Innovative approach to simulating the biodeterioration of industrial cementitious products in sewer environment. Part II: Validation on CAC and BFSC linings

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ABSTRACT

The development of a new test method for evaluating the resistance of manufactured cementitious products to biogenic acid attack, labeled BAC-Test for Biogenic Acid Concrete Test, was reported in Part I of this paper. The performance of the test in terms of sulfur-oxidizing bacteria selection and acid and sulfate production has been validated previously. In this second part, the representativeness of the degradation mechanisms of the cementitious materials is explored. Two segments of industrial pipes – ductile cast iron coated with cementitious linings (blast furnace slag cement (BFSC) and calcium aluminate cement (CAC) mortars) – were exposed to the test for 107 days. Then linings were analyzed by SEM coupled with EDS, EPMA, and XRD. Significant differences between BFSC and CAC linings were highlighted. Abundant cracking of the BFSC lining was observed, caused by precipitation of secondary ettringite, while no cracking was observed in the CAC lining. The CAC outer layer was composed mainly of AH3 gel. The decalcification front was deeper in the BFSC matrix than in the CAC one.

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1. Introduction

The biodeterioration of cementitious materials occurring in the headspace of sewer networks of urban wastewater systems is due, in particular, to the biological oxidation of hydrogen sulfide (H2S), produced in the stagnant zones, into biogenic sulfuric acid (H2SO4) [1]. No standardized test currently exists to qualify cementitious materials and products exposed to biologically induced deterioration in sewer systems [2,3]. Several tests with different designs and principles have nevertheless been proposed in the literature [2,4–7]. The purpose of this study was to develop a new biological test intended for products and materials in sewer systems. The design and the purpose of the test were described in the first part of this article [7]. The principle of the test was to inoculate the inner surface of cementitious linings of pipe products with an activated sludge consortium (consisting in a sample of wastewater from aerated reactor of a wastewater treatment plant) and to trickle a mineral solution containing a soluble sulfur source over the surface to ensure the selection and the activity of sulfur-oxidizing microorganisms in contact with the cementitious lining. The purpose of implementing trickling (thin layer of liquid medium at the surface of the material) was to avoid total immersion of the mortar samples in the biological medium and thus to better quantify the acid and sulfate actually produced in contact with the matrix. The leaching solution was collected downstream of the pipe product and analyzed in order to monitor sulfur-oxidizing selection, biogenic acid production, and dissolved cementitious cations (Al and Ca) as a function of time [7].

Pipe products consisting of ductile iron sewer pipes coated with an inner protective layer of cementitious mortars were tested in the study. Two types of cement mortars incorporating siliceous aggregates were investigated: one composed of blast furnace slag cement (BFSC) and the other composed of calcium aluminate cement (CAC). They were exposed to the test for 107 days [7]. For both linings, the analyses of the leaching solutions showed the acidification of the media, the pH of the leaching solutions dropping from 9 to 4 during the first 17 days, to reach values of around 3 after 107 days. This acidification phenomenon was associated with thiosulfate oxidation and sulfate production, leading to the dissolution of calcium and, in the last steps of the biogenic attack, to the dissolution of aluminum from the CAC lining. At the end
of the experiments, 16S RNA analyses confirmed the selection of sulfur-oxidizing bacteria on both linings. Behavior differences between the CAC and BFSC linings tested were highlighted in the first step of the biogenic acid attack, where the rate of calcium dissolution was higher on the BFSC lining than on the CAC lining. Finally, on the BFSC lining, at the end of the experiment, the biofilm maintained at the surface was more abundant than that on the CAC lining as measured by total volatile solids analyses.

The main objective of the second part of this article is to investigate the behavior of the BFSC and CAC linings after exposure in order to evaluate the representativeness of the chemical, mineralogical, and microstructural changes in the cementitious matrices by using short-term experiments. At the end of the test (107 days), the mortar linings were investigated using X-ray diffraction, scanning electron microscopy coupled with EDS, and electron probe microanalysis.

