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Toward an accelerated biodeterioration test to understand the behavior of Portland and calcium aluminate cementitious materials in sewer networks

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ABSTRACT

Sewer networks contain many aggressive and corrosive agents for pipe materials. One type of damage can be ascribed to concrete corrosion by biogenic sulfuric acid. According to field data, cementitious materials have different behaviors depending in particular on cement type: Those made with calcium aluminate cement (CAC) offer better performance than those made of ordinary Portland cement (OPC). The development of an accelerated and accurate laboratory test is essential to better understand the mechanisms involved for all cementitious materials. However, to define such a test, some additional knowledge is required. The present study deals with *in situ* experiments in order to determine the biochemical parameters

influencing the behaviors of OPC and CAC materials. Based on these determinations, supplemented by laboratory studies, it can be concluded that abiotic oxidation of hydrogen sulfide, bioreceptivity of the mineral surface, and growth of bacterial strains depend greatly on cementitious material types. All these results, complemented by literature data, lead to consideration of what the best parameters are to study biodeterioration of cementitious materials, and have been helpful in designing the biodeterioration chamber tested.

Keywords:

Biodeterioration

Cementitious materials

Sewer network

H₂S

Calcium aluminate cement

Portland cement

1 **1. Introduction**

2

3 In most industrialized countries, sewer systems are more than 40 to 50 years old and
4 now require major rehabilitation. From another perspective, in 1991 the Council of the
5 European Union adopted a directive on the need to treat urban wastewater properly.
6 Compliance with these regulations has always led and will probably always lead, to an
7 increase in the construction of sewerage and wastewater treatment plants. More recently, the
8 United Nations General Assembly declared 2008 as an International Year of Sanitation with
9 the objective of halving the number of people without access to safe water and adequate
10 sanitation by 2015.

11 Thus, the need to rehabilitate parts of the sewer network in large cities and to construct
12 new networks arising from EU directives and United Nations wishes now leads managers and
13 manufacturers to consider the best ways to build sustainable sanitation facilities and to
14 optimize sanitation management protocols.

15 Among the areas needing improvement, the degradation of materials, and particularly
16 biodeterioration of cementitious materials, appears fundamental. This is an extremely
17 dangerous and damaging phenomenon to sewer network structures, which was studied for the
18 first time by Olmstead and Hamlin (1900), who described the deterioration of bricks in the
19 sewer network of Los Angeles. Jointed mortar between the bricks disintegrated and ironwork
20 was heavily rusted. These authors also stated that the mortar joint had ballooned to two to
21 three times its original volume, leading to the destruction or the loosening of some bricks.

22 This type of damage can be ascribed to cementitious material corrosion by biogenic
23 sulfuric acid and represents 9% of the damage described in sewer networks (Kaempfer and
24 Berndt, 1999). Phenomena involved are depicted in Fig. 1. Relatively thick layers of
25 sedimentary sludge and sand accumulate at the bottom of the pipes, which leads to the

26 establishment of anoxic areas (typically 1 mm thick). Under these anaerobic conditions,
27 sulfate-reducing bacteria (SRB) can grow using oxidized sulfur compounds present in the
28 effluent as electron acceptor and excrete hydrogen sulfide (H_2S). Hydrogen sulfide degassed
29 in the aerial part of the pipe can impact the cementitious materials in two ways: either directly
30 by reacting with the cementitious materials and leading to a decrease in pH, or indirectly
31 through its use as a nutrient by sulfur-oxidizing bacteria (SOB), which produce sulfuric acid
32 (Islander et al., 1991; Roberts et al., 2002; Okabe et al., 2007). The cement matrix is then
33 dissolved by sulfuric acid and, depending on its composition, formation of expansive
34 secondary mineral products such as gypsum and ettringite is possible.

35 The present study focuses only on the second stage of the global process (i.e., the
36 biodeterioration of cementitious materials in the presence of H_2S), which can be broken down
37 into four steps, as shown in Fig. 1: abiotic oxidation of H_2S into elemental sulfur onto the
38 surface of cementitious material; oxidation of sulfur-containing molecules to sulfuric acid by
39 bacteria; diffusion of sulfuric acid into the degradation product layer; and acid attack on
40 healthy cementitious materials.

41 According to previous on-site experiments (Goyns, 2001, 2003; LCA 1; LCA 2)
42 cementitious materials made with calcium aluminate cement (CAC) perform better than those
43 made with ordinary Portland cement (OPC).

44 Most of the data published are based only on OPC studies. By contrast, the good
45 behavior of CAC in sewer networks is poorly documented. Therefore, it appears necessary to
46 better understand the deterioration mechanisms associated with CAC and OPC materials by
47 defining an accelerated test relevant to these materials, as well as to any other materials that
48 can be used in sewer networks.

