimens exposed to leaching [53,55]. It is probably not expansive as no  
391 microcracks are observed by SEM in this zone. The density of the  
392 anhydrous grains remains high in this zone, as can be observed in the  
393 SEM picture.
- 394 • After each cycle, zone 3 is mainly characterized by the dissolution of the  
395 anhydrous grains shown in the SEM picture and a lower density of the  
396 hydrated matrix (darker colour of the cement paste). The mineralogical  
397 pattern (Figure 6) shows that calcite is the main crystallized phase in this

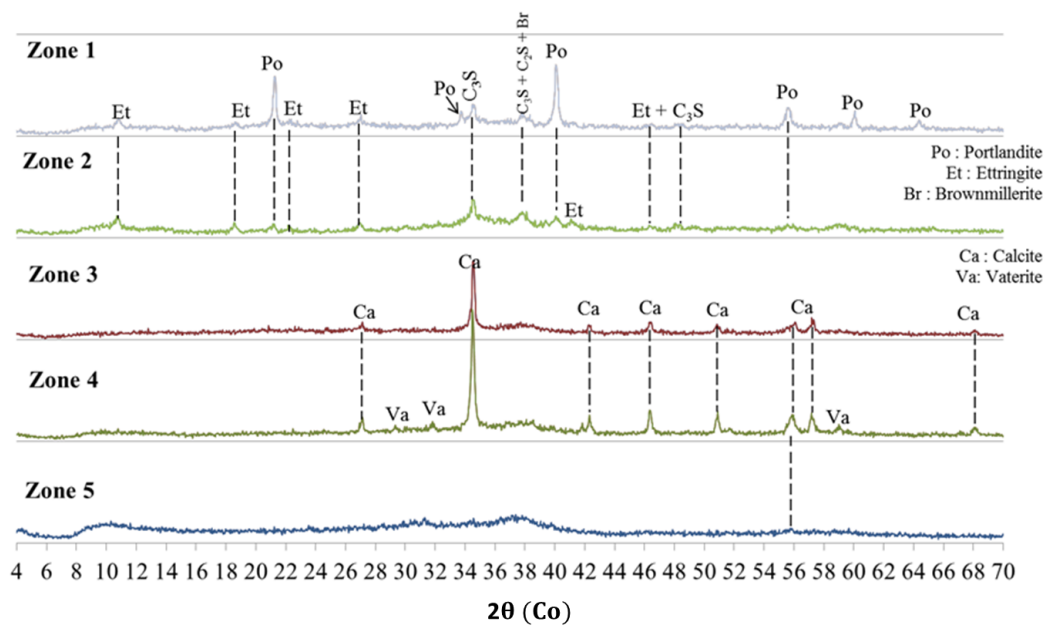
398 zone and that ettringite,  $C_3S$ ,  $C_2S$  and brownmillerite phases are  
399 dissolved. The chemical composition (Figure 5) shows the decrease in the  
400 sulfur content, correlated with the disappearance of the ettringite peaks  
401 and the decrease of the total amount of oxides. This zone is 180  $\mu m$  thick.

- 402 • Zone 4 is mainly composed of the two polymorphs of calcium carbonate  
403 ( $CaCO_3$ ), calcite and vaterite, which form for C/S ratio  $\geq 0.67$  in the C-S-H  
404 [56]. The chemical composition (Figure 5) shows the partial decalcification  
405 of the sample and a peak of phosphorous, probably brought by the  
406 biowaste. No peak of a crystallized phase containing phosphorus is visible  
407 on the diffraction pattern, at either 5 or 10 weeks, suggesting that an  
408 amorphous P-phase has precipitated. This zone is 30  $\mu m$  and 80  $\mu m$  thick  
409 respectively after the 5<sup>th</sup> and the 10<sup>th</sup> weeks, respectively, and shows a  
410 low density in the SEM image.
- 411 • Zone 5 is the outer layer, mainly visible after 5 weeks (70  $\mu m$  thick). This  
412 zone is mainly amorphous (Figure 6) and is likely to be composed of a Si-  
413 Al gel, containing phosphorus in its outer part. At 10 weeks, it can be  
414 assumed that this external zone was partially dissolved or detached from  
415 the matrix. The missing zone was determined to be around 150  $\mu m$  thick  
416 according to image analysis measurements performed on the cross  
417 section of the specimen.



