Biodeterioration of cementitious materials in biogas digester

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Abstract – In biogas production plants, concrete structures suffer chemical and biological attacks during the anaerobic digestion process. The attack on concrete may be linked to the effects of (i) organic acids; (ii) ammonium and CO_2 co-produced by the microorganisms' metabolisms; and (iii) the bacteria's ability to form biofilms on the concrete surface. In a context of biogas industry expansion, the mechanisms of concrete deterioration need to be better understood in order to propose innovative, efficient solutions. This study aims, firstly, to characterise the evolution of the biochemical composition of the biodegradable wastes during digestion so as to identify the compounds that are aggressive for concrete. Secondly, it aims to evaluate the mechanisms of concrete deterioration in anaerobic digesters. CEM I paste specimens were immersed in synthetic inoculated biowaste in anaerobic digestion conditions. The liquid fractions were analysed chemically. The alteration mechanisms of the cementitious matrices were investigated using XRD and SEM analyses. The maximal total concentration of organic acids was 65 mmol/L in the liquid fraction during the digestion process. The pH evolution showed two phases: acidification in the first few days and then a slow increase to pH 7–8. In only 4 weeks, an abundant biofilm developed on the cement paste surface. Biodeterioration leads to calcium leaching and carbonation of the cement paste.

Key words: Anaerobic digestion / cementitious materials / biodeterioration / organic acids / microstructure

Résumé – Biodétérioration des matériaux cimentaires dans les structures de méthanisation. Dans les digesteurs de méthanisation, le béton des structures subit des attaques d'origine chimique et biologique. L'attaque sur le béton serait liée à la combinaison des effets des acides organiques, de l'ammonium et du CO_2 produits par le métabolisme microbien et également à la capacité des bactéries à former des biofilms à la surface du béton. Le secteur de la méthanisation étant en pleine expansion, l'enjeu de ce travail est de progresser dans la compréhension des mécanismes de détérioration des bétons dans ces environnements afin proposer des solutions durables. Cette étude vise, dans un premier temps, à déterminer les caractéristiques chimiques des déchets organiques (pH, concentrations en composés chimiques agressifs) au cours de leur fermentation. Dans un second temps, les mécanismes de détérioration des bétons dans les conditions de méthanisation sont évalués. Des pâtes de CEM I ont été immergées dans un mélange de déchets organiques en conditions de digestion anaérobie. Le milieu a été analysé chimiquement tout au long du processus de digestion. Les pâtes de ciment ont été analysées par DRX et MEB+EDS. La concentration totale maximale en acides organiques était de 65 mmol/L dans les bioréacteurs. L'évolution du pH présentait deux phases : une acidification dans les premiers jours et une lente augmentation jusqu'à pH 7–8. En 4 semaines, un biofilm abondant s'est développé à la surface du matériau. La biodétérioration s'est traduite par la lixiviation du calcium et la carbonatation du matériau.

Mots clés : Digestion anaérobie / matériaux cimentaires / biodétérioration / acides organiques / microstructure

1 Introduction

Anaerobic digestion is a natural biological process of organic matter degradation in the absence of oxygen [1]. Complex organic matter undergoes several successive degradation reactions: hydrolysis, acidogenesis, acetogenesis and finally methanogenesis [2]. This process can be implemented intentionally (industrialised)

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in a digester, starting from organic wastes [3]. It leads to the production of biogas, a clean fuel similar to natural gas and containing methane with co-products such as solid or liquid digestates. Biogas appears to be a good alternative energy resource as it is relatively cheap and is available locally. Consequently, the industrial development of anaerobic digesters has become widespread throughout the world for many sources of wastes. Anaerobic digestion is becoming a key instrument in attempts to supply sustainable energy, with major development plans in Germany and in China. European policies support anaerobic digestion projects and France has the objective of increasing the number of installations by about 300% by 2020 [4].

Concrete is the most widely used material for the construction of structures in the biogas industry (pre-tank, digester, post-digester, storage tank, etc.) because it is economical, water- and air-tight, and offers high thermal inertia, among other advantages. Despite its safety and efficiency, the durability of concrete is reduced by the attacks of several aggressive chemical and biological components in the waste effluents in the course of the anaerobic digestion process. The degradation is notably due to acid components (various organic acids, including volatile fatty acids or VFA, especially acetic and propionic acids [5–8]), CO_2 [5, 9], and ammonium [5], produced by microbial oxidation processes and probably accentuated by the colonisation of the concrete surface by microbial biofilms. These attacks combined with mechanical stresses due to machine traffic and tank cleaning (high pressure water cleaning, scraping) during draining periods, result in loss of alkalinity, a decrease in mechanical resistance, progressive surface erosion and increased permeability of concrete. The consequences of such degradation of concrete structures are (i) economic: production yield is reduced by biogas leakage and repairing the structures, with the concomitant interruption of production during the repair work, is costly, and (ii) environmental: sealing defects lead to leakage of polluting effluents into the environment.