2. Typical chemical reactions within cementitious matrices exposed to biogenic sulfuric acid

Attack by biogenic sulfuric acid comprises the dissolution of cementitious phases because of acid–base reaction with H+, and the formation of sulfate-bearing secondary products, ettringite, and/or gypsum [8]. The simplified reactions of dissolution of the main hydrated phases of Portland cement matrix, Ca(OH)2, and calcium silicate hydrates (C-S-H), through acid attack are given in Eqs. 1 and 2, respectively [8]. A silica gel is formed from the leaching of Ca from the C-S-H. It should however be noted that C-S-H in OPC paste, as well as C-S-H in hydrated OPC partially substituted by Al-rich supplementary cementitious materials (SCM) such as slag, silico-aluminous fly ash, or metakaolin, incorporates a certain amount of aluminum [9–11]. These hydrates are usually noted C-A-S-H.

The composition, structure, and properties – notably the chemical stability – of the C-A-S-H in OPC with SCM is somewhat different from the hydrates in non-substituted OPC pastes [9,10], although all the information is not available in the literature yet [12]. Nevertheless, the dissolution of C-A-S-H by strong or weak acids leads to the formation of a silica gel containing aluminum [11,13,14]. For CAC-based matrices, the dissolution of calcium aluminate hydrate, C3A•H2O and C2A•H8, led to the formation of aluminum hydroxide or gibbsite (Eqs. 3 and 4 respectively), which dissolves at pH < 4 (Eq. 5) [15,16]:

\[
\text{Ca(OH)}_2 + 2H^+ \rightarrow \text{Ca}^{2+} + 2H_2O
\]

\[
\text{xCaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O} + 2xH^+ \rightarrow x\text{Ca}^{2+} + y\text{Si(OH)}_4 + (x + z - 2y)\text{H}_2\text{O}
\]

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 6\text{H}^+ \rightarrow 3\text{Ca}^{2+} + 2\text{Al(OH)}_3 + 6\text{H}_2\text{O}
\]

\[
2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O} + 4\text{H}^+ \rightarrow 2\text{Ca}^{2+} + 2\text{Al(OH)}_3 + 7\text{H}_2\text{O}
\]

\[
\text{Al(OH)}_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}
\]

For OPC pastes, the reaction of portlandite and C-S-H with sulfate forms gypsum (CaSO4•2H2O) [17–20] (Eqs. 6 and 7). Ettringite (3CaO·Al2O3·3CaSO4·2H2O) is formed through the reaction of gypsum with CaA [Eq. 8] [21] or with monosulfoaluminate (Eq. 9) [22] and, to a lesser extent, with CaAF, hydrated calcium aluminates, and AFm [22]:

\[
\text{Ca(OH)}_2 + SO_4^{2-} + 2H_2O \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]

\[
\text{xCaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O} + xSO_4^{2-} + 2H_2O \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + Si\text{(OH)}_4
\]

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 3\text{H}_2\text{O}
\]

3CaO·Al2O3·CaSO4·12H2O + 2CaSO4·2H2O + 16H2O → 3CaO·Al2O3·3CaSO4·32H2O

The mineralogical and chemical changes of CAC-based materials following the attack by sulfuric acid is not very well documented. Although theoretical Eqs. (10 and 11) provided by [22] and Eq. (12) provided by [23] mention the formation of gypsum and ettringite from C2AH8 and C3A•H8, experimental results only reported the formation of AH3 at the surface24,25]:

\[
2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O} + 2\text{SO}_4^{2-} \rightarrow 2\text{(CaSO}_4 \cdot 2\text{H}_2\text{O}) + 2\text{Al(OH)}_3 + \text{H}_2\text{O}
\]

\[
2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O} + 3\text{SO}_4^{2-} + 19\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + \text{Al(OH)}_3
\]

3CaO·Al2O3·6H2O + 3CaSO4 + 26H2O → 3CaO·Al2O3·3CaSO4·32H2O

Table 1 presents the molar volume of the main hydrates of ordinary binder-based materials and CAC materials, and of secondary compounds gypsum and ettringite [26]. The high molar volume of secondary phases compared to endogenous hydrates linked to local porosity accounts for the strong deterioration of the matrix because of local swelling, pressure increase in the porous network and then cracking of the cement paste.

