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Resistance of different types of concretes to cyclic sulfuric acid and sodium sulfate attack

F. Girardi, W. Vaona, R. Di Maggio *

Department of Materials Engineering and Industrial Technologies, University of Trento, Via Mesiano, 77, 38100 Trento, Italy

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ABSTRACT

An improvement in accelerated testing as a way of predicting durability was proposed in this study. Accordingly, the behavior of different concrete mixtures was examined in relation to a cyclic exposure to sulfuric acid and sodium sulfate solutions, recording the expansion and mass loss of the test specimens for about 5 years. Three different cements – i.e. Portland limestone, blast furnace slag and pozzolanic cement – were used, the latter two both with and without silica fume (SF), to prepare the concretes for the study. Scanning Electron Microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were used to correlate the samples' microstructure and deformation.

The lowest expansion was obtained by mixtures containing silica fume, although they were more susceptible to corrosion in acid. After a dormant period when no expansion occurred, the Portland limestone cement and blast furnace slag cement exhibited a large expansion that began suddenly and increased at an almost constant rate. This expansion correlated with the presence of cracks filled with calcium sulfate crystals in the core of the concrete samples.

For comparison, the expansion of concretes specimens left in a sodium sulfate solution was also measured. The dormant period in the two-step expansion process seen in the Portland limestone and blast furnace concretes was shorter in the cyclic testing in sulfate and sulfuric acid, which can be considered as a model of accelerated deterioration, than in the latter.

1. Introduction

The deterioration of concrete exposed to an aggressive environment poses problems in wastewater and sewage systems [1–5]. Concretes may deteriorate due to an inadequate mix design, but the aggressive nature of some environments warrants extra precautions to increase their durability [6]. An acid environment, as on the inner walls of sewer pipes, is one of the most harmful for concrete. According to the EN standard 206, aggressive environments are divided into exposure classes, depending on the severity of the attack. Sewer pipes come under exposure class XA3. The deterioration of concrete sewer pipes is a major problem if their service life is lesser of 30 years, because damaged pipes need maintenance or even replacement.

The processes leading to corrosion in concrete sewer pipes are highly complex. As reported by several authors [7–15], hydrogen sulfide produced by anaerobic wastewater is released into the wastewater flow, where it spreads to the atmosphere and condensates on the pipe wall above the wastewater. Micro-organisms, such as *Thiobacillus thiooxidans*, growing on this surface aerobically convert the hydrogen sulfide into sulfuric acid, which reacts with the concrete [16,17]. In most cases, the pH on the surface of the pipe is very low (as low as 0.5 in the worst case) [5].

The acid first attacks the calcium hydroxide and the C–S–H too, when portlandite is no longer available, making the first form gypsum and the second both anhydrous gypsum or an incoherent mass of hydrated silicate. This layer is highly porous and its growth depends on the rate of the acid's diffusion through the corroded layer to the reaction front, and on the rate of the acid's reaction with the as yet undamaged concrete. A previous paper [8] reported that the rates of corrosion by sulfuric acid of standard mortars are influenced by the continued deposition of calcium sulfate in the pores of corrosion layer. In a second step, calcium aluminate hydrate reacts with the sulfate ions from the sulfuric acid, forming ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$).

Calcium hydroxide reacts also with sodium sulfate, or other sulfates presents always in wastewater provided concentration of SO_4^{2-} is very high [5,18], giving secondary gypsum, which can form secondary ettringite. To extend the life of concrete sewage pipes, it is essential to find a way to control these processes.

There is evidence of the corrosion rate being higher just above the waterline, along the sides of the pipes, where fluctuating water levels wash away the sulfate deposits, continually reducing the

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* Corresponding author.
E-mail address: rosa.dimaggio@unitn.it (R. Di Maggio).

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Table 1
Mix proportions of concrete mixtures.

Aggregate type	Dolomite				
Fine (0–2 µm) (kg/m^3)	722	722	720	722	720
Fine (0/4 mm) (kg/m^3)	412	412	410	412	410
Coarse (3/8 mm) (kg/m^3)	621	621	620	621	620
Coarse (8/15 mm) (kg/m^3)	205	205	205	205	205
Cement designation (EN 197)	CEM II/A-LL	CEM III/A	CEM III/A	CEM IV/A (P)	CEM IV/A HSR
Cement (kg/m^3)	355	355	340	355	340
Silica fume (Meyco, MS610) (kg/m^3)	–	–	30	–	30
Acrylic superplasticizer (Glenium) (kg/m^3)	–	–	3	–	3
Water (kg/m^3)	140	140	133	140	133
w/c Ratio	0.39	0.39	0.39	0.39	0.39
Mass volume density (kg/dm^3)	2.501	2.532	2.490	2.502	2.516

N.B.: Each mass was determined at industrial plant, with an error equal to ±3%.

pipe wall's resistance. Moreover, the anaerobic conditions needed for hydrogen sulfide formation occur mainly when the sewage flow is slow. Since the formation of hydrogen sulfide and sulfuric acid is the controlling factor, the pH probably does not remain constantly below four (which coincides with a rapid concrete corrosion), but rises and falls with a scarcely predictable trend [15]. It seems that the concrete would need to be formulated to resist both acid and sulfate attack. It is worth adding that an alternate wetting and drying of the concrete is even more detrimental than a continuous exposure to chemical attack. Generally speaking, adding silica fume results in a concrete with a denser structure, better able to withstand sulfate attack, but it also reduces or eliminates the free, leachable calcium hydroxide [8,19]. Given this incongruence, the materials going into the concrete mixture have to be evaluated and selected to achieve the best compromise for the purposes of a long service life.