In the aim of improving the durability of digesters, this paper highlights the degradation mechanisms resulting from the microbiologically produced chemicals and caused by the microbes themselves in the waste fermentation process. While the actions of synthetic volatile fatty acids, CO_2 and ammonium on the cement matrix are quite well known [10–18], very few studies have so far investigated their combined action together with that of the microorganisms that produce them. The mechanisms of microbial adhesion to the concrete surface (biofilm) have also received little attention as yet. In this context, our preliminary work focused on (i) analysing the pH and the composition of a synthetic biowaste in terms of organic acid natures and concentrations during the anaerobic digestion process, and (ii) determining the mechanisms of microbiologically influenced deterioration of concrete. In this study, cement paste specimens were immersed in a batch process for 6 weeks, which is the average time required for biowaste to undergo complete digestion. During the experiment, the organic acid composition was analysed daily and the pH was measured continuously. The chemical, mineralogical and microstructural changes in the cement pastes were explored by SEM observations coupled with EDS analyses and XRD.

2 Materials and methods

2.1 Cementitious materials

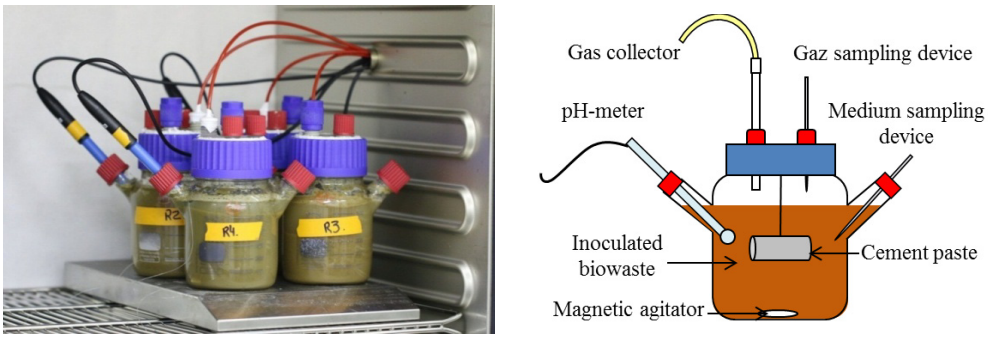
CEM I 52.5 cement pastes were made with a water/cement ratio of 0.40. The specimens were cast in cylindrical moulds 75 mm high and 25 mm in diameter. The pastes were removed from their moulds 24 h after pouring and stored in water at 20 °C for 28 days.

2.2 Preparation of synthetic biowaste

A model of biowaste, representative of the organic domestic waste produced in France, was prepared according to a process provided by IRSTEA of Antony (France). The composition of the model synthetic biowaste was (by mass): potatoes (8.1%), tomatoes (3.4%), minced meat (8.1%), milk powder (0.7%), crackers (4.1%), and water (75.6%). The whole mixture was blended for 10 min at 20 °C to obtain a homogeneous mixture. The biowaste was microbiologically inoculated to initiate the anaerobic digestion [19–25]. The microbial inoculum was sludge collected from a municipal waste water treatment plant in Toulouse (France). The organic loads, expressed as chemical oxygen demands (COD), were about 50 g/L for the biowaste and 20 g/L for the sludge (inoculum). In the literature, several ratios of inoculation, corresponding of the ratios between the quantity of inoculum and the quantity of biowaste (m/m), are reported to ensure a successful anaerobic digestion process [6, 20, 23, 25]. In our work, the strategy of sludge inoculation was adapted from the procedure of Elbeshbishy et al. [20] in which a ratio of 1 g COD(Inoculum)/g COD(biowaste) was used. The bioreactors (usable volume: 500 mL) were maintained at 37 °C in an operating mode oven during the whole experiment (Fig. 1).

2.3 Cement paste immersion in fermented biowaste under anaerobic digestion conditions

The cement paste specimens were immersed in bioreactors containing the inoculated biowaste for 6 weeks at 35 °C [26, 27]. The specimen was immersed immediately after the sludge inoculation of the biowaste. Cement pastes were exposed to all the successive degradation reactions of the biowaste during anaerobic digestion. The solid/liquid ratio (cement paste surface area/inoculated biowaste volume) for each bioreactor was approximately 224 $cm^2 \cdot L^{-1}$ (the in situ ratio in a standard digester is approximately 4 $cm^2 \cdot L^{-1}$). Control bioreactors containing inoculated biowaste without cement paste specimens were also run for 4 weeks as reference tests. The pH was continuously measured using a pH data acquisition system (WTW, Multi 3430).



(a) (b)

Fig. 1. (a) Picture of the experimental tests for the exposure of cement pastes to digested biowastes and (b) schematic representation of the anaerobic bioreactors placed on a magnetic plate for mixing purposes and kept in an oven regulated at 37 °C.

Fig. 1. (a) Image du dispositif experimental d'immersion de pâte de ciment dans un biodéchet en digestion anaérobie et (b) schéma de principe d'un bioréacteur anaérobie placé sur un dispositif d'agitation magnétique et maintenu à 37 °C dans une étuve.

