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Evaluation of the resistance of CAC and BFSC mortars to biodegradation: laboratory test approach

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Abstract. Biodeterioration of cementitious materials in sewer networks is a major concern for health and economic reasons. Essentially, it is due to the biological oxidation of H_2S into H_2SO_4 leading to a local progressive dissolution of the cementitious matrix and the precipitation of expansive products likely to provoke cracks. However, it is widely known that CAC has a better performance in such environments but the mechanisms are not very well understood. Nevertheless, previous studies focused mainly on measuring the mass loss of the specimens accompanied with little information on the chemical alteration of the cementitious matrix. This study aims to compare the performance of CAC and BFSC mortars in sewer conditions using laboratory test (BAC-test). Leaching kinetics were evaluated by concentrations measurements of cementitious cations in the leached solutions and of sulphate production by the microorganisms. Moreover, SEM observations coupled with EDS analyses allowed the identification of the chemical alteration of the cementitious matrix.

1. Introduction

Around 10% of sewer pipe failures were estimated to be due to microbial induced concrete corrosion (MICC) [1]. This phenomenon causes severe deterioration of the cementitious materials employed in sewer environments. Concrete sewer systems are composed of a lower liquid part and an upper aerial part (Figure 1). In the liquid part anaerobic sulphate reducing microorganisms (SRM) develop and reduce sulphate (SO_4^{2-}) in the wastewater stream to produce hydrogen sulphide (H_2S). In the aerial part H_2S condensates on the concrete surface resulting in a progressive decrease in pH, from 12 to around 9 in a first abiotic stage, leading to the development of aerobic sulphur oxidising microorganisms (SOM) [2,3]. Then, the dissociation of H_2S – due to the high relative humidity – produces sulphide ions which are oxidised into several sulphur species via several bio-chemical reactions. Sulphuric acid (H_2SO_4) is produced as the final product of the oxidising chain reactions of these sulphur species transformations. The H_2SO_4 – produced by microorganisms on the material's surface and possibly inside the cementitious matrix [4] – is at the origin of a severe attack on the cementitious material. The deterioration phenomenon is essentially due to the dissolution of the cementitious phases and to the secondary precipitation of expansive products, such as gypsum and/or ettringite.

In sewer environments, the higher resistance of calcium aluminate cement (CAC) compared to ordinary Portland cement (OPC) is widely recognised [5-11]. Thus, this study aims to compare the performance of

CAC and blast furnace slag cement (BFSC) in a laboratory test reproducing sewer conditions.

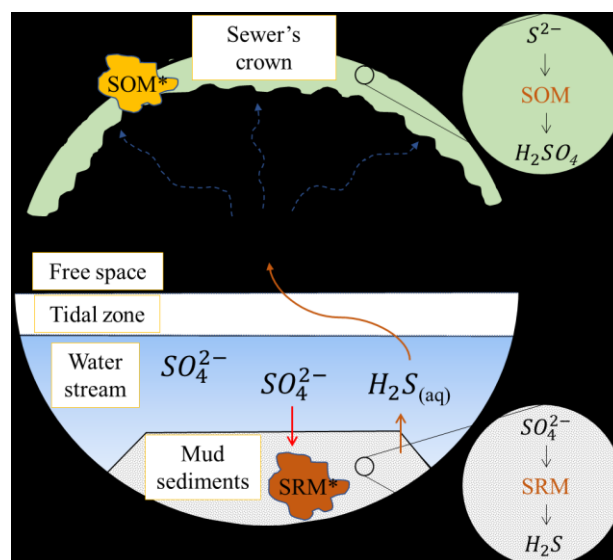


Figure 1. The sulphur cycle in the sewer system. *SRM: sulphate reducing microorganisms; *SOM: sulphur oxidising microorganisms

2. Materials and Methods

2.1. Cementitious mortars

The study was conducted on mortar specimens made of:

- A blast furnace slag cement containing 50% of slag, noted BFSC,

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Table 1. Chemical composition of CAC and BFSC binders

Oxides (wt.%)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	K ₂ O	SO ₃	Other oxides
CAC	37.9	5.1	52.1	1.6	0.3	2.1	0.4	< 0.05	0.5
BFSC	PC	68.2	22.7	2.5	0.2	0.5	0.5	2.3	3.0
	Slag	43.3	37.1	11.1	0.6	6.5	0.5	0.2	0.5

- A calcium aluminate cement containing around 50% of alumina, noted CAC.