3. Materials and methods

3.1. Pipe products

The pipe segments were 200 mm long and 80 mm in internal diameter (0.05 m² of exposed lining surface). Fig. 1 shows a longitudinal section of a Saint-Gobain PAM sewer pipe. The pipe is composed of a ductile cast-iron tube with a cement mortar lining (Fig. 1). The cementitious lining acts as a protective layer for the ductile iron structure of the sewer pipe (chemical, sacrificial protection against aggressive environments). The lining was 6 mm thick and was produced by centrifugation of mortar on the inner surface of the iron pipe (patented process [27]).

3.2. Experimental setup

The pilot apparatus for the BAC-Test was made up of two vertical parallel pipe-reactors, each mainly composed of a segment cut from a real sewer pipe (Fig.1). Before the start of the experiment, the surface of each cementitious lining was inoculated with an activated sludge consortium [7]. A constant flow of a mineral solution was trickled

Table 1

<table>
<thead>
<tr>
<th>Hydrated phases and precipitates</th>
<th>Cement paste</th>
<th>Molar volume (cm³•mol⁻¹)</th>
<th>Normalized molar volume (cm³•mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂ (Portlandite)</td>
<td>BFSC</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>(CaO)₃·SiO₂·(H₂O)₃ (CSH)</td>
<td>BFSC</td>
<td>59–78</td>
<td>59–78</td>
</tr>
<tr>
<td>3CaO·Al₂O₃·6H₂O (C₃A•H₈)</td>
<td>CAC</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>2CaO·Al₂O₃·8H₂O (C₂A•H₈)</td>
<td>CAC</td>
<td>184</td>
<td>91</td>
</tr>
<tr>
<td>Amorphous Al(OH)₃ (AH₃am)</td>
<td>CAC</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>CaSO₄·2H₂O (Gypsum)</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>3CaO·Al₂O₃·3CaSO₄·32H₂O (ettringite)</td>
<td>707</td>
<td>118</td>
<td></td>
</tr>
</tbody>
</table>
onto the cement surface. The area of surface exposed to the trickling solution was 50 cm². Thiosulfate was used as the sulfur source to avoid toxic H₂S, and to enable fast and quantifiable selection of sulfur-oxidizing activity at the lining surfaces. The inlet flow for the feed solution was 50 ml/h.

The test was run for 107 days, with a gradual increase of the thiosulfate inlet fluxes.

For both linings, the pH of the leaching solution decreased from 9 to 4 in the first 17 days of the experiment. The decrease of pH was linked with the transformation of thiosulfate by the biological activity, which produced H⁺ and sulfate in the trickling solution. After this first stage, the pH of the CAC lining stabilized during the next 57 days, and then due to an increase in the thiosulfate loading, a slight acidification was recorded, pH reaching around 3 during the last few days. For the BFSC lining, an overall acidification was also observed, pH reaching around 3.5 at the end of the experiment.

The test design enabled the rate at which thiosulfate was converted into sulfate to be monitored. During the first 63 days, the sulfate production rate increased regularly for both linings, with faster production recorded on the BFSC lining. The lower production rate on CAC highlighted the impact of the CAC lining on the first step of colonization by the sulfur-oxidizing bacteria. After the day 63, the sulfate production rate stabilized for both linings.

### 3.3. Sampling of the cementitious materials after exposure

Fig. 2 illustrates the different steps of the mortar specimen sampling prior to chemical and microstructural analyses. At the end of the exposure period (107 days), the pipe segments were sawn with a hand grinder to collect 5 cm × 5 cm specimens (ductile cast-iron envelope + mortar lining). The mortar linings were then easily detached from the iron tube. Afterward, the mortar lining pieces were sawn more accurately with a diamond saw to prepare 1 cm × 1 cm × 0.6 cm specimens intended for microstructural testing.