2.4 Analysis of organic acids by HPLC

Samples of 1.5 mL of biowaste were collected from the bioreactors twice a day for the first week then once a day until the end of the experiment using sterile needles and syringes. The samples were filtered at 0.2 μm in Eppendorf tubes and then stored in a freezer at –18 °C until their further analyses. The nature and concentrations of soluble organic acids in the liquid part of the biowaste samples were analysed by High Performance Liquid Chromatography (Eluant flow 0.6 ml/min, eluant H_2SO_4, Thermo Fisher U3000, Aminex HPX-87H BIO-RAD column).

2.5 Analysis of cementitious materials

Slides of cement paste specimens were sawn perpendicularly to their axes and embedded in an epoxy resin (Mecapres Ma2 by Presi). The specimens were dry polished using silicon carbide polishing disks (by Presi) according to the procedure described in Bertron et al. [11]. The polished sections were coated with carbon and were then characterised by Scanning Electron Microscopy (JEOL JSM-LV) combined with Energy Dispersive Spectrometry analyses (RONTEC XFlash® 3001).

The mineralogical changes were analysed by X-Ray Diffraction (Siemens D5000, Co cathode, 40 kV, 30 nA). The specimens were prepared according to the procedure described in Bertron et al. [12]. These analyses were performed on the plane sides of the cylinders. The first analysis was carried out on the plane external face of the specimen, which was then abraded and submitted to the next analysis. A control specimen was also analysed 5 weeks after pouring.

2.6 Observation of the microbial biofilms

The biofilm on the surface of the specimen was observed by SEM-FEG (JEOL 7100F TTLS combined with EDX XMax, 5 kW). Cement paste specimens were sawn carefully to preserve the biofilm developed at their surfaces. Before SEM observations, the biofilms on the cement pastes were chemically fixed and then dehydrated. The aim of the fixation was to create an artificial reticulation to preserve the integrity of the microorganism membranes during water extraction. The chemical fixation method required several steps: (i) 20 min of immersion in aldehyde fixator solution made of 2 volumes of glutaraldehyde (4%), 1 volume of phosphate buffer (pH 7.4, 0.4 M) and 1 volume of distilled water; (ii) two times 15 min of immersion in cleaning solution made of 1 volume of phosphate buffer (pH 7.4, 0.4 M), 2 volumes of sucrose solution (0.4 M) and 1 volume of distilled water.

The aim of the chemical dehydration was to replace water by volatile solvents, such as acetone and hexamethyldisilazane (HDMS). The chemical dehydration was progressively carried out by successive immersion of the specimens in solutions made of: acetone and water (50%–50%, 5 min), acetone and water (70%–30%, 5 min), acetone (30 min), acetone and HDMS (50%–50%, 10 min) and, finally, HMDS (100%) until complete evaporation.

After fixation and dehydration, the specimens were coated with a thin layer (in order to preserve the biofilm integrity) of gold before SEM observations.

3 Results

3.1 Tracking the production of organic acids and the pH evolution during the anaerobic digestion of biowastes

During the anaerobic digestion process, organic waste is biologically degraded and converted into clean biogas. According to Zhang et al. [28], the biodegradation process includes four main steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis, as shown in Figure 2. Firstly, high molecular materials and solid substrates (e.g., lipids

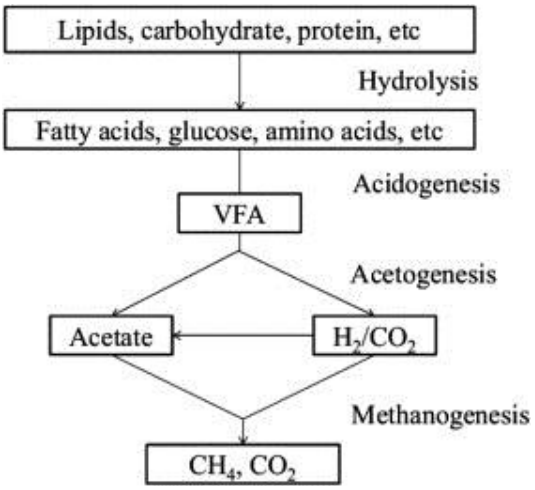


Fig. 2. Steps of the anaerobic digestion process of organic substrates (adapted from Zhang et al. [28]).

Fig. 2. Étapes réactionnelles d'une digestion anaérobie de substrats organiques (adapté de Zhang et al. [28]).

