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# Potential of low carbon materials facing biodeterioration in concrete biogas structures

Marie Giroudon<sup>1,2</sup>, Cédric Patapy<sup>1</sup>, Matthieu Peyre Lavigne<sup>2</sup>, Mialitiana Andriamiandroso<sup>1</sup>, Robin Cartier<sup>1</sup>, Simon Dubos<sup>2</sup>, Céline Bacquière<sup>1,3</sup>, Ludovic André<sup>1,3</sup>, Sébastien Pommier<sup>2</sup>, Xavier Lefevbre<sup>2</sup>, Martin Cyr<sup>1</sup>, Alexandra Bertron<sup>1</sup>

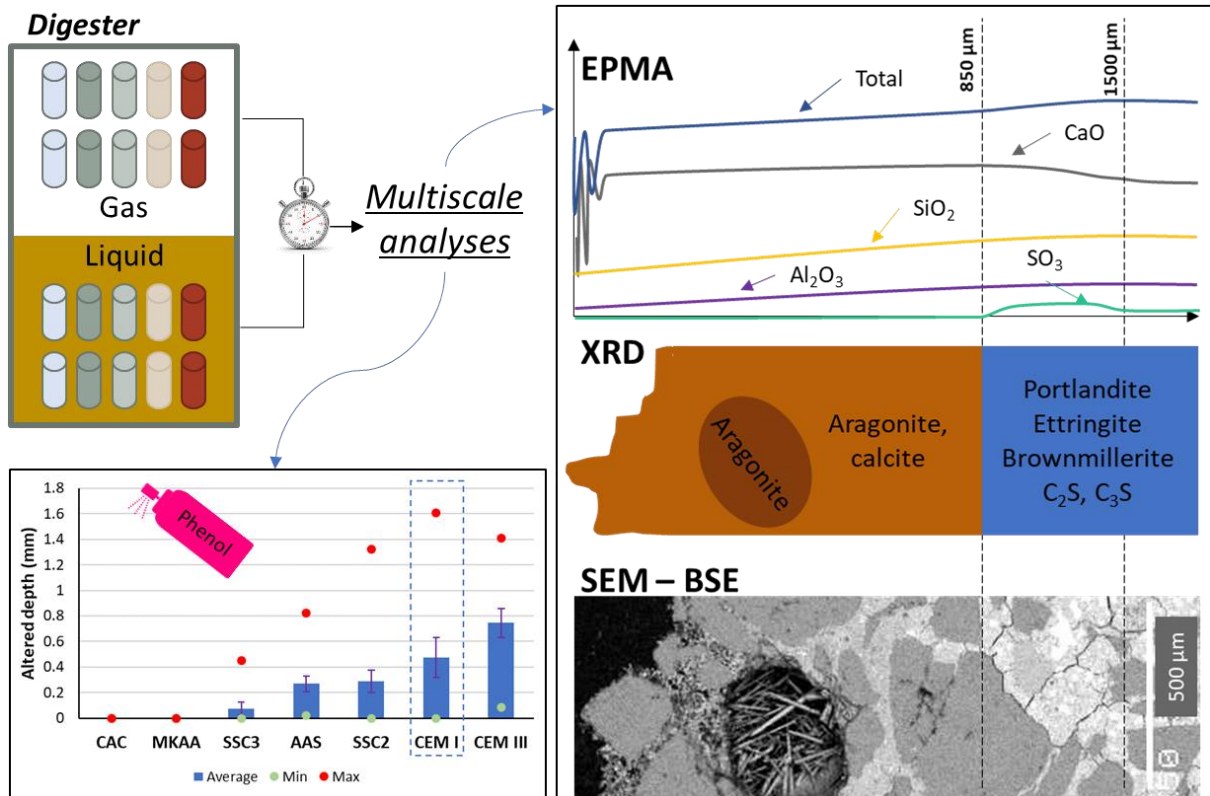
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## 17 Graphical abstract



## 19 Abstract

20 Anaerobic digestion, a renewable energy source, is the degradation of organic waste into  
21 biogas, mainly composed of  $\text{CH}_4$  and  $\text{CO}_2$ . The sector is expanding rapidly due to its multiple  
22 environmental and economic benefits. This process is implemented industrially in concrete  
23 structures that are in direct contact with the biowaste being digested and the gas produced.  
24 Both phases can damage concrete through (i) the presence of volatile fatty acids, dissolved  
25  $\text{CO}_2$ , ammonium, and microbial biofilm in the liquid phase, and (ii) high concentrations of  $\text{CO}_2$   
26 and various concentrations of  $\text{H}_2\text{S}$  in the gas phase. In order to develop more sustainable  
27 concrete biogas units, long-term, in-situ experiments were carried out in a semi-industrial  
28 scale digester to provide new insights into the performance levels and deterioration  
29 mechanisms of various low- $\text{CO}_2$  binders, including alkali-activated metakaolin (geopolymer),  
30 alkali-activated slag (AAS), and supersulfated cements (SSC), in comparison to calcium  
31 aluminate cement (CAC) and Portland cement based matrices. In the running conditions  
32 explored, carbonation of the cementitious matrices was predominant over other  
33 deterioration phenomena in both the digester liquid and the gas phases. Alkali-activated  
34 metakaolin and calcium aluminate cement performed better with few degradations observed.  
35 Supersulfated cements and alkali-activated slag showed an intermediate behaviour with good  
36 performance in the acidic liquid phase but low performance in the  $\text{CO}_2$ -rich gas phase.

## 37 Introduction

38 Anaerobic digestion is a bioprocess transforming organic matter, such as food or agricultural  
39 waste, into a renewable energy through the action of microorganisms, in anaerobic  
40 conditions. This bioprocess produces biogas mainly composed of  $\text{CO}_2$  (20% to 50%) and  $\text{CH}_4$   
41 (50% to 70%), and digestate, generally used as an agricultural amendment [1].

42 Anaerobic digestion treatment units are mainly made of concrete because this material is not  
43 only easy to implement and economical but is also waterproof and airtight, and has good  
44 thermal inertia. In digesters, concrete is in contact with the fermenting biowaste and also  
45 possibly with the gas produced by the bioprocess, since the liners covering the upper walls [2]  
46 may possibly peel off or be punctured. In the liquid phase, microorganisms produce  
47 intermediate metabolites such as volatile fatty acids (VFA), dissolved  $\text{CO}_2$  and  $\text{NH}_4^+$  ions  
48 (produced during acidogenesis and/or contained in some waste [3]), which are aggressive to  
49 concrete. The reaction of these metabolites with the hydrated binders leads to the dissolution  
50 of its initial phases, a partial decalcification, a loss of density, and secondary precipitation of  
51 calcium carbonates [4–9]. Moreover, the presence of microbial biofilm on the concrete  
52 surface can locally accentuate the intensity of damage and the kinetics of degradation  
53 [5,10,11] through the generation of locally high concentrations of aggressive metabolites. In  
54 the gas phase, the very high proportion of carbon dioxide ( $\text{CO}_2$ ) associated with the high  
55 relative humidity (RH) inside the digester, between 53% and 90% according to Obileke et al.  
56 [12], is favourable to the carbonation of the cement phases (carbonation kinetics is maximum  
57 for RH between 40% and 80% [13]). Moreover, biogas also contains hydrogen sulphide ( $\text{H}_2\text{S}$ ),  
58 which is known to cause biogenic acid attack of concrete in sewer networks due to the  
59 formation of sulfuric acid biologically produced in the presence of oxygen [14–19]. During  
60 anaerobic digestion, the gas phase does not normally contain oxygen. However, the digesters

61 can be opened during the emptying of liquid-state digesters or for the reloading of solid-state  
62 digesters. Thus, the structures are actually subjected to alternate anaerobic/aerobic  
63 conditions. Also, Koenig and Dehn [6] identified concrete damage caused by sulfuric acid in a  
64 digester where desulfurization was carried out using atmospheric oxygen.

65 If the sustainable development of the rapidly expanding biogas sector is to be ensured, there  
66 is a need to develop durable, environmentally friendly concrete structures for biogas  
67 production units. To date, very little information is available in the literature on the  
68 performance of traditional and low-carbon binders in these environments under real-life  
69 conditions. Ordinary Portland cement (OPC), blast furnace slag cement, calcium aluminate  
70 cement and metakaolin-based geopolymer have already been tested in laboratory conditions  
71 [4,5,8,9,20], while Portland-based cements (OPC, OPC with additions, slag cement) have been  
72 exposed in situ [6]. In this context, the present work aims to evaluate the durability of several  
73 binders exposed in situ in a semi-industrial-scale digester. Long-term exposure was applied,  
74 for about two years, to low-carbon mortars and pastes based on slag cement, alkali-activated  
75 metakaolin, alkali-activated slag and supersulfated cements as well as mortars based on  
76 Portland and calcium aluminate cements in the liquid and the gas phases of the digester. The  
77 composition of the liquid and gas phase was monitored. After the exposure, the altered depths  
78 of the mortars were measured to establish a ranking of the performance of the different  
79 materials. The main degradation mechanisms of the various materials were also analysed by  
80 microscale analyses (scanning electron microscopy coupled to energy dispersive  
81 spectrometry, and X-ray diffraction).

