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Behaviour of different cementitious material formulations in sewer networks

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ABSTRACT

Sewer networks are subjected to degradation, including biodeterioration of materials, in the presence of biogenic sulfuric acid, leading to costly repairs. To ensure durable structures, it is essential to select the best adapted materials. Two cementitious materials based on ordinary Portland cement (OPC) or calcium aluminate cement (CAC), were subjected to biodeterioration in the headspace of an operating sewer network. After a few month OPC materials started to deteriorate whereas CAC materials were still intact. The better durability of CAC materials is due to the presence of alumina providing a combination of protective mechanisms. On-site environmental parameters were monitored and analysed in the context of the biological and chemical mechanisms involved in material degradation. These data will eventually feed into the development of a representative, reproducible and accelerated laboratory test.

Key words | aluminium, biodeterioration, calcium aluminate cement (CAC), cementitious materials, hydrogen sulfide (H_2S), Portland cement

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INTRODUCTION

Sewer networks are structures built to transport wastewater from its point of production to treatment plants. Severe constraints are applied to these structures, which result in premature deterioration. These include root intrusion, joint displacement, cracks and hole formation leading to a significant volume of leakage with an overall risk for the environment and public health. For example, it is estimated that 500 million m^3 of contaminated water per year can leak into soil and ground-water in Germany (Kaempfer & Berndt 2009).

Hydrogen sulfide (H_2S) is indirectly responsible for biodeterioration (US EPA 1974, 1985; Vollertsen *et al.* 2008). This poisonous gas is produced by the reduction of sulfates, sulfites and other oxidized sulfur species in sludge and sediments accumulating at the bottom of the sewer. These deposits create anoxic conditions which favour the growth of a biofilm that may contain sulfate-reducing microorganisms (i.e. *Desulfovibrio* spp., *Desulfobulbus* spp.) (Vincke *et al.* 1999). H_2S is emitted into the headspace. In the presence of this gas, a second biofilm colonizes the inner surface of the sewer. This biofilm is composed of a succession of sulfur-oxidizing microorganisms that oxidize H_2S into sulfuric acid. This acid streams down the wall of the structure, dissolves metals and cementitious matrices, and leads to the formation of non-cohesive and/or expansive products such as gypsum and/or ettringite. If the biodeterioration of cementitious materials is not properly managed, it may lead to severe structural deterioration leading to significant repair costs.

However, this is based on the study of ordinary Portland cement (OPC) and is not relevant for all cementitious materials. As an example, calcium aluminate cement (CAC) materials performed much better in sewer network conditions subjected to biogenic deterioration (Alexander & Fourie 2011) despite the fact that they can dissolve in sulfuric acid at pH below 3 (Herisson *et al.* 2013). A report from the Concrete Manufacturers Association in South Africa (PIPES 2009) proposes a material factor (M_F) for the deterioration of different types of cementitious materials used in sewer networks, based on 14 years' observation of a real sewer. M_F is the ratio of corrosion rate for the alternative material being considered and a standard concrete (OPC

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Table 1 | M_F values of various materials (PIPES 2009)

Cement	Aggregates	Deterioration rates (in mm y^{-1})	M_F
OPC	Siliceous	7.5	1
CAC	Siliceous	1.9	0.25
CAC	CAC		0.025

and siliceous aggregate). As shown in Table 1, the composition of cementitious materials is a crucial factor in biodeterioration.

However, there is no universal laboratory test that mimics biogenic acid formation in sewer networks in order to assess any material's durability. As a result, there is no standard for comparing the best adapted materials in those deleterious environments.

This study focused on monitoring the biodeterioration of CAC and OPC specimens exposed in severely corroded sewer networks. Such monitoring was to gain better knowledge of the intrinsic and extrinsic bio-physico-chemical parameters governing cement material biodeterioration.

MATERIALS AND METHODS

Specimens studied

Mortars are generally used for repairs or as coatings for precast concrete or cast-iron pipes. The behaviour of this type of material can be extrapolated to that of concrete. For the various test series presented in this paper, mortar specimens were cast with OPC or CAC, for which the chemical oxide compositions are given in Table 2. For all specimens, the water to cement and siliceous sand to cement ratios were 0.37 and 1.44 respectively. After demoulding, specimens were stored at room temperature and kept in these conditions to allow natural carbonation. Porosities were similar for both materials (9.8% for OPC and 8.9% for CAC).