418

419 **Figure 5. Chemical composition after 10 weeks of immersion and chemical**  
 420 **composition of the outer layers of the CEM I paste after 5 weeks [7]**  
 421 **according to the distance to the surface (EPMA) (top) and SEM**  
 422 **observations of the polished section in BSE mode (bottom)**



**Figure 6. Mineralogical analysis by XRD of CEM I paste immersed for 5 and 10 weeks**

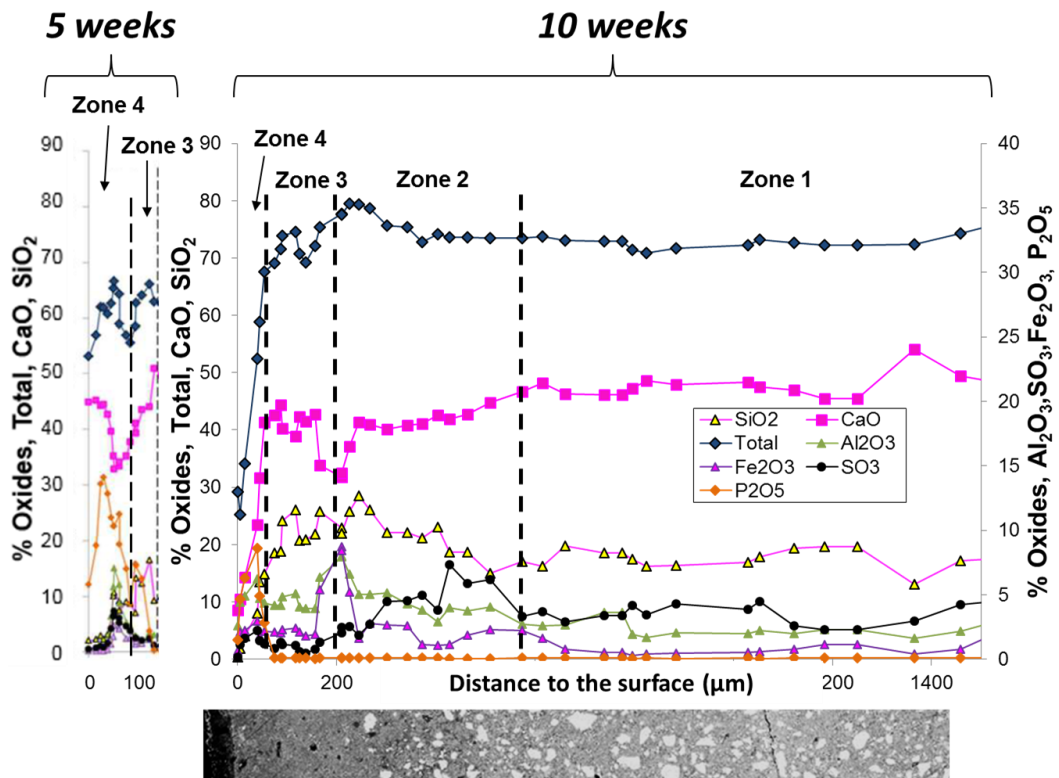
### 3.4.2 CEM I-Ox paste

The chemical composition profiles, according to the distance to the surface, of the CEM I-Ox paste sample at 10 weeks of immersion, and the image of the same specimen by SEM in BSE mode are presented in Figure 7, right side. The left side of the figure gives the chemical composition profile of the outer layers of the CEM I-Ox paste immersed for 5 weeks in the fermenting biowaste. The mineralogical characterization by XRD of each zone is presented in Figure 8. In light of the chemical and mineralogical analyses, four zones can be distinguished after 5 and 10 weeks, with differences in the composition of the outer layer between the two exposure times. The zonation is as follows:

- Zone 1 corresponds to the unaltered zone. Its mineralogical and chemical composition is similar to that of zone 1 of the CEM I paste.
- As for the CEM I paste specimen, Zone 2 shows a slight decalcification with an increase of the sulfur oxide content. From a mineralogical point

440 of view, portlandite peaks are reduced whereas ettringite peaks are  
441 intensified, which could be correlated with the increase of sulfur oxides  
442 content. This zone is 400  $\mu\text{m}$  thick and the SEM image shows a less  
443 dense structure here than in zone 1.

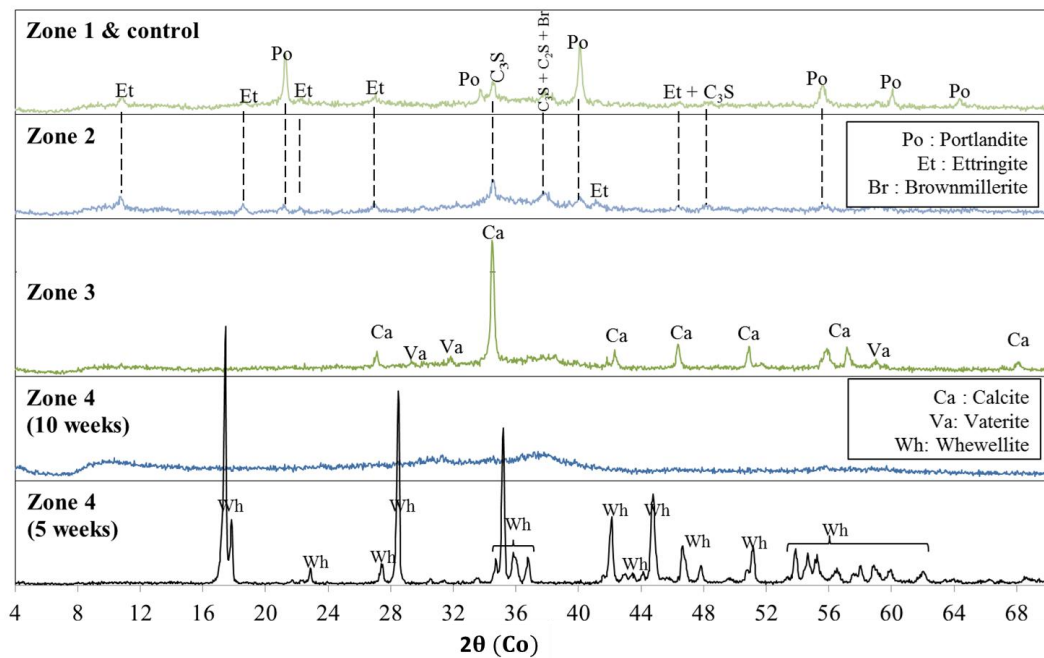
- 444 • Zone 3, 180  $\mu\text{m}$  thick, contains mainly calcium in the form of calcite  
445 and vaterite. Anhydrous grains are no longer observed in the SEM  
446 image and the paste density has decreased.
- 447 • For zone 4, two different patterns are observed at 5 and 10 weeks of  
448 exposure to the biowaste. At 5 weeks, this zone is mainly composed of  
449 calcium and phosphorus. The CaO content is related to the  
450 precipitation of the calcium oxalate salt (whewellite), preserved on the  
451 surface, the XRD pattern being very similar to that of the surface  
452 before the immersion (Figure 1). The phosphorus enrichment is  
453 probably due to diffusion and fixation of this element from the biowaste.  
454 At 10 weeks, the calcium content tends to zero in the outer part of this  
455 zone. Whewellite has been dissolved and the XRD diffractogram  
456 shows an amorphous pattern of the remaining cement matrix.



