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Mechanisms of cementitious material deterioration in biogas digester

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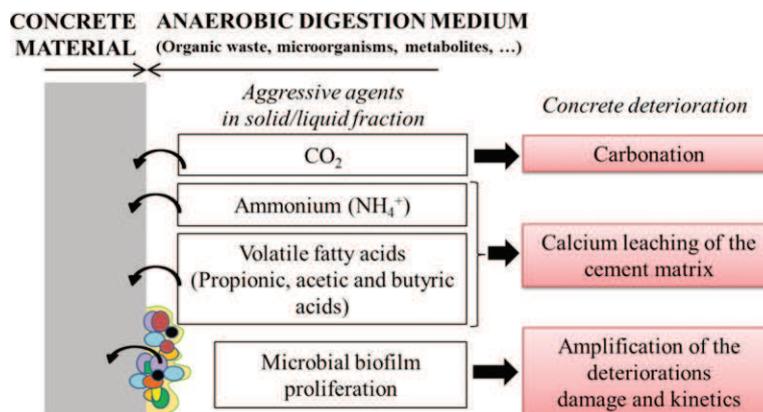
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HIGHLIGHTS

- Anaerobic digestion is a microbial waste treatment producing energy.
- Microbial activity during digestion causes deterioration of concrete digesters.
- The biodeterioration of cement paste in anaerobic digestion bioreactors is evaluated.
- Cement paste biodeterioration combines calcium leaching and carbonation in bioreactors.
- Microorganisms should be considered as aggressive for concrete in European standards.

GRAPHICAL ABSTRACT



ABSTRACT

Digesters produce biogas from organic wastes through anaerobic digestion processes. These digesters, often made of concrete, suffer severe premature deterioration caused mainly by the presence of fermentative microorganisms producing metabolites that are aggressive towards cementitious materials.

To clarify the degradation mechanisms in an anaerobic digestion medium, ordinary Portland cement paste specimens were immersed in the liquid fraction of a running, lab-scale digester for 4 weeks. The anaerobic digestion medium was a mixture of a biowaste substrate and sludge from municipal wastewater treatment plant used as a source of anaerobic bacteria.

The chemical characteristics of the anaerobic digestion liquid phase were monitored over time using a pH metre, high performance liquid chromatography (HPLC) and ion chromatography (HPIC). An initial critical period of low pH in the bioreactors was observed before the pH stabilized around 8. Acetic, propionic and butyric acids were produced during the digestion with a maximum total organic acid concentration of 50 mmol L⁻¹. The maximum ammonium content of the liquid phase was 40 mmol L⁻¹, which was about seven times the upper limit of the highly aggressive chemical environment class (XA3) as defined by the European standard for the specification of concrete design in chemically aggressive environments (EN 206).

The changes in the mineralogical, microstructural and chemical characteristics of the cement pastes exposed to the solid and liquid phase of the digesters were analysed at the end of the immersion period by X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDS) and electron-probe micro-analysis (EPMA). A 700-µm thick altered layer was identified in the cement paste specimens.

Keywords:

Biodeterioration
Anaerobic digestion
Cementitious materials
Organic acids
Ammonium
Biofilms

The main biodeterioration patterns in the bioreactors' solid/liquid phase were calcium leaching and carbonation of the cement matrix.

1. Introduction

Microbial production of sustainable energy, such as biogas, is possible through the natural biodegradation of organic matter in anaerobic conditions, also called anaerobic digestion (Frank and Smith, 1988). The anaerobic digestion process consists of four consecutive degradation reactions called hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The methanogenesis step is responsible for the production of biogas, mainly composed of 65% methane (CH_4) and 35% carbon dioxide (CO_2), and of co-products such as digestate, which is used as agricultural fertilizer (Evans and Furlong, 2003).

Biogas is a cheap and locally available renewable energy resource. Therefore, the industrial development of the anaerobic digestion process has become worldwide, permitting the valorization of many sources of organic wastes.

In a biogas plant, biogas production is carried out in anaerobic digesters for the conversion of large volumes of organic wastes (Fig. 1). The converted biogas is used either directly for heating the digester or for local distribution, e.g. gas and electricity in a nearby city.

The construction material commonly used for the digester structures is concrete. Concrete is economically competitive and shows high performance in terms of water- and air-tightness, and thermal inertia.

Structural concrete in digesters is exposed to digesting organic waste, the solid/liquid phase (in the submerged part of the structure), and to the resulting biogas, the gas phase (mainly in the emerged part) (Fig. 1). Many chemical and biological agents in the gas and in the solid/liquid phases of the digester may lead to irreversible damage on cementitious materials, which consequently threaten the durability of the concrete structures. The main consequences of the deteriorations of structural concrete are financial and environmental. On the one hand, the income from biogas production is reduced because of (i) the lowered production yield caused by the biogas leakage and (ii) the structural repairs, which require production to be stopped. On the other hand, the leakage of polluting effluents into the nearby environment becomes possible through sealing defects.

One recent study reports observations of deterioration patterns of concrete that are probably due to the microbial deterioration processes in a biogas digester fed with silage as the biowaste (Koenig and Dehn, 2016). The authors conclude that concrete deteriorations were caused by biogenic sulfuric acid attack in the gas phase and erosion of the concrete skin, slight leaching and carbonation in the solid-liquid fermenting waste. The altered layer of concrete samples in the solid-/liquid phase after one year and a half of exposure was around 1 mm thick, independently of the concrete mixes used for the samples, which were designed according to European standard EN 206 (Koenig and Dehn, 2016).

However, the solid/liquid phase in a biogas digester contains several aggressive agents: (i) a mix of volatile fatty acids (VFA) (Breure and Van

Andel, 1984; Lata et al., 2002, Koenig and Dehn, 2016), and ammonium (Karakashev et al., 2005; Yenigün and Demirel, 2013), which can be responsible for concrete leaching (Bertron et al., 2005; Escadeillas, 2013), and (ii) CO_2 (Cohen et al., 1979) which can lead to concrete carbonation (Magniont et al., 2011) (Fig. 2). These chemical compounds are produced in large quantities by cooperating microbial communities involved in the anaerobic digestion process (Fernández et al., 2008). They are able to structure their biofilms "intelligently", i.e. to self-organize into biofilms that optimize the exchange of substances (metabolites, ions, etc.) and to create an environment in which local physicochemical conditions are favourable to microbial cooperation. The biofilm organization contributes to a more efficient degradation of organic substrates and to a higher biogas yield (Ahring, 2003; Langer et al., 2014). But biofilm formation on cement paste intensifies the deterioration kinetics and phenomena (Magniont et al., 2011) (Fig. 2).

Table 1 illustrates the diversity of maximal concentrations of volatile fatty acids during anaerobic digestion of various substrates as reported in the literature. The concentrations of organic acid during anaerobic digestion vary considerably according to the substrates fermented (Table 1).