## 82 1 Materials and methods

### 83 1.1 Binders

84 Cement pastes and mortars were manufactured from the following binders:

- 85 • an OPC CEM I 52,5 R Lafarge – Port la Nouvelle (CEM I), used as a reference binder;
- 86 • a slag cement, CEM III/B 42,5 N Lafarge – La Malle (CEM III) containing 71% of ground  
87 granulated blast furnace slag (GGBS);
- 88 • a calcium aluminate cement, Imerys Aluminates – Calcoat® RG (CAC);
- 89 • a metakaolin-based geopolymer (metakaolin from Argeco Développement; sodium  
90 silicate of modulus  $\text{SiO}_2/\text{Na}_2\text{O} = 1.7$ , Betol 47T Na-Silicate from Wöllner;  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of  
91 the geopolymer = 3.6) (MKAA);
- 92 • an alkali-activated slag (AAS) from ECOCEM, the GGBS being activated by 10% of  
93 sodium silicate of modulus  $\text{SiO}_2/\text{Na}_2\text{O} = 1.7$ , Betol 47T Na-Silicate from Wöllner;
- 94 • two supersulfated cements from ECOCEM (SSC2 and SSC3):
  - 95 ○ SSC2 contained >75% GGBS and 20% calcium sulfate;
  - 96 ○ SSC3 contained >75% GGBS, 20% calcium sulfate and an activator.

97 Chemical compositions of the binders are given in Table 1.

98 *Table 1. Oxide compositions of the binders in mass percentages and loss of ignition (l.o.i) (%) – ICP-OES analyses – n.d. = not*  
99 *detected*

	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	l.o.i
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<b>CEM I</b>	20.00	66.20	4.85	2.64	n.d.	0.14	1.06	0.27	3.01	0.06	1.64
<b>CEM III</b>	30.00	48.80	9.48	2.78	n.d.	0.50	2.72	0.48	2.93	0.23	1.89
<b>CAC</b>	5.58	38.30	51.60	1.65	0.37	0.07	0.50	2.24	0.02	0.13	0.24
<b>Metakaolin</b>	68.10	1.38	25.60	3.58	0.32	0.03	0.22	1.22	n.d.	0.05	2.58
<b>GGBS</b>	33.19	41.75	11.16	0.58	0.55	0.31	7.38	0.77	0.06	0.03	0

100

101 The CEM I, CEM III, CAC, AAS and SSC pastes were poured with a water/binder ratio (W/B) of  
102 0.30 and the associated mortars were poured with a W/B ratio of 0.40. The metakaolin-based  
103 alkali-activated pastes and mortars were manufactured according to Pouhet's procedure [21]  
104 by mixing metakaolin, liquid sodium silicate, water – and sand for the mortars. The precise  
105 designs of SSC are confidential. The pastes and mortars were mixed using an adaptation of the  
106 French standard NF EN 196-1 (using the water/binder ratios defined above but without sand  
107 for the pastes). Two types of moulds were used: cylindrical PVC moulds 75 mm high and 25  
108 mm in diameter for CAC pastes only, and cylindrical PET plastic pillboxes 70 mm high and 35  
109 mm in diameter for the other pastes and all the mortars. After casting, the PVC moulds were  
110 covered with plastic film and the pillboxes were closed with their lids. Immediately after  
111 pouring, a heat treatment was applied to the CAC specimens (pastes and mortars) in order to  
112 promote the conversion of the metastable hydrates  $CAH_{10}$  and  $CAH_8$  into stable hydrates  
113  $C_3AH_6$  [22]. For this purpose, the CAC specimens were placed in a climatic chamber at 35°C and  
114 85% RH, and the temperature was gradually increased so as to reach 70°C after 3 hours. This  
115 temperature was maintained for a further 3 hours to allow the conversion. Finally, the  
116 specimens were placed in a storage chamber (20°C). The MKAA samples were removed from  
117 their moulds after 7 days of curing according to the recommendations of Pouhet [21]. Those  
118 based on CEM I and CAC underwent an endothermic cure of 28 days. Finally, the slag-based  
119 specimens, i.e. CEM III, AAS and SSC, had a longer 90-day endothermic cure in order to  
120 promote the formation of hydrates and therefore the reduction of porosity [23,24] as well as  
121 the development of their mechanical strength [25]. At the end of their curing period, all the  
122 samples were stored in closed plastic bags at 20°C. The mortars were sawn in half before  
123 exposure in order to double the number of samples.

## 124 1.2 Semi industrial scale digester

### 125 1.2.1 The SOLIDIA experimental platform

126 Samples were exposed to real anaerobic digestion conditions using the SOLIDIA platform at  
127 Bélesta-en-Lauragais (Haute-Garonne, France). This experimental platform was implemented  
128 by the CRITT GPTE<sup>1</sup> team of Toulouse Biotechnology Institute for research purposes. The  
129 experimental platform can be fed directly with biowaste or digestate from the CLER VERTS  
130 company, which specializes in the recovery of organic waste. Two tanks are dedicated to liquid  
131 anaerobic digestion on the SOLIDIA site. The digesters (2 m in diameter, about 3.5 m high,  
132 designed to contain 8 m<sup>3</sup>) are made of polyethylene and insulated.

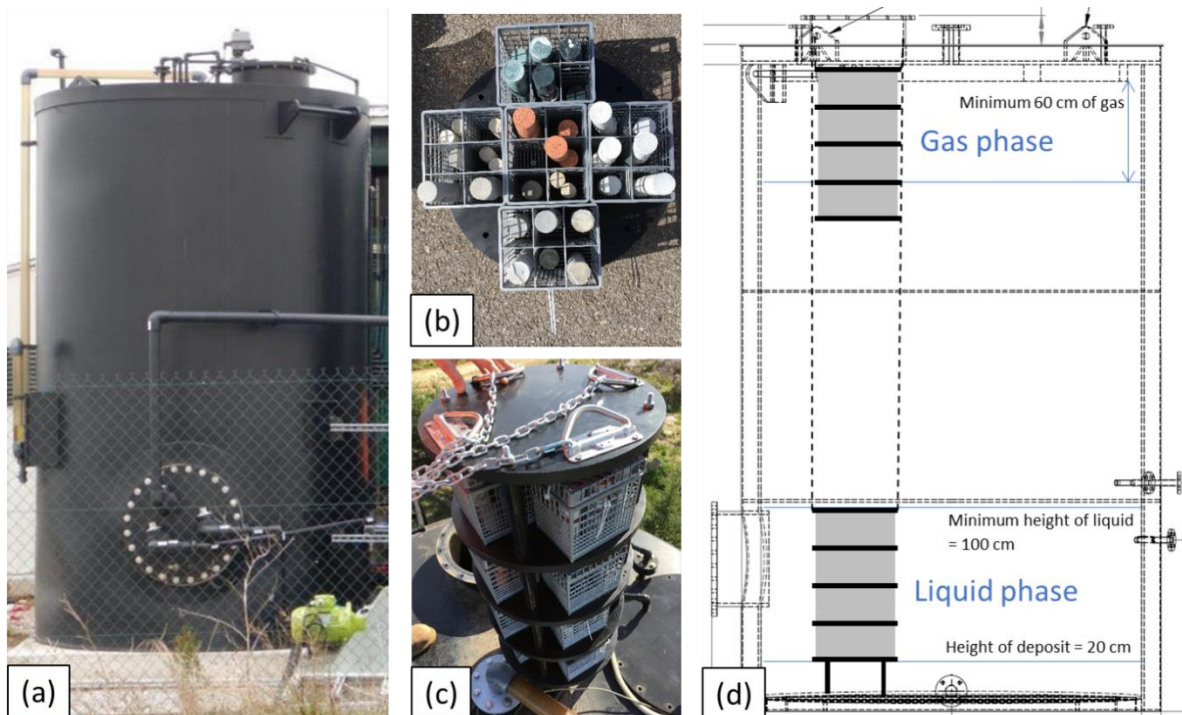
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<sup>1</sup> CRITT GPTE: Centre Régional d'Innovation et de Transfert de Technologies, Génie des Procédés – Technologies Environnementales (Regional Centre for Innovation and Technology Transfer, Process Engineering – Environmental Technology)

133 1.2.2 Exposure conditions of the samples

134 • Distribution of the samples

135 The samples were exposed to both the liquid and the gas phases, in a single tank (Figure 1 (a)).  
136 To allow smooth circulation of the gas and liquid, the samples were placed in dishwasher  
137 cutlery baskets (Figure 1 (b)). The baskets were hung on two polypropylene structures set at  
138 different heights in the digester (Figure 1 (c)) (one structure for the gas phase and one for the  
139 liquid phase). The structures were then introduced into the digester through the manhole and  
140 fixed using chains (see Figure 1 (d)). The layout of the structures was designed considering the  
141 minimum and maximum filling levels and also the estimated height of the solid deposit fringe  
142 at the bottom of the tank, as shown in Figure 1 (d).