457

458 **Figure 7. Chemical composition of the CEM I-Ox paste after 10 weeks of**  
 459 **immersion and chemical composition of the outer layers of this paste after**  
 460 **5 weeks of immersion according to the distance to the surface (EPMA)**  
 461 **(top), and SEM observations of the polished section in BSE mode (bottom)**





**Figure 8. Mineralogical analysis by XRD of the CEM I-Ox paste immersed for 10 weeks and 5 weeks (Zone 4)**

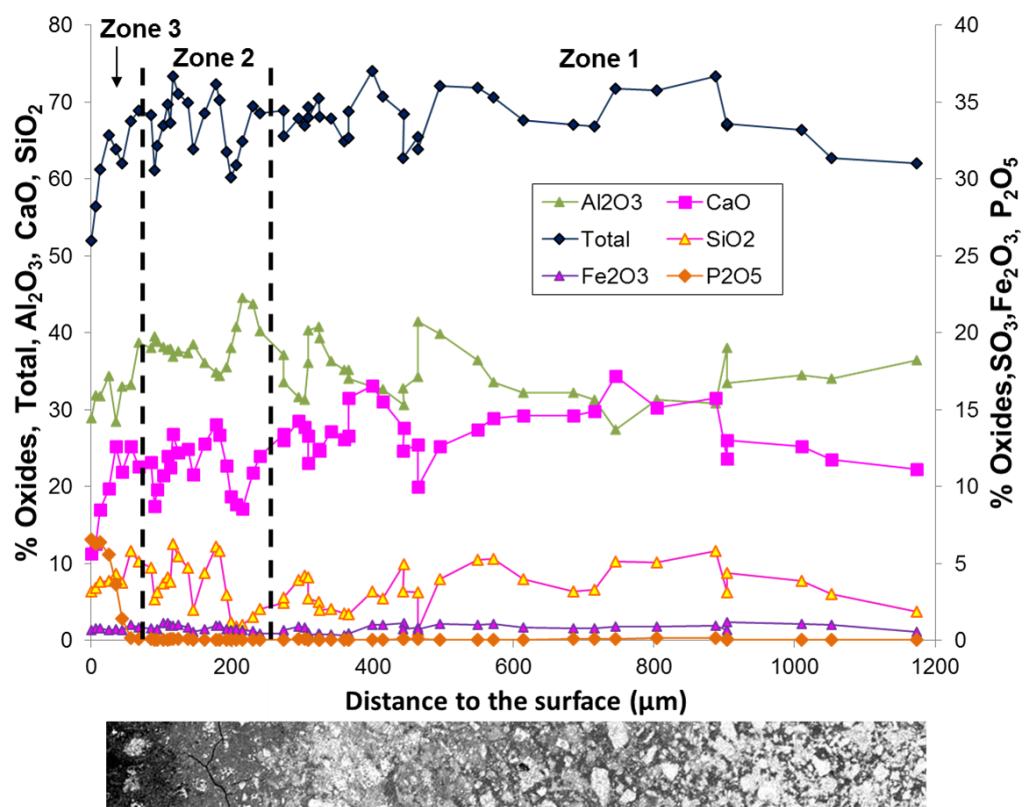
### 3.4.3 CAC paste

The chemical composition of the CAC paste after 10 weeks of immersion is presented in Figure 9, together with a BSE-mode SEM image of the sample.

Chemical compositions are similar after 5 and 10 weeks. The mineralogical analyses from the core to the surface are presented in Figure 10. Three zones are distinguished:

- Zone 1 has similar composition to that of a sound specimen, i.e. it is mainly made of aluminium and calcium, and contains crystalline anhydrous (calcium aluminium oxides (CA), mayenite ( $C_{12}A_7$ ), brownmillerite ( $C_4AF$ ), gehlenite ( $C_2AS$ )) and hydrated phases ( $C_3AH_6$ , gibbsite ( $AH_3$ ),  $C_2AH_8$ ), usually found in aluminate cement matrices. It shows a high density (lighter grey zone on the SEM images).