The ammonium concentration in anaerobic digesters can reach 55 mmol L^{-1} (1000 mg L^{-1}) (McCarty, 1964). McCarty highlighted that the concentrations of ammonium should not exceed 1500 mg L^{-1} otherwise the anaerobic digestion is inhibited. However, other authors have measured concentrations of a few grams per litre (Karakashev et al., 2005; Yenigün and Demirel, 2013).

Finally, dissolved CO_2 , mainly in the form of bicarbonate, is present in the fermented biowaste and is monitored to control operating industrial digesters (Cohen et al., 1979; Jenkins et al., 1991). Considering all the studies on concrete aggressive agents in anaerobic digestion, the anaerobic digestion liquid phase appears to lead to highly variable environments that are harmful for cementitious materials.

Environments aggressive towards concrete are classified in the European standard EN 206. Chemically aggressive aqueous media are classified in three classes of increasing aggressiveness: XA1, XA2 and XA3, according to the aggressive agents identified in the media and their concentrations. As far as biowastes are concerned, the standards notably consider the following criteria in the classification of chemically aggressive media: the pH, the aggressive carbon dioxide concentration (aggressive CO_2) and the ammonium ion concentration (NH_4^+).

The present study aimed to (i) identify the chemical composition of the liquid fraction of the waste according to time during the anaerobic digestion process (in terms of pH, and concentrations of volatile fatty acids and ammonium), (ii) evaluate the capability of the microorganisms in the biowaste to colonize the cementitious material in the form of a biofilm, and (iii) characterize the mechanisms of biodeterioration of cementitious materials in contact with the solid/liquid phase of an anaerobic digester. Ordinary Portland cement paste samples were immersed in biowaste in anaerobic batch conditions for 4 weeks, which is the time required to achieve complete digestion of a biowaste. The concentrations of organic acids and ammonium, and the pH in the liquid phase were monitored over time during the experiment. The concentration of CO_2 in the liquid phase was measured occasionally. The biofilm on the specimen surface was observed by Field Emission Gun Scanning Electron Microscope (FEGSEM). The chemical, mineralogical and microstructural changes of the cement pastes after immersion in the solid/liquid phase were explored by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectrometry (EDS), X-ray Diffraction (XRD) and Electron Probe Micro-Analysis (EPMA).

Caption:

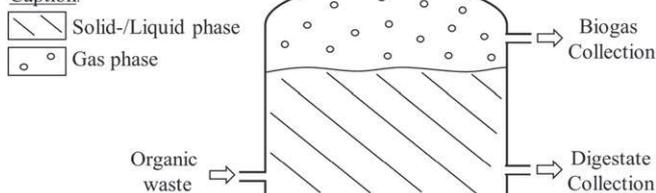


Fig. 1. Anaerobic digester scheme.

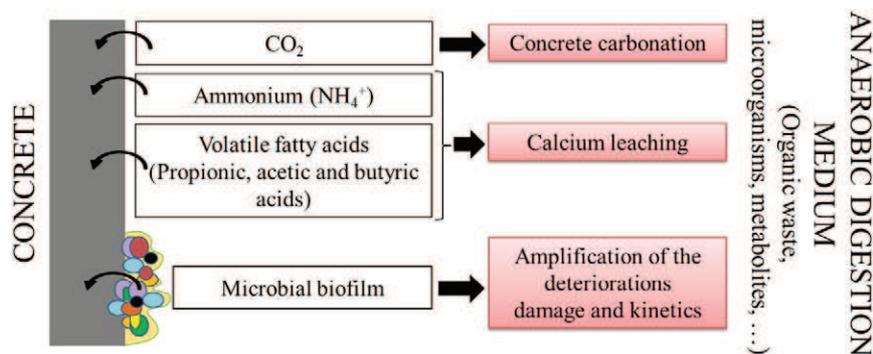


Fig. 2. Scheme of the bio induced deterioration of concrete in the solid/liquid phase of an anaerobic digester.

2. Materials and methods

2.1. Cementitious materials

Samples of ordinary cement pastes (CEM I 52.5 R CE CP2 NF; Lafarge, factory of Le Teil, France) were made with a water/cement ratio of 0.40. Cylindrical moulds (height 75 mm, diameter 25 mm) were used to cast the specimens. After the pastes had been removed from their moulds (24 h after pouring), the curing period of the specimens was 28 days in water at 20 °C.

2.2. Preparation of synthetic biowaste

The composition of a synthetic biowaste representative of the proportions of organic domestic waste was provided by IRSTEA of Antony (France). The composition is given in Table 2.

The biowaste was homogenized by blending for 10 min at 20 °C. It was then inoculated in order to initiate the anaerobic digestion process (Neves et al., 2004). Here, the inoculum was a sludge sampled from a municipal wastewater treatment plant in Toulouse (France). The organic loads, expressed as chemical oxygen demands (COD), were 50 g L⁻¹ for the substrate (biowaste) and 20 g L⁻¹ for the inoculum (sludge). Proper establishment of the anaerobic digestion process depends on the inoculum/substrate (biowaste) quantity ratio (Elbeshbishy et al., 2012). The inoculation was operated with an optimal ratio of 1 g COD(inoculum)/g COD(biowaste) as already reported in a previous work (Voegel et al., 2015). Therefore, biowaste was diluted in inoculum to reach this ratio. The immersion was operated in anaerobic bioreactors (usable volume: 500 mL) at 37 °C (Lettinga, 1995; Khanal, 2008) in a thermostatically controlled incubator during the complete biowaste digestion (Fig. 3).

2.3. Immersion of cement pastes in the digesting organic waste

The tests of cement paste specimen immersion were performed in triplicate, conducted in three replicate anaerobic bioreactors containing the inoculated biowaste, for 4 weeks at 37 °C (Fig. 3). Directly after the inoculation of the biowaste, the cement paste specimens were

immersed in the bioreactors. The solid/liquid ratio (cement paste surface area/inoculated biowaste volume) used for each bioreactor was approximately 224 cm² L⁻¹ (industrial scale digesters provide a lower ratio, of about 4 cm² L⁻¹). Three reference bioreactors were also run in digestion without cement paste specimens. The pH in the bioreactors was monitored by a pH data acquisition system (WTW, Multi 3430) throughout digestion (Voegel et al., 2015).

2.4. Analysis of organic acids, ammonium and dissolved carbon dioxide in the liquid phase of the digesting biowaste

The analysis of the liquid phase required regular samplings of 1.5 mL of biowaste in digestion from the bioreactors, using sterile needles and syringes. The nature and concentrations of the organic acids were determined in the liquid phase of the biowaste samples by High Performance Liquid Chromatography analysis (Thermo Fisher U3000; column: Aminex HPX-87H BIORAD; eluant: H₂SO₄; flow rate: 0.6 mL min⁻¹) (Voegel et al., 2015). The concentrations of ammonium in the liquid phase of the fermented biowaste samples were analysed by Ionic Chromatography (Thermo Electron ICS 3000, column: CS16; pre-column; cartridge holder; eluant: 30 mM methanesulfonic acid, flow rate: 1.0 mL min⁻¹). Moreover, some occasional analyses of total inorganic carbon were performed with an analyser of total carbon and total inorganic carbon (TOC-SHIMADZU Combustion) in order to determine the soluble CO₂ produced by the microbial activity.