Cylindrical mortar specimens (6 cm diameter, 14 cm high) were prepared with a PVC tube anchor for their suspension in the sewer network. Specimens were exposed in the headspace of a sewer network after 6 months' conditioning in a controlled laboratory atmosphere (20 ± 2 °C and 40% relative humidity).

On-site exposure

Site characterization

The sewer had experienced severe deterioration of the concrete walls. The cementitious matrix was non-cohesive and exposed aggregates were clearly visible. In some areas, a significant gypsum layer had formed. In the headspace of the sewer network, a temperature and H_2S sensor (myDatasensH_2S® from Microtronics) was used to measure the previously mentioned parameters every minute. Hence it was possible to note that the annual temperature cycle had a maximum in summer (around 30 °C) and a minimum in late winter (around 8 °C). H_2S gaseous concentration values measured for 1 year were 0–250 ppmv, with an average value of 100 ppmv.

Sampling and analyses

At each sampling time (i.e. every 4 months), samples were photographed, weighed and the surface pH was measured. Three sets of samples were exposed. While one of them was left undisturbed, a second one was gently brushed at each sampling time with a nail brush and then washed in tap water before being re-weighed to estimate the proportion of degradation by-products generated. The third one was used to study microbial diversity.

Microbial diversity. Biofilm microbial diversity was studied using molecular techniques. One set of specimens was scraped with a brush impregnated with a guanidine thiocyanate solution (pH 7.5) to extract and preserve total DNA from biofilms. DNA specimens were held in the guanidine thiocyanate solution at −80 °C for transport and storage until analysis. DNA was extracted using an MP Biomedical kit, the Fast DNA® SPIN Kit for Soil as described by Ettenauer *et al.* (2012). The extracted DNA was amplified

Table 2 | Composition of the two cements (%)

	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_3	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	–	–

LOI: loss on ignition; IR: insoluble residue.

by polymerase chain reaction (PCR) and used for capillary electrophoresis single-strand conformation polymorphism (CE-SSCP) analysis. Two specific sets of primers were used to target prokaryotes and eukaryotes species. Primers w104 (6-FAM labelled) and w49 (Godon *et al.* 1997) were used for prokaryotes, while primers w131 (TET labelled) and w16 were used for eukaryotes. The amplification mix contained 1.25 units of Pfu Turbo (Stratagene, La Jolla, CA), 5 mL of 10× buffer, 200 mM dNTP, and 200 ng of each primer, with water added to make up a final volume of 50 mL. The thermal profile used for amplification was as follows: incubation at 94 °C for 2 min, then 25 cycles of denaturation at 94 °C for 30 seconds, 61 °C for 30 seconds and 72 °C for 30 seconds. This robust molecular fingerprint tool allows the study of microbial diversity present in environmental ecosystems. One μL of total extracted DNA was used per PCR-SSCP amplification. The CE-SSCP analysis was carried out with ABI 3130 (Applied Biosystems) as described by Delbes *et al.* (2000, 2001).

ATP analyses. On site, condensed water in equilibrium with mortar was collected and analysed to determine the adenosine triphosphate (ATP) content. ATP is the molecular unit of currency of intracellular energy transfer in every living entity. The higher the ATP content, the higher the activity of cells or microorganisms. Water condensation in the PVC tube anchor and in contact with mortar was recovered in order to measure ATP content with an ATPmeter type Novalum® from Charm Science using WaterGiene® swabs. These swabs, initially made for use in the food industry, are quantitative, easy to use and give repeatable results.

Aluminium ion. *In-situ* condensed water was also analysed to quantify the dissolved aluminium ions. Aluminium ion concentrations were measured by inductively coupled plasma atomic emission spectroscopy (ULTIMA 2000 from Jobin-Yvon) according to NF EN ISO 11885 standard.

RESULTS AND DISCUSSION

Table 3 gives an overview of the changes of cementitious materials of undisturbed specimens exposed on site. After 2 years' exposure, the OPC mortars were highly deteriorated. They had lost their physical integrity and deterioration products were detached, inducing a mass loss of around 14% with a surface pH of around 1.5. In contrast, CAC mortars kept their original geometry and showed a slight weight gain (≈ +1%) with a surface pH of 3.5. As specimens had been exposed in the same environment, the difference in durability was due to matrix composition and more particularly to cement type.