There are currently no methods available for assessing the performance of hydraulic cements in both acid- and sulfate-rich environments. The ASTM describes two test methods for assessing their performance in sulfate-rich environments (ASTM C452 and C1012), both of which have been criticized because they seem unable to predict field performance adequately. Among the several issues concerning these tests, it is worth noting that they are carried out on mortars, not concretes, only taking expansion due to ettringite formation into account. Acid attack is generally ignored, though it causes mass loss and may accelerate the deterioration process induced by sulfate exposure.

A reliable method for the accelerated testing of sulfate resistance is therefore of growing interest for the production of concretes with Portland and other cements. In this study, the sulfate resistance of concretes was assessed using a test method that included a monthly acid attack. The damage was evaluated by measuring both expansion and mass loss. For comparison, a test was also carried out using sodium sulfate alone, as required by the ASTM C1012 "Test Method for Length Changes of Hydraulic-Cement Mortars Exposed to a Sulfate Solution".

In this study, an accelerated test procedure was used to assess the effect of composition on the long-term durability and microstructure of a concrete in conditions resembling those of sewer pipes as closely as possible. The test method involved the cyclic exposure of concrete samples to sodium sulfate (50 g/l) and sulfuric

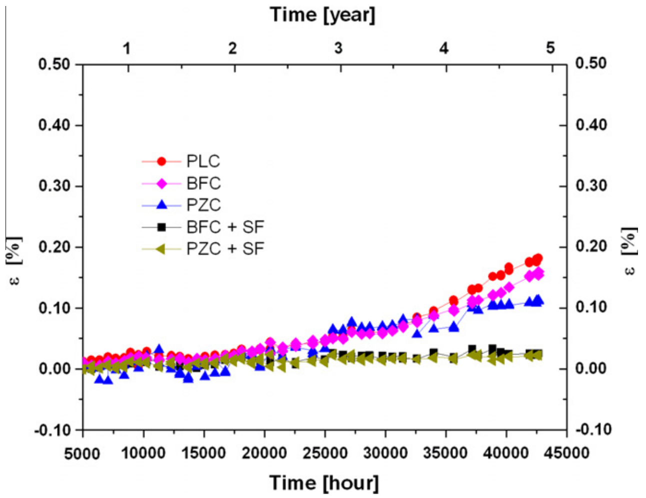

Fig. 1a. Percentage of expansion of samples under sulfate attack vs. time.

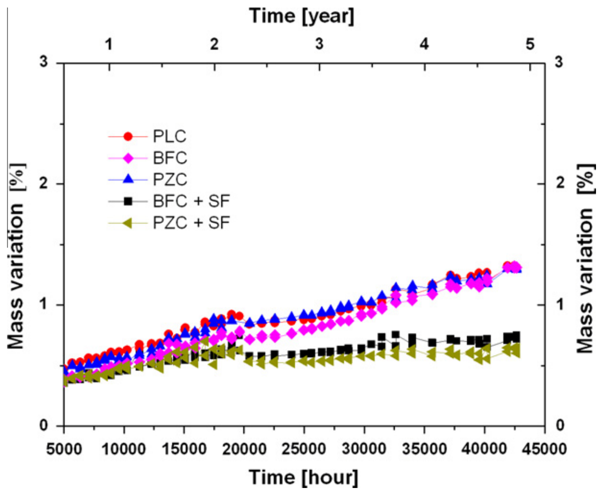

Fig. 1b. Percentage of mass loss of samples under cyclic sulfate and acid attack vs. time.

Table 2
Concrete compressive strength.

Cement	Additives (type and amount)	R_c (cubic sample) (MPa ± 5) 28 days	R_c (cylindrical sample) (MPa) 28 days
CEM III/A + silica fume (30 kg/m^3)	Superplasticizer (3 kg/m^3)	72	66 ± 3
CEM II/A-LL	–	79	62 ± 5
CEM IV/A (P)	–	73	63 ± 7
CEM III/A	–	80	66 ± 5
CEM IV/A HSR + silica fume (30 kg/m^3)	Superplasticizer (3 kg/m^3)	82	58 ± 7

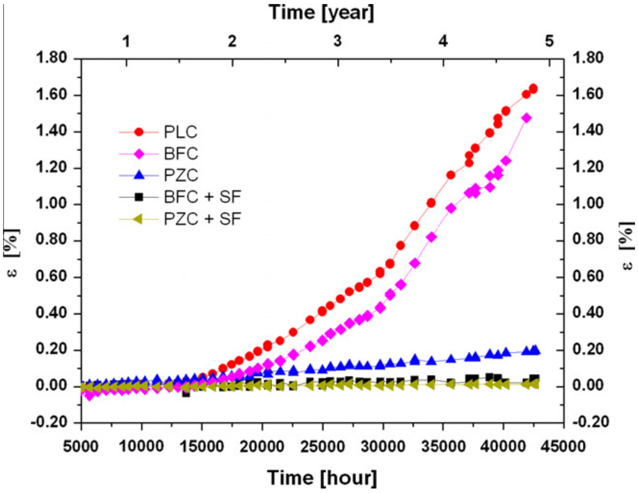

Fig. 2a. Percentage of expansion of samples under cyclic sulfate and acid attack vs. time.

acid (pH = 2) solutions at 20 °C. This test method is an attempt to approximate the real conditions in sewer pipes and the results are indicative of the concrete's long-term performance. The concretes investigated contained Portland limestone cement (PLC) or blast furnace slag cement (BFC), or sulfate-resistant pozzolanic cement, the latter two with and without silica fume, at a constant water/cement ratio (w/c 0.39).