2.5. Observation of microbial biofilms on cementitious materials

The surface of the cement paste specimens was observed with a scanning electron microscope at the end of the 4 weeks of immersion to observe any biofilm that had developed. Cement paste specimens were first sawn carefully to avoid any damage to the surface. The cement pastes were then treated for biofilm fixation and dehydration (Voegel et al., 2015). Firstly, the biofilms were fixed on the samples for 20 min in aldehyde fixator solution made of glutaraldehyde (4%), phosphate buffer (pH 7.4, 0.4 M) and distilled water. Secondly, the specimens were cleaned twice for 15 min in a solution made of phosphate buffer (pH 7.4, 0.4 M), sucrose solution (0.4 M) and distilled water.

Table 1
Maximum volatile fatty acid concentrations in mmol L⁻¹ (mg L⁻¹) during anaerobic digestion of several substrates (nm: not mentioned) (Breure and Van Andel, 1984; Cohen et al., 1979; Hill and Holmberg, 1988; Lata et al., 2002; Wang et al., 2009).

Authors (year of publication)	Substrate	Acetic acid	Propionic acid	Butyric acid
Cohen et al. (1979)	1% Glucose	17.55 (1054)	95 (1.28)	5673 (64.39)
Breure and Van Andel (1984)	Gelatin	4.54 (20,743)	4.83 (358)	1.12 (99)
Hill and Holmberg (1988)	Manure	16.49 (990)	26.38 (1954)	5.86 (516)
Lata et al. (2002)	Vegetables	66.61 (4000)	20.25 (1500)	39.72 (3500)
	Tea	66.61 (4000)	6.75 (500)	nm
Wang et al. (2009)	Mix ethanol + acetic/propionic/butyric acids	68.69 (4125)	38.55 (2856)	39.22 (3456)
		26.64 (1600)	4.05 (300)	20.43 (1800)

Table 2

Composition of the biowaste in percentages by mass of organic substitution fractions from organic domestic waste in (IRSTEA of Antony, France).

Organic substitution fractions	Composition by mass (%)
Potatoes	8.1
Tomatoes	3.4
Minced meat	8.1
Milk powder	0.7
Crackers	4.1
Water	75.6

Finally, the samples were progressively dehydrated by successive immersion in solutions made of acetone and water and then hexamethyldisilazane (HMDS) until total evaporation. The specimens were coated with a thin layer of gold before SEM observations (Field Emission Gun, JEOL 7100F TTLS).

2.6. Analysis of chemical and mineralogical changes in cementitious materials

The cylindrical cement paste specimens were sliced perpendicularly to their longitudinal axis with a thin diamond saw. The slices of cement paste, which were a few millimetres thick, were embedded in an epoxy resin (Mecaprex MA2 by Presi) and dry-polished using silicon carbide polishing disks (Presi) according to the procedure described in Bertron et al. (2009). After carbon coating of the polished sections, chemical analyses were performed with an Electron Microprobe (Cameca SXFive, 15 kV, 20 nA, scanning area of the beam: $2 \times 2 \mu\text{m}^2$) on one hundred points on the flat, polished sections, from the surface in contact with the liquid phase of biowaste in digestion to the centre of the specimen. The points analysed were carefully chosen to measure only the hydrated paste and avoid residual anhydrous grains. The following elements were analysed: Ca, Si, Al, Fe, S, P and Ti for each point. The counting time was 10 s on peak and 5 s on the background on each side for all elements but titanium. For titanium (minor element used for the correction method) the counting time was 30 s on peak and 10 s on the background on each side (Bertron et al. 2009). Calibration was performed on natural and synthetic standard materials before each series of analyses. Elemental mass percentages were expressed as mass percentages of the associated oxides. For cementitious materials, the sum of oxides is normally around 75% (Bertron et al. 2009). The complement to 100 covers non-analysed elements, such as H, C, and elements in small quantities that were not included in the analysis program. It should be noted that most of the complement to 100 could be attributed to bound water in hydrated calcium silicate hydrates (C-S-H), portlandite (CH), ettringite (AFt), etc. In the case of chemical attack, such as leaching, the loss of less stable and more mobile elements (Ca,

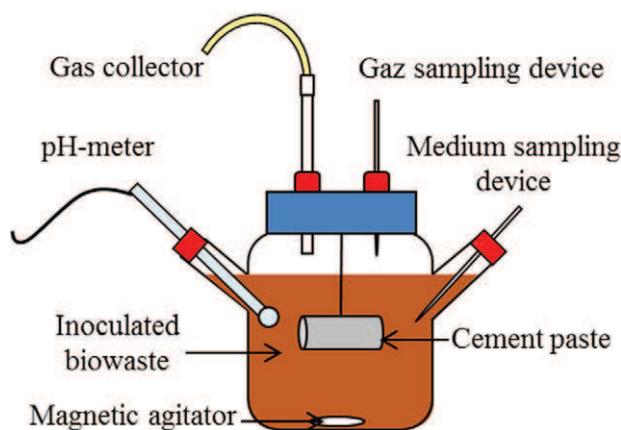


Fig. 3. Schematic representation of the anaerobic bioreactors placed on a magnetic plate for mixing purposes and kept in an oven regulated at 37 °C.

Na and K for example) leads to an increase in the proportion of more stable elements (Si, Al, Fe, etc.) since microprobe analysis gives the relative contents of the elements in the probed volume. To obtain the absolute evolution of the element concentrations, the microprobe data was processed according to a method detailed by Bertron et al. (2009). The TiO_2 content was used to calculate correction factors since it has been shown that titanium present in the form of rutile titanium oxide is very stable over the pH interval between 3 and 9.5 (Knauss et al., 2001).

The changes in mineralogical composition in the depth of the specimens were characterized by X-Ray Diffraction (Siemens D5000, Co cathode, 40 kV, 30 nA). The preparation of the specimens is described in Bertron et al. (2005). The plane sides of the cylinders were analysed. The plane face of the specimen directly exposed to the biowaste in digestion was first analysed. Then it was abraded and submitted to the next analysis. A control specimen was also analysed at the end of the curing period (four weeks).