During exposure, some specimens were brushed to mimic the tidal zone effect. The monitoring of mass before and after brushing enabled a diagram to be plotted as a function of time (Figure 1). The masses brushed away were calculated by the mass of the degradation products removed during brushing divided by the mass before brushing. The mass losses were not uniform and it can be noted that mass loss rates were high during the autumn/winter season. These cooler seasons favour the condensation of water vapour on the specimen surface, which in general enhances biofilm development. Moreover, wetting and drying cycles accelerate the process of acidic corrosion. During wetting events, acidic solutions penetrate into the material. If dryness causes desiccation, it will result in salt crystal formation. Generally, crystals require an increase volume, causing development of a porous network within the material and thus promoting cracks (Sand 1997; Allahverdi & Škvára 2000). Colonization of cracks may be particularly harmful to cementitious materials because

Table 3 | Visual changes in OPC and CAC mortars exposed on site over 2 years

	T 0	4 months	1 year	2 years
OPC				
CAC				

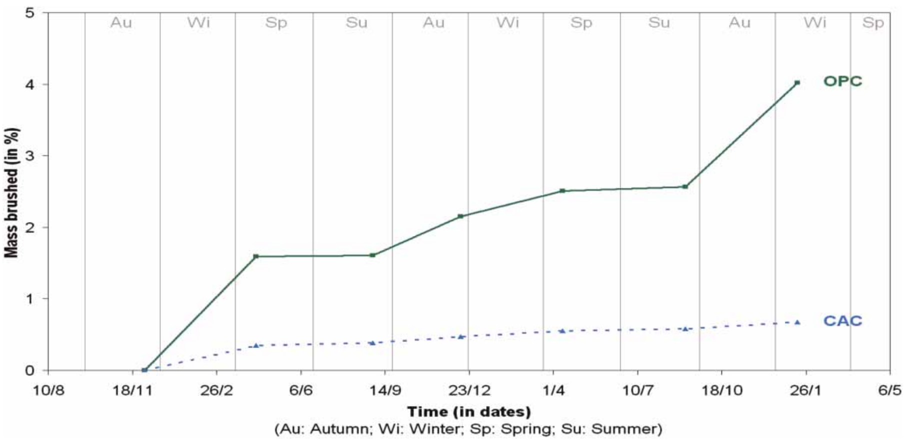

Figure 1 | Evolution of mass loss following OPC and CAC specimen brushing.

these cracks are a way for aggressive substances to spread. They also allow the penetration of microorganisms and metabolised substances in the interstices, which may lead to an increase in the material's internal pressure, thus worsening biodeterioration (Roux 2008).

Biodeterioration is caused by the metabolic activity of microorganisms that are well known in the case of OPC (Islander *et al.* 1991; Okabe *et al.* 2007). The specimens were studied for microbial diversity by CE-SSCP analyses in order to have an overview of biodiversity without identification of microorganisms involved in the process. Figure 2 shows the prokaryotic CE-SSCP spectra of the two mortars exposed for 4 months. Each peak represents a species and the peak height reflects the relative abundance of the species in the population. Prokaryotic (Figure 2) and eukaryotic (Figure 3) biodiversity appears to differ depending on the cement type and it evolves

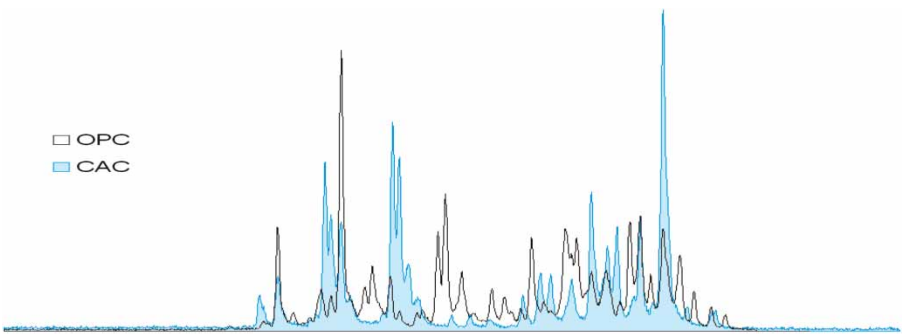

Figure 2 | SSCP diagram of bacterial DNA extracted on OPC and CAC mortars after 4 months' exposure.