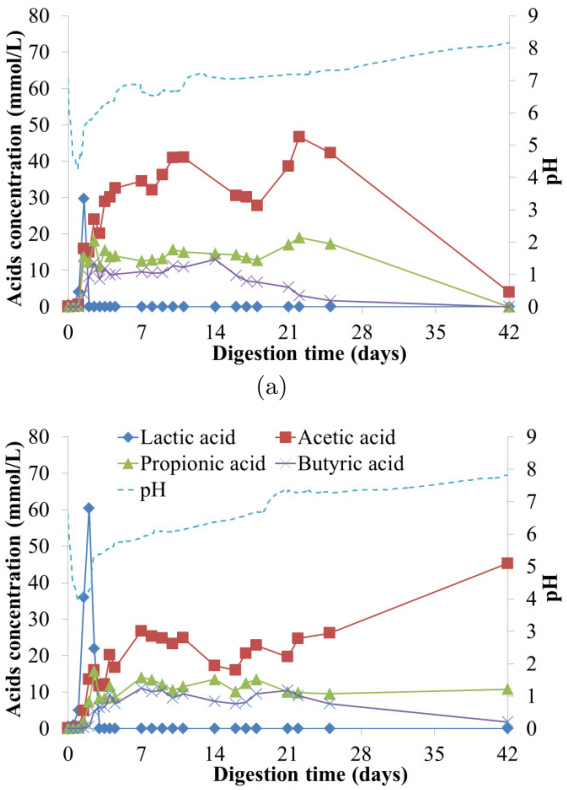


Fig. 3. Concentration of acids and pH during the anaerobic digestion of biowaste in presence (a) and in absence (b) of ordinary cement paste sample in the bioreactors.

Fig. 3. Concentrations en acides et pH pendant la digestion anaérobie de biodéchet en présence (a) et en absence (b) de pâte de ciment ordinaire dans le bioréacteur.

and carbohydrates, protein) are hydrolysed by fermentative bacteria into small molecular materials and soluble organic substrates (e.g., fatty acids and glucose, amino acids). Secondly, small molecular materials and soluble organic substrates are degraded into volatile fatty acids (organic acids) and by-products (e.g., NH_3, CO_2 and H_2S) are formed. Thirdly, the organic substrates produced in the second step are digested into acetate, H_2, CO_2 which may be used by methanogens for methane production.

Anaerobic bacteria need different pH ranges for their growth, e.g., a comprehensive pH range of 4.0–8.5 is required for the fermentative bacteria producing organic substrates (e.g., fatty acids and glucose). In particular, a range of 6.5–7.2 promotes the growth of methanogenic bacteria [28]. Organic acids produced by fermentative bacteria determine the pH within the mix of the digested biowastes.

Figure 3 shows the evolution of the biowastes (containing the cement paste or not) in terms of nature and concentrations of organic acids and the corresponding pH during a complete cycle of anaerobic digestion (4 weeks).

The decrease in pH in the first few days was correlated with a significant rate of production of lactic acid and volatile fatty acids, such as acetic, propionic and butyric acids.

The pH values obtained in this study indicate the proper setting up of the different digestion phases. The pH decreased from 6 to 4 in the first day. Then, the pH slowly increased to 7 and 8. Interestingly, the presence of cement material in the bioreactor seemed to accelerate the establishment of the pH in the range favourable for methanogenesis (Fig. 3). This was probably due to the release of hydronium ions from the cementitious matrix into the medium.

Acetic, butyric and propionic acids are typical metabolites from microbial anaerobic microorganisms [5–7, 29]. In contrast, the lactic acid production occurring in the first day is less common. The production of lactic acid was probably linked with the presence of milk powder in the biowaste. Lactic acid was nevertheless completely degraded in the first 3 or 4 days. The three VFAs showed high production rates in the first few days. Then, the concentrations of these acids remained constant at about 10 mmol/L for butyric acid, 15 mmol/L for propionic acid and between 30 and 40 mmol/L for acetic acid in the presence of cement paste. Without cement paste, the concentrations of these acids remained constant at about 10 mmol/L for butyric and propionic acid and between 15 and 25 mmol/L for acetic acid. The concentrations of acids then tended to 0 at the end of the experiment, except for acetic and propionic acids in the absence of cement paste in the bioreactor. This change in pH has an impact on microbial metabolism and may result in the activation of the metabolic pathway leading to butyric acid production and/or the inhibition of the production of lactic acid. The total amount of acids analysed was higher in the presence of cement paste in the mix, with a total maximal amount of 65 mmol/L, than in the absence of cement paste (total concentration of 50 mmol/L), except at the end of the experiment.