3. Results

3.1. Production of organic acids, ammonium, dissolved carbon dioxide (carbonates) and evolution of the pH during the anaerobic digestion of biowastes

Fig. 4 gives the evolution of the pH and the mean values of organic acid concentrations in the liquid fraction contained in the bioreactors with or without the cement paste specimens (Fig. 4). In Fig. 4 (a), the first days of decreasing pH from 6 to 4 corresponded to a significant

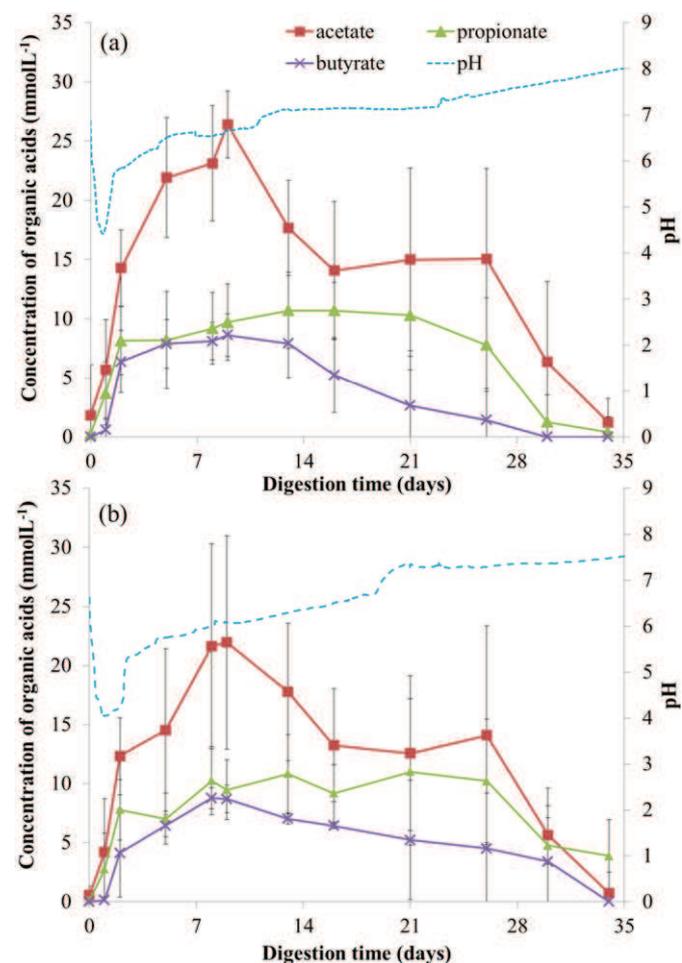
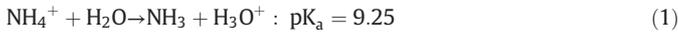


Fig. 4. Evolution of the pH and the concentrations of organic acids during anaerobic digestion of biowaste in presence (a) and in absence (b) of cement paste specimens.

production of acetic, propionic and butyric acids, which are typical volatile fatty acids metabolized by microorganisms in anaerobic digestion (Jeris and McCarty, 1965). The total maximum concentration of organic acids reached about 50 mmol L⁻¹ on day 9. After this first acidification stage, the pH slowly rose to 7–8 and reached the pH conditions of methanogenesis. After 9 days of digestion, the concentrations of acids decreased, except for propionate, which started depleting after 15 days. The complete digestion of the substrate was marked by the entire consumption of all the volatile fatty acids at the end of the experiment. The bioreactors without cement paste samples followed the same evolution as the bioreactors with the samples but with slightly lower organic acid concentrations.

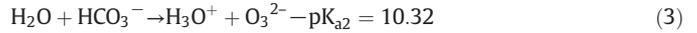
Fig. 5 shows the evolution of the ammonium concentration in the fermented biowaste in presence and in absence of cement paste samples in the bioreactors. The ammonium production increased quickly from 1 mmol L⁻¹ (10 mg L⁻¹) to nearly 20 mmol L⁻¹ (500 mg L⁻¹) in two weeks with and without the cement paste samples in the bioreactors. After four weeks of digestion, the ammonium content reached nearly 40 mmol L⁻¹ (800 mg L⁻¹). According to Eq. (1), ammonium should be mainly in the form of ammonium ion in the pH conditions (7.0–8.0), which were significantly lower than the pKa of the acid and conjugate base NH₄⁺/NH₃, of 9.25.



The ranges of ammonium concentration of the exposure classes (marked XA1, XA2 and XA3) for chemical attacks on concrete as defined by the European standard (EN 206) are reported in Fig. 5. The ranges are 0.83–1.66 mmol L⁻¹ (15–30 mg L⁻¹) for XA1, 1.66–3.33 mmol L⁻¹ (30–60 mg L⁻¹) for XA2 and 3.33–5.55 mmol L⁻¹ (60–100 mg L⁻¹) for XA3.

The concentrations of dissolved CO₂ were measured through analysis of total inorganic carbon content in the fermenting medium at 3 weeks of experiment. At this time, the pH of the biowaste was 7.7. The mean value of total inorganic carbon in the medium was 146 ± 46 mg L⁻¹ (5 samplings). In the pH condition, the major form of dissolved CO₂ was bicarbonate ion HCO₃⁻ (95% by mass), according to the predominance curve of dissolved carbonates (Eqs. (2) and (3)). Calculations gave the mean amount of HCO₃⁻ as 2.3 mmol L⁻¹ ± 0.2 mg L⁻¹ (or 139 ± 16 mg L⁻¹) in the fermented media. The other form present at pH 7.7 was carbonic acid H₂CO₃ (5% by mass) with a mean content of

$$0.1 \pm 0.02 \text{ mmol L}^{-1} (7 \pm 1.7 \text{ mg L}^{-1}).$$



3.2. Microbial biofilm formation on the surface of the cementitious material

The cement paste surfaces after 4 weeks of immersion in the bioreactors are shown in Fig. 6. The surface of the cementitious material was entirely covered by biofilm (Fig. 6 (a)). The measurements performed during the observation session suggested a total biofilm thickness of about 100 μm. The biofilm contained microorganisms with spherical (Fig. 6 (d)) and elongated shapes, called coccus and rod (bacillus) morphologies.

3.3. Deterioration of cement paste immersed in the solid/liquid phase of a biowaste in anaerobic digestion

The chemical composition profiles, analysed by EPMA, of the specimen as a function of the distance to the surface exposed to the solid/liquid phase of the biowaste in digestion, is shown on Fig. 7. The observation of the same specimen by SEM in back-scattered electron (BSE) mode is also presented under the graph. A chemical zonation of the specimen was identified and is represented on Fig. 7 (zones 1 to 5). The average chemical composition of the cementitious matrix in the different zones is given in Table 3. Fig. 9 gives the mineralogical characterization by XRD of the different zones of the cement pastes, as defined on Fig. 7, after 4 weeks of exposure to the biowaste.