The chemical composition of the cements is presented in Table 1. The preparation of the specimens was done according to the French Standard *NF EN 196-1*. 450g of cement and 1350g of standardized silica sand mixed with 225g of water then vibrated from 1 to 2 mins until the disappearing of air bubbles rising to the surface. The water to cement ratio was 0.5.

BFSC mortars were kept in sealed bags at 20°C and CAC mortars were cured for 2h at 70°C with 100% RH to accelerate the conversion process of the hydration products and to obtain stable phases such as C₃AH₆. Afterwards, CAC mortars were cured for 22h at 20°C with 100% RH and finally put in sealed bags at 20°C.

2.2. Durability test: BAC-test

The BAC-test, for Biogenic Acid Concrete was developed at INSA Toulouse to assess the resistance of cementitious based materials to biogenic acid attack. Figure 2 shows the BAC-test experimental pilot design [6, 7]. The test pilot was made up from a 200-liter tank (1), connected to the test apparatus by plastic tubes used to transport the solution from the tank via flow pumps (2) and drop it on the top of the specimens (3) which were covered with the inoculum obtained from an activated sludge. The specimens were laid on inclined supports with a low slope to optimize the retention time of the solution in contact with the cementitious material [8].

The feeding solution was composed of tetrathionate (K₂S₄O₆) as a soluble reduced sulphur source and other nutrients, such as nitrogen, phosphorus, iron, chloride and oligo-elements, required for microorganisms' growth, dissolved in deionized water [6]. Downstream of the specimens the leaching solutions were punctually collected (4) and filtered at 0.45 µm to eliminate all microorganisms that could have fallen into the collecting tubes and to stop any further biochemical reaction in the collection tubes. The liquid samples were, then, stored in at 4 °C after measuring the pH. These samples were used to measure the concentration of Ca²⁺, Al³⁺ and SO₄²⁻ in the leaching solution. At the end of the test, the cement paste specimens were collected for microstructural and chemical analyses and degraded depth measurements. The representativeness and reproducibility of the test method were demonstrated in previous campaigns [6-8].

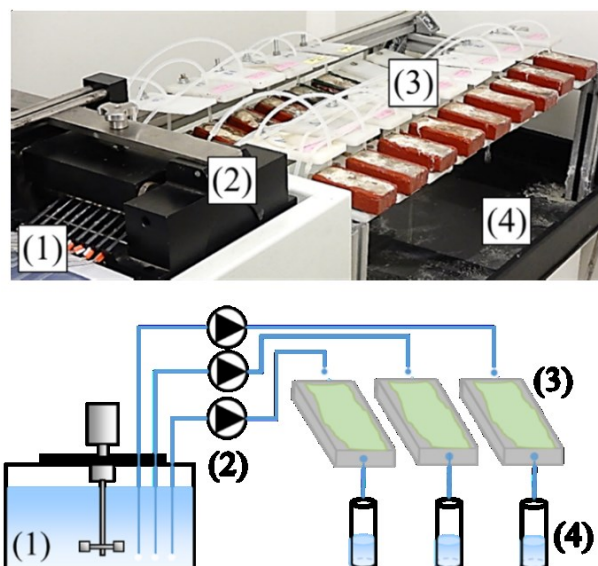


Figure 2. The BAC-test experimental pilot and a schematic layout of the test

2.3. Methods

2.3.1. Analyses of the aggressive solutions during the exposure

Leaching solution samples were filtered at 0.45 µm and then acidified using HNO₃ Plasma-Pure at 2% of the liquid volume. The concentrations of Ca and Al in the solutions were measured by ICP-OES (Optima 7000 DV machine).

The same samples analysed by ICP were, then, diluted with a factor of 10 to reduce the peak of HNO₃ and to be able to distinguish the sulphate peak. The concentrations of sulphate were measured using Dionex ICS-39 with an AS-11 HC column and KOH as eluent.

2.3.2. Analyses of the degraded materials

Flat sections were sawn and put into a resin – Mecapex MA2+ with the appropriate catalyser – before being polished and coated with a carbon film. These sections were used for microstructural observations and chemical analyses using a scanning electron microscope (JEOL JSM-6380LV with accelerating voltage 15kV) in back scatter electron (BSE) mode and were completed with elemental mapping analyses using energy dispersive spectroscopy (Rontec XFLASH 3001).