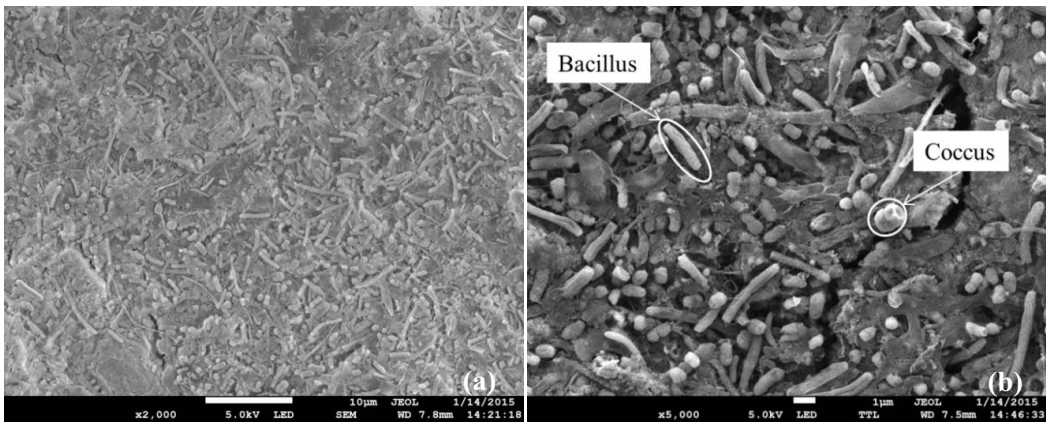


Fig. 4. SEM observations of ordinary cement paste surface colonised with a microbial biofilm after 4 weeks of exposure to biowastes under anaerobic digestion process.

Fig. 4. Observations MEB de surfaces de pâte de ciment ordinaire colonisées par un biofilm microbien après 4 semaines d'immersion dans un biodéchet en conditions de digestion anaérobie.

3.2 Highlighting microbial biofilm formation on the cement paste surface

Figure 4 shows the SEM observation of the surface of the cement paste specimens immersed in the fermented biowastes for 4 weeks. A biofilm developed and the coverage of the sample surface by the microbial biofilm was total.

Various shapes and sizes of microorganisms were observed inside the biofilm. The shapes of methanogenic microorganisms are mainly described in the literature as rod (bacillus), curved rod, spiral and coccus types [30]. Here, the microorganisms making up the biofilm had a variety of aspects. Some had clearly spherical shapes (Fig. 4b), corresponding to a coccoid morphology. Others were stretched or elongated, suggesting long rods. The length of the rod-like microbial cells varied between 1 μm and 10 μm (Fig. 4). These results match those observed by Zellner et al. [31] who identified rod and coccus shaped microorganisms in the microbial flora of a fixed-bed anaerobic methanogenic bioreactor.

3.3 Assessing the chemical degradation of cement paste immersed in anaerobic digestion conditions

3.3.1 Chemical changes

Figure 5 shows SEM observations in BSE (Back-Scattered Electron) mode of a polished cross section of a specimen exposed to anaerobic digestion conditions for 4 weeks. A chemical zonation of the specimen was identified by EDS analyses. The typical compositions of the various zones, marked zones 1 to 5 and shown on Figure 5, are given in Table 1. From the core of the specimen to the outer layer, zonation was as follows:

– Zone 1, or sound zone, showed a high density of anhydrous residual grains (white grains on the SEM picture). The chemical composition of this zone was similar to that of an unaltered control specimen (Tab. 1),

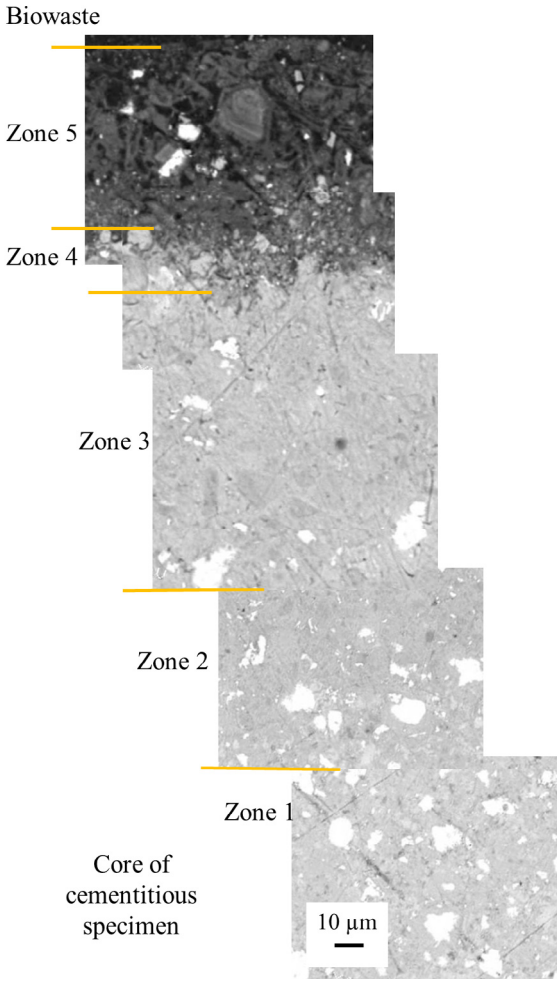


Fig. 5. Observations by SEM of the different zones on a polished section of ordinary cement paste exposed to anaerobic digestion conditions for 4 weeks.

Fig. 5. Observations MEB des différentes zones d'une section polie de pâte de ciment ordinaire immergée en conditions de digestion anaérobie pendant 4 semaines.

Table 1. Average chemical composition (calculated on 6 analyses of circular zones 5 μm in diameter) and standard deviations in mass percentages in the different zones defined on Figure 5 (d.l.: detection limit).