- 477       • Zone 2, 180 µm thick, shows a slight decalcification, and therefore a  
478       slight relative enrichment of Al. Mineralogical analyses show the same  
479       phases as in zone 1 overall. However, some slight differences can be  
480       noted: the peaks of the anhydrous phases, CA and gehlenite are less  
481       intense closer to the surface; in contrast, gibbsite peaks ( $\text{AH}_3$ )  
482       increased. Aragonite is detected, probably due to the carbonation of  
483       katoite  $\text{C}_3\text{AH}_6$  [57]. Moreover, the density of the paste decreases  
484       (darker background on the SEM image).
- 485       • Zone 3 shows an enrichment in phosphorus with an intense  
486       decalcification and a decrease of the aluminium content. However, no  
487       peak of a crystallized P-bearing phase is observed on the diffraction  
488       pattern. The total oxides content decreases from 65 to 50%. The  
489       mineralogical analysis shows intense peaks of  $\text{AH}_3$ , the broad bases of  
490       which characterize the poorly crystallized character of this phase. The  
491       density of the peripheral zone remains relatively high.



492

493 **Figure 9. Chemical composition of the CAC paste after 10 weeks of**  
 494 **immersion according to the distance to the surface (EPMA) (top), and SEM**  
 495 **observations of the polished section in BSE mode (bottom)**

496



513 increased quickly during the first few days of digestion and then stabilized at  
514 values around 55 mmol.L<sup>-1</sup>. Both cycles showed similar aggressive conditions in  
515 terms of concentrations of aggressive metabolites (VFA, ammonium and  
516 dissolved CO<sub>2</sub>) and pH values. This means that concrete structures in which  
517 anaerobic digestion takes place will undergo repeated aggression when they are  
518 replenished in fed-batch, or a continuous aggression in the case of continuously-  
519 fed digesting installation.

520 These concentrations of aggressive metabolites in the liquid phase of the  
521 bioreactors give information on the aggressiveness of the environment for  
522 concrete. Table 3 summarizes the limit values for solutions according to the  
523 exposure classes as given in FD P 18-011 [31] for the concentrations of  
524 aggressive CO<sub>2</sub> and the ammonium, together with the pH. Considering that, for  
525 each cycle, the pH increased to values up to 6.5 after 7 days, the pH of the  
526 anaerobic digestion in normal operation should not lead to aggressive conditions  
527 for concrete according to the French information document FD P 18-011 [31]  
528 where the upper limit of pH of the XA1 exposure class is 6.5. The standard  
529 documents [30,31] also take the presence and the concentration of ammonium  
530 and dissolved CO<sub>2</sub> into account. The maximum concentration values measured  
531 during the anaerobic digestion (55 mmol.L<sup>-1</sup> for ammonium and 2.3 mmol.L<sup>-1</sup> for  
532 dissolved CO<sub>2</sub>) made the liquid phase of the anaerobic digestion a highly  
533 aggressive medium for cement based materials (class XA3 according to Table 3):  
534 the maximum concentration of ammonium measured was more than 7 times the  
535 upper limit considered in the XA3 range (3.33 – 5.55 mmol.L<sup>-1</sup>) and the dissolved  
536 CO<sub>2</sub> concentration was above the lower limit of the XA3 class (1.67 mmol.L<sup>-1</sup>). It  
537 also can be noticed that ammonium and bicarbonate concentrations of several  
538 grams per liter have been found in fully functioning industrial digesters [58–60].

539 Moreover, it can be highlighted that neither document considers the presence  
540 and concentration of VFA, even though several authors [17,33] have shown that  
541 the acid concentration is a much more significant parameter than the pH in the  
542 evaluation of the aggressiveness of certain types of acids, including organic  
543 acids.