### 3.4. Microstructural characterization by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS)

Microstructural observations and chemical analyses of exposed and control mortar lining specimens were performed using a scanning electron microscope (Jeol JSM-6380LV, pressure: 60 Pa, accelerating voltage: 15 kV) fitted with an EDS detector (Rontec XFlash® 3001). The observations were performed on fractures and on flat polished sections previously coated with a carbon film. The flat polished sections were prepared as described in [28].

### 3.5. Oxide composition of the cement paste by electron probe microanalysis (EPMA)

The chemical composition of mortars was analyzed using an electron microprobe (CAMECA SX 50). The accelerating voltage was 15 kV, the current was 10 nA, and the scanning area of the beam was 2 × 2 μm². The counting time was 10 s on peak and 5 s on the background on each side for all elements. The measurements were performed on flat, polished, carbon-coated sections up to the core of the specimen (about 6 mm depth) and were expressed according to the distance from the inner surface of the lining (inoculated surface). These analyses were performed on two specimens (reproducibility). A control specimen (sound lining) was also analyzed. The following elements were analyzed: Ca, Si, Al, Fe, Mg, S, K, Na, and Ti. Calibration was performed on natural and synthetic standard materials before...
each series of analyses. These standards are listed in [28], with the confidence intervals on the mass percentage of each analyzed element and the corresponding detection limits. The analysis points were chosen with care so as to explore the hydrated paste only and to avoid residual anhydrous grains [28–30].

3.6. Mineralogical analyses by X-ray diffraction (XRD)

Mineralogical analyses were performed on the specimens using X-ray diffraction (SIEMENS D5000, cobalt cathode; anode voltage: 35 kV; current strength: 35 mA) [28–30]. The measurements were performed on two specimens as a function of the distance from the inner surface. The first analysis was carried out on the inner surface of the specimen, which was then gently abraded manually with a polishing disc and subjected to the next analysis. The depth of analysis was deduced by measuring the thickness of the remaining lining specimen with a vernier caliper. Because the mortar specimens to be analyzed were collected from cylinders (Figs. 1 and 2), they were curved. Nevertheless, the diameter (80 mm) of the cylinders was large compared to the transversal length of the specimens (about 10 mm) and the inner surfaces were thus flat enough for the XRD analyses to be performed in satisfactory conditions.

3.7. Water intrusion porosimetry

Water intrusion porosity tests were performed on the sound specimens according to the GranDubé recommended procedure [31]. The collected samples were kept in a vacuum for 4 h to eliminate the air contained in the pores. Afterward, the porosity of the specimens was filled with water under vacuum conditions for 12 h. The samples were then weighed hydrostatically before being dried for 24 h at 105 °C and then weighed in air. The specific and apparent densities and the porosity were deduced from these successive weighings as described in [31].

4. Results

4.1. Analyses of the control specimens

The placing of cementitious linings inside the pipes by centrifugation [27] leads to spatial segregation of the different mortar compounds. Fig. 3 shows SEM observations in BSE mode of cross sections of CAC and BFSC control specimens. The linings, 5.6 mm thick, show a double-layered structure composed of the following:

(i) the outer layer (in contact with the ductile cast-iron tube) made of mortar (4.0 mm thick, siliceous aggregates, zone a on Fig. 3). The CAC mortar layer showed more compact granular packing with smaller aggregates than the BFSC mortar

(ii) a 1.6-mm-thick paste layer (internal part of the lining and in contact with the biofilm). Within this paste layer, two zones can be distinguished: zone b, 1200–1300 μm thick, a dense cement paste layer, and zone c, an outer, low density, 300- to 400-μm-thick layer (which corresponds to the laitance layer and which is carbonated). No initial cracking was observed in either of the control linings.

The average oxide compositions of the two control specimens measured by EPMA analyses are presented in Table 2.

The water porosity of control specimens of mortar linings is given in Table 3. The porosity was measured (i) on the paste layer, (ii) on the mortar layer, and (iii) on the total specimens for each type of lining. The paste and mortar layers in each zone were collected by sawing with a diamond saw.