2. Experimental

2.1. Materials

The concretes were prepared in accordance with EN standard 206 for the XA3 class with a w/c ratio $\leqslant 0.45$ and $R_{ck} \geqslant 45$ MPa. R_{ck} is the compressive characteristic resistance ($R_{ck} = R_{cm} - k\delta$, where $\delta = [\Sigma(R_{ci} - R_{cm})^2/(n-1)]^{1/2}$ and $k = 1.4$), the value for which there is a probability of 95% that each experimental strength result R_{ci} is higher than R_{ck}. Five concrete pipes were prepared with calcareous aggregate at the Eurobeton industrial plant in Salorno. The pipes were 30 cm in internal diameter and 200 cm long. Their minimum thickness was 57 mm and the maximum 100 mm (at the bottom). Their chemical composition and the concrete mix designs are detailed in Table 1. The two mixtures prepared with silica fume also contained an acrylic superplasticizer admixture. The aggregate was a crushed dolomitic limestone.

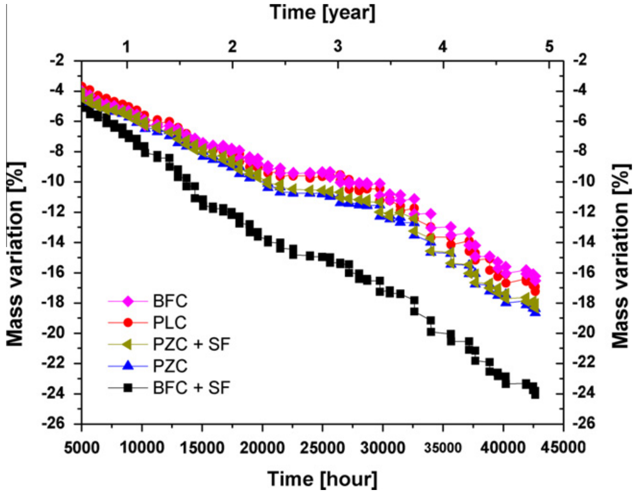

Fig. 2b. Percentage of mass loss of samples under cyclic sulfate and acid attack vs. time.

To compare the chemical resistance of different cements, PLC (CEM II/A-LL 42.5 R), BFC (CEM III/A 42.5), pozzolanic cement (CEM IV/A (P) 42.5) and pozzolanic with low aluminate content (CEM IV/HSR 42,5) were considered. As detailed in Table 1, some samples also contained silica fume (SF).

The pipes were removed from the mould after 1 day, then matured in the open air and sprinkled by water when relative humidity was below 80%. The temperature was 27 ± 5 °C. After 30 days, three sets of cylindrical samples 30 mm in diameter and 140 mm high were cored directly from the pipes. A set was used to measure the samples' compressive strength, and the results are given in Table 2. The other two sets were used for each of the two chemical tests, described in the following paragraph.

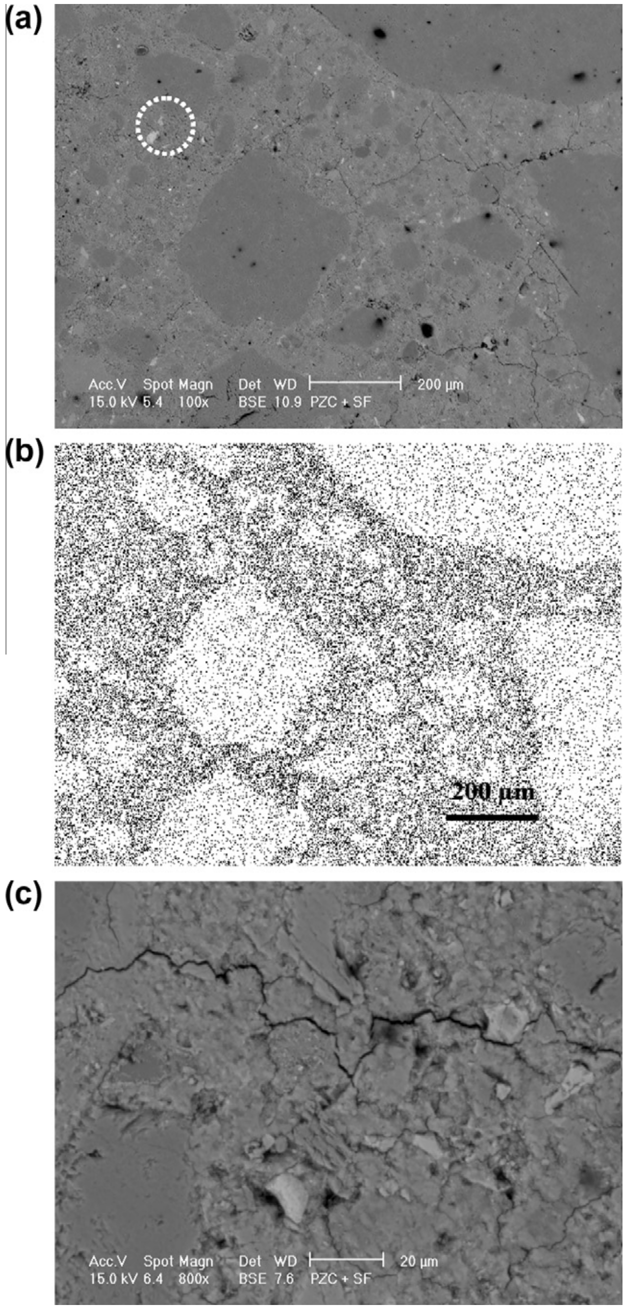

Fig. 3. SEM image (a) and X-ray maps for sulfur (dark) (b) of polished surface of concrete with pozzolanic cement and SF after about 40,000 h under cyclic sulfate and acid attack. (c) Magnification of the area in the white dotted circle in (a).