49 Many studies have already been performed with different accelerated tests aimed at
50 mimicking the bio-physicochemical conditions encountered in sewer networks. Some of them

51 (Monteny et al., 2000; Roy et al., 2001; De Belie et al., 2004) simply proposed chemical tests
52 as the phenomenon can be considered at its last step as an acid attack. The basis of these tests
53 is the immersion of concrete samples into a sulfuric acid solution for about one month, after
54 which the sample's weight loss is measured. Some of the proposed tests are complemented by
55 a step of sample surface brushing in order to mimic the tidal area effect in the pipe and
56 therefore to create the worst possible conditions. In general, the results obtained by these
57 chemical tests are not in agreement with *in situ* experimental results.

58 Some other studies deal with biochemical accelerated tests by introducing
59 microorganisms, in order to more closely simulate reality. A Heidelberg University
60 (Germany) group (Hormann et al., 1997; Schmidt et al., 1997) worked on the design of a
61 simulation chamber using only one bacterial strain (*Acidithiobacillus thiooxidans*). Mortar
62 samples were placed in a reactor and for 5 min h⁻¹ they were immersed in the culture media.
63 This test has two major disadvantages: Being immersed in a culture medium at pH 3.5 leads
64 to a chemical test rather than a biological one, and the washing of the sample each hour
65 modifies the sample surface conditions.

66 A University of Ghent (Belgium) team (Vincke et al., 1999; De Belie et al., 2004) has
67 developed a test that recreates the worst conditions encountered in sewer networks. Samples
68 of mortars were exposed to cycles of deterioration: 3 days of exposure to 250 ppm of H₂S, 10
69 days of immersion in the culture medium of *A. thiooxidans*, 2 days of washing by water, and
70 finally 2 days of drying. This test is far from realistic conditions and some of the steps are not
71 justified considering *in situ* conditions. Moreover, with this test, biodeterioration of samples is
72 also disturbed by chemical reactions at the sample surface.

73 The University of Hamburg (Germany) has developed a biodeterioration chamber that
74 allows recreating the conditions met in sewer systems (Milde et al., 1983; Sand et al., 1992,
75 1994; Ehrich et al., 1999). For this purpose, a wide chamber (1 m³) with air circulation (250

76 m³ h⁻¹) and controlled relative humidity (close to 98%) and temperature (approximately 30°C)
77 is used. The mortar samples are sprayed with a solution of mineral salts essential for the
78 growth of 12 bacterial strains isolated from the sewer network of Hamburg. The atmosphere
79 in this chamber contains between 15 and 20 ppm of H₂S. This accelerated test appears to
80 represent *in situ* mechanisms and displays an acceleration factor of 24 compared to on-site
81 conditions (Sand et al., 1992; Ehrich et al., 1999).

82 This present paper focuses on both *in situ* and laboratory studies carried out on mortar
83 samples, with the objective of providing useful knowledge concerning the effect of
84 biodeterioration on Portland and calcium aluminate cements. Moreover, these new data are
85 analyzed in order to improve the accelerated biodeterioration tests currently examined.

86

87 **2. Materials and methods**

88

89 *2.1. Samples*

90

91 Mortars were cast with OPC or CAC. Their chemical oxide compositions are given in
92 Table 1. For all samples, the water-to-cement and siliceous-sand-to-cement ratios are,
93 respectively, 0.37 and 1.44.

94 For laboratory studies, samples were cast in 2x2x16 cm³ moulds. After one-day
95 hydration, they were sawn in order to obtain seven samples of 2x2x2 cm³. Each of them has
96 three molded faces and two sawed faces. For *in situ* experiments, cylindrical samples (6 cm
97 diameter, 14 cm high) were prepared with a PVC tube anchor for their suspension in a sewer
98 network. The two types of sample are shown in Fig. 2. All the samples were kept in plastic
99 bags until studies in order to avoid desiccation.

100

101 2.2. *In situ* experiments

102

103 Cylindrical mortar samples were exposed in two sewer networks. The first one (Site 1)
104 has a low biodeterioration potential with an H₂S concentration between 0 and 20 ppm and a
105 temperature between 18 and 25°C. Site 2 is much more aggressive, with an H₂S concentration
106 ranging from 100 to 200 ppm and a temperature ranging from 25 to 30°C.

107 For each site, samples are suspended in a PVC box located in the headspace of the
108 sewer network. There are three replicates of each kind of mortar sample.

