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Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete

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ABSTRACT

In situ failure of laboratory tested coatings against biogenic sulfuric acid (BSA) corrosion of concrete in sewers has lead to new approaches that affect microbial activity. This paper reports on the performance of concrete surfaces containing antimicrobial polymer fibers or metal-zeolites in preventing BSA corrosion. Additionally, the effectiveness of commercial surface treatments and admixtures was measured by means of accelerated chemical exposure and microbiological simulation tests. The biocidal effect of antimicrobial additives was quantified by means of incubation tests on mortar specimens. The presence of antimicrobial compounds resulted in a 3–12-fold decrease of the bacterial activity, as observed from ATP measurements. The largest deterioration from the accelerated tests was noticed for a cementitious coating. The antimicrobial and silicates admixtures did not result in a protective effect towards degradation under the given test conditions. The best protection was obtained with a polyurea lining and an epoxy coating. No loss of coating integrity could be observed after 8 and 10 cycles of microbiological and chemical testing, respectively.

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1. Introduction

Worldwide, municipal wastewater systems are facing biogenic sulfuric acid (BSA) corrosion of concrete. This corrosion severely compromises the integrity of the infrastructure, necessating costly repair and premature replacement of failed structures. In Flanders (Belgium), biogenic corrosion represents a cost of about 10% of the total sewage treatment expenditures [1].

BSA corrosion is a result of the sulfur cycle that occurs in sewer networks. Under anaerobic conditions, sulfate reducing bacteria (SRB) produce hydrogen sulfide (H_2S) from sulfur compounds present in the sewage. Upon emission to the sewer atmosphere, H_2S is converted under aerobic conditions to sulfur chemically, and subsequently, to sulfuric acid microbiologically. This occurs by a succession of different sulfur oxidizing bacteria (SOB), such as thiobacilli, present on the surface. The reaction of the sulfuric acid with the concrete results in the formation of expansive products such as gypsum and ettringite. This results in cracking, material loss and eventually a loss of structural integrity [2–6].

Several methods have been developed to control BSA corrosion in sewer systems, targeting different links in the corrosion chain; Type (1): Application of chemical or biological technologies that decrease the amount of hydrogen sulfide emission [7]; Type (2): Application of admixtures [8,9], protective coatings [10–13] or acid-resistant cement [14] that prevent the chemical attack of concrete; Type (3): Usage of antimicrobial coatings [15–17] or admixtures that decrease or eliminate microbial activity. The latter have also been explored for the inhibition of algal [18] and fungal growth [19] .

While antimicrobial surfaces have already been introduced in a variety of sectors, such as medicine and dentistry and the food industry [20], antimicrobial concrete for the prevention of BSA corrosion is a relatively new research area. Yamanaka et al. [21] obtained some inhibition of microbial activity when cultures of *Thiobacillus* were exposed to concrete with addition of calcium formate in the mixture. Shook and Bell [22] reported on the effectiveness of a water-stabilized silicone quaternary ammonium salt (Conshield®), added to a concrete admixture to inhibit the growth of thiobacilli. Furthermore, an antimicrobial concrete consisting of fibers treated with biocides (Fibermesh fibers containing the Microban B additive) was developed for the improvement of hygienic conditions of concrete built agricultural premises [23]. While this fiber concrete is reported to be very effective in inhibiting the growth of fungi as well as bacteria, such as *Escherichia coli* and also *Staphylococcus aureus*, no reports are available on the inhibition of SOB.

In the last two decades, several investigations have been carried out concerning the use of zeolites supporting bactericidal metal ions, such as silver and copper ions [24]. The durability of the

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activity of the antimicrobial compounds and the low toxicity for humans have resulted in an extensive use of these antimicrobial ceramics in a wide range of areas [25,26]. Recently, an antimicrobial concrete containing zeolites with silver and copper ions (Zeomighty manufactured by Shinanen Zeomic Co, Japan) was introduced on the Japanese market. According to the tests performed by the manufacturer, a concentration of metal zeolites of 1% to cement weight is optimal for the inhibition of the growth of thiobacilli (http://www.zeomic.co.jp/english/05_01_zeomighty.html) [27].