The CAC lining showed much lower porosity than the BFSC one. In particular, the paste layer (in contact with the biofilm) of the BFSC lining was twice as porous as the CAC lining. These porosity measurements combined with the oxide compositions (Table 3) indicate that the paste layers (zones in contact with the biofilm) of the two linings had comparable calcium contents (30% for the BFSC lining and 25% for the CAC lining).

4.2. Characterization of the exposed mortar linings

4.2.1. Cementitious lining inspections using SEM observations coupled with EDS analyses

Fig. 4 shows observations of cross sections of the linings exposed to the test: the CAC lining (Fig. 4(A)) and the BFSC lining (Fig. 4(B)). The left sides of Fig. 4(A) and Fig. 4(B) correspond to the inoculated surfaces of the two linings.

For the CAC lining (Fig. 4(A)), no crack was visible anywhere in the specimen. The paste showed high density and compactness except in a 100-μm-thick, very porous, and decalcified outer layer (previously in contact with the biofilm).

For the BFSC lining (Fig. 4(B)), micro-cracks were present in the paste layer of the specimen (no crack was observed in control specimens prepared by the same method) (Fig. 3(B)). At around 400 μm in from the surface, a thicker crack, almost parallel to the surface, was notably visible (observable with the naked eye) (Fig. 4(B, C)). Fig. 4(D) shows a front view of the BFSC lining specimen after the abrasion of the first 400 μm of the cement paste. This optical microscope observation confirms the quite intense cracking at this depth in the BFSC lining (see Section 3.2.2).

4.2.2. Chemical composition profiles with EPMA

The results of EPMA analysis of the BFSC lining exposed to the test, according to the distance from the inoculated surface, are shown in Fig. 5. The paste and mortar layers, as well as zones a, b, and c, as defined in Fig. 3 on the BFSC control specimens, are reported on the graph. Moreover, three zones (distinct from zones a, b, and c) can be observed on the chemical profiles.

From the core to the surface:

- Zone 1, or the unaltered zone, has the same average chemical composition as the control specimen (Table 2).
- Zone 2, from 700 to 100 μm below the surface, is enriched in sulfur and is partially decalcified. This zone comprises the main crack identified with SEM (Fig. 4(B,C)). The location of the crack (about 400 μm depth) corresponds to the highest amount of sulfur recorded on the whole profile. The average SO3 content reaches 5.6% in mass for the exposed specimen (average content of 4.5% for the control specimen). Silicon and aluminum are preserved in this zone.
- Zone 3, the outer layer, 100-μm thick, is strongly decalcified and its SO3 content progressively tends to zero toward the surface. Al2O3 and SiO2 contents are maintained in this zone.

The results of EPMA analysis of CAC lining exposed to the test, according to the distance from the inoculated surface, are shown in Fig. 6. On the graph, zones (a) and (b) observed on the control specimen (Fig. 3(A)) are reported. Moreover, two zones can be observed on the chemical profiles. From the core to the surface, they are as follows:

- Zone 1, or unaltered zone, having the same average chemical composition as the control specimen (Table 2).
- Zone 2, 160-μm thick, which is (i) enriched in sulfur (up to 1.7% of SO3 vs. an average of 0.06% in the rest of the paste), (ii) almost fully decalcified, and (iii) mainly composed of aluminum.
4.2.3. Mineralogical characterization by XRD

Fig. 7 shows the mineralogical characterization by XRD of the BFSC lining specimen exposed to the test for zones 1 to 3 described previously (Fig. 5) and for the surface of the specimen (in contact with the biofilm):

- Zone 1 has the same mineralogical composition as the control specimen. Peaks of the hydrated phases ettringite and portlandite are visible, as well as the C-S-H halo at the center of the graphs. Peaks of the anhydrous phases C₃S and merwinite are also present. A major peak of quartz is also found, probably because of the presence of siliceous sand grains in the plane surface analyzed (close to the mortar layer).
- In zone 2, peaks of portlandite have disappeared, and intense peaks of ettringite suggest that secondary precipitation of this phase has occurred. This is consistent with EPMA results and the decrease of calcium content and the enrichment of sulfur oxide in this zone (Figs. 4 and 5), which comprises the main crack (Fig. 4(B,C)).
- In zone 3, ettringite peaks have disappeared. Calcite peaks are present, as are those of residual anhydrous grains C₃S and merwinite.
- The surface of the BFSC specimen, in contact with the biofilm, is mainly amorphous (Fig. 7).