109 For each sampling (i.e., every 4 months), different parameters are monitored: visual
110 changes, weight, and surface pH. Moreover, one of the three cylindrical samples is used to
111 study biofilm microbial diversity using molecular techniques. Samples are scraped with a
112 brush impregnated with a guanidine thiocyanate solution (pH 7.5) to extract and preserve total
113 DNA from biofilms. DNA samples are held in the guanidine thiocyanate solution at -80°C for
114 transport and storage until analyzed. DNA is extracted using an MP Biomedical kit, the Fast
115 DNA[®] SPIN Kit for Soil, which allows extraction and cleansing of the genetic material from a
116 sample with an environmental background (e.g., ground, faeces, wastewater, sludge). This kit
117 provides the advantage of quick isolation (less than 30 min) of the genomic DNA for use in
118 PCR (polymerase chain reaction). The DNA extracted is amplified by PCR and used for CE-
119 SSCP analysis (Capillary Electrophoresis Single-Strand Conformation Polymorphism). This
120 molecular fingerprint tool allows for the study of microbial diversity present in environmental
121 ecosystems. One microliter of total extracted DNA is used per PCR–SSCP amplification. The
122 w104 (6-FAM labelled) and w49 (Godon et al., 1997) are used for the V3 region of 16S
123 ribosomal DNA. The PCR-SSCP amplification mix contains 1.25 units of *Pfu Turbo*
124 (Stratagene, La Jolla, CA), 5 µl of 10× buffer, 200 µM of dNTPs (tri-phosphate
125 desoxyribonucleotides), and 200 ng of each primer, with water added to a final volume of 50

126 μl . The thermal profile used for amplification of ribosomal RNA genes is as follows:
127 incubation at 94°C for 2 min, and then 25 cycles of denaturation at 94°C for 30 s, 61°C for 30
128 s, and 72°C for 30 s. The CE-SSCP analysis is carried out with ABI 3130 (Applied
129 Biosystems) as described by Delbes et al. (2000, 2001).

130 Water condensation in the PVC tube anchor and in contact with mortar was also
131 recovered in order to measure pH and ATP content. This latter parameter is determined by an
132 ATPmeter type Novalum[®] from Charm Science using WaterGiene[®] swabs. These swabs,
133 initially made for use in the food industry, are quantitative, give repeatable results, and are
134 easy to use.

135

136 *2.3. Laboratory experiments*

137

138 Considering two of the four biodeterioration steps (see Fig. 1), tests were carried out to
139 determine the influence mortar sample type had on the results and to propose a way to take
140 into account this influence in an accelerated test.

141

142 *2.3.1. Sulfuric acid impact*

143 Cubic samples were immersed in sulfuric acid solutions (pH 1 and 2) for a week, as
144 proposed by Espinosa et al. (1996). Twice a day, a part of the solution was sampled for
145 elemental analysis and solid samples were weighed. Chemical analyses were made by ICP-
146 OES with an ULTIMA 2000 Jobin-Yvon.

147

148 *2.3.2. Abiotic oxidation of H₂S*

149 Samples of mortar were exposed to 20 ppm of H₂S for three months. Each month, a
150 sample was removed to be analyzed by environmental scanning electron microscopy (ESEM).

151 Observations were made with an ESEM type Quanta 400 from FEI. Chemical analyses were
152 made using an energy dispersive X-ray spectroscopy system, EDAX DX 4i, from Oxford
153 Instruments.

154

155 **3. Results and discussion**

156

157 *3.1. Field experiments*

158

159 The first step to get a better understanding of the mechanisms involved in cementitious
160 materials' biodeterioration is to determine the consequences of *in situ* exposure on samples of
161 such materials.

162 After four months in sewer networks, the two sites affected the samples differently. As
163 expected, site 1 was less damaging than site 2. Upon opening the manhole giving access to the
164 exposure boxes, a preliminary observation on the exterior of the boxes was made. The
165 samples exposed on site 1 kept their original appearance, while the box suspended in site 2
166 had a clear yellow-white color with the presence of significant deposits on the top of the box
167 (Fig. 3).

168 Figure 4 presents the visual appearance of the mortar samples. For site 1, one can
169 notice little change on samples compared to the controls. A thin coat of whitish color
170 containing glittering crystals was observed on the surface of all samples. This layer is barely
171 visible in the Fig. 4 photos. The OPC samples of this site are slightly darkened locally while
172 CAC samples displayed a slightly bluish tint.

173 Site 2 samples displayed more advanced deterioration. Most of the samples had
174 changed color and phenomena associated with bursting were observed on the upper face. The
175 OPC samples became totally black and a relatively thick deposit (around 5 mm) formed at the

176 retention zones (at the top of the test tubes or in the macro-porosity of the samples). The top
177 also had burst under the formation of expansive mineral phases. The CAC samples hung in
178 this site became partially black with white deposits covering the surface of the samples.