Over the years, a wide range of laboratory tests has been developed for the evaluation of Types (2) and (3) methods (see introduction section for explanation) against BSA corrosion [28,29] (a detailed overview of these tests can be found in [28]). Schmidt et al. [30], however, showed that a high resistance to sulfuric acid in chemical tests does not always implicate a high resistance against BSA corrosion.

In this research, two types of antimicrobial concrete based on polymer fibers or metal zeolites were tested regarding their efficiency to prevent BSA corrosion in sewers. In addition, the effectiveness of a number of commercially available admixtures and surface treatments against sulfuric acid corrosion was measured. The choice of these treatments was guided by the ease of application in practice. Attention was given to treatments that could be applied during or immediately after production of the pipes in the factory.

The protective effect was investigated by means of chemical and microbiological tests developed at our lab. Furthermore, a test was developed to quantify the inhibition of bacteria as a result of the presence of antimicrobial compounds.

2. Materials and methods

2.1. Mortar specimens

Three series of mortar mixtures were produced: one reference mixture (RM) and two antimicrobial mixtures. The reference mixture had the following composition: 450 g CEM I 52.5 N, 1350 g sand and 292.5 g water (w/c 0.65). Antimicrobial mixtures had the same composition as the reference mixture with exception of the addition of copper/silver zeolites (ZM) (1 weight% on cement base; zeolites contain 3.5% silver and 6.5% copper) or antimicrobial fibers (FM) (1000 g/m^3). Standardized mortar prisms ($40 \times 40 \times 160$ mm^3), prepared according European Standard EN 196-1, were cured for 28 days under humid atmosphere (95% R.H., 20 °C) and afterwards cut into prisms with dimensions $40 \times 20 \times 0.8$ mm^3. As the surface pH of fresh mortar specimens was too high (12–13) to allow bacterial growth, specimens were subjected to 3 weeks of accelerated carbonation (70% R.H., 10% CO_2, 20 °C). After this period, the specimens were placed in demineralised water for 2 weeks. The resulting surface pH was measured with pH indicator strips and amounted to about nine. Tests were performed on a moulded surface.

2.2. Concrete specimens

The specimens for the chemical and microbiological tests had the following dimensions (height (H) and diameter (D) in mm): $H = 75$, $D = 220$ and $H = 15$, $D = 80$, respectively.

The first test series consisted of concrete with commercially available admixtures and coatings. For these series, specimens were obtained from a Belgian pipe manufacturer (composition see Table 1). Cores were drilled perpendicular to the inner surface of the pipe. From these cores, a slice was cut off near the inner surface of the pipe. Subsequently, the flat surfaces were polished. The different sets were designated with the following codes: sewer pipe reference concrete (SP RC), concrete with hydrous silicate admixture (SAC), epoxy coating (EC), polyurea lining (PUL) and a cementitious coating (CC). The properties of the different products are given in Table 2. Coatings were applied by the pipe manufacturer in accordance with the technical data instructions. Coatings were applied on the curved side of the cylinders (Fig. 1). The specimens of the CC series, however, consisted entirely of the coating itself. In order to prevent side-effects from the ingression of sulfuric acid beneath the curved outer surface via adjacent sides, these polished sides were also coated with the EC (Fig. 1). Both chemical and microbiological tests were performed on these series.

The second test series consisted of concrete with antimicrobial components. For these series, specimens were prepared in the laboratory. The different sets were designated with the following codes: laboratory reference concrete (L RC), concrete with antimicrobial fibers (FC) and concrete with antimicrobial zeolites (ZC). The concrete mixtures were cast into 150 mm compressive strength cubes and stored at 90% R.H. and 20 °C for 28 days (demolded after 24 h). Compressive strength was determined on three specimens per composition at an age of 28 days, according the Belgian standard NBN B15-220. The composition and compressive strength of these specimens are presented in Table 1. Only the microbiological tests were performed on these series.