The chemical and mineralogical zonation from the core to the external layer of the specimen was as follows:

Zone 1, or the sound zone, had a chemical and a mineralogical composition identical to that of an unaltered control specimen. The typical peaks of hydrated phases, such as portlandite and ettringite, and of anhydrous grains, such as tricalcium silicate or alite (3CaO·SiO₂), dicalcium silicate or belite (2CaO·SiO₂) and brownmillerite (4CaO·Al₂O₃·Fe₂O₃), were present (Fig. 9). Furthermore, the density of anhydrous residual cement grains was high (white grains on the SEM picture) (Fig. 7).

Zone 2 showed a slight decalcification and an enrichment in sulphur (Fig. 7), which may be correlated with the dissolution of portlandite and the intensification of the ettringite peaks compared to zone 1 (Fig. 9). The density of residual anhydrous grains was lower than in zone 1. This zone was 500-μm thick (Fig. 7).

Zone 3 was slightly decalcified (Fig. 7). Calcite was the main crystallized phase. Ettringite was dissolved. Alite and belite peaks had disappeared, which was in accordance with SEM observations showing a very low amount of residual anhydrous grains in this zone (Figs. 7 and 8). This zone was 100 μm thick.

Zone 4 was just a few tens of μm thick and showed phosphorus enrichment (Fig. 8). Phosphorus was most probably brought by the biowaste. SEM observations coupled to EDS analyses showed some precipitates mainly composed of P, Ca and Si at different places in this thin layer (Fig. 8). The proportions of Ca, P and Si of these precipitates (Table 3) were typical of apatite minerals (Elliott et al., 2002), which may be confirmed by the small peaks resembling those of hydroxyapatite observed on Fig. 9. Finally, the average CaO/SiO₂ ratio in this zone (about 1.95, Table 3) suggested that the calcium silicate hydrates (C-S-H) had been dissolved.

Zone 5 was the outer layer (50-μm thick) previously covered by the biofilm. This zone was less dense than the other zones (dark zone on the SEM picture of Fig. 7) and mainly amorphous (Fig. 9). This zone was almost completely decalcified and enriched in aluminium and silica compared to the zones closer the specimen core. Also, the phosphorus content in this zone, although lower than in zone 4, remained high.

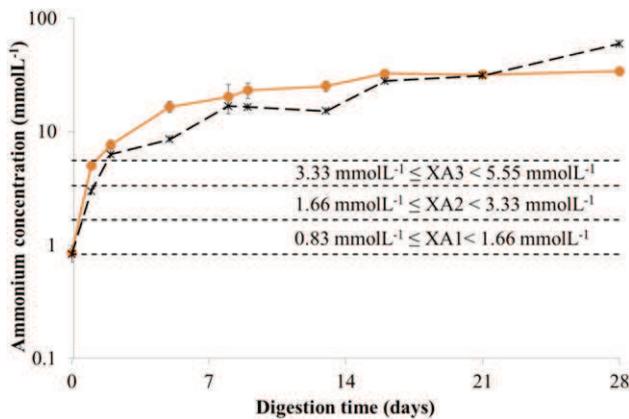


Fig. 5. Evolution of the concentration of ammonium during the anaerobic digestion of biowaste in presence (continuous line) and in absence (dotted line) of cement paste samples in the bioreactors. Limit values of the exposure classes (15 mg L⁻¹ ≤ XA1 < 30 mg L⁻¹, 30 mg L⁻¹ ≤ XA2 < 60 mg L⁻¹ and 60 mg L⁻¹ ≤ XA3) for chemical attacks in aqueous environments in the standards (European standard EN NF 2061 and French documentation file FD P18-011) are reported for comparison.

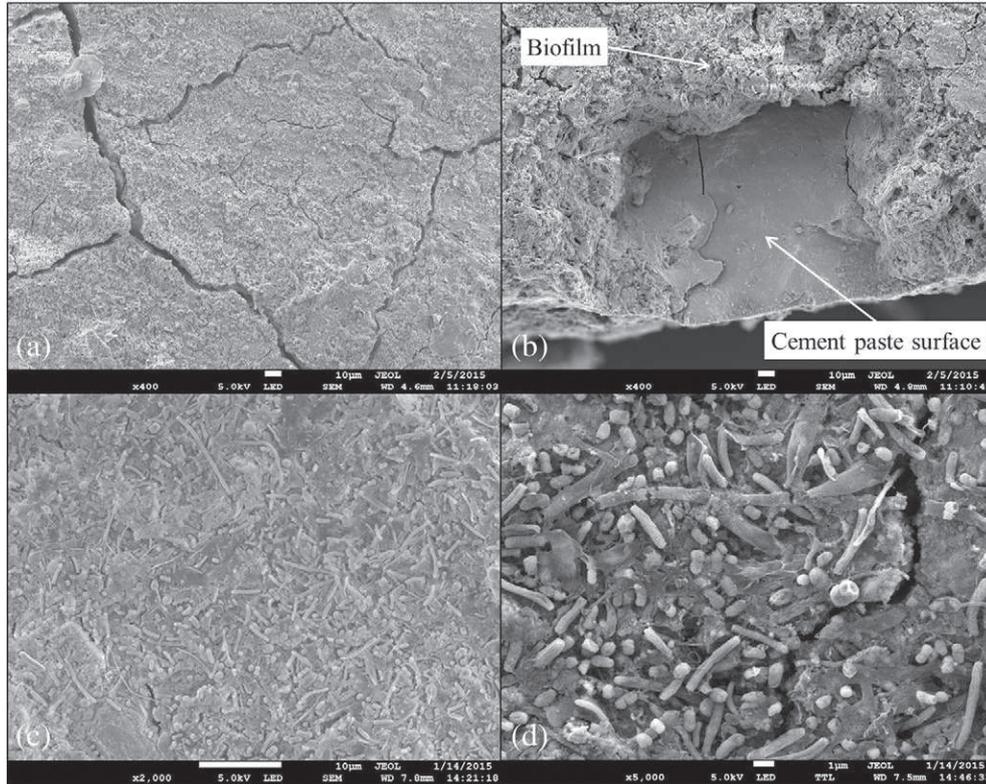


Fig. 6. SEM observations of ordinary cement paste surface colonized with a microbial biofilm after 4 weeks of exposure to biowaste under anaerobic digestion process. ((a) global biofilm surface, (b) view of the cement paste under the biofilm thanks to a little nick made on the biofilm, (c,d) focus on biofilm details.)

4. Discussion

Ordinary cement paste specimens were exposed to the solid/liquid phase of a biowaste during a complete anaerobic digestion process. This work aimed to quantify the concentrations of aggressive agents

against concrete in the liquid phase of fermenting biowaste, to identify the capability of the microorganisms in the biowaste to colonize the cementitious material in the form of a biofilm, and to determine the mechanisms of cementitious material biodeterioration in the solid/liquid phase of an anaerobic digester.

