



## **UNDERSTANDING BIODETERIORATION MECHANISMS OF A CALCIUM ALUMINATE–BASED COATING AFFECTED BY SUBSTRATE CRACKING**

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**Keywords:** wastewater treatment plant, calcium aluminate cement, biodeterioration, durability, cracking.

### **ABSTRACT**

Calcium aluminate cement (CAC)-based coatings have demonstrated superior resistance to microbially-induced concrete deterioration (MICD) in wastewater infrastructures and are widely used to protect Portland cement-based concrete. However, in the penalizing case of cracking within the underlying substrate, cracks might propagate into the coating and act as pathways for aggressive agents. This study investigates the behavior of a thin sprayed CAC-based coating in the presence of cracks to understand the mechanisms that govern the coupling of cracks and biodeterioration.

Representative cracks were generated in coated mortar specimens using a displacement controlled three-point bending test, producing different crack width ranges: 150-200  $\mu\text{m}$  (complying the Eurocode 2 recommendations) and beyond 700  $\mu\text{m}$ . These specimens were exposed to the Biogenic Acid Concrete (BAC) test, which reproduces the aggressive conditions encountered in sewer networks. During the exposure period, the leaching solutions collected from the exposed surfaces were analysed followed by microstructural and chemical analyses of the structure using coupled SEM-EDS analysis.

Results show that the leaching of calcium was not significantly impacted in the presence of cracks. SEM-EDS observations revealed the formation of newly precipitated phases within the crack openings. These phases are suggested as a potential physical barrier, limiting the penetration of aggressive agents and contributing to the crack sealing of the coating in the stated conditions of exposure.

### **INTRODUCTION | BACKGROUND**

Wastewater treatment facilities are constructed mainly using cement-based materials that undergo progressive degradation throughout their service life.

Approximately 10% of their concrete deterioration has been attributed to biodeterioration processes arising from coupled biological and chemical activity<sup>1</sup>. This form of degradation is primarily associated with the production of hydrogen sulfide ( $H_2S$ ) and its subsequent biological oxidation to sulfuric acid ( $H_2SO_4$ ) by sulfur-oxidizing microorganisms.

Calcium aluminate cements (CAC) have shown superior resistance to microbially-induced concrete deterioration (MICD) in wastewater infrastructures<sup>2,3</sup> and are widely used in coatings to protect Portland cement-based concrete. The key factor in this resistance lies in its chemical and microstructural nature. However, cracks develop in the protected structure and might propagate into the coating, serving as preferential pathways for the ingress of aggressive agents into the underlying concrete<sup>4</sup>.

In this context, this paper studies the behavior of a thin CAC-based coating, developed by Imerys, in the presence of cracks to improve the understanding of the mechanisms that govern the coupled effect of cracks and biodeterioration. Using a controlled 3-point bending test, cracks of different crack width ranges were initiated: 150-200  $\mu m$  and more than 700  $\mu m$ . These specimens were exposed to BAC test during which the leaching solutions collected from the exposed surfaces were analyzed and coupled microstructural and chemical analyses were performed.

## METHODS

Fiber-reinforced mortars were cast into the substrate formulation using CEM III/A 42.5 N-LH cement, suitable for exposure class XA3 according to EN 206, and amorphous metallic fibers in 7 cm x 7 cm x 28 cm molds, with a water-to-cement ratio (w/c) of 0.47. The prisms were submerged in water for 14 days then covered in plastic bags at 20°C for 14 days.

The coating is based on calcium aluminate cement and calcium aluminate synthetic aggregates. It was mixed with 14% by mass water using a portable mixer and then sprayed onto one face of the substrate prisms with a target thickness of 5 mm. The composite specimens were then kept for 7 days in the lab in ambient temperature then cracks were introduced into the substrate-coating composite specimens using a three-point bending test on a servo-hydraulic press under displacement control.

To evaluate the influence of cracking on the coating's protective performance, different surface crack-width ranges were investigated: a crack width between 150 and 200  $\mu m$  falling below the Eurocode 2 crack-width limit and a crack width exceeding 700  $\mu m$ .

Biodeterioration was studied using the BAC test, developed at INSA Toulouse<sup>5</sup>, which simulates sewer conditions through biofilm inoculation and continuous feeding with a reduced sulfur source ( $K_2S_4O_6$ ). The exposed specimens included uncoated substrates (CEM III) and CAC-coated substrates with different ranges of crack width. Biodeterioration was monitored through analysis of the leached solutions using ICP-OES analyses for the quantification of the cementitious leached cations and acid ( $H^+$ ) calculations were based on sulfate and sulfite quantification using HPIC. These analyses were followed by SEM-EDS microstructural and chemical characterization after the end of the exposure period.

## KEY FINDINGS

The standardized calcium leaching results are presented in Figure 1 in which the results are presented for a CEM III-uncoated substrate, a CAC-coated uncracked substrate and cracked substrates with two ranges of surface crack width: one between 150 and 200  $\mu\text{m}$  and one whose width exceeds 700  $\mu\text{m}$ . The cumulative leached calcium was normalized<sup>6</sup> by its initial content in the material per unit surface area of the exposed surface as a function of the quantity of acid produced on the exposed surface calculated from the quantified sulfite and sulfate.