143

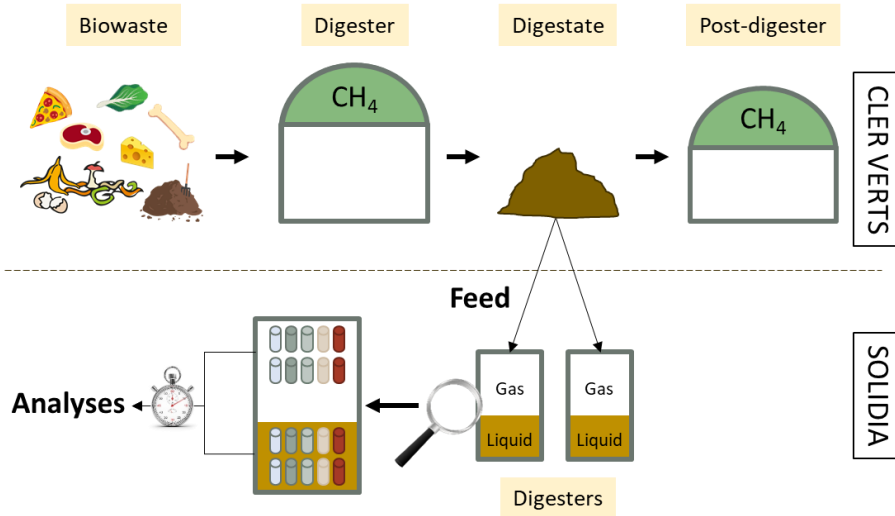
144 *Figure 1. (a) Semi industrial scale digester used for the in-situ exposure – SOLIDIA, Béléssta-en-Lauragais, (b) samples*  
145 *compartmented in dishwasher baskets, (c) assembly of the baskets on a polypropylene structure, and (d) positioning of the*  
146 *basket structures in the digester*

147 The samples intended for the liquid phase were inserted in the digester on 18<sup>th</sup> March, 2019,  
148 whereas those for the gas phase were inserted on 6<sup>th</sup> June, 2019. The former were removed  
149 from the liquid phase on 24<sup>th</sup> June, 2021 whereas the latter were removed from the gas phase  
150 on 16<sup>th</sup> March, 2021. Thus the total exposure duration was approximately 2 years and 3  
151 months in the liquid phase and 1 year and 10 months in the gas phase. The extracted samples  
152 were stored in closed plastic bags and kept in a storage chamber at 20°C until characterization.

153 • Digester feeding and composition of the liquid and gas phases

154 The CLER VERTS industrial digester is fed with biowaste from restaurants or unsold products  
155 from large and medium-sized retail outlets. It can treat vegetables, fruits, cereals, milk, meat,  
156 eggs, fish, and also agricultural waste such as manure and slurry [26]. The digestate produced  
157 is used to feed the SOLIDIA tanks. Usually, it is further degraded in a post-digester to produce

158 more methane (Figure 2). The use of a digestate as substrate leads to matter that is less  
 159 biodegradable than biowaste, and thus to less aggressive conditions for the materials.



160

161 *Figure 2. Feeding of the SOLIDIA digesters*

162 The chemical compositions of the liquid phase were analysed on the following dates:  
 163 28/01/2020, 04/02/2020, 25/09/2020, 03/11/2020, 10/12/2020 and 21/06/2021. The results  
 164 are shown in Table 2.

165 *Table 2. Composition of the liquid phase of the digester at six dates during the immersion (n.m. = not measured; n.d. = not  
 166 detected < 1 mg/L)*

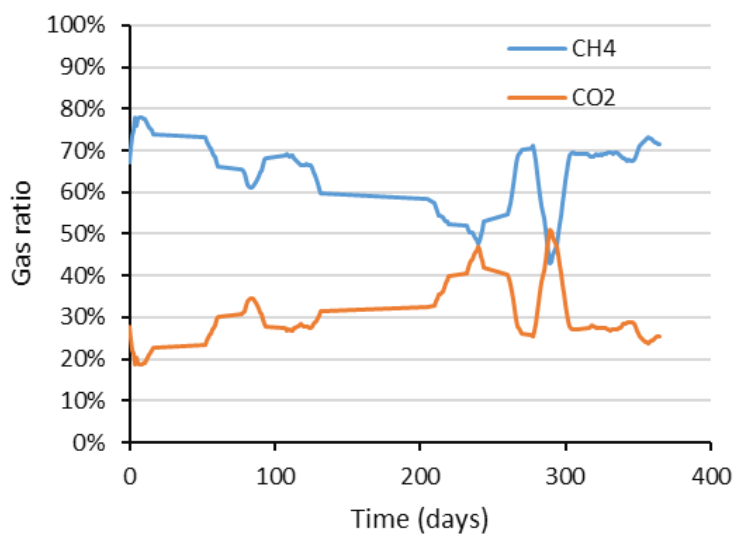
Date	28/01/2020	04/02/2020	25/09/2020	03/11/2020	10/12/2020	21/06/2021
Duration of immersion	≈ 10 months	≈ 10.5 months	≈ 18 months	≈ 19.5 months	≈ 20.5 months	≈ 27 months
Inorganic carbon (gC/L)	n.m.	n.m.	3.01	1.58	n.m.	3.69
[Cl <sup>-</sup> ] (mg/L)	1165.3	1163.2	3267.0	1889.8	2417.8	3446.3
[NH <sub>4</sub> <sup>+</sup> ] (mg/L)	1487.4	1473.3	3589.4	3056.8	4001.9	3479.7
[Mg <sup>2+</sup> ] (mg/L)	59.8	55.8	27.4	6.1	10.0	12.0
[K <sup>+</sup> ] (mg/L)	1578.5	1528.3	1536.0	914.6	1264.9	1353.3
[Na <sup>+</sup> ] (mg/L)	845.5	846.5	1113.0	840.4	880.2	1067.4
[Ca <sup>2+</sup> ] (mg/L)	31.9	14.0	819.6	247.8	185.6	218.7
pH	7.75	8.04	n.m.	n.m.	n.m.	n.m.
VFA tot (mg/L)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

167

168 The liquid phase of the digester was rich in CO<sub>2</sub> and contained high concentrations of Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>  
 169 and K<sup>+</sup> (> 1 g/L), and Na<sup>+</sup> and Ca<sup>2+</sup> (several hundred mg/L). VFA concentrations were below the  
 170 level of detection, which is consistent with the fact that VFA are continuously consumed in an  
 171 efficient continuously fed digester. In previous laboratory experiments, lower ion  
 172 concentrations were measured: NH<sub>4</sub><sup>+</sup> concentrations remained below 1 g/L, Na<sup>+</sup>  
 173 concentrations were about 100 mg/L, and K<sup>+</sup> concentrations were several hundred mg/L  
 174 [4,5,8,9]. Mg<sup>2+</sup> concentrations were similar both in situ and in laboratory experiments [4].

175 Carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) contents were measured online during a previous  
176 campaign run in 2015 [27]. Variations in gas composition occurred in the tank, with CO<sub>2</sub>  
177 contents that varied from 25% to 60% and CH<sub>4</sub> contents that varied from 30% to 70% of the  
178 gas phase.

179 Moreover, the gas phase composition was analysed during the first year of exposition (March  
180 2019 to March 2020). Figure 3 shows the CH<sub>4</sub> and CO<sub>2</sub> ratio (compared to the total amount of  
181 CH<sub>4</sub> and CO<sub>2</sub>) in the gas phase of the digester during this period. No measurement of the H<sub>2</sub>S  
182 concentration was performed. In comparison with the previous measurements of 2015, low  
183 amount of CO<sub>2</sub> was observed in the tank. This could be explained by the presence of a large  
184 amount of cementitious pastes in the digester, which could have reacted with both the  
185 gaseous and dissolved CO<sub>2</sub>.



186

187 *Figure 3. CH<sub>4</sub> and CO<sub>2</sub> ratio (compared to the total amount of CH<sub>4</sub> and CO<sub>2</sub>) in the gas phase of the digester between March*  
188 *2019 and March 2020*

### 189 1.3 Analyses of the materials

190 The characterization of the deterioration of materials exposed to anaerobic digestion  
191 consisted of (i) the macroscopic analysis of the samples and (ii) the characterization of their  
192 microstructural, chemical and mineralogical alteration.