Fig. 8 shows the mineralogical characterization by XRD of the CAC lining specimen exposed to the test for the gel zone described previously (zone in contact with the biofilm) and for the surface of the specimen (in contact with the biofilm):

- Zone 1 shows typical anhydrous (CA, C₁₂A₇) and hydrated (C₃AH₆, AH₃) crystallized phases of CAC matrices. In the layer in contact with the biofilm (zone 2), the structure is poorly crystalline with precipitation of AH₃ (in its crystallized and amorphous forms) and dissolution of C₃AH₆ and of the other crystallized phases.

Fig. 3. Observation with SEM (BSE mode) of control specimens, cross sections of mortar linings, (A) the CAC lining and (B) the BFSC lining, and zoom on zones b and c.
and calcium released by the matrix and then the reaction of gypsum to the primary formation of gypsum from the reaction between sulfate and monosulfoaluminate (Eq. 9) in the matrix and/or in the trickling solution and the saturated conditions at the surface, which favored the precipitation of gypsum could also be used, such as the inclination of the pipe (from the vertical), to increase the hydraulic residence time and thus the accumulation of the biological and leached products at the surface of the lining. In another experimental campaign carried out since then, where zones not saturated with water were created at the surface of the linings and where the use of tetrathionate as a substrate enabled higher sulfuric acid production, gypsum formation was observed at the surface of the BSFC lining [36]. Other ways of optimizing the test design to favor the precipitation of gypsum could also be used, such as the inclination of the pipe (from the vertical), to increase the hydraulic residence time and thus the accumulation of the biological and leached products at the surface of the lining. In this case, gypsum should precipitate at the surface of the cementitious materials.

However, although the formation of gypsum is favorable to the representativeness of the test, it does not necessarily favor intensification of the deterioration phenomena.

The role of gypsum during the biodeterioration of the cementitious materials in a sewer environment is controversial, with a positive aspect detected by XRD either at the surface or in the cementitious matrix. The thickness of the altered layer (zones 3 on Fig. 6) was 160 μm.

5.2. Comparison with degradation mechanisms reported in the literature

Regarding BSFC lining, cracking due to the secondary formation of gypsum and/or ettringite has been widely observed on concrete made of ordinary binders (generally OPC) in sewer networks exposed to high concentrations of H₂S for several years [17–19,34]. The precipitation front, evidenced by the longitudinal crack at a depth of about 400 μm in the matrix, supports the description of the biogenic attacks on clinker-based mortars (BSFC) in two steps [34]: first a surface phenomenon with biological production of acid and sulfate, and then the penetration of acid and sulfates into the material with local precipitation of ettringite [2,35]. Nevertheless, the absence of gypsum at the surface, in the conditions of the experiment, needs to be discussed in terms of representativeness and intensification.

The calculations of the saturation index (SI) for gypsum from the concentrations of calcium leached and sulfate produced in the leaching solution during the tests are presented in Fig. 9 for the CAC lining and the BSFC lining. These calculations confirmed that no gypsum precipitated at the surface of the BSFC lining in the experimental conditions of the present test. Nevertheless, the saturation index recorded during the last 40 days of the test was between −1 and 0 for both linings, which was close to conditions inducing gypsum precipitation. The absence of gypsum may have been due to the low residence time of the trickling solution and the saturated conditions at the surface, which favored the leaching of calcium released by the cement matrix and of the sulfur substrate. In another experimental campaign carried out since then, where zones not saturated with water were created at the surface of the linings and where the use of tetrathionate as a substrate enabled higher sulfuric acid production, gypsum formation was observed at the surface of the BSFC lining [36]. Other ways of optimizing the test design to favor the precipitation of gypsum could also be used, such as the inclination of the pipe (from the vertical), to increase the hydraulic residence time and thus the accumulation of the biological and leached products at the surface of the lining. In this case, gypsum should precipitate at the surface of the cementitious materials.