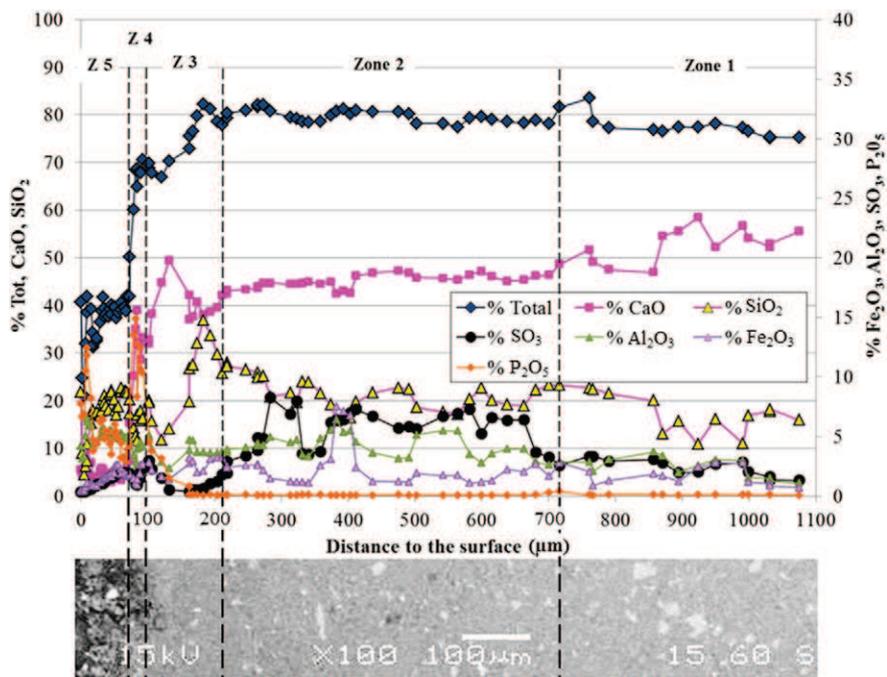


Fig. 7. Chemical composition profile of an ordinary Portland cement paste immersed in the solid/liquid phase of a biowaste in anaerobic digestion conditions for 4 weeks according to the distance to the surface in contact with the medium (EPMA), and SEM observations of the polished section in back-scattered electron (BSE) mode.

Table 3
Average chemical composition and standard deviations in mass percentages in the different zones defined in Fig. 7.

Oxides	Average chemical composition by mass (%)		
	Zone 3	Zone 4	Zone 5
% CaO	39.22 ± 4.78	29.97 ± 6.75	5.09 ± 1.75
% Al ₂ O ₃	3.92 ± 0.84	3.75 ± 0.62	5.02 ± 0.68
% SiO ₂	24.01 ± 8.24	15.37 ± 2.12	17.70 ± 4.82
% P ₂ O ₅	1.57 ± 1.87	11.47 ± 2.15	5.66 ± 2.28
% SO ₃	1.24 ± 0.98	1.55 ± 0.52	1.22 ± 0.57
% Tot	74.22 ± 5.48	64.84 ± 6.31	37.02 ± 4.74

4.1. Composition of the liquid fraction of the fermenting biowaste and potential aggressiveness for cementitious material

The growth of microorganisms in anaerobic digestion requires different pH ranges, e.g., a pH range of 4.0–8.5 is needed for the fermentative microorganisms producing organic substrates (e.g., fatty acids and glucose). In particular, a more restricted pH range of 6.5–7.2 stimulates the growth of methanogens (Zhang et al., 2014).

The evolution of organic acids, in terms of nature and concentrations, and pH during the whole digestion is represented on Fig. 4, the duration of which (4 weeks) matched a whole cycle of anaerobic digestion. The pH evolution suggested that anaerobic digestion was properly established. The presence of cement paste specimens in bioreactors did not affect the anaerobic digestion process. pH, organic acid and ammonia concentrations changed in a similar way with or without the addition of cement paste (Figs. 4 and 5).

Anaerobic digestion showed an initial pH drop (<2 days) from 6 to 4–5 before a slow pH increase, reaching the pH values corresponding to methanogenesis conditions in 4 weeks (Fig. 4). The maximal total concentration of volatile fatty acids, including acetic, propionic and butyric acids, was about 50 mmol L⁻¹ in the biowaste under digestion. In terms of ammonium content, the total ammonium production had reached nearly 1000 mg L⁻¹ after 4 weeks. Besides being present in the initial biowaste before the digestion, ammonia (NH₃) and ammonium (NH₄⁺) accumulated during the breakdown of proteins and were the foremost inhibitors of the anaerobic digestion process. The range of concentrations (up to 40 mmol L⁻¹) measured in the fermenting biowaste was in accordance with the data available in the literature and below critical thresholds (80 mmol L⁻¹) that can cause inhibition of the biogas production process (McCarty, 1964). CO₂ was co-produced during the

anaerobic digestion of the biowaste. Occasional analyses made on dissolved CO₂ content in the fermenting mix showed an HCO₃⁻ concentration of 2.3 mmol L⁻¹ (or 140 mg L⁻¹) (pH of 7.7 at the sampling time). The concentration of CO₂ in the bioreactor was thus much lower than the concentrations that may be reached in industrial anaerobic digestion media, i.e. 2000–3000 mg L⁻¹ (McCarty, 1964) corresponding to the saturation level (the solubility of CO₂ in water at 25 °C and 1 atm is 34 mmol L⁻¹ or 0.77 mg L⁻¹).

Based solely on pH data collected during the anaerobic digestion of biowaste, despite a short initial period with a pH below 7.0, anaerobic digestion media in normal operation should not be classified as aggressive environments for cement based materials, considering their stable pH of 7.0–8.0 (>6.5 which is the upper limit of the XA1 exposure class according to NFD 18–011). Nevertheless, when considering the ammonium and the CO₂ concentrations collected during anaerobic digestion of biowaste, the anaerobic digestion media in normal operation have to be considered as highly aggressive for cement based materials (XA3 exposure class according to EN 206 and NF D 18–011). For example, the concentration of ammonium, from two days after the start of the experiment ([NH₄⁺] = 9 mmol L⁻¹) to the end ([NH₄⁺] = 40 mmol L⁻¹), was significantly higher than the concentration range of class XA3 (3.33–5.55 mmol L⁻¹).

The concentrations of ammonium measured (up to 40 mmol L⁻¹) in this study were about seven times the upper limit (5.55 mmol L⁻¹) of the XA3 exposure class and still lower than the anaerobic digestion inhibition concentration (around 80 mmol L⁻¹) given by McCarty (1964). It may be noted that the French documentation file FD P18–011 recommends an external or internal protection in cases when the concentration of an aggressive agent exceeds the upper limit of the XA3 classification in the media.

It should additionally be noted that these standards do not consider the nature of the acids, notably the organic acids, their concentration, nor the specific impact of the microorganisms, individually or in the form of a biofilm, in the classification of aggressive media. Yet, several studies have highlighted the significant role of these two parameters in the deterioration of the cementitious matrix in various biological media (Nica et al., 2000; Leemann et al., 2010a; Larreur-Cayol et al., 2011; Magniont et al., 2011; Bertron and Duchesne, 2013; Bertron, 2014).