#### 193 1.3.1 Macroscopic characterization: altered depths

194 The macroscopic analysis measured the altered depth (loss of alkalinity) by spraying  
195 phenolphthalein on two flat sawn sections of the sample. The colour change from violet (in  
196 the inner, alkaline zone of the sample) to transparent (in the outer layer in contact with the  
197 gas or liquid phase) indicated the altered depth. Two hours after the spraying, each side of a  
198 sample was scanned and the images were analysed using ImageJ software: the altered depths  
199 were measured at 32 points of measurement around the circumference. The average, 95%  
200 confidence intervals using Student's law, and minimum and maximum values of the 32  
201 measurements are considered in the exploitation of the results.



### 202 1.3.2 Microscopic characterization

203 Thorough microscopic characterization was carried out in order to understand the various  
204 mechanisms of material deterioration. A diamond saw was used to collect circular slices from  
205 the samples for solid analyses. Quarter slices of mortars were prepared for Scanning Electron  
206 Microscopy (SEM) in backscattered electron mode (BSE) (JEOL JSM-LV, 15 kV) and Electron  
207 Probe Micro-Analysis (EPMA) (CamecaSXFive, 15 kV, 20 nA). The sections were embedded in  
208 an epoxy resin (Mecaprex Ma2+ from Presi), and dry polished using silicon carbide polishing  
209 disks (Presi; ESCIL, P800–22  $\mu\text{m}$ , P1200–15  $\mu\text{m}$  and P4000–5  $\mu\text{m}$ ). The flat, polished sections  
210 were then coated with carbon. The chemical composition changes were characterized using  
211 EPMA chemical profiles, from the surface to the core according to the distance to the surface.  
212 The analysis spots were chosen with particular care through point-by-point selection in order  
213 to analyse hydrated paste and not residual anhydrous grains. Trend curves, based on the  
214 analysis of three chemical composition profiles for each material, are used below to present  
215 the chemical modifications of the mortars (EPMA). The mineralogical alterations were  
216 assessed by qualitative X-Ray Diffraction analyses (XRD) (Bruker D8 Advance, Cu anti-cathode,  
217 40 kV, 40 nA, 15 min,  $2\theta$ : 4 to  $70^\circ$ , 0.25 s per step in  $0.02^\circ$  increments) on the upper side of  
218 the paste samples. The plane side of the slices was first analysed, then the slice was  
219 successively abraded and analysed in order to characterize the mineralogical changes with  
220 depth, until sound paste was reached.

221 The degraded depths observed on the trend curves are not directly comparable with the  
222 phenolphthalein spray results since they rely on only a few chemical profiles that are not  
223 representative of the global composition of the material. This point is further addressed in the  
224 discussion.

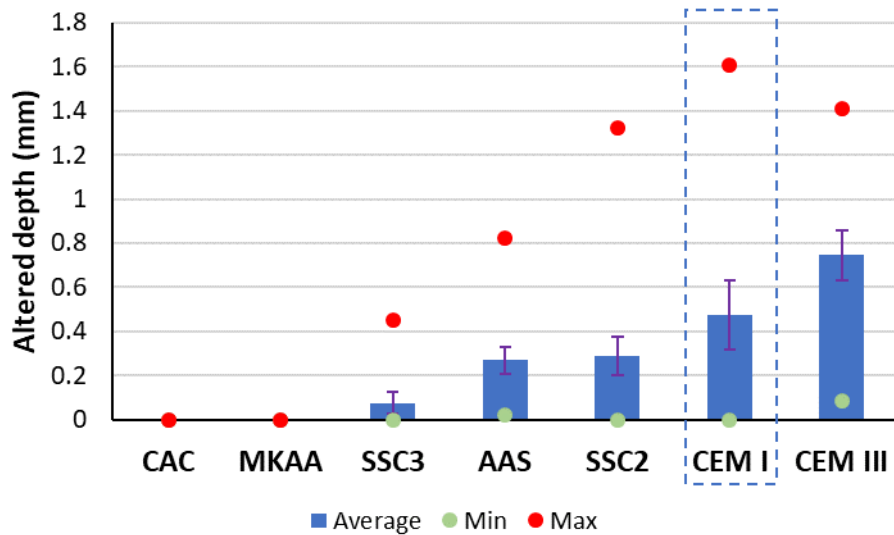
## 225 2 Results

226 The materials were divided into three subclasses with regard to the nature of the binder:  
227 Portland cement-based materials (CEM I and CEM III), aluminium-rich materials (CAC and  
228 MKAA) and activated slag-based materials (AAS and SSC).

### 229 2.1 Deterioration of materials in the liquid phase

#### 230 2.1.1 Altered depths of specimens

231 Figure 4 gives the altered depths of the different mortars exposed to the liquid phase of the  
232 digester for 2 years and 3 months. The average value of 32 measurements is provided for each  
233 mortar, together with the minimum and maximum values measured and the corresponding  
234 confidence intervals. The different material types are presented in increasing order of their  
235 degraded depth in order to establish their relative performance levels, with the CEM I-based  
236 mortar as the reference.



237

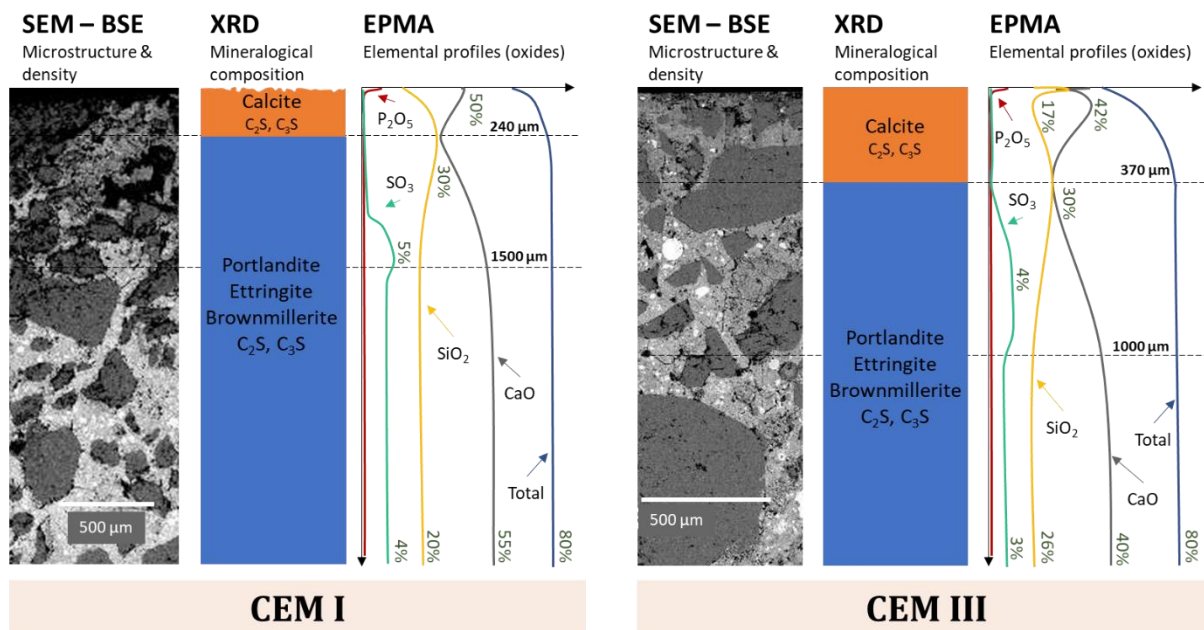
238 *Figure 4. Performance ranking of the mortars according to their altered depth after 2 years and 3 months of exposure to the*  
 239 *liquid phase of the digester – blue dashed frame corresponds to the CEM I-based reference mortar*

240 Mortars made with CAC and MKAA did not show altered depths with this test (no colour  
 241 change of the phenolphthalein on the whole cross section of the specimens). The SSC3, AAS  
 242 and SSC2-based mortars had lower degraded depths than CEM I: respectively  $0.075 \pm 0.049$   
 243 mm,  $0.269 \pm 0.063$  mm, and  $0.287 \pm 0.088$  mm versus  $0.474 \pm 0.156$  mm. CEM III mortars  
 244 presented the greatest degraded depths ( $0.745 \pm 0.114$  mm). The disparity between minimum  
 245 and maximum values highlights a non-homogeneous alteration of the mortars on the  
 246 circumference of the slices, probably linked with an uneven development of the biofilm on  
 247 their surface [28].

#### 248 2.1.2 Microstructural, chemical and mineralogical alteration of CEM I and CEM III mortars

249 Figure 5 summarizes the results of the SEM observations, the XRD analyses and the EPMA  
 250 analyses.

251 The materials based on CEM I and CEM III mainly experienced dissolution and carbonation,  
 252 calcite being the main crystallized mineralogical phase identified in the outer zone. The  
 253 anhydrous phases were dissolved in the outer zone, where Ca leaching and a slight loss of  
 254 density were observed in the SEM image. A sulfur enrichment occurred in the intermediate  
 255 zone. Slight enrichments in  $P_2O_5$  were observed close to the surface of the CEM I and CEM III  
 256 mortars (up to 0.42% and 0.64% in mass, respectively). No major mineralogical change was  
 257 observed deeper than 370  $\mu\text{m}$  from the surface of the specimens. These mechanisms were  
 258 similar to those previously observed in laboratory experiments [4,5].