3. Results and discussion

3.1. Bacterial activity and sulphate production

Figure 3 shows the pH evolution of the leaching solutions for the specimens subjected to biogenic sulphuric acid for 52 days. For the first 3 days, the pH increased for both materials because of the leaching of the very outer layer of cement pastes once in contact with the solution. During these 3 days, microorganisms' selection was being done as SOM have found a sulphur substrate ($K_2S_4O_6$) which allowed them to develop and to create the biofilm.

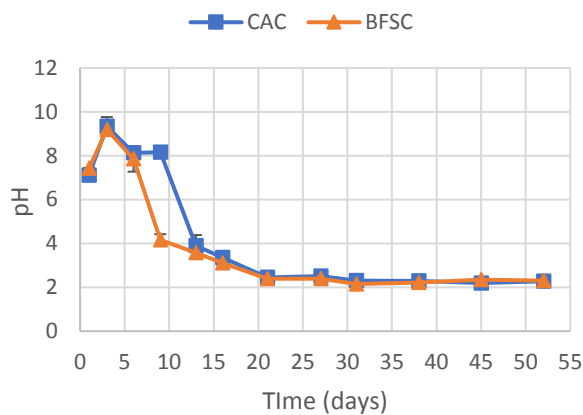


Figure 3. pH evolution of CAC and BFSC leaching solutions exposed to BAC-test

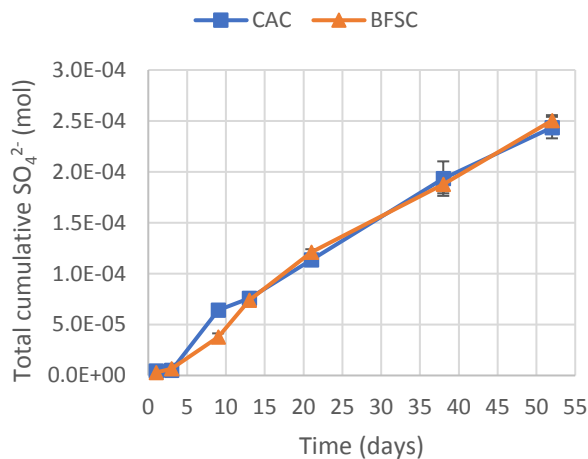


Figure 4. Total cumulative SO_4^{2-} produced by microorganisms on top of CAC and BFSC materials

The first 3 days marked the development of the neutrophilic sulphur oxidizing bacteria (NSOM). The activity of these microorganisms was limited by the high pH and therefore, the amount of produced sulphate was relatively low (Figure 4), leading to a slow progressive decrease of the pH. However, CAC showed a slightly higher buffer effect compared to BFSC as the pH took several additional days to reach acidic values. Nevertheless, starting from 21 days, the pH of both materials stabilised around 2.5 until the end of the test, in accordance with other experimental campaigns [8, 12],

showing the high aggressiveness of the chemical conditions set by the BAC test.

Nonetheless, quantification of sulphate in the leaching solution showed that the amount of sulphate produced by microorganisms on both materials' surface was very similar, as shown on Figure 4.

3.2. Cementitious cations leaching

Figure 5 shows a significant difference in the amount of leached calcium between CAC and BFSC, although, the same amount of sulphate was produced on both materials' surface (Figure 4). The total cumulative leached Ca^{2+} per initial total Ca^{2+} in the BFSC binder was found to be two times higher compared to CAC. The same behaviour was observed on Al^{3+} leaching with 0.002 molCa/molCa and 0.008 molAl/molAl for CAC and BFSC respectively.

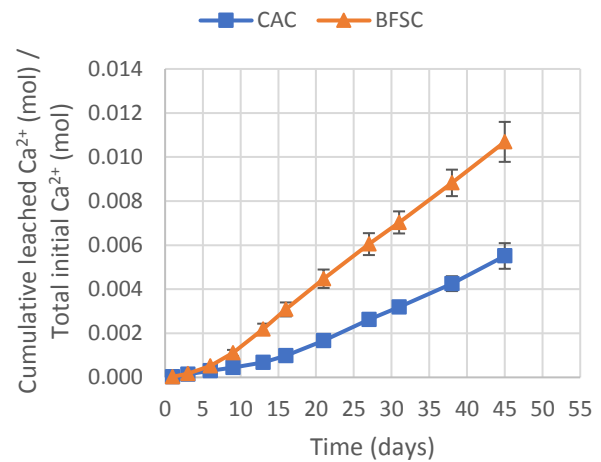


Figure 5. Cumulative leached Ca^{2+} by initial binder content during the exposition of CAC and BFSC to the BAC-test