4.2. Biofilm proliferation at the surface of the cementitious materials

The phenomena of biodeterioration are often exacerbated when a surface layer of microorganisms, called biofilm, grows on the surface of the altered material. The aggressive products secreted by microorganisms are concentrated in the close vicinity of the material surface and result in accelerated damage (Nuhoglu et al., 2011; Magniont et al., 2011).

After only 4 weeks of exposure in the solid/liquid phase of the fermenting biowaste, a rich biofilm, a hundred microns thick, was already observed by scanning electron microscopy on the cement paste surface of the cementitious material exposed to the fermenting biowaste. It should be mentioned that the optimal pH conditions for microorganisms involved in anaerobic digestion to live are 4.5–6.3 for hydrolytic bacteria and acidogens, 6.8–7.5 for acetogens and 6.2–7.6 for methanogens (McCarty, 1964; Prescott et al., 1996; Evans and Furlong, 2003). However, cementitious materials have initial pH around 12–13. The surface colonization was probably made possible because of the production of metabolites (organic acids, CO₂ and ammonium) by the planktonic microorganisms in the first hours of the digestion process, which caused initial deterioration of the material (calcium leaching and carbonation, as analysed with EPMA, SEM + EDS and XRD) and probably decreased the surface pH to suitable conditions for microbial colonization (Magniont et al., 2011). This surface conditioning is a key step enhancing the bioreceptivity of the cementitious material (Guillite, 1995; Manso et al., 2014).

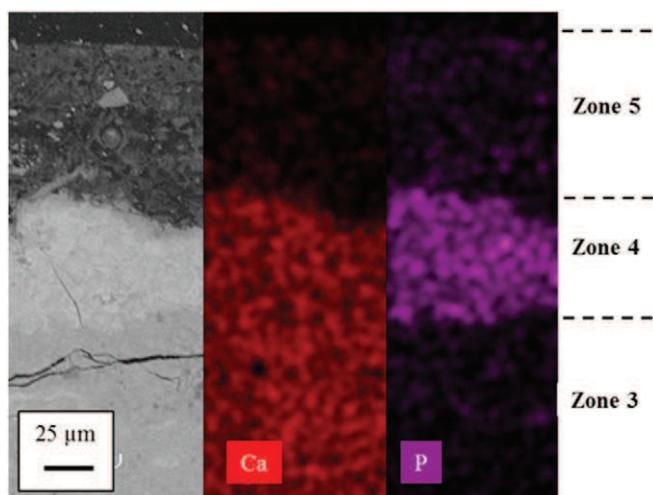


Fig. 8. SEM observation in BSE mode and chemical mapping of calcium (Ca) and phosphorus (P) EDS in the outer zones (zones 3 to 5 as defined in Fig. 6) of an ordinary cement paste immersed in solid/liquid phase of biowaste in anaerobic digestion conditions for 4 weeks.

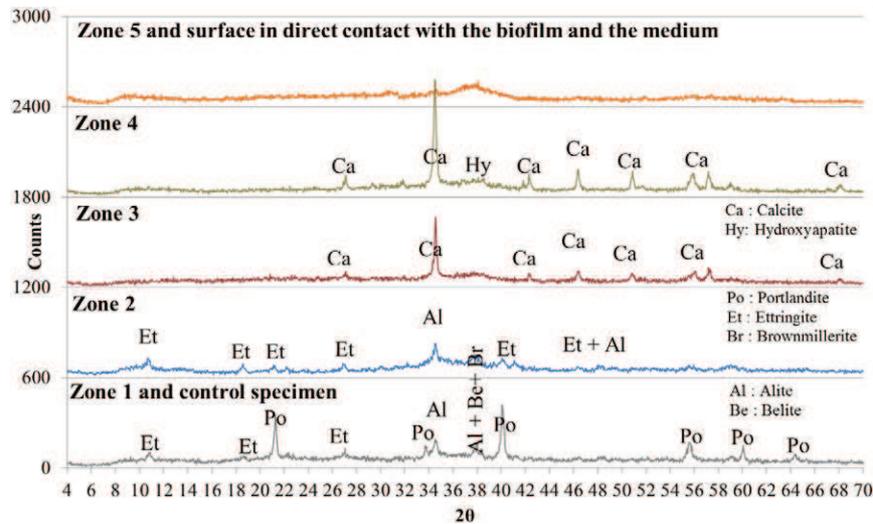


Fig. 9. Mineralogical analyses by XRD of ordinary cement paste immersed in the solid/liquid phase of biowaste in anaerobic digestion conditions for 4 weeks.

SEM observations showed a complex mixture of microorganisms with rods and cocci morphologies in the biofilm on cementitious materials. Zellner et al. observed the same morphologies in biofilm in anaerobic digester reactors (Zellner et al., 1996).

The presence of a biofilm suggests greater local microbial activity on the surface of cementitious material than in the medium (i.e. heterogeneous catalytic phenomenon). For that reason, the consequences on the distribution and the concentration of soluble chemical species have to be considered. Thus, concentrations of metabolites obtained in the biowaste during anaerobic digestion are certainly lower than those actually produced locally on the surface of cement pastes.

4.3. Chemical alteration mechanisms on cementitious materials exposed to the solid/liquid phase of fermenting biowaste in the anaerobic digester

A chemical and mineralogical zonation of cementitious specimens exposed to the solid/liquid phase of biowaste in digestion was highlighted. Five zones with different chemical and mineralogical compositions were identified, with zone 1 corresponding to the non-altered core of the specimen and zone 5 being the outer layer in contact with the biowaste. After four weeks of immersion, the total thickness of the altered layers (zones 2 to 5) was 700 μm . Organic acids, CO_2 and ammonium are the agents aggressive to concrete that were identified in this work. The metabolites reacting with the calcium-bearing components of the cement matrix were responsible for calcium leaching and carbonation phenomena in the cement matrix. It should be noted that the presence of microorganisms on the surface may have led to specific conditions of concentrations of aggressive agents and of pH (namely high acid, CO_2 and ammonium concentrations and low pH) locally (Magniont et al., 2011). Phosphorus enrichment of the cement matrix was also detected.

4.3.1. Calcium leaching phenomena

Calcium leaching of the cementitious matrix was observed, probably due to the attack of organic acids (Koenig and Dehn, 2016) and ammonium in the biowaste.

A cement matrix in a medium containing organic acids undergoes acid-base reactions occurring between the acids and the highly alkaline cement phases. In the case of ordinary cement paste, these reactions lead to the formation of calcium salts or complexes and water (Bertron and Duchesne, 2013; De Windt et al., 2015). The volatile fatty acids in anaerobic digestion (acetic, propionic and butyric acids) have very soluble calcium salts (Bertron et al., 2007; Bertron and Duchesne, 2013). The attack by these specific acids induces calcium leaching

from the matrix and formation of a Si-Al-skeleton gel with high porosity and low mechanical properties (Bertron et al., 2007), the main hydrates of the cement matrix ($\text{Ca}(\text{OH})_2$, C-S-H and C_4AHx) being dissolved.