179 One of three samples of each formulation was brushed to remove the deterioration
180 products that had formed. This test aimed to represent a tidal zone with the loss of the
181 deterioration products occurring during every rise in the water level. While samples exposed
182 on site 1 did not present real alteration, samples brushed from site 2 showed a significant loss
183 of weight. Mass loss of OPC samples (1.59%) was four times higher than those of CAC
184 (0.35%) on site 2.

185 The pH of all samples was also measured on four sample faces: top face, one on the
186 bottom face, and two on the sides (Fig. 5). It can be observed that there was a pH increase
187 from the top face to the bottom face.

188 The sampling of sub-aerial biofilm growing on cementitious material surfaces allowed
189 extraction and quantification of the total DNA. It can be seen that the OPC samples (total
190 DNA extracted after four months: 10 ng cm⁻² for site 1 and 155 ng cm⁻² for site 2) are more
191 bioreceptive than the CAC ones (total DNA extracted after four months: 4 ng cm⁻² for site 1
192 and 48 ng cm⁻² for site 2). Both exposure sites favor bacterial development, but samples from
193 site 2 display up to 15 times more biomass than samples from site 1.

194 CE-SSCP analysis performed of the bacterial extracted DNA reveals that the cement
195 composition has a major role in the establishment of the biofilm, considering that the
196 microbial diversity decreases from OPC to CAC (data not shown). In addition, site location
197 has a strong impact: Samples from site 1 present a lower microbial diversity compared to
198 those from site 2.

199 The analysis of condensed water in the PVC tube anchor showed that pHs are always
200 close to 1. By contrast, ATP concentrations from OPC samples (1.1×10^8 relative light units)

201 are much higher than those from CAC samples (3.8×10^4 RLU), indicating greater microbial
202 activity. All results (mass loss, DNA quantity, and microbial activity) indicate that CAC
203 seemed to inhibit bacterial strains, their activity, and, as a consequence, the degradation of
204 cementitious materials.

205 Moreover, the *in situ* experiments showed that the environmental conditions
206 significantly influenced the biodeterioration of cementitious materials, as shown by the
207 concentration of H₂S and temperature.

208 Several hypotheses can be made based on *in situ* experiments. The main element of
209 CAC materials, aluminum, may have a major role in the good behavior of these materials by
210 acting like an inhibitor for microorganisms involved in the biodeterioration process. The
211 surface state may also influence a part of the phenomenon, considering that hydrates present
212 in the two materials are quite different. To answer these questions, additional laboratory
213 experiments are required. Such experiments should aim to design an accelerated test
214 reproducing the bio-physicochemical processes occurring in sewer networks.

215

216 3.2. Study of biodeterioration mechanisms

217

218 According to *in situ* experiments, the biodeterioration mechanisms of cementitious
219 materials in sewer systems occur via a sulfuric acid attack. Sulfuric acid interacts with some
220 of the chemical compounds of the cementitious material, thereby forming characteristic
221 phases (Okabe et al., 2007), such as gypsum or ettringite. Despite the fact that chemical
222 experiments are not suitable for the classification of cementitious materials in terms of
223 durability in sewer networks, it is interesting to carry out these tests in order to observe ions,
224 especially aluminum, leached into solution.

225 For that purpose, we plunged cubes of mortar 2 cm per side into solutions of sulfuric
226 acid at pH 1 or 2, for one week (Fig. 6).

227 Chemical analyses were performed on the acidic solution to monitor the leaching of
228 ions in solution every 24 h. Figure 7 indicates that whatever the mortar type, calcium
229 concentration reaches values of the order of 10 mg cm^{-2} , but the behavior of the aluminum
230 differs depending on the type of mortar. It dissolves sparsely in solution in the case of OPC
231 and reaches values of 10 mg cm^{-2} for CAC. Aluminum is known to have bacteriostatic
232 properties (Karlik et al., 1980; Munns et al., 1981; Wood et al., 1988; Exley and Birchall,
233 1992) so it is possible that that is one explanation for the good behavior of CAC materials in
234 the *in situ* experiments.

235 Monitoring of the sample mass was also performed and the results are reported in Fig.
236 8. The CAC lost up to twice the weight that Portland cement did during an acid attack by
237 immersion at pH 1. Similar trends were observed at pH 2.