2.2. Chemical test procedures

The concrete samples' chemical resistance to the following types of attack was investigated at 20 ± 2 °C:

(a) a cyclic immersion in 2 l of sodium sulfate (Na_2SO_4) solution 50 g/l, replenished monthly, combined with one 6-h immersion a month in 2 l of sulfuric acid solution with a pH 2;
(b) continuous immersion in 2 l of sodium sulfate (Na_2SO_4) solution 50 g/l, replenished monthly.

Every month, the length and weight of each sample (after that stainless steel studs had been mounted on both ends of the specimen) were measured at about 20 °C. Their weight was recorded, after surface-drying the samples with a cloth, using a technical balance with a sensitivity of 0.001 g. Their length was measured with a digital comparator with a precision of 0.001 mm. Microstructural analyses were carried out after about 40,000 h of testing to monitor the deterioration of all the concretes involved in the cyclic test. Immediately after cutting, the surface of the slices underwent a phenolphthalein test (EN 9944). The same samples, after polishing, were examined by scanning electronic microscopy (SEM, Philips LX30) using energy-dispersive X-ray analysis (EDX).

3. Results

Fig. 1a shows the percentage expansion of the samples exposed to continuous sulfate attack alone. After a dormant period of about 20,000 h, the expansion rate suddenly increased and all the three specimens containing no SF expanded in two steps [19–21]. No such situation was seen in the two concretes containing SF. Even after about 40,000 h of testing, the expansion of the concretes containing SF is negligible. On the other hand, the control specimens exposed to a sulfate solution alone showed a constant slow increase in mass due mainly to the formation of calcium sulfate (Fig. 1b).

Fig. 2a shows the percentage of expansion of all the specimens exposed to both sulfate and acid attack. By comparison with the control specimens, the dormant period of the concretes containing no SF was much shorter, while the expansion rate and total expansion were much greater. The expansion of the concretes containing SF was much the same as in the samples not exposed to sulfuric acid.

Fig. 2b shows the mass variation with time of the specimens exposed cyclically to sulfuric acid and sulfate solutions. The slope of the experimental curves is negative: the mass loss is due to the sulfuric acid reacting with the alkaline substances in the concretes (cement paste and aggregate). Portlandite reacts with sulfuric acid forming calcium sulfate more quickly than C–S–H. The aggregate also reacts with the acid, becoming coated with calcium sulfate. It is also worth noting that the specimens proving less expansive (those containing SF) are more likely to lose mass under acid attack. This is because the SF negatively affects their acid resistance [14,16]. This is particularly true of a concrete with BFC and SF.

The core of all the specimens appeared alkaline under phenolphthalein test carried out after about 40,000 h of attack. The sample containing pozzolanic cement and SF revealed a basic reaction on the surface too: this suggests a limited effect of the sulfate and acid attack in this material, as evidenced by the negligible expansion recorded. This result is confirmed by SEM image (Fig. 3a) on