Ammonium salts are highly aggressive for the cementitious matrix because of an exchange reaction between NH_4^+ in the medium and Ca^{2+} in the cement paste (Escadeillas, 2013).

In this work, the chemical and mineralogical compositions of zone 2 (transition zone where portlandite was dissolved and non-expansive ettringite precipitated) and of zone 5 (an amorphous zone mainly composed of Si and containing Al and P) were typical of a leaching process resulting from the exposure of cementitious materials to VFA (Bertron et al., 2007) and ammonium (Escadeillas, 2013).

4.3.2. Phosphorus enrichment in the cement matrix

The chemical analyses by EDS and EPMA revealed enrichment in phosphorus in zone 4. This enrichment in the Ca-P component was due the presence of phosphorus in the substrate used in our experiment. It would not necessarily occur in the various environments that may be encountered in other anaerobic digestion media. Hydroxyapatite may have precipitated following the reaction between calcium released by the cement matrix and phosphorus diffused from the medium. This precipitation could not be confirmed by XRD, which may be explained by the formation of an amorphous calcium phosphate precursor (Christoffersen et al., 1989). Amorphous calcium phosphate is one of the most frequent forms of calcium phosphate minerals in biological organisms (Eanes, 1998) and is the precursor of hydroxyapatite, which is a major part of bone structure (Rey et al., 2009).

It should be noted that Meyer and Eanes (1978) reported that this amorphous form was stable in pH between 7 and 9 (Meyer and Eanes, 1978). This pH condition might be encountered in zones 4 and 5, zone 4 being the place with the highest concentration of P (Figs. 7 and 8) as the pH decreases from the core of the matrix (pH 12–13) to the outer layer in contact with the biofilm (pH 7 or lower). There was no ettringite left in zone 3, which means that the pH was lower than 10.6 (Duchesne and Bertron, 2013), and calcite precipitated in zones 3 and 4, indicating preferential pH conditions between 8.5 and 9.5 (Tai et al., 2006; Ruiz-Agudo et al., 2011). Finally, it is not known whether this precipitation has a protective effect on the cement matrix through the creation of a diffusion barrier.

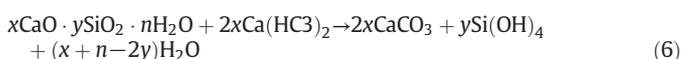
4.3.3. Carbonation of the cement matrix

CO_2 is one of the main metabolites of methanogens as it constitutes 35% of the final biogas produced in an anaerobic digestion process. In aqueous environments, the presence of dissolved carbon dioxide may

lead to both carbonation and dissolution of the cement matrix. The total CO₂ in the medium includes free and bound CO₂. The free CO₂ contains aggressive and stabilizing CO₂ (Escadeillas and Hornain, 2008). The stabilizing CO₂ is the quantity required to maintain the bicarbonates in solution with the following reaction Eq. (4).



The aggressive carbon dioxide is the excess free CO₂ beyond the stabilizing CO₂. The degradation with aggressive CO₂ leads to subsequent dissolution and precipitation mechanisms. The water in contact with the cement material becomes progressively saturated in bicarbonates. Calcium carbonate, with its very low solubility, can precipitate through the reaction between bicarbonate in solution and calcium-bearing hydrates such as portlandite and C-S-H as shown in Eqs. (5) and (6).



This phenomenon decreases the porosity of the cementitious material (Escadeillas and Hornain, 2008). The calcium carbonate precipitated reacts with carbon dioxide and forms calcium bicarbonate, according to Eq. (7).



Calcium bicarbonate is more soluble than calcium carbonate and will consequently be dissolved in water (Yin et al., 2015). So, the leaching of lime, the formation of bicarbonates, and the precipitation of carbonates is repeated until the lime runs out (Escadeillas and Hornain, 2008).

In this study, an average concentration of 2.3 mmol L⁻¹ (or 140 mg L⁻¹) of dissolved CO₂ (in the form of HCO₃⁻ at the pH of 7.7 in the fermented medium) was measured in the medium. However, as suggested by Magniont et al. (2011), more aggressive conditions, including higher CO₂ concentrations and lower pH, may be encountered at the interface between the biofilm and the specimen surface than in the surrounding medium. Leemann et al. highlighted that, in low pH conditions, as in an acidic environment, calcite would not precipitate even in presence of carbonates because of the insufficient buffering capacity of the CaO content in the cement material towards the acidic environment (Leemann et al., 2010b). Actually, calcite was not identified on the surface of the specimen in this experiment.

Calcite was detected deeper in the specimen, i.e. in zones 3 and 4. Other authors have also concluded that carbonation can be induced by bacteria producing CO₂ in an environment enriched with microorganisms (Lajili et al., 2008; Magniont et al., 2011). Calcite precipitation in the cementitious material has also been reported as a providing possible protection against agents that are aggressive to concrete, by filling the porosity of the material (Leemann et al., 2010b).

5. Conclusion

Biodeterioration of cementitious material exposed to the solid/liquid fraction of fermenting biowaste was investigated by immersing ordinary cement pastes in bioreactors in laboratory conditions. The liquid phase of the digesters was analysed over time to measure the evolution of pH, and the concentrations of volatile fatty acids and ammonium. CO₂ concentration was also measured.

A maximum total concentration of 50 mmol L⁻¹ of volatile fatty acids (acetic, propionic and butyric acids) was produced during the process. Despite a short period of biowaste acidification at the beginning of the experiment, the pH in the bioreactors stabilized in the 7–8 range. Large amounts of ammonium ion, up to 8 times the upper limit of the

class of highly aggressive environments for concrete (XA3) in European standard EN 206, were formed during the anaerobic digestion.

The biodeterioration of the cementitious material in the solid/liquid phase of anaerobic digestion bioreactors was identified as a combination of calcium leaching and carbonation. The cement paste surface was covered by a biofilm several tens of μm thick after 4 weeks of exposure to digesting biowaste. The deterioration mechanisms highlighted through this study suggest that specific chemical conditions may have developed under the biofilm and that these conditions may have been more aggressive for the cementitious material than what was obtained from the analysis of the bulk environment.

It should be noted that the European (EN 206) standards for the design of concrete subjected to aggressive environments consider neither the presence of volatile fatty acids and their concentrations nor the presence of microorganisms (in the environment or in the form of a biofilm on the material) as potential aggressive agents, which appears to be a shortcoming of these standards.

Further research will focus on understanding the specific impact of attached microorganisms in deterioration. Microorganisms capable of colonizing the surface of cement pastes will also be identified using DNA-based microbial population analyses.

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