Tableau 1. Moyenne des compositions chimiques (calculée sur 6 zones circulaires de 5 μm de diamètre) et écart-type en pourcentage massique dans les différentes zones définies sur la Figure 5 (d.l. : limite de détection).

	Zone				
Element	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5
Aluminium	3.46 ± 0.27	10.69 ± 2.14	4.86 ± 0.38	4.58 ± 0.68	15.15 ± 0.38
Silicon	28.39 ± 2.58	14.16 ± 6.35	31.69 ± 1.71	22.10 ± 3.87	52.44 ± 6.77
Phosphorus	0.32 ± 0.00	0.29 ± 0.07	0.48 ± 0.16	26.28 ± 3.04	12.63 ± 4.03
Sulfur	4.09 ± 0.31	19.26 ± 7.30	4.28 ± 1.11	3.07 ± 0.78	2.25 ± 0.54
Calcium	62.80 ± 2.18	54.53 ± 2.17	57.44 ± 1.78	43.26 ± 4.28	11.66 ± 4.28
Chloride	<d.l.	<d.l.	<d.l.	<d.l.	4.65 ± 0.16

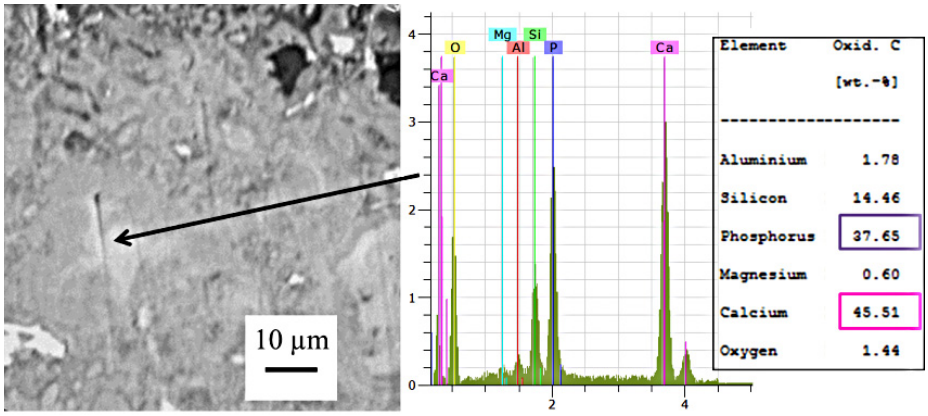


Fig. 6. Observation and composition chimique, en pourcentage d'oxydes, d'un précipité observé dans la zone 4 du coupon immergé en conditions de digestion anaérobie pendant 4 semaines.

Fig. 6. Observation et composition chimique, en pourcentage d'oxydes, d'un précipité observé dans la zone 4 du coupon immergé en conditions de digestion anaérobie pendant 4 semaines.

- Zone 2 was slightly decalcified and was enriched in sulphur. The density of residual anhydrous grains was lower than in zone 1. This zone was 50 μm-thick.
- Zone 3, 100 μm-thick, was slightly decalcified. Most residual anhydrous grains had been dissolved.
- Zone 4, a few tens micrometers thick, had a high phosphorus content. Phosphorus was most likely brought by the medium. Precipitates mainly composed of P, Ca and Si were observed at different places in this thin layer (Fig. 6). The proportions of Ca, P and Si of these precipitates were typical of apatite minerals [32].
- Zone 5, the outer layer previously in contact with the biofilm, was 50 μm thick. The density of this zone was very low. Nearly complete decalcification occurred in this zone. The aluminium and silica contents were high than in the zones closer to the centre.

3.3.2 Mineralogical changes

The mineralogical characterisation of the different zones of the cement pastes, as defined in Section 3.3.1, was performed by XRD analyses after 4 weeks of exposure to the fermented biowaste in anaerobic conditions. Figure 7 presents the X-ray patterns obtained in the core (zone 1) and in the altered zones (zones 2, 3, 4 and 5).

- Zone 1 showed the same mineralogical characteristics as the control specimen. Peaks of portlandite, ettringite and anhydrous grains of C_3S and C_2S were present.
- In zone 2, portlandite peaks had disappeared. The intensity of ettringite peaks was higher than in zone 1. These observations can be related to the slight decalcification and to the increase in sulphur content highlighted through EDS analyses.
- In zone 3, the only crystallised phase was calcite.
- Zone 4 showed peaks of calcite and of hydroxyapatite
- Zone 5 was completely amorphous.

4 Discussion

4.1 Composition of anaerobic digestion medium and potential aggressiveness

In this study, cement paste specimens were exposed to the complete anaerobic digestion cycle of a mix of biowaste, which included 4 main successive reactions of conversion (hydrolysis, acidogenesis, acetogenesis, methanogenesis, Fig. 1). The aim was notably to identify the steps of the anaerobic digestion that were the most aggressive toward cementitious materials.