238 As reported by previous studies (Monteny et al., 2000; De Belie et al., 2004;
239 O'Connell et al., 2010; Magniont et al., 2011), an accelerated biodeterioration test cannot rely
240 on a simple immersion test in an acidic solution. For evidence, *in situ* experiments indicate
241 that cementitious materials made with CAC are less deteriorated than those with OPC, but
242 with chemical tests, CAC materials are more deteriorated than OPC. Furthermore, surface pH
243 of the CAC materials for *in situ* experiments never decreases below 3.5 - 4. This limit
244 corresponds to the stability of the alumina (Lamberet et al., 2008). Using a pH lower than 4
245 for the acid attack is not representative of conditions met by CAC materials.

246 Thus for the accelerated biodeterioration experiment, it is necessary to involve
247 microorganisms to recreate the real decrease of pH.

248 According to the literature, biodeterioration mechanisms of cementitious materials in
249 sewer networks also bring in a succession of microorganisms clearly identified in the case of

250 OPC (Islander et al., 1991; Okabe et al., 2007). It is thus necessary to recreate this bacterial
251 succession in the laboratory to be able to gradually lower the pH of the surface of the mortar
252 samples.

253 The first stage of biodeterioration of cementitious materials in sewer systems is the
254 transformation of hydrogen sulfide into elemental sulfur on the surface of the materials. It
255 seems that the oxidation of hydrogen sulfide in sewer networks can follow two paths (Parker,
256 1947) depending on the state of degradation of cementitious materials. On healthy materials,
257 sulfides can be oxidized chemically and produce thiosulfate ($S_2O_3^{2-}$) or tetrathionate ($S_4O_6^{2-}$).
258 In contrast, on deteriorated concrete with a lower pH, sulfide can be oxidized into elemental
259 sulfur. However, transformation of sulfides can also involve microorganisms. Suzuki (1999)
260 states that H_2S can be transformed by sulfur-oxidizing microorganisms following some other
261 mechanisms. Therefore, it appears that the oxidation of H_2S is not well understood and that
262 our knowledge about the mechanisms involved needs to be expanded.

263 To study the significance of this step, 20 ppm of gaseous H_2S was maintained in
264 contact with mortar samples for three months. Examination performed with SEM (Fig. 9)
265 revealed a heterogeneous and diffuse sulfur deposit on the surface of OPC materials, while
266 CAC materials did not display this.

267 Deposits of sulfur in the case of OPC materials seem to be favored in the periphery of
268 aggregates. In fact, this corresponds to a transition zone rich in calcium for OPC materials. It
269 can be concluded that the transformation of H_2S into elemental sulfur requires the
270 intervention of a catalyst in the form of cations, such as calcium for this study, but also of
271 metallic cations (Fe, Cu, Zn, etc.) for other studies (U.S. EPA, 1992; Nielson et al., 2005;
272 Firer et al., 2008).

273 The difference of deposition of elemental sulfur on the surface of mortar samples for
274 OPC and CAC could be an additional reason for the good behavior of CAC in the face of

275 biodeterioration features of sewer systems. Furthermore, it indicates that H₂S gas has a major
276 role in the processes of biodeterioration because it has different oxidation/deposition behavior
277 according to materials composition. Thus it is necessary to have H₂S for a suitable accelerated
278 biodeterioration experiment.

279

280 3.3. Development of an accelerated experiment

281

282 To create a simple, effective, and reproducible accelerated test, it is important to have
283 a completely homogeneous air volume with the environment controlled for temperature,
284 relative humidity, and concentration of H₂S. Considering these parameters, a biodeterioration
285 chamber of a cubic meter, homogenized by a powerful ventilating system, was chosen. The
286 relative humidity was purposely maintained at a very high level to allow water condensation
287 at 30°C. This temperature was chosen because it corresponds to the optimal growth
288 temperature of the selected bacteria. The H₂S is continuously injected at 20 ppm.

289 According to Parker (1947), Islander et al. (1991), Robert et al. (2002), and Okabe et
290 al. (2007), only a few bacterial strains are involved in biodeterioration of cementitious
291 materials by oxidizing sulfur-containing molecules. The growth patterns of these bacteria are
292 different depending on environmental conditions, and there is a succession of bacteria for
293 colonization that is determined by the material surface pH (Islander et al., 1991; Lamberet et
294 al., 2008). The selected bacterial strains for the present study were *Halothiobacillus*
295 *neapolitanus*, *Starkeya novella*, *Thiomonas intermedia*, and *Acidithiobacillus thiooxidans*.
296 The first three are neutrophilic and the last is acidophilic.

297

298 Various parameters were selected for biodeterioration monitoring:

- 299 • Sample weight

- 300 • Surface material pH, which is a crucial parameter as shown by Islander et al. (1991)
301 and Roberts et al. (2002), since it allows to highlights progress of the process.
- 302 • X-ray diffraction and thermal analysis (DTA-TG), in order to understand the
303 transformation of materials during the degradation.
- 304 • Biochemical analysis aimed at determining the number of microbial cells growing on
305 the surface. This analysis is correlated to ATP activity measurement and microbial
306 protein content determination.