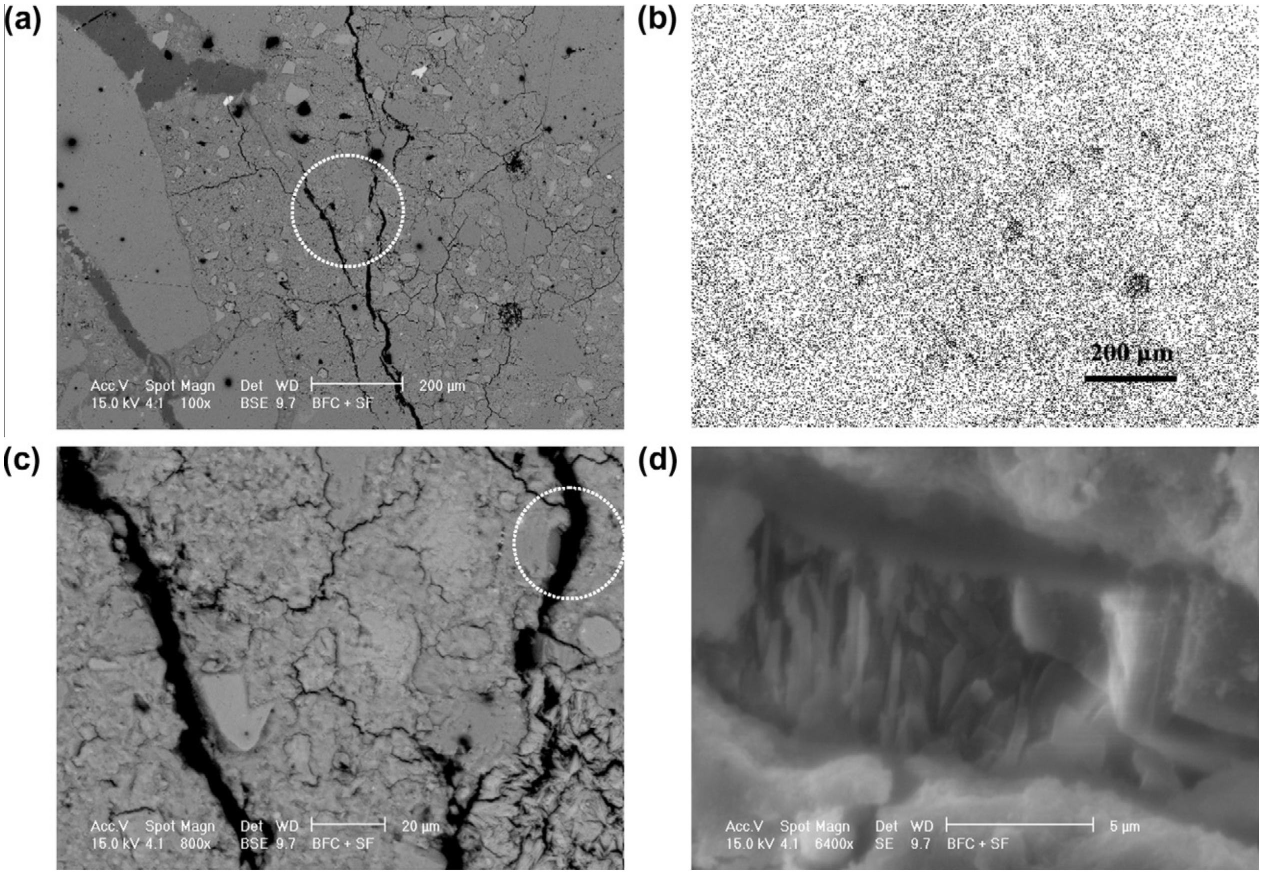

Fig. 4. SEM image (a) and X-ray maps for sulfur (dark) (b) of polished surface of concrete with BFC and SF after about 40,000 h under cyclic sulfate and acid attack. (c) Magnification of the area in the white dotted circle in (a). (d) Magnification of the interior of a crack.

this sample: the surface of the sample shows no cracks or signs of a preferential path of acid attack. Fig. 3b is the X-ray map for sulfur of the same sample, showing there are low signs of sulfur filling the voids and entrained air spaces. The magnification of the sample's edge shows that the attack has induced a general erosion of surface, whereas the interior part is dense with a few small microcracks visible (Fig. 3c) in the sample.

The microstructure of the concrete produced with BFC and SF shows, especially at higher magnification (Fig. 4a and c), features a bit different from the previous sample. Some microcracks appears and in the interior of one of the largest cracks are visible crystalline platelets (Fig. 4d). The EDX of these crystals shows mainly calcium and sulfur in atomic ratio compatible with that of gypsum.

Fig. 5a shows the cutting surface of the sample made with pozzolanic cement with no SF, which expanded more than in the two previous ones. It seems there are no cracks, but in the transition zone is clearly visible the presence of a phase different from cement paste The corresponding X-ray map for sulfur (Fig. 5b) shows that in the transition zone there is a concentration of sulfur. Fig. 5c shows a magnification of a transition zone containing columnar crystals: EDX analysis confirmed again the high sulfur content in these crystals and a atomic Ca/S comparable with that of gypsum.

The morphological pattern of the PLC concrete observed by SEM analyses consists of a disintegrated surface area around a more intact interior, where only microcracks appear. In the external area, extensive cracking was observed around aggregate and through the paste, with occasional cracking through aggregate particles. Most of the cracks were black, due to loss of material during sample cutting and polishing. Aggregate particles on the outside zone became detached, leaving empty sockets. Gaps were also macroscopically visible around some aggregate particles. Fig. 6a is a SEM image showing the extent of the damage in the core of the sample: it is visible a web of cracks in the cement paste and again the presence of sulfate in the transition zone. In Fig. 6b it can be seen that the concentration of sulfur is higher in the transition zone. Fig. 6c and d shows the transition zone, where gypsum crystallized, and the magnification of those crystals. The EDX in Fig. 6e confirms that they are gypsum. For comparison, it is worth noting that the PLC sample submitted to sulfate attack alone showed no incoherent areas in the outermost layer, but some microcracks containing flat sulfate crystals were apparent, albeit to a lesser extent than in the sample immersed in both the acid and the sulfate solutions.

The BFC concrete with no SF (Fig. 7a–c) shows morphological features similar to PLC, suggesting that the acid attacks along a preferential pathway and sulfate phases crystallize afterwards.

No visible and well definite corrosion layer was observed on the surface of the specimens through SEM observation. Moreover, crystals of sodium and calcium sulfate were observed to coat some part of the surface aggregate in the external part of PLC specimen.

4. Discussion

The three selected cement types are those typically used by manufacturers of concrete pipes and the PLC taken as a reference in this study is often even more common than ordinary Portland cement (OPC). The addition of silica fume is always assumed to increase the cement's strength and resistance to chemical attack. It is also assumed, however, that PLC concrete should benefit considerably from adding silica fume in terms of a conspicuously reduced expansion, but only when a high percentage of cement is replaced. On the other hand, the effect of adding small quantities of silica fume to concretes with BFC and pozzolanic cements is by no means certain.

Our results indicate that concretes exposed alternately to an acid and a sulfate environment exhibit two opposite types of behavior: a considerable expansion with little mass loss (pozzolanic, BFC and PLC cements without SF), or a negligible expansion with a pronounced mass loss (pozzolanic or BFC cement with SF). The deterioration caused by exposing the concrete to acid and sulfate can be discussed in relation to two mechanisms, i.e. the dissolving of its components and the expansive action of the reaction products. This study considered both aspects and confirmed that silica fume helps to prevent expansion, but fails to reduce mass loss under acid attack. Several authors have found that the use of pozzolana or silica fume can reduce the percentage mass loss of concretes exposed to dilute acids, but not when concentrated acids are involved [12,16,20,22]. Recent experiments showed that PLC concretes coated with amorphous silica using sol–gel process expand less and have a greater mass loss than their uncoated counterparts [23].