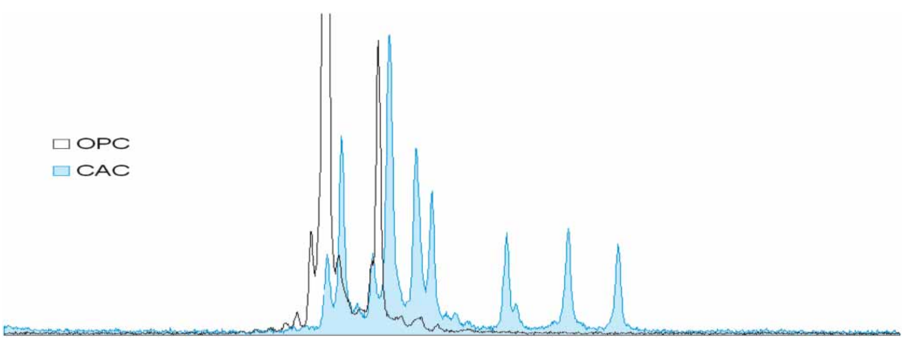

Figure 3 | SSCP diagram of eukaryote DNA extracted on OPC and CAC mortars after 8 months' exposure.

completely differently over time (data not shown). However, as only single specimens were analysed in this instance, definite conclusions regarding differences in the microbial community compositions cannot be drawn from this study.

Hence the matrices generated by the two cement types have a role in microbial selection but they also have a role in the amount of biomass that develops on the surface of materials, as shown in the DNA concentration extracted from biofilms at multiple sampling times (Table 4).

Aluminium is known to have a potential bacteriostatic effect (Illmer & Erlebach 2003). The aluminium ion dissolved in condensed water in the PVC tubes of the specimens was monitored, regardless of the compound, in order to ascertain its impact on bacterial activity. The evolution of ATP as function of total dissolved aluminium (Figure 4) shows that there is an inhibition of microorganisms at 350 mg L^{-1} of aluminium ion, also reported by Ehrich (1998) for a similar environment.

Table 4 | Total DNA content (in ng cm^{-2} of material) extracted on the material surface exposed

	T 0	4 months	9 months	1 year	1.3 years
OPC	0.8	10.3	1.3	70.6	16.9
CAC	0.5	3.5	3.1	8.1	3.8

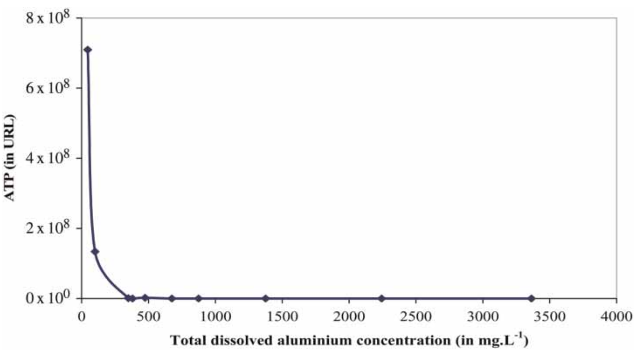

Figure 4 | ATP measurement on *in-situ* specimens condensed water of OPC and CAC as a function of total aluminium ion concentration at low pH (1–2) after a year's exposure.

The difference in durability between OPC and CAC materials is due to a difference in colonization resulting from the presence of aluminium ions at the surface of CAC materials. During biogenic acid attack, CAC hydrates react to form an alumina gel (AH_3 in cement chemist notation) which is stable between pH 9 and 3–4 (Figure 5). Below this acidic threshold, the alumina gel dissolves, releasing aluminium ions that likely have a bacteriostatic effect on some microorganisms (Figure 4; Herisson 2012). The stability of this layer over a wide pH range ensures a better acid neutralization capacity and prevents the establishment of acidophilic microorganisms like *Acidithiobacillus thiooxidans*, known to be one of the greatest acid producers responsible for deterioration (Parker 1947; Roberts *et al*. 2002). Another advantage of CAC materials is that alumina gel will precipitate in the porosity and on the surface, limiting acid penetration and hence protecting the material from the aggressive environment (Fryda *et al.* 2010). The formation of this AH_3 layer makes the surface smoother and could limit biofilm adhesion.