307

308 This biodeterioration chamber is expected to enable accelerated testing similar to the
309 biodeterioration chamber designed by the Hamburg University research team (Milde et al.,
310 1983; Sand et al., 1992, 1994; Ehrich et al., 1999). However, in contrast with Ehrich et al.
311 (1999), four bacterial strains purchased from DSMZ collection were introduced into the
312 chamber. The use of referenced bacterial strains allows this test to be replicated anywhere in
313 the world the laboratory is located.

314 Currently the biodeterioration chamber is being tested with different mortar samples and
315 preliminary results are promising.

316

317 **4. Conclusions**

318

319 On-site experiments provide important data relevant to a better understanding of
320 biodeterioration of cementitious materials. In fact, it has been found that CAC materials
321 perform better than those with OPC, and the biomass that develops on the surface of the
322 former is different and less abundant. The good behavior of CAC materials could be due to
323 their high aluminum content, which could inhibit the growth of microorganisms.

324 Studies carried out in the laboratory indicate that the simple chemical tests (with the
325 addition of sulfuric acid) do not allow estimation of the service life of materials in sewer
326 systems. The work performed with H₂S showed that the presence of H₂S was required when
327 one wants to design an accelerated experiment because the materials do not display the same
328 sulfur deposition behavior without it.

329 An accelerated biodeterioration chamber suitable for studying the durability of
330 cementitious materials in sewer networks also needs the addition of sulfur-oxidizing bacteria
331 to recreate the pH decrease observed *in situ*.

332

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334

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338

339

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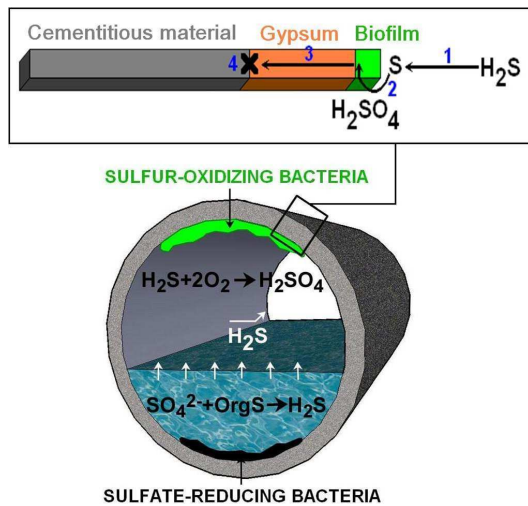
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469 **Captions**



470

471 **Fig. 1.** Schematic representation of sulfur cycle in sewer network with the four steps involved
 472 in the biodeterioration of cementitious materials.

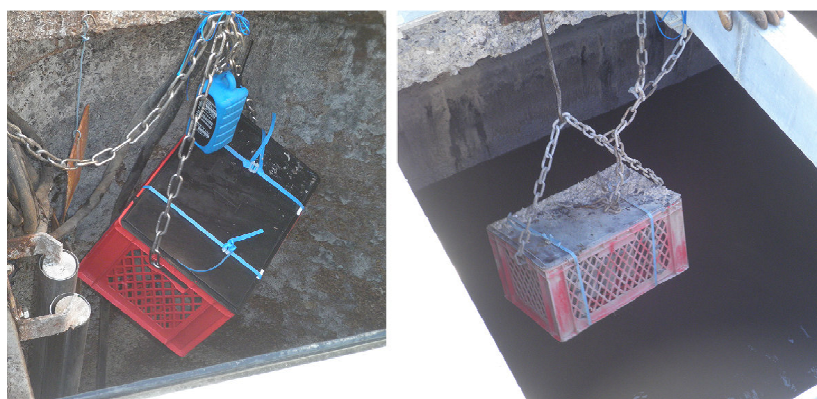
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475 **Fig. 2.** Laboratory samples on the left and on-site samples on the right.