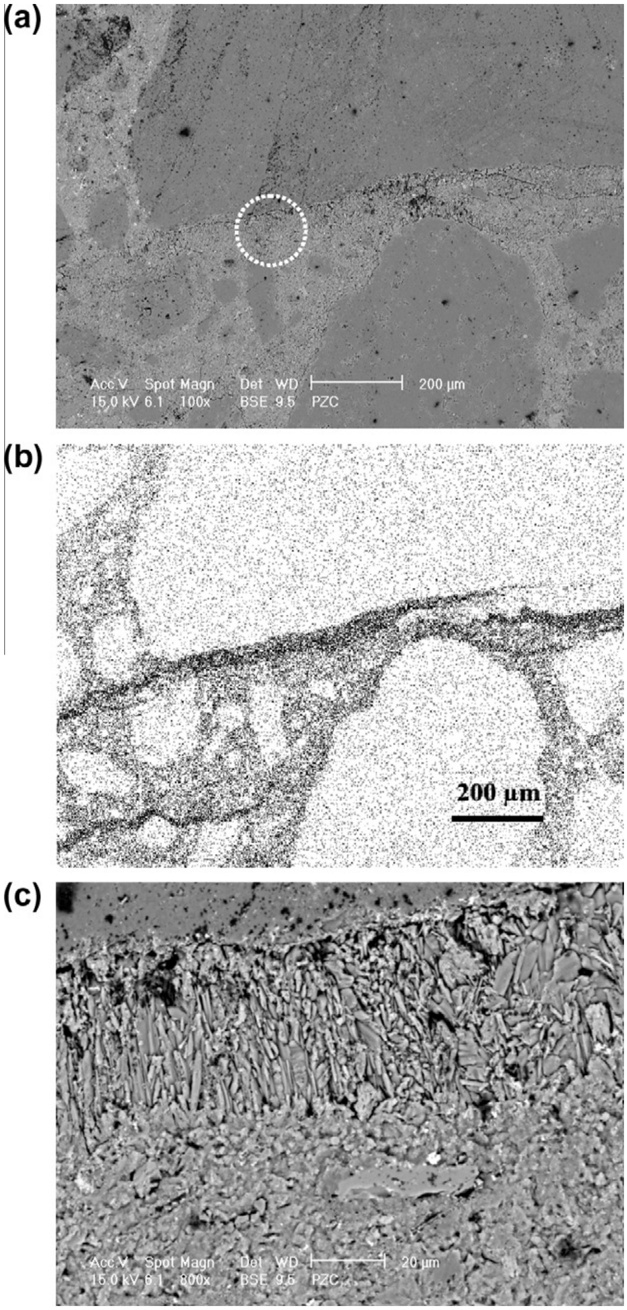

Fig. 5. SEM image (a) and X-ray maps for sulfur (dark) (b) of polished surface of concrete with pozzolanic cement after about 40,000 h under cyclic sulfate and acid attack. (c) Magnification of the area in the white dotted circle in (a).

Dissolution is due mainly to portlandite reacting with the acid [16] according the following reaction:

$$CH_{(s)} + H_2SO_{4(aq)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)} \qquad (1)$$

When concrete is attacked by sulfuric acid, porosity increases fast in the concrete, at least until the portlandite has been used up completely. The geometry and distribution of the porosity are more important than its total volume. Concrete permeability is an important parameter in degradation kinetics, which depend on the diffusion of the aggressive species. Meantime the nucleation of gypsum occurs in a pervasively way. In fact, the tinier the space where crystal growth takes place, the higher the developed stresses causing expansion. In concretes without SF, the reaction (1) promotes more expansion than mass loss. They are richer of free