5.1. Degradation mechanisms of BSFC and CAC linings.

Significantly different degradation patterns were observed for the BSFC and CAC linings exposed to the biogenic acid attack for 107 days.

The BSFC lining showed intense cracking of the outer zone of the paste layer (the main crack being observed at a distance of about 400 μm from the surface) because of the precipitation of secondary ettringite. The outer layer of the paste zone was also decalcified and mainly amorphous. These alteration phenomena were the consequences of the biofilm producing acid and sulfate at the surface of the specimen through the oxidation of thiosulfate in the trickling medium. In particular, the precipitation of ettringite may have been due to the reaction of sulfate with monosulfoaluminate (Eq. 9) in the matrix and/or in the trickling solution and the saturated conditions at the surface, which favored the precipitation of gypsum could also be used, such as the inclination of the pipe (from the vertical), to increase the hydraulic residence time and thus the accumulation of the biological and leached products at the surface of the lining. In this case, gypsum should precipitate at the surface of the cementitious materials.

For the CAC lining, after the exposure time, an amorphous layer was observed at the surface of the material. This layer, in contact with the biofilm, was decalcified and mainly composed of AH₃ (EPMA analyses showed that the zone was mainly composed of Al, and AH₃ peaks were identified through XRD), the other hydrated and anhydrous crystallized phases being dissolved. It was also enriched with sulfur in its outer zone, probably because of absorbed substrate, since no secondary sulfate-bearing compounds, such as gypsum or ettringite, were observed at the surface of the CAC lining specimen.
for the cementitious matrix observed in stagnant sulfuric acid tested by the formation of a protective layer at the surface of the material [22,36], or with a negative aspect when the gypsum layer is described as a favorable medium for colonization by the microbial community, in addition to its swelling properties [34,37].

Regarding the CAC lining, it was mentioned in Section 2 that the phenomena governing the degradation of calcium aluminate cement-based materials exposed to biogenic acid attack in a sewer were rather poorly documented in the literature. The formation of AH₃ and the absence of secondary sulfur-bearing compounds (ettringite/gypsum) at the surface and in the lining is consistent with other studies in the literature [4,38]. AH₃ is stable for pH from 9 to 3–4 [16,38]. The monitoring of released aluminum during the last 40 days of the experiment, as presented in the first part of this article [7], highlighted the intensity of the biogenic acid attack, which led to the dissolution of the AH₃ hydrogel (reaction 5). The absence of gypsum and ettringite may have been due to (i) local chemical conditions that were not favorable (saturation index presented on Fig. 9) despite the release of calcium from the outer layer [8,15] and to (ii) the protection provided by the alumina gel formed during the biogenic attack (AH₃) and the low porosity of the CAC matrix, limiting the penetration of sulfate [8,37].
It should be noted that, as for BSFC linings, gypsum was observed at the surface of CAC specimens exposed to the test with tetrathionate and unsaturated zones [36]. The deterioration processes observed inside the matrix were the same as those observed in the present study.

Finally, it may be concluded that the degradation phenomena occurring in the cement matrix of CAC and CEM III were globally in accordance with in situ and laboratory data found in the literature.

5.3. Resistance of the tested materials to biogenic acid attack and capability of the test design to discriminate two linings in short-term experiments