544 The presence and impact of microorganisms, in the form of a biofilm or not, are  
545 not considered either by the FD P18-011 [31] regulation. However, the  
546 establishment of a microbial biofilm between the 5<sup>th</sup> and the 10<sup>th</sup> week was clearly  
547 a factor increasing the deterioration kinetics of the CEM I-Ox paste. In contrast,  
548 the CAC paste was particularly resilient to the biofilm proliferation and was the  
549 material that showed the strongest resistance against the biodeterioration.

550 Several studies agree that microorganisms are acting as accelerating agents on  
551 the deterioration of concrete, aggravating its biodeterioration [7,8,28,29,61]. More  
552 particularly, a study by Magniont et al. [28] has highlighted the clear influence of a  
553 biofilm formation of *E. coli* intensifying the CEM I degradation. In addition, it was  
554 also demonstrated that the ability of bacteria to create a biofilm could be very  
555 harmful for concrete structures [5,28]. According to the non-aggressive pH-  
556 conditions, the dissolution of the external zone (Si-Al gel) of the CEM I paste  
557 presently observed after 10 weeks of exposure can be explained by particularly  
558 severe local conditions brought by the establishment of a biofilm at the surface.

559 Lastly, the standard considers temperatures between 5 and 25 °C while the  
560 anaerobic digestion process occurs mostly at mesophilic conditions (around 37  
561 °C) in the industrial sector [11]. Even if a rise in temperature increases reaction  
562 rates and finally the concrete degradation kinetics, this factor is not taken in  
563 account for the exposure classes.

564 **Table 3. Limit values for exposure classes for liquid environments**  
565 **according to FD P 18-011 [31]**

Aggressive agents	Aggressiveness class according to NF EN 206 [30]			In the biowaste studied
	XA1	XA2	XA3	
<b>Aggressive CO<sub>2</sub> (mg.L<sup>-1</sup>)</b>	≥ 15 and ≤ 20	> 40 and ≤ 100	> 100	101
<b>NH<sub>4</sub><sup>+</sup> (mg.L<sup>-1</sup>)</b>	≥ 15 and ≤ 30	> 30 and ≤ 60	> 60 and ≤ 100	990
<b>pH</b>	≤ 6,5 and ≥ 5,5	< 5,5 and ≥ 4,5	< 4,5 and ≥ 4,0	7.5

566

567 **4.2 Performances of tested materials in relation with biofilm-materials**  
568 **interaction phenomena**

569 The CEM I paste showed the highest deterioration kinetics, with the greatest  
570 degraded depths after 5 and 10 weeks and complete biofilm coverage observed  
571 at 5 weeks of exposure. The early microbial colonization of the CEM I paste could  
572 be explained by the topology of the surface of CEM I, especially the abundance  
573 of micrometric holes, which Voegel et al. [27] found to be favourable to adhesion  
574 and microbial proliferation.

575 The oxalic acid treatment has resulted after 5 weeks in a less intense degraded  
576 depth than in the CEM I specimen, a chemical composition close to that of a  
577 sound sample, and no biofilm coverage. This resistance against the microbial  
578 biofilm growth could come from the surface texture created on the CEM I treated  
579 by oxalic acid: according to Voegel et al. [27], considering the characteristics of  
580 its surface height distribution, the CEM I-Ox paste covered by calcium oxalate  
581 was less favourable to microbial growth. However, after 10 weeks of immersion,  
582 the salt was no longer observed and the sample was covered by biofilm. The  
583 CEM I-Ox paste then showed the same degradation mechanisms as the CEM I