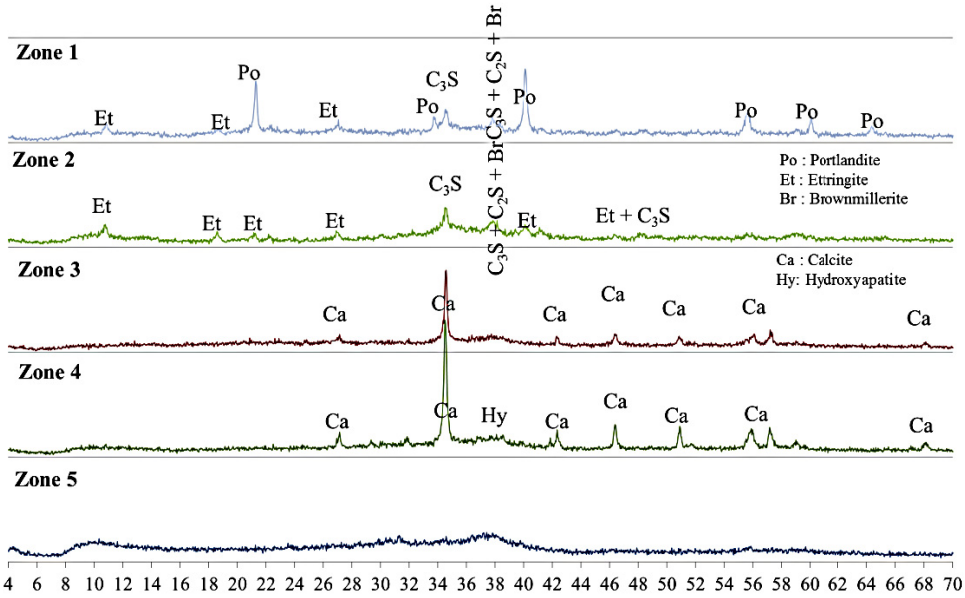


Fig. 7. X-ray traces of ordinary cement paste specimens immersed in inoculated biowaste in anaerobic fermentation conditions for 4 weeks.

Fig. 7. Analyses par DRX de pâte de ciment ordinaire immergée dans un biodéchet inoculé en conditions de digestion anaérobie pendant 4 semaines.

The pH of the anaerobic digestion process, presented in Figure 3, showed an initial decreasing step from 6 to 4–5 during 2 days before slowly increasing to reach the pH value of 7–8 in 5 weeks. In terms of composition of acids, lactic acid and volatile fatty acids (acetic, propionic and butyric acids) were produced during the anaerobic digestion with a maximal total concentration of about 65 mmol/L. The presence of cement pastes in the waste was found to accelerate the increase of pH. In addition, CO_2 and ammonium were also co-produced and so were probably present in the digestion medium. McCarty [5] reported concentrations of CO_2 in the range of 2000–3000 $mg{\cdot}L^{-1}$ and ammonium in the range of 50–200 $mg{\cdot}L^{-1}$ in classic anaerobic digestion media. To develop a complete assessment of the anaerobic digestion aggressiveness on cement based materials, additional analyses to evaluate the evolution of CO_2 and ammonium concentrations in the biowaste should be performed.

In terms of pH conditions, despite a short initial period in which the pH was low, anaerobic digestion media should be classified as a deleterious environment for cement material according to their stable pH of 7–8. However, CO_2 and ammonium concentrations reported in the literature suggest that the anaerobic digestion media should be considered as highly chemically aggressive (XA3) toward concrete according to the European standard EN NF 206-1. Nevertheless, it should be noted that this standard does not consider the nature and concentration of the acids or the presence of microorganisms in the chemical aggressive environment classification, although these two components were identified as aggressive to the cement matrix [33, 34].

4.2 Microbial colonisation at the surface of the cementitious materials

Biodeterioration is often exacerbated when the presence of a surface layer of microorganisms and their products is identified on the surface of the altered material. Such microbial layers are known as microbial biofilms and contain high concentrations of products from the microbial metabolism. Generally, biofilms are in direct contact with the material rather than dispersed in the surrounding environment. Thus, the aggressive products secreted by microorganisms are concentrated in close proximity to the material surface and result in accelerated damage of concrete material. The first cases of microbiologically induced concrete biodeterioration were especially detected in constructions like sewer pipes [35, 36], waste water treatment facilities [37], cooling towers [38], gas and oil platforms, marine structures, and other structures where various microorganisms (like bacteria, microscopic fungi, algae and lichen) are usually present at high concentrations.

Anaerobic digestion environments are rich in microorganisms that have the ability to organise themselves as multispecies biofilms. Several types of biogas production processes operate continuously with fermentative and methanogenic biomass immobilised in the form of aggregates or solid particles that are easy to separate (fixed bed or fluidised bed methods). We investigated whether these microorganisms involved in anaerobic digestion were able to install themselves on concrete and truly colonise the surface exposed to the fermenting biowastes.