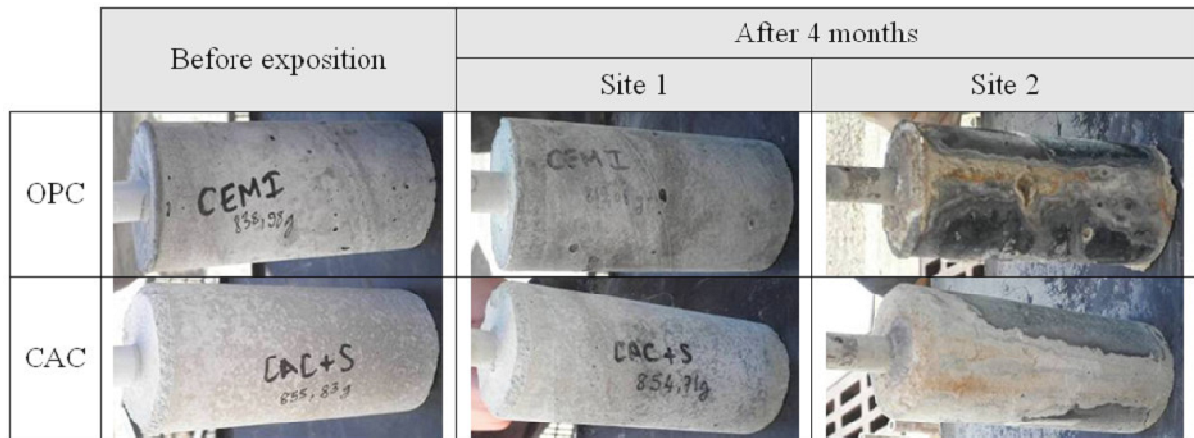
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478 **Fig. 3.** Exposed boxes after four months in sewer networks. Site 1 is on the left, site 2 on the
 479 right.

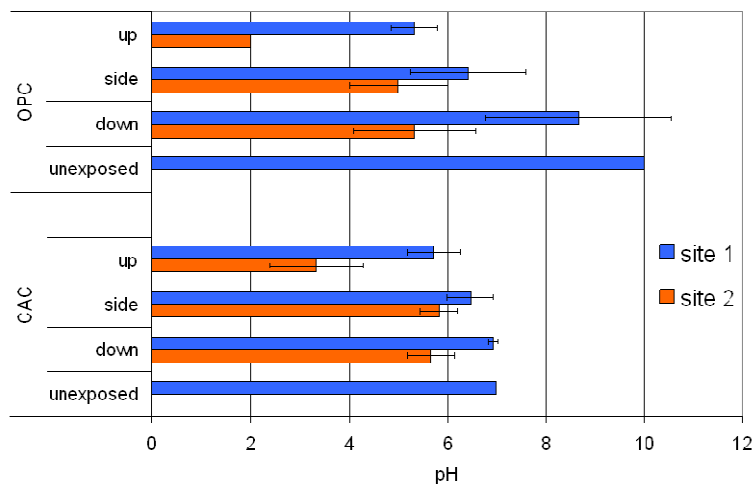
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482 **Fig. 4.** Photos of the exposed samples after four months in the two sewer networks.

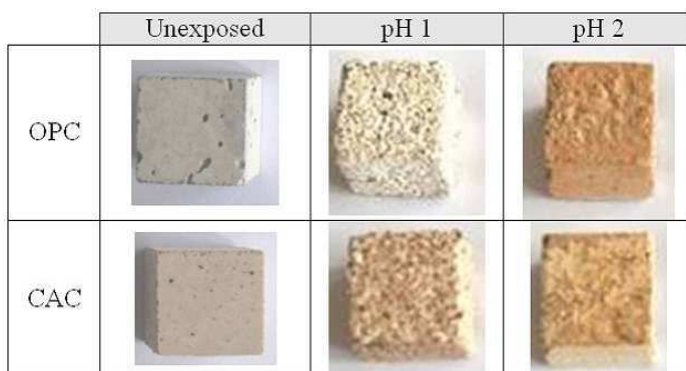
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485 **Fig. 5.** Change of surface pH of samples after four months in a sewer network.