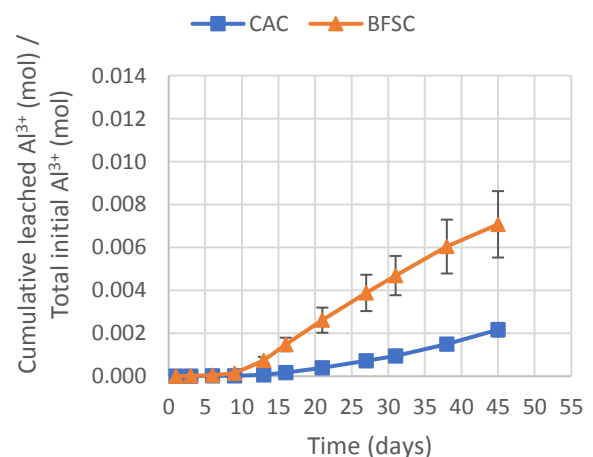


Figure 6. Cumulative leached Al^{3+} by initial binder content during the exposition of CAC and BFSC to the BAC-test

The different behaviour between CAC and BFSC could be explained by the different chemistry of the cement and the chemical stability of their phases. For

instance, katoite (C_3AH_6) and gibbsite (AH_3) are the main phases of CAC while C-(A)-S-H is the dominant phase – along with AFm/AFt phases – of BFSC. On one hand, AH_3 is known for its high chemical stability in acidic environments (down to pH 3-4), moreover, the dissolution of C_3AH_6 results in the production of additional AH_3 inside the cementitious matrix.

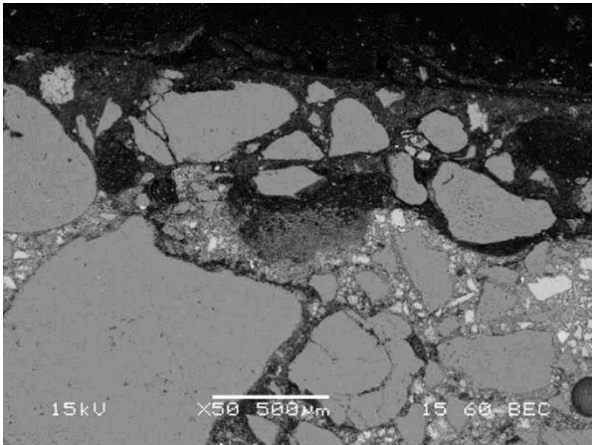
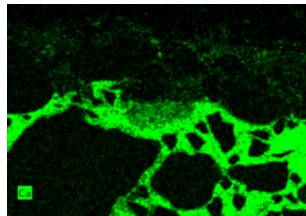
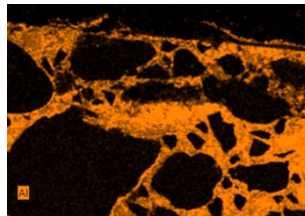
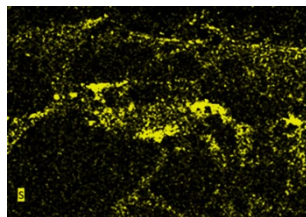
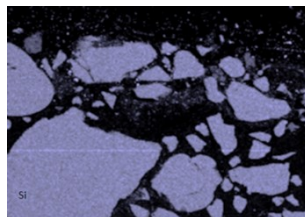
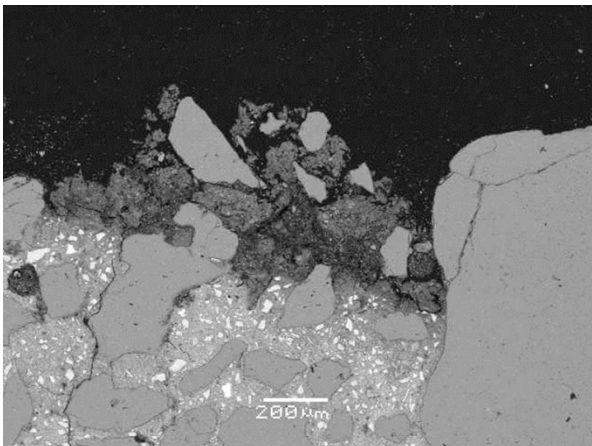
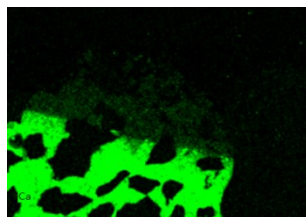
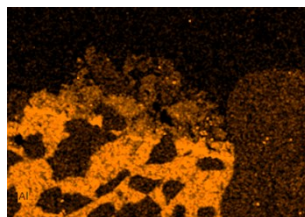
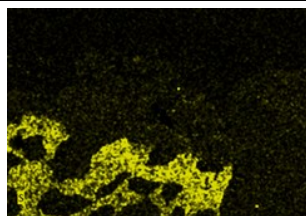
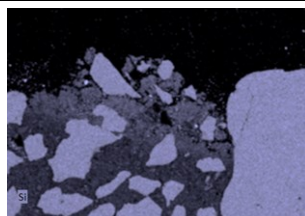
Also, some authors reported the capacity of the aluminium gel to create a physical barrier against the sulphur penetration [13,14]. However, the aggressive exposure conditions of the BAC-test induced such acid flow on the material's surface that the impact of the gel physical barrier properties was lowered [15]. Sulphur may also have penetrated the material before the formation of the surface gel as several studies showed ettringite precipitations near the degradation front, under the alumina gel [7, 16, 17].