In the literature, the better resistance of the CAC materials in a biogenic acid environment is reported to be due to (i) the higher acid neutralization capacity of CAC than of OPC-based materials [38,39], (ii) the formation of a stable alumina gel (AH3) at the surface of the material during the biogenic attack, which leads to a decrease of the porosity [38], and (iii) a bacteriostatic effect of the cementitious matrix and/or the leaching products (aluminum in particular) [38]. More generally, several intrinsic properties of the material can influence the bioreceptivity of the materials, as surface properties (hydrophobicity or hydrophilicity, roughness, etc.). However, this field of study concerning CAC matrix is not well documented today. Nevertheless, it was shown in the first part of the paper that the selection of optimal sulfur-oxidizing activity was delayed on the CAC lining, most probably because of its chemical and mineralogical composition, both initially and after the surface alteration by the biogenic acid attack [7]. The quantification of biological activity by sulfur mass balances, the amount of organic matter produced (80 mg of total volatile solid (TVS) for the CAC lining versus 330 mg TVS for the BFSC one), and the analysis of the microbial diversity [7] highlighted the impact of the CAC lining on the global microbial activity. Other studies have confirmed the influence of CAC materials on microbial populations involved in biogenic attack [40], especially in the first step of the attack (neutrophilic sulfur-oxidizing bacteria such as Starkeyella Novella and Thiomonas Intermedia) [40,41], while, in the last step, Acidithiobacillus thioxidans, for example, seems to be unaffected or less affected by CAC materials or by the leaching product [41–43]. Nevertheless, the mechanisms of the effect of CAC materials on the microbial population, which might account for the better resistance of CAC in sewer-like environments, is not well understood yet.

Concerning the test evaluation, the degraded layer depths were 700 μm for the BSFC lining and 150 μm for the CAC lining after 107 days of exposure, which, in absolute terms, confirms the better resistance of the CAC lining compared to the BSFC one. The degraded layer depths divided by the total number of moles of acid produced during the experiment, per square meter of exposed surface (5.2 mol of H+ on the BSFC lining and 4.7 mol on the CAC lining), were (i) 135 μm/mol H+/m² for the BFSC lining and (ii) 32 μm/mol H+/m² for the CAC lining. After 150 days of test in an H2S chamber, Ehrich et al. obtained: (i) ~80 μm/mol H+/m² for a BFSC mortar with siliceous aggregates and (ii) ~50 μm/mol H+/m² for a CAC mortar with siliceous aggregates (with the assumption that the mass loss of the samples was uniform over the specimens) [4]. These results show the same tendencies for cementitious-based materials against biogenic acid attacks. Moreover,
they highlighted that lining production industrial process could intensify the differences between products compared to mortars produced in the laboratory. In particular, the paste layer of the lining is denser in the case of the CAC lining (porosity of 16.5%) than in the BSFC one (porosity of 33.8%) (Table 3). This is likely to limit the diffusion of the aggressive agents inside the cementitious lining during the first step of the biogenic acid production.

Finally, the experiment confirmed the different behavior of BFSC and CAC linings as already highlighted in the literature [4,6,44,45], which validates the test in terms of discrimination between two manufactured products. The test also enables the initial structure of the lining (induced by the industrial process) to be taken into account.

6. Conclusions

A new biological test method (labeled Bact-Test for Biogenic Acid Concrete Test) was designed for the evaluation of manufactured pipe products intended for sewer networks. Cementitious linings were inoculated with an initial diversified consortium (inoculum composed of environmental microbial populations selected only by the wastewater collecting and treatment system) at the beginning of the test. Thiosulfate, used as a sulfur source, was trickled over the surface of the linings. After 15 weeks of exposure in a controlled environment, a sulfur-oxidizing biofilm developed at the surface of the materials, leading to chemical and microstructural transformations of the cementitious materials similar to those observed in sewer networks exposed to H2S. Moreover, the test discriminated between two types of cementitious linings (BFSC and CAC) in terms of performance (degraded layer depth). The study also highlighted the impact of the lining nature on the selection and the activity of the bacterial consortium.

Concerning the intensification of the biogenic acid attack, a polythionate – tetrathionate – identified as a biological intermediate in thiosulfate oxidation will be used as the sulfur substrate in order to increase the acid production (1.5 atom of H+ per oxidized sulfur atom of the tetrathionate molecule, against 1 atom of H+ for the thiosulfate molecule). The reproducibility of the test is currently being evaluated by another experimental campaign run under the same conditions.

In situ testing has also started in the framework of a collaborative research program (DURANET) in order to evaluate the accelerating factor of the test.

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