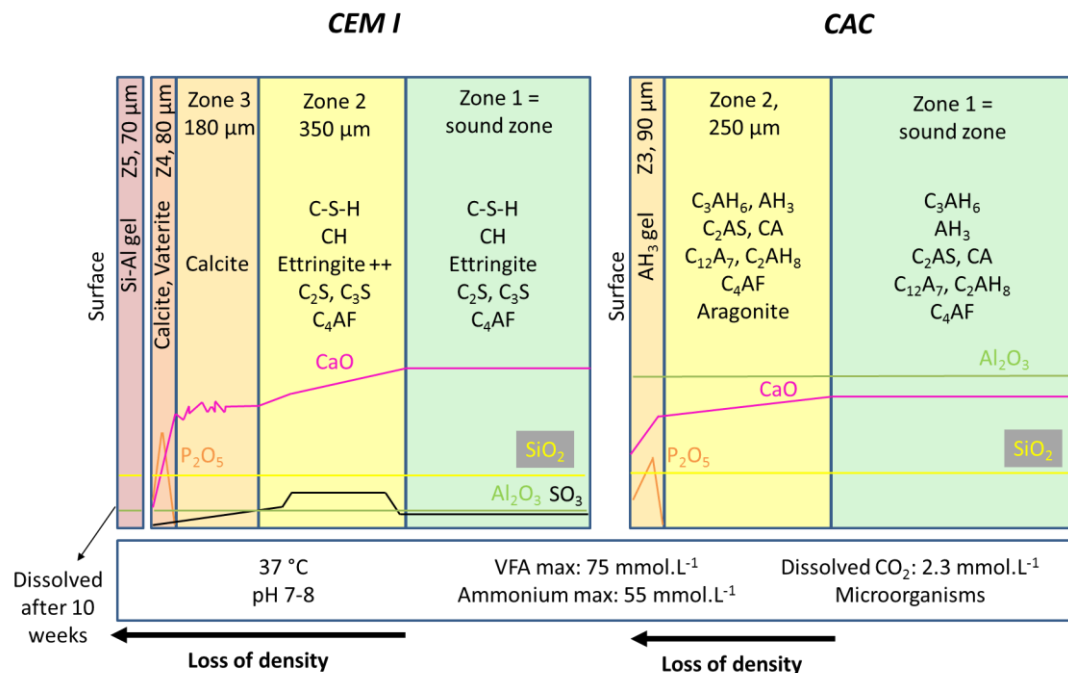
584 paste, with a large degraded depth. Thus, the treatment seemed to have a  
585 protective effect for a limited duration only: it allowed degradation to be delayed  
586 by delaying the biofilm formation on the surface, which underlines the worsening  
587 effect of this formation. The oxalic acid surface treatment probably provided two  
588 types of protection: the delay of biofilm formation and the presence of a layer of  
589 calcium oxalate, which was initially stable against acid attacks, thus protecting  
590 the matrix, but dissolved in the short term, revealing a surface composition close  
591 to that of the non-treated CEM I favourable to microbial proliferation.

592 Although the CAC pastes presented surfaces favourable to proliferation [27], this  
593 material showed the highest durability, with the smallest degraded depths after  
594 10 weeks and only a non-uniform weak surface coverage by a microbial biofilm.  
595 The anhydrous phases of the CAC paste were the most preserved and the  
596 aluminate cement showed some peaks of crystallized  $AH_3$ . However, a halo  
597 baseline characteristics of amorphous compounds is also observed on the  
598 surface layer.

#### 599 **4.3 Biodeterioration mechanisms**

600 Figure 11 summarizes the main chemical and mineralogical changes in the CEM  
601 I and CAC pastes exposed to the anaerobic digesting biowaste for two cycles,  
602 together with exposure conditions and degraded depths.