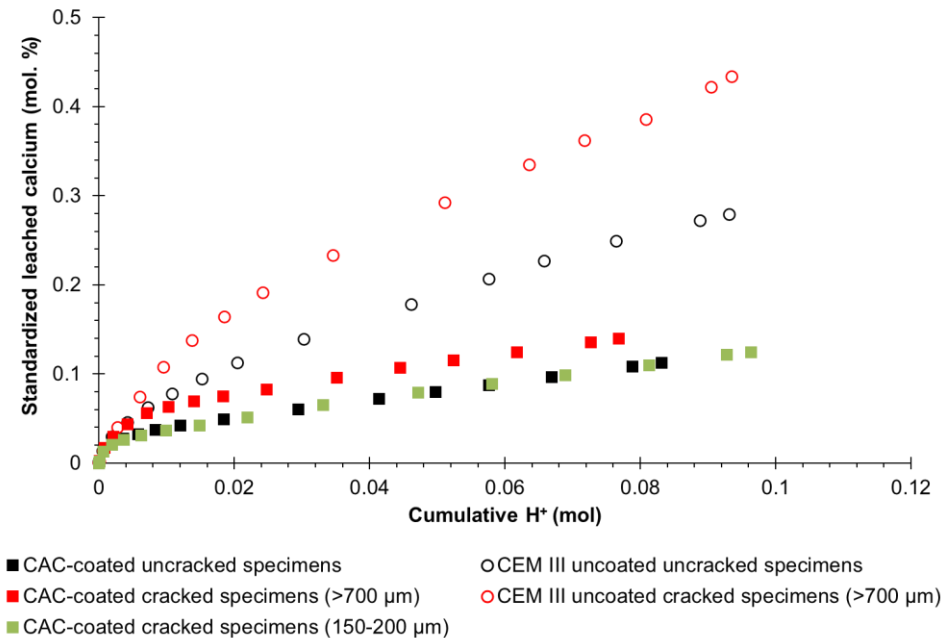


Figure 1. Evolution of the standardized leached calcium as a function of acid production during the 3-month exposure period

The presence of the CAC-based coating on the CEM III-based substrate, reduced calcium leaching by up to three times compared to the uncoated substrate, demonstrating the coating's superior resistance relative to the underlying material. Among the crack-width ranges in the coated specimens, the one between 150 and 200  $\mu\text{m}$ , which complies with Eurocode 2, had no impact on calcium leaching. In contrast, although wider cracks (>700  $\mu\text{m}$ ) increased calcium leaching, the coating's performance was not fully compromised as leaching remained substantially lower than in uncoated specimens. Moreover, this range of cracks significantly increased the leaching of calcium in CEM III uncoated cracked specimens.

At the end of the exposure period, SEM-EDS analyses were performed on specimens from different experimental campaigns. In all coated samples, a newly-formed phase was detected near the exposed surface and within the crack openings (Figure 2). While it partially clogs a crack of width between 400 and 600  $\mu\text{m}$ , it appears to completely fill the smaller crack (150-200  $\mu\text{m}$ ). Its presence likely contributes to the enhanced performance of the coating even in the presence of cracks. In contrast, this phase was not observed in CEM III-based cracked substrates (>700  $\mu\text{m}$ ).

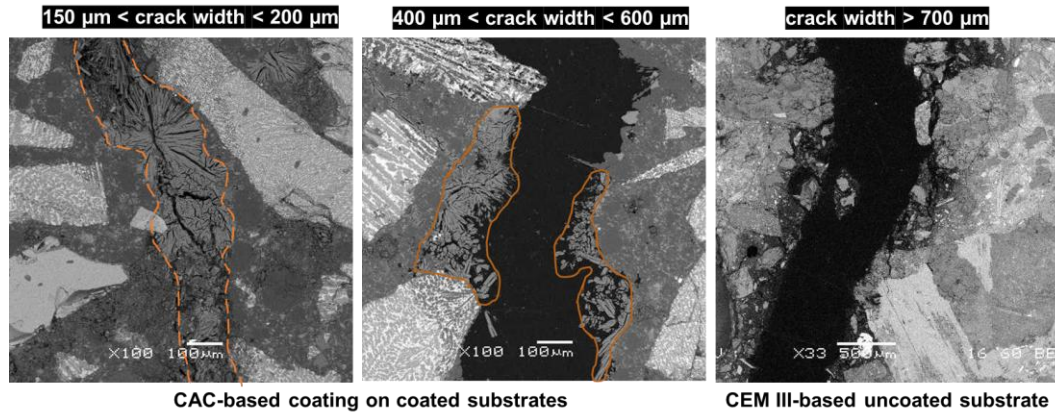


Figure 2. SEM images showing the newly-formed phases (in orange) in the crack opening

## CONCLUSIONS

This study investigated the biodeterioration mechanisms of calcium aluminate cement-based (CAC) coatings spray-applied onto CEM III-based substrates under simulated sewer conditions using the BAC test in the presence of cracks. The results demonstrated that the application of this CAC coating significantly reduced calcium leaching compared to uncoated CEM III substrates, confirming its protective performance and the reliability of the BAC test in evaluating biodeterioration of complex coating systems. While cracks compatible with Eurocode 2 limitations (150–200  $\mu\text{m}$ ) showed negligible impact on calcium leaching, wider cracks ( $>700 \mu\text{m}$ ) increased leaching without completely compromising the protective function. SEM-EDS analyses revealed the formation of a phase near the surface and within cracks in the coating, which likely contributes to its superior resistance to biodeterioration. These results suggest the potential of the CAC coating to engage self-healing mechanisms under such aggressive conditions.

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