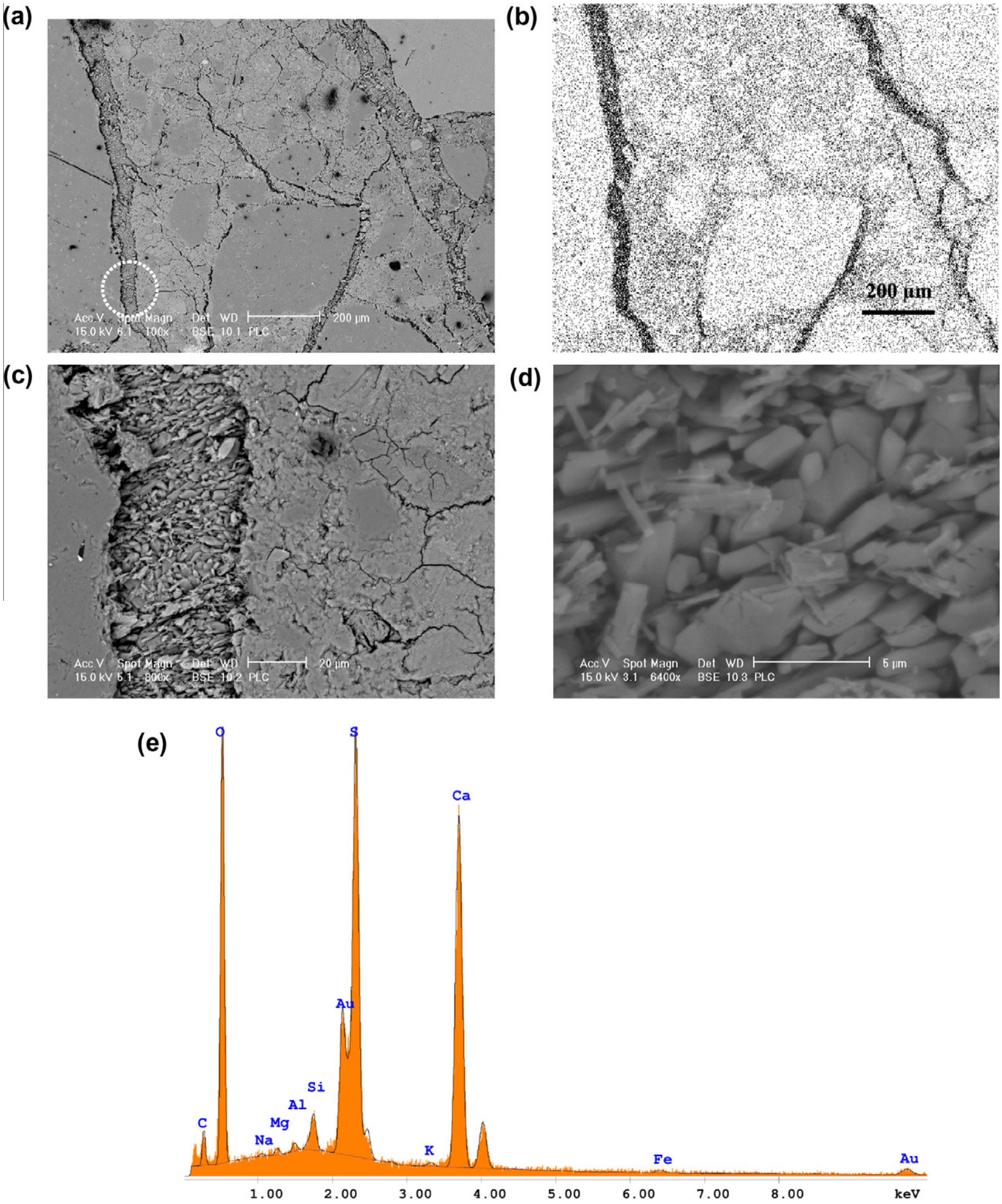

Fig. 6. SEM image (a) and X-ray maps for sulfur (dark) (b) of polished surface of concrete with PLC cement after about 40,000 h under cyclic sulfate and acid attack. Magnifications of the (c) area in the white dotted circle of (a), (d) crystals in the transition zone and (e) their EDX analysis.

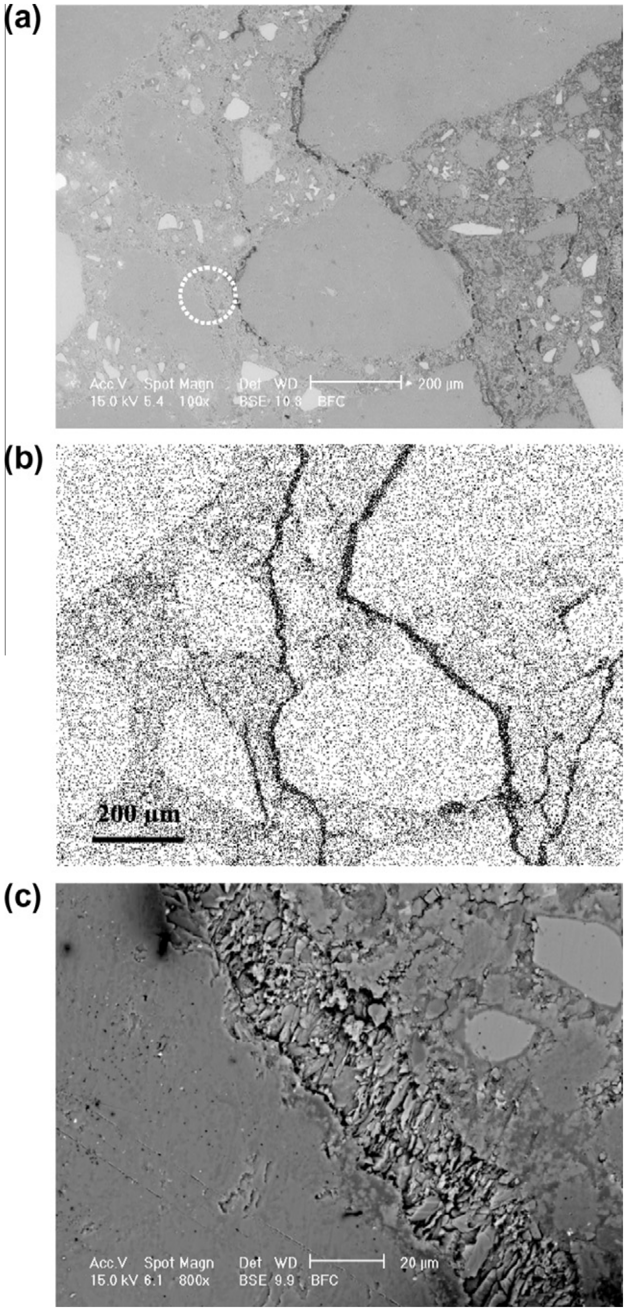

Fig. 7. SEM image (a) and X-ray maps for sulfur (dark) (b) of polished surface of concrete with BFC after about 40,000 h under cyclic sulfate and acid attack. (c) Magnification of the area in the white dotted circle in (a).

portlandite, especially in the zone transition, so that microcracks were first formed just there. In fact the largest grains of gypsum were grown around aggregate as a side effect of the pervading sulfate attack.

In concretes with SF, there is little portlandite available for reaction with the acid, because it has already reacted with the SF, producing C–S–H and reducing the cement paste's permeability at the same time. Thus, acid attack is consequently restricted to the surface and also to C–S–H in transition zone according to decalcification reaction (2).

$$C_3S_2H_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_4 \cdot 2H_2O_{(s)} + C_2S_2H_{2(s)} \tag{2}$$

The rate of mass loss from concretes with SF is not constant, but starts slowly and increases with time, confirming that reaction (2) is slower than (1). After some time, it causes the aggregate detachment from the specimen's surface. This separation contributes more than the cement paste to mass loss, due to the high percentage of aggregate in the concrete. Indeed, the surface of the concretes with SF is generally worn down, even if the acid cannot degrade the interior, which remains intact. Furthermore, the largest mass loss of BFC + SF samples is due to the reaction between sulfuric acid and the alkaline component of the slag.