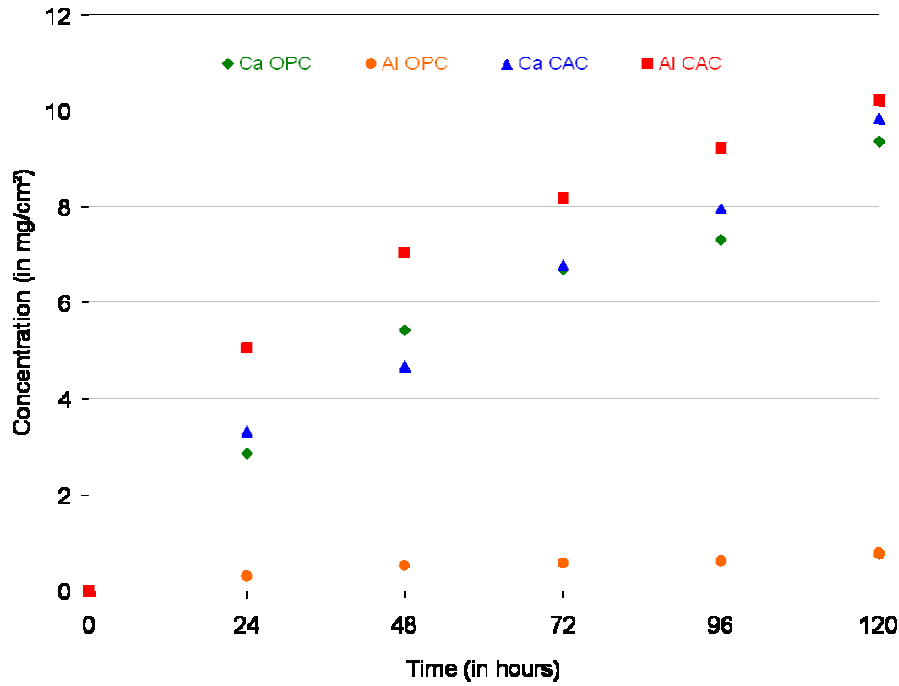
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488 **Fig. 6.** Change of mortars immersed in sulfuric acid solution for a week.

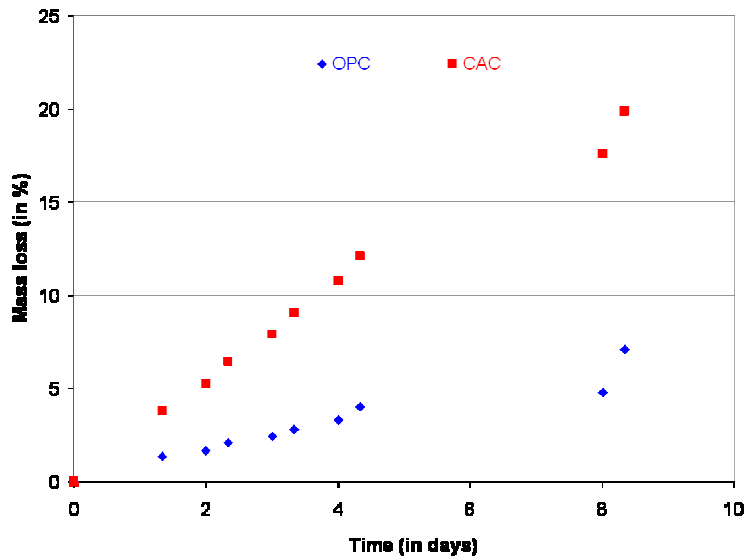
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491 **Fig. 7.** Change of calcium and aluminum concentrations in acidic solution (pH 1) with OPC
 492 and CAC materials.

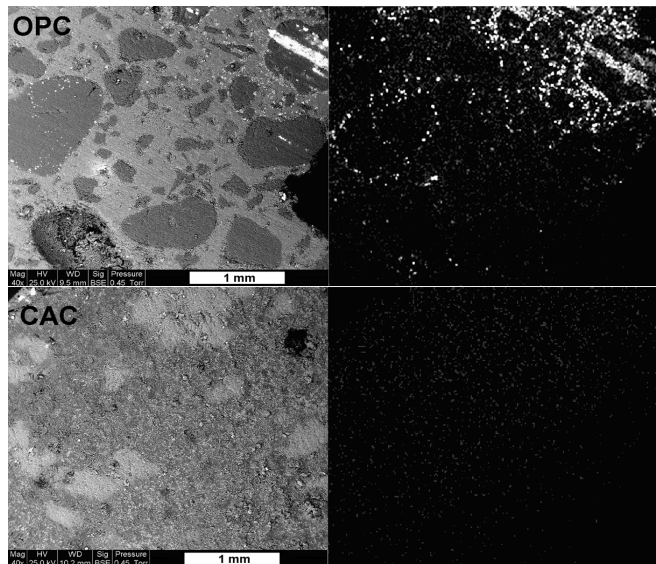
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495 **Fig. 8.** Mass loss of samples over time during an immersion in sulfuric acid (pH 1).

496



497

498 **Fig. 9.** SEM images of OPC and CAC surfaces exposed for 3 months to 20 ppm of H₂S, on
 499 the left. Sulfur mapping is on the right.

500

501

502 **Table 1**

503 Composition of the two cements.

	Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	MgO	TiO ₂	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	LOI	IR
OPC	5.07	63.93	20.87	3.31	0.83	0.24	3.39	1.01	0.20	0.94	0.94	0.26
CAC	51.87	37.06	5.31	2.25	0.54	2.19	0.15	0.31	0.05	0.19	-	-

504 LOI: Loss On Ignition; IR: Insoluble Residue

505