On the other hand, C-(A)-S-H, AFm and AFt phases are unstable in acidic medium, which might result in the total decalcification of C-(A)-S-H [18], leaving a very porous Si-Al gel with no cohesive properties. Furthermore, the dissolution of AFm/AFt phases could act as an internal source of SO_4^{2-} , which might accelerate the degradation.

3.3. Degradation mechanisms

At the end of the test, the mortars samples were collected for chemical analyses. Backscattered electron images from SEM observations and chemical elemental (Ca, Si, Al and S) maps of polished sections obtained for CAC and BFSC are shown in Table 2.

Table 2. Chemical elemental mapping of CAC and BFSC samples after 52 days of exposure to biogenic acid using the BAC-test

CAC			
	Ca	Al	
			
	S	Si	
			
BFSC			
	Ca	Al	
			
	S	Si	
			

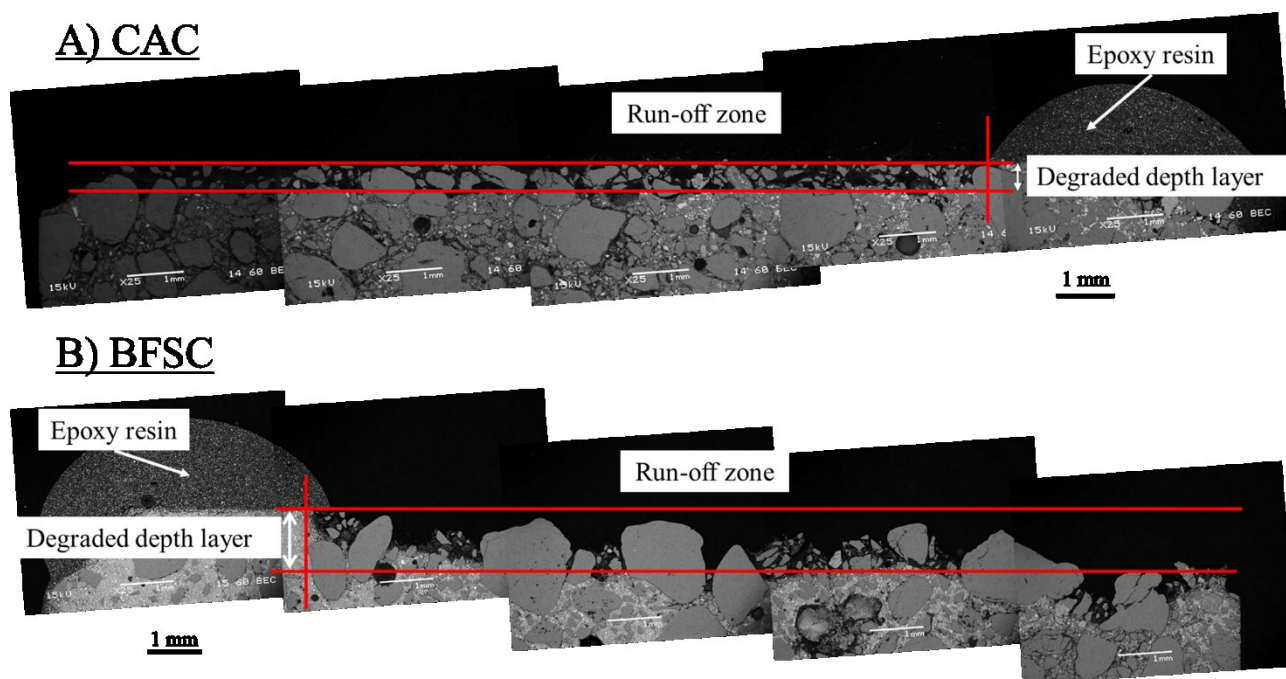


Figure 7. SEM observations (BSE images) of deteriorated mortars sample (A) CAC and (B) BFSC after 52 days of exposure to biogenic acid using the BAC-test

Regarding the CAC sample, a relatively homogeneous dark grey zone was observed at the surface which corresponded to a more porous and highly decalcified layer of the specimen. The average thickness of the decalcified layer was approximately 500 μm . However, as this altered layer was enriched in Al, previous works demonstrated that $\text{Al}(\text{OH})_3$ was the main mineral in this zone [7-10]. Also, while CAC mortars did not initially contain any S, the degradation front between the altered layer and the sound zone exhibited local enrichments of S, which confirmed the diffusion of sulphur species inward the cementitious specimen.

However, the nature of the S-based minerals was not determined in this study but it is likely to be mainly gypsum as reported in [7, 11]. The silicate sand did not suffer any degradation. Nonetheless, some aggregates got detached from the specimen due to the dissolution of the binder.

Regarding the BFSC sample, three zones were identified parallel to the surface. The outer zone was completely dissolved due to the high aggressiveness of the acid attack. Also, the silica sand got detached from this zone and felt apart. The totally dissolved zone had an average thickness of 600 μm . The second zone – called degraded zone – had a dark grey shade and corresponded to the highly deteriorated zone at the surface of the specimen. The thickness of this strongly deteriorated zone was estimated