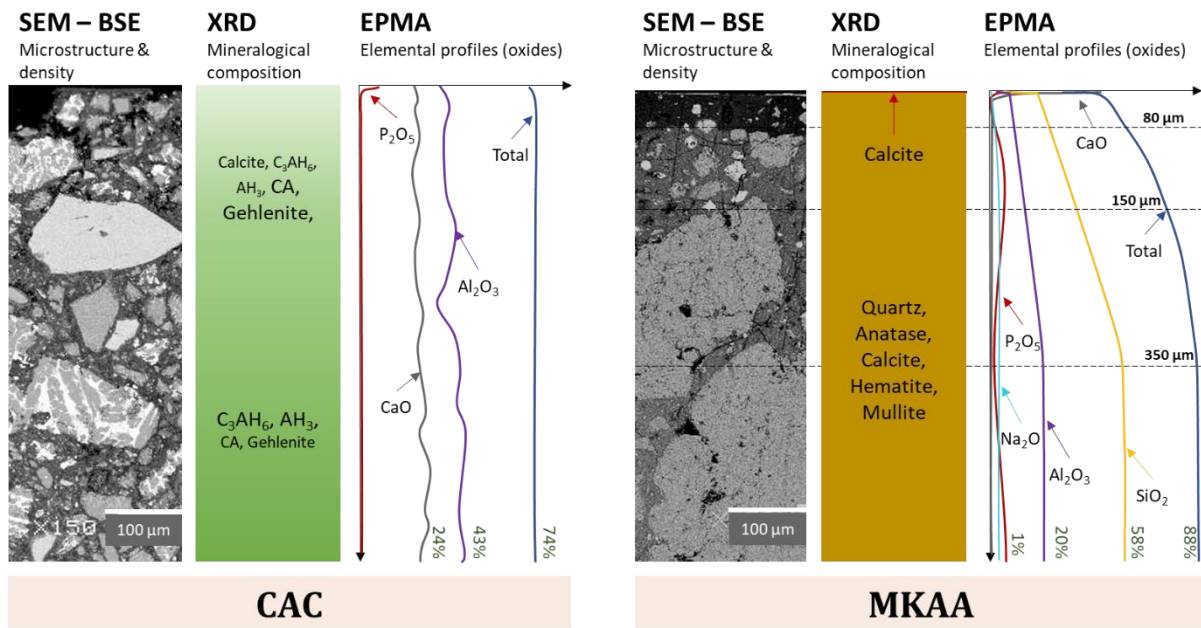
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260 *Figure 5. BSE-SEM images and mineralogical and chemical compositions of the different zones of the CEM I and CEM III mortars*  
 261 *after 2 years and 3 months of exposure in the liquid phase of a digester*

262 2.1.3 Microstructural, chemical, and mineralogical alteration of CAC and MKAA mortars

263 CAC mortar was slightly biodeteriorated but presented no major change in chemical and  
 264 mineralogical compositions (Figure 6). A slight enrichment in P<sub>2</sub>O<sub>5</sub> occurred near the surface  
 265 (up to 0.28% in mass) and calcite precipitated.

266 A thin external carbonated layer was observed on the MKAA mortar (brighter layer in the SEM  
 267 image) associated with the intensification of the calcite peaks in the XRD patterns and an  
 268 enrichment in CaO coming from the liquid (since the geopolymer did not initially contain CaO)  
 269 (EPMA). Under the carbonated layer, over 80 μm, the paste had a significantly lower density  
 270 than the sound core. K<sub>2</sub>O (not shown) and Na<sub>2</sub>O were leached over 150 μm (from 3.4% to 1%  
 271 and 0.7% to 0.3% respectively). The alteration of the material up to 350 μm deep resulted in  
 272 the dissolution of the matrix, as in previous studies [4,5]. This deterioration was probably due  
 273 to the acidic component of the liquid medium since similar dissolution has already been  
 274 observed during acid attacks in other studies [29–31].



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Figure 6. BSE-SEM images and mineralogical and chemical compositions of the different zones of the CAC and MKAA mortars after 2 years and 3 months of exposure in the liquid phase of a digester

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2.1.4 Microstructural, chemical and mineralogical alteration of AAS, SSC2 and SSC3 mortars

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Figure 7 shows the mineralogical and chemical alterations (analysed by XRD and EPMA

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respectively) and SEM images of the AAS, SSC2 and SSC3 samples.

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According to the mineralogical and chemical analyses, the alteration mechanism of the AAS

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material was mainly surface carbonation, expressed by the intensification of the calcite signal

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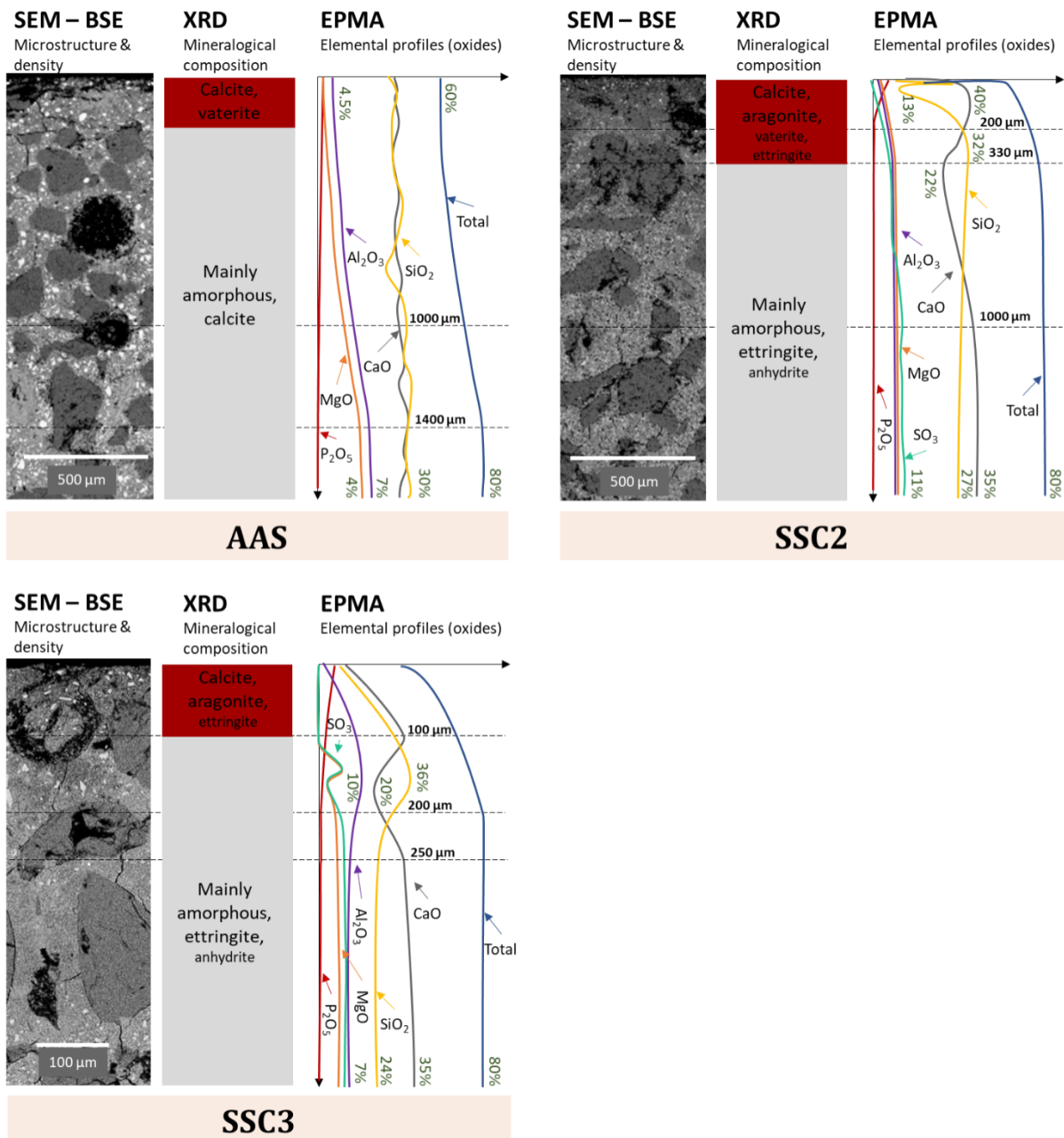
(XRD) in the outer layer and the precipitation of calcite and vaterite. However, no major

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change in the mortar chemical composition was spotted. A slight enrichment in  $P_2O_5$  (up to

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0.8% at 18  $\mu m$  deep) was observed in the outer layer.