As concerns expansion, a negligible expansion developed at a constant rate in the concretes containing SF, while expansion occurred in two steps in the concretes with no SF. Our results are in agreement with the findings of previous studies by Santhanam et al. on concretes submitted to sulfate attack alone [19–21].

Generally speaking, expansion may occur as a result of the formation of gypsum ($CaSO_4 \cdot 2H_2O$), which is the product of both the previously-discussed reactions under acid attack, and/or ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) [14–22,25]. Previous research suggests that gypsum formation during sulfate attack is expansive [24–27], but ettringite might form afterwards, contributing to expansion. The rate and type of deterioration also depends on the concentration of the aggressive substances: if the concentration of SO_4^{2-} is high, then gypsum will form; if it is low, ettringite will form. Our test was carried out with a strong concentration of reagents (33,800 ppm of SO_4^{2-}) and exposing a large specific area (the samples had a high area/volume ratio) [18,26], so calcium sulfate (not ettringite) is the main product, which crystallized in cracks. On the other hand, the crystals embedded in cracks revealed an atomic Ca/S ratio compatible with that of calcium sulfate, rather than ettringite.

Gypsum nucleates during the induction period in microcracks, causing expansion, first in the transition zone around aggregate and then in the cement paste. As discussed before, the consequence of the attack is subsequently the growth of the sulfate phase in the cracks, shaped like columns (or plates in the smallest cracks). In concretes without SF, cyclic immersion in a sulfuric acid solution had the effect of carrying the attack even in the core, so the gypsum formed deeper in the sample. The end result was a shorter dormant period being needed before expansion became macroscopic.

In concretes with SF, neither gypsum nor ettringite could form to any great extent in the internal cement paste because of the absence of free portlandite and because it was more difficult for the attack to penetrate. The time it takes to induce nucleating crystals capable of causing expansion is consequently too long in the conditions chosen for this study. Indeed, the expansion of concretes containing SF was negligible and much the same when samples were immersed in sulfuric acid and sodium sulfate solutions, or in sodium sulfate alone.

To predict the life expectancy of concrete sewer pipes, even a phenomenological tool could be important for comparing the resistance and behavior of different concrete mixtures in cyclic contact with sulfuric acid and sodium sulfate. Although it cannot predict the concrete's absolute life in quantitative terms, the results of our cyclic test enable the concrete's behavior and reduction in thickness to be assessed more quickly and more reliably than tests based on sulfate attack alone. When the temperature and concentration of the aggressive agent are increased, the rate of deterioration is reportedly greater [14,21,24,28]. Our test could be improved, for example, by using an acid attack once a week. For sewage applications, on the other hand, it may be of more interest to study the concrete's behavior at temperatures lower than room temperature [28]. Although the damage of concrete is generally attributed to "sulfate attack", actually sulfate can come from different sources and cations, as magnesium or ammonium, can intensify the attack [4,29]. Thus the reliability of an accelerated test in this field would be bound to benefit from using a more complex solution, prepared by mixing different salts.

5. Conclusions

We studied the deterioration of five concretes with different compositions exposed cyclically to a solution of sodium sulfate (50 g/l) and also to a solution of H_2SO_4 with a pH 2 for 6 h once a month. The extent of the damage caused was evaluated by measuring mass loss and expansion. The results, charted for about 5 years, enabled the following conclusions to be drawn.

On the whole, the concretes containing SF were less expansive, but they lost mass at a faster rate than those without SF. BFC and pozzolanic concretes containing SF expanded the least. The concrete containing BFC and SF revealed a negligible expansion, but a considerable mass loss. Finally, the greatest expansion and most severe damage were recorded in pozzolanic, BFC and PLC cements without SF. After an induction period of about 10,000 h, it was observed in the three concretes without SF a sudden increase in the expansion rate and the whole expansion process is decoupled in two stages, the first at lower expansion rate than the second one.

SEM and EDX analyses indicated that concretes with SF contained very a few microcracks, some of them enclosing microcrystalline gypsum. Those without SF (especially PLC and BFC concretes) were severely damaged on the surface and in the interior: cracks formed and became filled with gypsum around the aggregate particles and where the damage was particularly severe, within the cement paste and through the aggregate particles.

The method developed in this study proved very useful in comparing the resistance and behavior of different concrete mixtures alternately in contact with sulfuric acid and sodium sulfate. To classify the suitability of different mixtures in terms of the long-term durability of concrete sewer pipes, we considered both the disruption caused by sulfate expansion and the reduction in thickness in sulfuric acid due to mass loss. The latter is at least as important as the former for the purposes of long-term durability. Since we proved that mixtures less expansive lose mass at faster rate, design should pay attention to use a mixture suitable for containing expansion combined with an oversizing of the initial pipe thickness. The mixtures could be classified in order of increasing sulfate resistance as follows: mixtures with PLC, mixtures with BFC, mixtures with pozzolanic cement, mixtures with BFC plus SF, and mixtures with pozzolanic cement plus SF.

For the purposes of comparison, the behavior of the concretes left permanently in a sodium sulfate solution was also studied. Of course, no mass loss was recorded in this case, while there was a slow, continuous increase in weight due to the effect of calcium sulfate salt deposition. The classification of the five concrete samples' sulfate resistance remained the same, although the concretes without SF expanded much less than in the cyclic test including immersion in acid. The typical cracks filled with columnar crystals of gypsum were only detectable in BFC and PLC concretes at very high SEM magnification. The induction period was also longer than in the cyclically-tested samples, i.e. the differences in the five concretes' expansion behavior took almost 40,000 h to appear clearly after immersion in sulfate solution alone, whereas they took only 20,000 h when the samples were also submitted to cyclic immersion in sulfuric acid. The cyclic test adopted for this study can consequently be considered as a model of accelerated deterioration.

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