at 500 μm . Finally, the inner zone had a similar grey shade as the core of the specimen and corresponded to the sound zone. The degraded zone was highly decalcified and was mainly composed of Si and Al. It might be due to the decalcification of C-(A)-S-H, leading to the precipitation of an amorphous Al-Si gel on the surface. Moreover, S was detected at the degradation front between the degraded zone and the unaltered zone, which could be

used as an indirect validation of the diffusion of sulphate – produced by SOM – to deeper zones. Lastly, the silica aggregates did not suffer any chemical alteration but still got detached from the specimen as for the CAC specimen.

Figure 7 presents the profiles of the cross-sections of CAC and BFSC obtained by SEM. An epoxy resin – on the right and left sides for CAC and BFSC respectively – was used to identify the initial surface of the material which served as a reference for the degraded depths estimations.

The total degraded depth was measured using image analyses techniques and was obtained by averaging the surface of the dissolved and the degraded zones over the initial sound zone surface. The total degraded depths for CAC and BFSC were estimated at 500 μm and 1100 μm respectively.

4. Conclusion

In this study, CAC and BFSC mortars were exposed to an accelerated biodegradation laboratory test (BAC-test) for 52 days.

The main results highlighted the better performance of CAC over BFSC. The chemical and mineralogical compositions of the binders were key players facing the biogenic sulfuric acid attack. The better thermodynamic stability of C_3AH_6 and AH_3 compared to C-(A)-S-H, AFm and AFt phases could explain the better resistance of calcium aluminate based materials. Furthermore, the degradation of C_3AH_6 by sulphuric acid led to the precipitation of additional AH_3 which has a high chemical stability in acidic environments (down to pH 3-4). However, the severe conditions of the BAC-test significantly reduced the importance of the barrier effect

of the gel as the enrichment of sulphur at the degradation front confirmed the diffusion of sulphur species inside the cementitious matrix despite the presence of the alumina gel on the surface. These results came in accordance with the literature [15]. In summary, the degraded zone was less deteriorated in the case of CAC matrix than in the case of BFSC one.

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