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Figure 7. BSE-SEM images and mineralogical and chemical compositions of the different zones of the AAS, SSC2 and SSC3 mortars after 2 years and 3 months of exposure in the liquid phase of a digester

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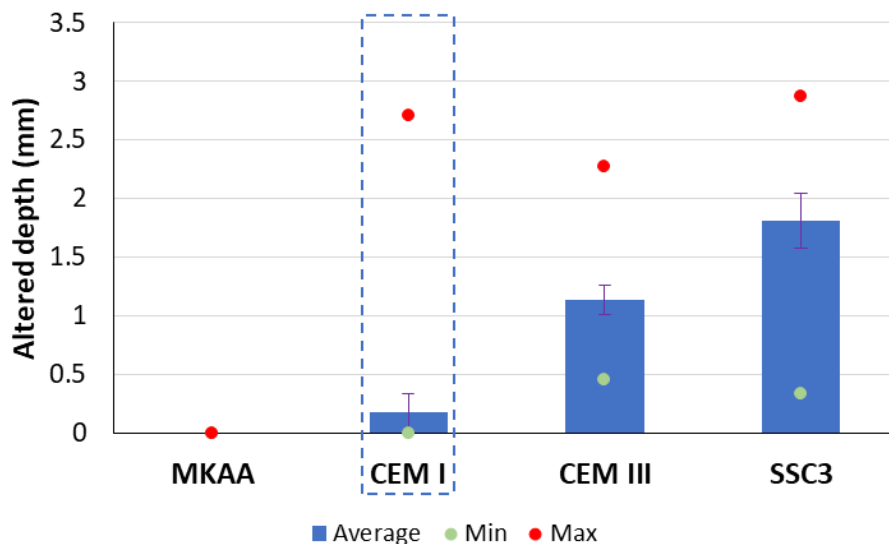
XRD analyses showed the precipitation of the crystallized calcium carbonate phases in the outer layer of the SSC2 and SSC3 mortars. Calcite and aragonite precipitated in both mortars whereas vaterite was identified only in SSC3. This is consistent with the chemical composition profiles, which showed a slight decalcification in depth, and then an increase in the calcium oxide content associated with the decrease in the contents of other oxides up to the surface of the mortars, corresponding to carbonation and leaching. The density of the mortars decreased close to the surface (darker zones in the SEM image). An enrichment in phosphorus was observed in the outer layer (up to 0.5% at 38 μm deep for SSC2 and up to 0.6% at 20 μm deep for SSC3).

298 Thus, the degradation phenomena observed on the three slag-based materials (AAS, SSC2 and  
 299 SSC3) were mainly surface carbonation and leaching, with a slight enrichment in phosphorus  
 300 in the outermost few tens of microns. However, according to the chemical composition  
 301 profiles, the sensitivities of the slag-based materials to the attack were significantly different:  
 302 SSC3 had a degraded depth of 250  $\mu\text{m}$ , SSC2 of 1000  $\mu\text{m}$  and AAS of 1400  $\mu\text{m}$ .

## 303 2.2 Deterioration of materials in the gas phase

### 304 2.2.1 Altered depth of specimens

305 Figure 8 shows the altered depths of the different mortars that were exposed to the gas phase  
 306 of the digester (average values of the 32 lengths measured for each), together with the  
 307 minimum value and the maximum value measured, and the corresponding confidence  
 308 intervals. The results are presented in increasing order of degraded depth so as to establish  
 309 the relative performances of the samples, the CEM I-based mortar being used as a reference.  
 310 Unfortunately, the liquid level rose during the in situ exposure and the CAC-based mortars  
 311 were submerged, so could not be studied and compared with the other samples. As the SSC3  
 312 mortar was the most efficient slag-based material in the liquid phase, it was chosen to be  
 313 studied in the gas phase.



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315 *Figure 8. Performance ranking of the mortars according to their altered depth after 1 year and 10 months of exposure to the*  
 316 *gas phase of the digester – blue dashed frame corresponds to the CEM I-based reference mortar*

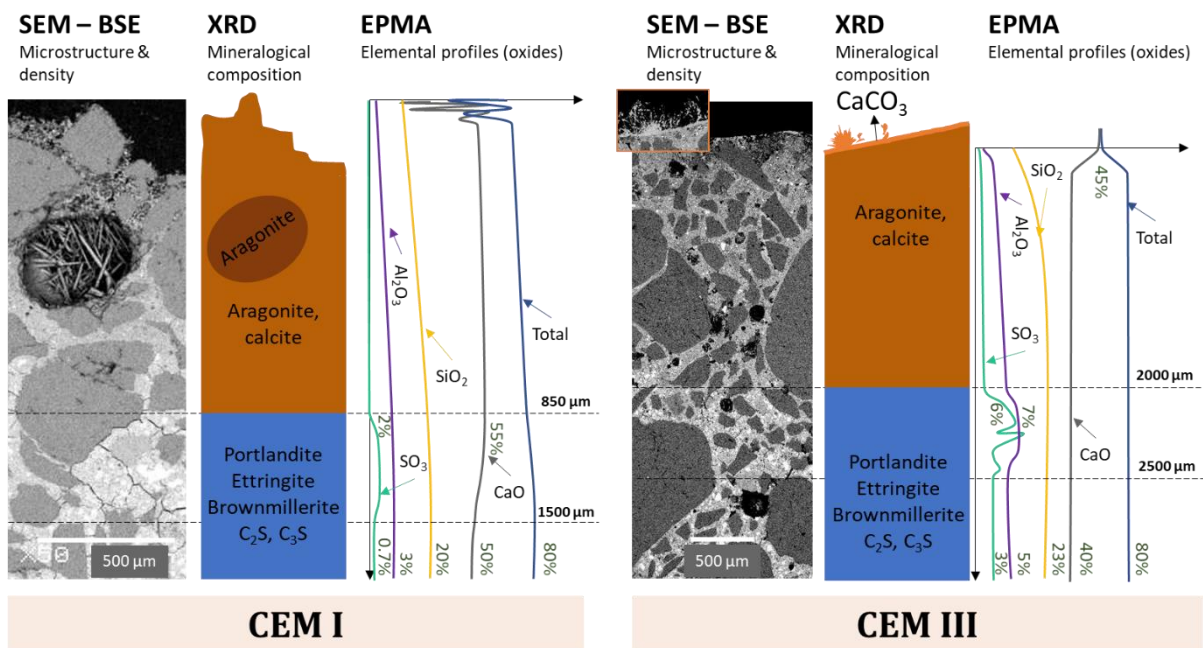
317 As for the specimens immersed in the liquid phase, this test highlighted no altered depth on  
 318 the MKAA-based mortar, and the CEM III-based mortar showed deeper altered depth ( $1.135 \pm 0.122$  mm)  
 319 than the CEM I-based mortar ( $0.183 \pm 0.158$  mm). However, in the gas phase, the  
 320 SSC3 mortar showed lower performance than the CEM I-based mortar, with significantly  
 321 higher altered depth ( $1.813 \pm 0.231$  mm). A great disparity in the distribution of the alteration  
 322 depth was noted.

### 323 2.2.2 Microstructural, chemical and mineralogical alteration of CEM I and CEM III mortars

324 The structural, chemical and mineralogical analyses of the CEM I-based mortar (Figure 9)  
 325 highlighted carbonation in the surface layer, with the precipitation of calcite and aragonite,  
 326 needle-shaped aragonite crystals [32] being observed on the SEM images inside the porosity.

327 Few anhydrous grains remained in this external zone, which was less dense than the core.  
 328 From 850  $\mu\text{m}$  to 1500  $\mu\text{m}$  deep, an enrichment in sulphur was observed in the chemical  
 329 composition profile, associated with a denser paste and microcracks in the SEM image. This  
 330 could correspond to a local precipitation of secondary ettringite. No phosphorous enrichment  
 331 was spotted. The mortar was sound from 1500  $\mu\text{m}$  deep.

332 The alteration of CEM III-based mortar was very similar to that of the CEM I-based mortar. A  
 333 whitish deposit was visible (to the naked-eye) on the surface of the sample, which  
 334 corresponded to a thin layer of calcium carbonate unevenly covering its surface (SEM image).  
 335 Moreover, large, needle-shaped precipitates were observed in places. XRD analyses showed  
 336 the presence of calcite and aragonite. The external 2000  $\mu\text{m}$  thick zone was less dense than  
 337 the core of the specimen with few remaining anhydrous grains. From 2000  $\mu\text{m}$  to 2500  $\mu\text{m}$   
 338 deep, the matrix showed higher density, microcracking, and an enrichment in sulfur, up to  
 339 15% at some places, which could be the sign of ettringite precipitation in this area. The mortar  
 340 was sound from 2500  $\mu\text{m}$  deep. Note that, for this sample, the degradation was not  
 341 homogeneous and probably depended on the uneven covering of the surface by calcium  
 342 carbonate crystals, which may have prevented the penetration of aggressive agents by  
 343 clogging the porosity.