**Figure 11. Chemical and mineralogical changes and degraded depths of CEM I and CAC pastes exposed to the liquid-solid phase of an anaerobic digestion bioreactor after 10 weeks of immersion and their conditions of exposure.**

#### 4.3.1 CEM I paste

In accordance with Voegel et al. [7], the analyses for the ordinary Portland cement showed alteration mechanisms corresponding to a combination of (i) leaching resulting from the exposure of cementitious materials to VFA [62] and ammonium [20], and (ii) carbonation due to the presence of aqueous CO<sub>2</sub> [21]. As the biowaste contained little or no sulfur, it is likely that the relative enrichment in sulfur at depth, expressed by the formation of secondary non-expansive ettringite, was due to the movement of sulfur from the outer layer, where S-bearing phases were dissolved, into zone 2. The peak of phosphorus in zone 4 was associated with the presence of phosphorus in the substrate [7]. Unlike the CAC paste, the CEM I paste was significantly affected by biofilm formation, leading to an external zone that was totally decalcified: anhydrous grains were completely dissolved after only 5 weeks of immersion, from zone 5 to zone 3.

#### 621 4.3.2 CAC paste

622 In contact with biowaste, the CAC paste underwent chemical and mineralogical  
623 changes. Several phenomena were identified, such as surface decalcification,  
624 (incomplete) dissolution of the anhydrous grains and the hydrates on the surface,  
625 precipitation of calcium carbonates at depth and a phosphorous peak in the  
626 intermediate zone. It could also be noted that the peripheral zone maintained a  
627 relatively high density. The fact that the CAC paste performs best could be linked  
628 to lower colonization of the CAC pastes compared to other binders [63,64].  
629 Herisson et al. [65] explained this by the bacteriostatic effect of aluminium,  
630 present in large amounts in the CAC cements. It should be noted that, when  
631 considering very aggressive sulfur oxidizing conditions comparable to those in  
632 sewer networks, Buvignier et al. [61] showed no direct effect of the aluminium on  
633 the bacteria responsible for the acid attack, which the authors attributed to the  
634 adaptation of the microbial biofilm to high Al concentrations. The particular effect  
635 of CAC on microbial biofilm development was also observed in different  
636 conditions by Peyre Lavigne et al. [66] (sulfur-oxidizing biofilms) and Dalod et al.  
637 [63] (photosynthetic biofilms). Results of both studies suggested that the biofilm  
638 development and/or activity was slowed down on the CAC substrates compared to  
639 the one grown on ordinary binder based materials. Moreover, Peyre Lavigne et  
640 al. [66] showed that the biofilm on CAC was less dense, and drier, and with lower  
641 microbial diversity compared to biofilm grown on other binders. Moreover,  
642 according to the literature, the formation of an aluminium gel ( $\text{Al}(\text{OH})_3$ ) on the surface  
643 leads to better durability of calcium aluminate cement matrices, since this gel is  
644 known to be stable at moderately acidic pH [37].

#### 645 5. CONCLUSION

646 In this study, cement paste specimens were exposed to the anaerobic digestion  
647 liquid phase of laboratory reactors for 10 weeks. At the end of the experiment, all  
648 the cementitious materials tested: made of CEM I (ordinary Portland cement),  
649 CAC (calcium aluminate cement) or CEM I-Ox (CEM I treated with oxalic acid)  
650 were covered by biofilm and presented biodeterioration. The pastes were  
651 affected by alteration mechanisms including leaching, carbonation and  
652 phosphorus enrichment. However, it should be noted that differences of  
653 behaviour were highlighted according to the material. The treatment with oxalic  
654 acid seemed to protect the specimen from biodeterioration by preventing the  
655 formation of biofilm during the first 5 weeks. Calcium oxalate therefore seems to  
656 have a proliferation inhibiting effect, at least in the short term. After this period,  
657 CEM I and CEM I-Ox followed the same degradation kinetics and mechanisms,  
658 with the formation of secondary non-expansive ettringite at depth. CAC paste  
659 showed the best durability performances and smallest degraded depth in the long  
660 term. Moreover, the anhydrous phases of the CAC paste were the best preserved  
661 and some of them were still present in the surface layer. This good durability  
662 could be linked to a less dense coverage by the biofilm but probably also to the  
663 CAC mineralogy and to the formation of a peripheral gel of  $AH_3$ , stable at  
664 moderately acidic pH.

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