CAC materials may be wrongly excluded from use in sewer networks because they are not resistant in highly acidic conditions (pH 1–2). However, due to their particular properties they can perform better than OPC materials. According to Scrivener & De Belie (2013), chemical acid attack and biogenic acid attack involve two different processes because, as one can see in the case of CAC materials, the material matrix could have an influence on the growth of microorganisms and hence on acid production. Moreover, the deteriorated layer plays a different role in the two phenomena (Alexander & Fourie 2011). For chemical acid attack, this layer becomes a beneficial barrier against acid penetration, limiting exchanges. However, for

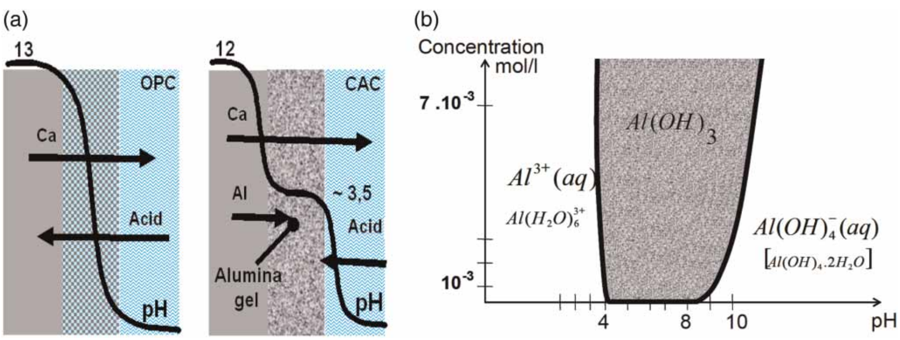

Figure 5 | (a) Schematic representation of acid attack on OPC and CAC (Fryda *et al.* 2010). (b) Stability diagram of alumina ($Al(OH)_3$) (Lamberet *et al.* 2008).

biogenic acid attack, a degraded layer composed mainly of gypsum creates excellent conditions for the growth of microorganisms. They penetrate into this soft layer and produce sulfuric acid close to the intact material. Under these conditions, the degraded layer contributes to the attack of the parent cement material.

Identification of durable materials in sewer networks needs a laboratory accelerated test that mimics the conditions of these aggressive conditions involving a range of selected microorganisms. A few groups have worked to design an accelerated test (Hormann *et al.* 1997; Vincke *et al.* 1999) but they are very different from real conditions except that of Hamburg University (Ehrich 1998) which is now out of operation. According to Scrivener & De Belie (2013), the Hamburg accelerated test is the most representative test of bacteriogenic deterioration developed to date but it used as the inoculum sludge from the Hamburg sewage system.

With the aim of standardizing this method, DNA extracted on site from biofilms at each sampling will be used to perform pyrosequencing analyses in order to identify microorganisms likely to be involved in the biodeterioration process. Using those microorganisms instead of an unknown microbial consortium sampled from a local sewer system, and growing them properly, will accelerate the biodeterioration of any materials sensitive to biogenic acid. This reproducible test will allow the ranking of material durability after about a year.

CONCLUSION

Sewer networks are prone to many causes of deterioration, including, in the presence of H_2S, the biodeterioration of cementitious materials by acid produced by microorganisms. This complex phenomenon has been studied in detail for OPC materials and mechanisms are suggested in the literature, but these mechanisms are not relevant to CAC materials.

Experiments confirm that CAC materials are more durable on account of their composition. They are based on calcium aluminate hydrates that react with acid and result in the precipitation of an alumina gel. This alumina layer creates a physical barrier to acid penetration, stabilizes pH around the alumina solubility threshold (3–4) and has a bacteriostatic effect. This study highlights that active biofilms will not readily colonize CAC material surfaces and will not evolve as biofilm does on OPC materials.

Bearing in mind the need to build and repair sewer networks subjected to biogenic deterioration, there is a need to design a representative laboratory test that mimics realistic deleterious conditions. This test must involve selected acid-producing microorganisms able to grow on cementitious materials in order to observe the interaction between the cementitious matrix and biofilm development with optimized conditions based on *in-situ* experiments. Eventually, this reproducible test will be a way to test any new materials before using them in sewer networks.

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