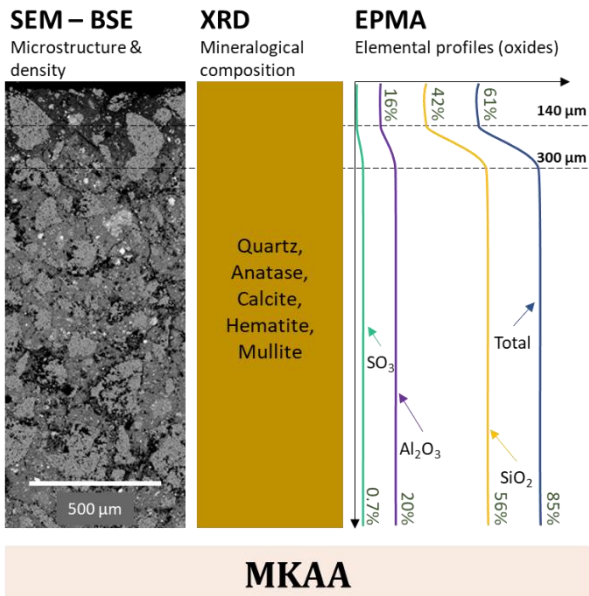


344

345 *Figure 9. BSE-SEM images and mineralogical and chemical compositions of the different zones of the CEM I and CEM III mortars*  
 346 *after 1 year and 10 months in the gas phase of a digester*

347 2.2.3 Microstructural, chemical and mineralogical alteration of MKAA mortar

348 Figure 10 shows the structural, mineralogical and chemical composition of the MKAA mortar  
 349 after its exposure to the gas phase of the digester. Only slight leaching was observed from the  
 350 chemical composition profile, illustrated by a less dense matrix (SEM image).  $\text{Na}_2\text{O}$  was slightly  
 351 leached (from 1.5% to 1%) on the outer 140  $\mu\text{m}$  (not shown for easier reading of the graph).  
 352 No mineralogical change was observed by XRD analyses. The material was sound from 300  $\mu\text{m}$   
 353 deep.



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*Figure 10. BSE-SEM images and mineralogical and chemical compositions of the different zones of the MKAA mortar after 1 year and 10 months in the gas phase of a digester*

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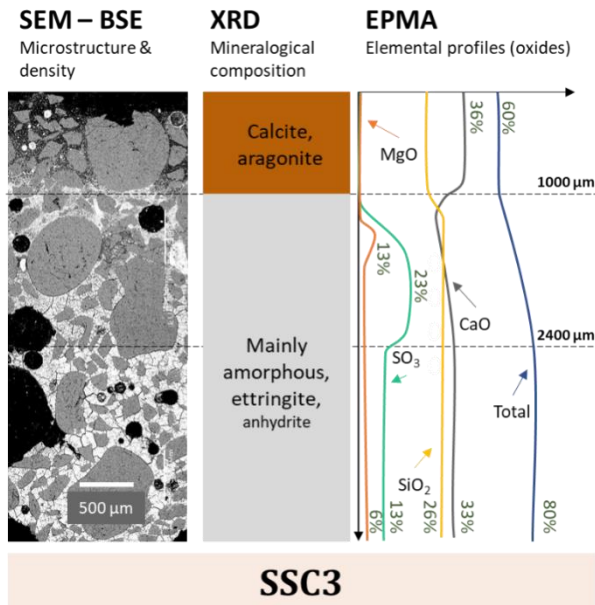
#### 2.2.4 Microstructural, chemical and mineralogical alteration of SSC3

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Several zones could be observed in the SSC3-based mortar exposed to the gas phase (Figure 11). Beyond 2400 μm, the specimen was unaltered, with the chemical composition corresponding to a sound SSC paste. Microcracks were present but were probably due to the high ettringite content of the sound hydrated binder. From 2400 μm to 1000 μm deep, the EPMA chemical analyses showed a slow decrease of the total oxides content, a slow decalcification associated with a sulfur enrichment and an increase of the relative SiO<sub>2</sub> content. In the SEM image, this zone showed a lower density than the sound core, and microcracks. The external zone (up to 1000 μm) showed a poorly dense matrix, where calcite and aragonite were the only crystallized phases detected. Sulfate and magnesium were completely leached, while the calcium content was high (about 35%) and the total oxide content was stable, due to carbonation.

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Figure 11. BSE-SEM images and mineralogical and chemical compositions of the different zones of the SSC3 mortar after 1 year and 10 months in the gas phase of a digester

### 372 3 Discussion

#### 373 3.1 Deterioration mechanisms

##### 374 3.1.1 Liquid phase

375 In the liquid phase, the main degradation phenomena were leaching and carbonation, as  
 376 calcium carbonates, mainly calcite but also aragonite and vaterite, precipitated in the outer  
 377 layers of all the mortar. The joint presence of the three crystallized polymorphs of calcium  
 378 carbonates could be due to the high RH and temperature in the environments considered, but  
 379 also to the carbonation of C-S-H and ettringite [33–38]. This carbonation was linked to the  
 380 high concentration of dissolved CO<sub>2</sub> in the liquid phase due to the microbial production of CO<sub>2</sub>  
 381 in the liquid, and in the biofilm, in direct contact with the materials. Moreover, the sulfur  
 382 enrichment observed for CEM I, CEM III and SSC3 mortars was probably due to the  
 383 precipitation of non-expansive secondary ettringite. This phenomenon is classically observed  
 384 in materials exposed to leaching because of the diffusion of sulfates from the altered zone  
 385 inwards [4,39,40].

386 An enrichment in phosphorus was systematically observed on the surface of the mortars but  
 387 no phosphorus-rich crystallized phases were identified by XRD. Moreover, the depth of  
 388 phosphorus penetration was not the same for all the materials. Since this phosphorus  
 389 enrichment was probably due to the penetration of exogenous phosphorus from the  
 390 fermenting biowaste [41], the depth of penetration may have been related to the diffusion  
 391 properties of the cementitious matrix.

392 Despite an intense carbonation and the associated dissolution of the initial Ca-bearing phases  
 393 and precipitation of calcium carbonates, there was no significant variation in the calcium  
 394 content inside the materials. This may have been due to the high calcium content of the

395 surrounding liquid medium (several hundred mg/L, Table 2) which did not favour the leaching  
396 of calcium from the matrix to the external medium.

397 The degradations observed under anaerobic digestion conditions in situ were similar to those  
398 observed in laboratory studies [4,5,8,9,42], where the authors showed a combination of  
399 leaching and carbonation, with surface phosphorus enrichment for CEM I and CEM III pastes.  
400 In the laboratory and in situ, the CAC and MKAA specimens were the best preserved under  
401 these aggressive conditions. In the present study, the AAS and SSC materials also underwent  
402 a combination of carbonation and leaching, and were better preserved than the Portland-  
403 based materials CEM I and CEM III. As the composition of the liquid was not the same as in the  
404 laboratory experiments (the substrate nature and the frequency of substrate supply were  
405 different), this could have resulted in different biofilm coverage (density, variety and number  
406 of microorganisms), different amounts of metabolites in contact with the materials and  
407 different deterioration patterns. The composition of the biofilm and its thickness were not  
408 studied in the different configurations, which makes it impossible to establish possible  
409 correlations.

#### 410 3.1.2 Gas phase

411 The main degradation phenomenon in the gas phase was carbonation. However, the  
412 carbonation was more intense than in the liquid phase since greater carbonated depths and  
413 well-crystallized aragonite and calcite were observed in the SEM images, in the pores and on  
414 the surface of the materials. This carbonation was linked to a medium not saturated with  
415 water, but with high RH, and to the high proportion of CO<sub>2</sub> in the gas phase (up to 60%).

416 In contrast with the observations of Koenig and Dehn [6], no precipitate of elementary or  
417 amorphous sulfur was identified on the surface of the materials, nor was any secondary  
418 precipitation of gypsum observed at depth. As the digester was fed with digestate, it is likely  
419 that the sulfur had already been converted into H<sub>2</sub>S in the previous industrial digester, which  
420 could explain the absence of H<sub>2</sub>S in the semi-industrial scale one. Moreover, unlike in Koenig  
421 and Dehn's study, there was no treatment of H<sub>2</sub>S by microaeration here and therefore no  
422 possibility of oxidizing the potential residual H<sub>2</sub>S into sulfuric acid. This low-H<sub>2</sub>S environment  
423 is similar to what can be encountered in industrial digesters degrading biowaste containing  
424 little sulfur or in post-digesters.

#### 425 3.2 Relative performances of cementitious binders

426 The altered depths observed on the chemical composition profiles contradict the classification  
427 obtained by phenolphthalein spraying. This could be explained by the very great  
428 heterogeneity of the degradations along the surface of the material, highlighted by the  
429 disparity of the measured altered depths. Thus, a reliable performance ranking cannot be  
430 made on the basis of localized chemical composition profiles. For this reason, only the altered  
431 depths obtained by phenolphthalein spraying were used for the performance ranking,  
432 although this indicator is not particularly suitable for alkali-activated materials [43].