In only 4 weeks, an abundant biofilm developed on the cement paste surface, despite an initial pH of 13 on the

cementitious surface exposed to the fermenting biowaste. However, as mentioned previously, the optimal pH for microorganisms involved in anaerobic digestion to thrive is around 4.5–6.3 for hydrolytic and acidogenic bacteria, in the range of 6.8–7.5 for acetogenic bacteria and around 6.2–7.6 for methanogenic bacteria. The metabolites (acids, CO_2 and ammonium) secreted initially by planktonic microorganisms (in suspension in the liquid phase of the biowaste) probably initiated the material deterioration (most likely through leaching and carbonation, as analysed with SEM+EDS and XRD) and provided suitable pH conditions for the microorganisms to colonise it [33]. These phenomena enhanced the bioreceptivity of the cementitious material [39].

The bacterial communities involved in the biofilm formation have not yet been identified. However, morphological analysis of the biofilms by SEM observations revealed a complex and irregular mixture of rod and coccus shaped microorganisms. This is in accordance with earlier observations [31], which showed these same shapes involved in a biofilm in anaerobic digester reactors. Further analyses of the diversity of the microbial populations will be needed in order to identify the microorganisms developing at the surface of the cementitious specimens.

It should be noted that the formation of biofilm on the material surface may have consequences on the distribution and the concentration of soluble chemical species. The microorganisms are the motor of the anaerobic digestion as they catalyse the reactions of conversion of the organic substrates. Thus, measurements of organic acid concentrations carried out in the biowaste during anaerobic digestion are certainly lower than what was actually produced locally on the surface of cement pastes.

4.3 Chemical degradation mechanisms on cementitious materials in anaerobic digestion conditions

Cementitious materials in anaerobic digestion media are subjected to several chemical degradation mechanisms.

The attack of the anaerobic digestion medium implemented in this study on the cementitious specimens expressed itself through chemical and mineralogical zonation. The aggressive components in the medium (organic acids, CO_2 and ammonium) induced (i) calcium leaching and (ii) carbonation of the cement matrix.

The acids in the medium (VFA and lactic acids) are characterised by their very soluble calcium salts [34, 40]. The attack by these acids leads to calcium leaching from the matrix and to the formation of a Si-Al-skeleton gel with high porosity and low mechanical properties [15]. In this study, the chemical and mineralogical composition of zone 2 (transition zone typical of calcium leaching phenomena) and of zone 5 (Si-Al gel outer layer) were typical of a leaching process resulting from the exposure of cementitious materials to VFA [15], pure strong acids [41] and ammonium [42].

CO_2 is produced during respiration of the microorganisms and also as a metabolite during anaerobic digestion in the methanogenesis phase. CO_2 leads to the carbonation of the specimen [43]. The precipitation of calcite is linked to the diffusion in the cementitious matrix of dissolved CO_2 produced by microorganism respiration in the aggressive medium [33,43,44]. HCO_3^{2-} combined with Ca^{2+} released by the cement paste, and precipitated in the form of calcite in zones 3 and 4, where suitable conditions no doubt occurred.

A phosphorus-bearing layer was also identified by chemical analyses in zone 4. Hydroxyapatite probably precipitated because of the combination of calcium released from the cement matrix with phosphorus diffused from the medium.

Finally, it should be mentioned that microorganisms play a key role in deterioration in an agricultural environment [45, 46]. As highlighted by Magniont et al. (2011), microorganisms in the form of a biofilm on the surface are more aggressive than their metabolites alone [33]. In accordance with our comment in the previous section, Magniont et al. explained that the presence of microorganisms on the surface probably led to particular conditions of acid concentrations and pH (high acid concentrations and low pH) locally. These conditions may explain (i) the intense alteration of the outer layer of the specimens observed in our study (total decalcification of the matrix) despite a pH close to neutrality, and (ii) the conditions suitable for calcite precipitation in zones 3 and 4 inside the matrix rather than at its surface.

5 Conclusion

The anaerobic digestion process was followed in bioreactors filled with biowaste microbiologically inoculated by sludge from a municipal waste water plant in laboratory conditions. Ordinary cement paste specimens were immersed in bioreactors and were thus exposed to the successive degradation steps of the anaerobic digestion cycle of the biowaste.

The investigation of the liquid fraction of the biowaste during digestion showed a massive production of acids (lactic acid and volatile fatty acids: acetic, propionic and butyric acids) in a maximal total concentration of 65 mmol/L. The rapid production of acids led to a short period of biowaste acidification corresponding to the first 3 days of the study. During the five and a half weeks that followed, the pH stabilised in a region close to 8.0. After the 4 weeks of cement paste exposure to digesting biowaste, an abundant biofilm estimated to be several tens of μm thick was observed on the material surface.

The biodeterioration was expressed by a combination of leaching and carbonation phenomena. Phosphorus-bearing precipitates were also detected in the cementitious matrix. Further research will focus on deciphering the specific impact of attached microorganisms in the deterioration. Microorganisms capable of colonising the surface of cement pastes will also be identified using DNA-based microbial population analyses.

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