433 In the liquid medium, where carbonation and leaching were predominant, the materials were  
434 ranked in increasing order of performance as follows: CEM III < CEM I < SSC2 < AAS < SSC3 <  
435 CAC & MKAA. In the gas phase of anaerobic digestion, where conditions were favourable for

436 intense carbonation, the materials studied were classified in increasing order of performance:  
437 SSC3 < CEM III < CEM I < MKAA.

438 The difference in the composition of the media led to a different ranking according to the type  
439 of environment, in particular for AAS- and SSC-based materials, which were less degraded than  
440 Portland cements in the liquid phase, but not in the gas phase.

441 The use of slag is known to increase the chemical resistance of materials to leaching and acid  
442 attack by reducing the calcium and portlandite contents of the binder in favour of C-(A-)S-H  
443 [44,45]. High acid resistance is also reported for alkali-activated slag-based materials and is  
444 also due to their specific C-(N-)A-S-H (or C-(K-)A-S-H) phase assemblage [29,46–50]. However,  
445 the properties specific to the use of slag (reduced or no portlandite content, higher proportion  
446 of C-(A-)S-H of lower Ca/Si ratio) are not beneficial to the resistance to carbonation. Under  
447 carbonation, the C-(A-)S-H are decalcified by decreasing the Ca/Si ratio and that can lead to a  
448 silicate polymerization and to the formation of an amorphous silica gel, together with  
449 precipitation of calcium carbonates. For extensive carbonation, this can result in significant  
450 shrinkage, loss of cohesion, increased porosity, cracking and a decrease of the micro-  
451 mechanical properties, with increased diffusion coefficients [51–58]. Moreover, the density of  
452 ettringite-based materials (SSC) tends to decrease as a result of carbonation since a large  
453 amount of bound water is released during carbonation reactions [59,60]. On the contrary, the  
454 carbonation of CEM I paste does not seem to have had a negative effect on the durability of  
455 the material. In the presence of portlandite, the precipitation of calcium carbonates clogs the  
456 porosity, which leads to a decrease in pore volume and pore connection of the paste [53,61].  
457 These phenomena explain both the good behaviour of AAS- and SSC-based materials in the  
458 liquid phase and their less good behaviour in the CO<sub>2</sub>-rich gas phase [62–64]. Besides, the  
459 better performance of SSC3 compared to SSC2 showed that an improved design (addition of  
460 an activator) can significantly improve the performance of the material. Finally, the poorer  
461 performance of CEM III in the liquid phase was probably due to the combined sensitivity of  
462 slag cement to carbonation, and a relatively low leaching resistance (compared to AAS- and  
463 SSC-based materials). On the one hand, the presence of portlandite in the CEM III paste, a  
464 phase sensitive to leaching (compared to C-A-S-H), was not beneficial for the material. On the  
465 other hand, portlandite could have acted as a sacrificial phase during the carbonation reaction  
466 but it may have been dissolved by leaching before its combination with carbonates forming  
467 clogging calcium carbonates.

468 In contrast, the CAC and MKAA materials had the lowest degradation after exposure, whether  
469 in a carbonating and leaching environment (CAC & MKAA) or in an intense carbonation  
470 environment (MKAA only). This is in accordance with previous studies showing that CAC-based  
471 and MKAA materials performed best in anaerobic digestion conditions [4,5,8,20]. The good  
472 performance of CAC-based samples could be due to the lower colonization of the material by  
473 microorganisms (compared with OPC-based materials) [8,65–68] and/or to the beneficial  
474 formation of an aluminium gel (AH<sub>3</sub>) on the surface, which is known to be stable at moderately  
475 acidic pH, i.e. up to pH 4 [15,69]. The degradation of the MKAA materials in the liquid phase  
476 was mainly expressed by the dissolution of the matrix, as classically encountered during acid  
477 attacks [29–31,50]. The sodium content of the matrix was lower in the liquid phase than in the

478 gas phase, indicating that alkalis leaching was probably higher in the liquid medium. However,  
479 no silica gel acting as a barrier layer was identified in the present study. This was probably due  
480 to the neutral pH of the liquid medium, since silica gel precipitates at low pH in short-term  
481 exposure [50,70], but also to the presence of calcium in solution, leading to the precipitation  
482 of calcium carbonates. In the gas phase, the carbonation only marginally affected the MKAA  
483 mortars. The overall good performance of MKAA materials was probably due to its chemical  
484 and mineralogical composition and also to the stability of its geopolymer framework due to  
485 its high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio [66]. However, a reservation can be made regarding the  
486 characterization of the MKAA geopolymer, since alkalis from the pore solution were not  
487 analysed and sodium carbonates were not measured. Actually, the alkalis in these matrices  
488 are mainly in the pore solution and are rapidly carbonated due to the high connected porosity  
489 of the material [71]. The carbonation products are very soluble and therefore offer very little  
490 protection. In order to enable full understanding of the alteration of the materials, an  
491 additional study of their transfer properties would be necessary, in particular for MKAA, which  
492 is known to have high, interconnected porosity [72].

### 493 3.3 Normative context

494 The non-harmonized European standard EN 206+A2/CN [73] and the French information  
495 document FD P 18-011 [74] classify chemically aggressive environments in three classes of  
496 increasing aggressiveness, XA1 to XA3, especially for waters and for gases in wet conditions.  
497 The aggressiveness of water depends on its concentration of aggressive agents – aggressive  
498  $\text{CO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and low total alkali strength (TAC) – and its pH, whereas the  
499 aggressiveness of gases in wet environments depends on their  $\text{SO}_2$  and  $\text{H}_2\text{S}$  concentrations.

500 The liquid medium of neutral pH was  $\text{CO}_2$ -rich (1 – 3 gC/L) and contained high ammonium  
501 concentrations (1000 – 4000 mg/L), low magnesium concentrations (6 – 60 mg/L), and no  
502 sulfate. The attack by this medium resulted in the leaching and carbonation of the materials.  
503 The attack by the gas medium, mainly composed of  $\text{CO}_2$  (25% to 60%) and  $\text{CH}_4$  (30% to 70%)  
504 led to carbonation of the matrices. While the main alterations observed in this study resulted  
505 from carbonation of the binders,  $\text{CO}_2$  is not considered aggressive to the cementitious matrix  
506 according to the standards. Moreover, in these two  $\text{CO}_2$ -rich environments, CEM III mortars  
507 were more deteriorated than CEM I mortars, while French standards and guidelines  
508 recommend the use of blast furnace cement in environments that are chemically very  
509 aggressive (XA3) [73–75], such as agricultural structures. Thus, it might be relevant to consider  
510 the additional effect of  $\text{CO}_2$  on the recommended cements, for liquid or gaseous aggressive  
511 environments.

### 512 Conclusion and perspectives

513 This study assessed the performance of different low carbon mortars, together with a  
514 reference Portland cement-based mortar, toward anaerobic digestion media. Although the  
515 liquid and gaseous media were very different, it appears that the major mechanism in both  
516 environments and for all materials was carbonation on the surface. In view of these results, it  
517 is very likely that (i) the liquid phase contained few VFA and that (ii) the gas phase contained  
518 little or no  $\text{H}_2\text{S}$  during the exposure of the materials.

519 In addition, the phenolphthalein tests allowed the materials' performance to be ranked and,  
520 in the current conditions of exposure:

- 521 • CAC and MKAA materials showed the best behaviour, whether in the liquid or the gas  
522 phase of the digester;
- 523 • Because of their good behaviour in an acid environment but their sensitivity to  
524 carbonation, the activated slag-based materials (AAS and SSC) behaved better than  
525 Portland-based materials (CEM I and CEM III) in the liquid phase but not in the gas  
526 phase;
- 527 • Due to the sensitivity of slag-Portland cements to carbonation, in the gas phase and in  
528 the liquid phase, slag cement (CEM III) was more degraded than Portland cement (CEM  
529 I).

530 Thus, future work could focus on the great variability of the compositions of the liquid and  
531 gaseous phases over time, according to the inputs and depending on the installations. In  
532 addition, and considering the high cost of using CAC or MKAA concrete, it would be interesting  
533 to (i) study the use of cementitious coatings by assessing their transfer properties and (ii) focus  
534 on improving the design of the least expensive low-carbon materials, such as AAS and SSC, so  
535 that they can be used industrially and resist both the gas and the liquid phases. Finally,  
536 consideration should be given to reviewing the standards and recommendations concerning  
537 the various binders to be used in these media, in particular by considering the great variability  
538 of the media compositions.

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543 original draft, visualization.

544 Cédric Patapy: Conceptualization, methodology, validation, writing: review & editing,  
545 supervision.

546 Matthieu Peyre Lavigne: Conceptualization, methodology, validation, resources, writing:  
547 review & editing, supervision

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556 Alexandra Bertron: Conceptualization, methodology, validation, writing: review & editing,  
557 supervision, project administration, funding acquisition.

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