2.3. Incubation on mortar coupons

Suspensions of SOB [31] were placed on the surface of mortar specimens and incubated for 24 h for the quantification of the biocidal effect of antimicrobial mortar mixtures.

Prior to the experiments, mortar specimens were sanitized by means of rinsing with ethanol (70%) and subsequent drying in an oven at 80 °C for 15 min. Next, after cooling in a laminar flow, specimens were completely immersed for 10 min in Petri dishes containing sterile demineralized water. Subsequently, for each mixture, four moist mortar specimens were placed in a closed Petri dish (15 cm diameter). The specimens were allowed to equilibrate

Table 1
Composition and 28-days compressive strength of the laboratory concrete mixtures.

Code	Components	Quantity (kg/m^3)	Compressive strength (MPa)
RC[a]	CEM I 52.5 HSR LA R	350	63.18 ± 0.20
	Water	130	
	Fine aggregate	811	
	Coarse aggregate (Porphyry)	1137	
FC	RC		60.48 ± 1.11
	+Antimicrobial fibers	0.9	
ZC	RC		58.26 ± 0.30
	+Antimicrobial Ag^+/Cu^+ zeolites	3.5	

[a] Composition according to pipe manufacturer. (RC = reference concrete, FC = concrete with antimicrobial fibers, ZC = concrete with antimicrobial zeolites; HSR = high sulphate resistant cement).

Table 2
Properties of the commercially available treatments provided by the manufacturer.

Product	Composition	Density (kg/dm^3)	Hardness (shore)	Thickness (mm)	Application condition
Polyurea lining	2 component epoxy primer	–	–	0.350	Airless spray system
	2 component polyurea	–	92 (A)[a] 46 (D)[a]	1.5–2.5	Hot spray system Can be applied after demolding (primer necessary)
Epoxy coating	Solvent free epoxy resins, polyamine derivates as curing compounds	–	74 (D)[b]	0.400	–Can be applied after demolding (no primer necessary) –Hot spray system
Cementitious coating	Portland cement with organic and inorganic additives	2.1	–	3	Can be applied after demolding
Silicate admixture	Complex catalyzed hydrous silicate solution	–	–	–	0.75% on cement weight

[a] Hardness according ASTM D 1474.
[b] Hardness according DIN 53505; all the above information was provided by the different manufacturers and suppliers.

for 5 min in the closed Petri dish. As such, the moisture was homogeneously distributed with no visible water drops remaining on the surface. Then, 100 μL of nutrient medium (10 g/L $Na_2S_2O_3{\cdot}5H_2O$, 3 g/L KH_2PO_4, 0.1 g/L NH_4Cl, 0.1 g/L $MgCl{\cdot}6H_2O$ and 0.14 g/L $CaCl{\cdot}2H_2O$) was homogenously distributed over the surface of each specimen with a pipet to promote bacterial growth and biofilm formation. After 15 min, the lid of the Petri dish was opened for a period of 10 min, to allow superficial drying of the surface. Finally, 100 μL of an active SOB culture (7.22×10^8 cells/mL) was distributed over the surface with a pipet. The bacterial culture was obtained after centrifugation (10 min, 3000 g) of 50 mL of 2 weeks old mixed cultures of SOB [31], washing and suspension of the pellet in 50 mL of fresh nutrient medium. This was done to prevent possible adverse effects of the low pH and high concentration of sulfate ions in the original suspension on the biocidal activity of the mortars.

Immediately after the application of the microorganisms, the Petri dish was closed, removed from the laminar flow and stored under laboratory conditions (20 ± 3 °C). In order to prevent rapid drying of the specimens, a small Petri dish containing sterile demineralised water was placed together with the specimens in the larger Petri dish. Furthermore, the Petri dish was sealed at the sides with Parafilm M (Parafilm, USA).

After a period of 24 h, the surface of each specimen was sampled with a sterile cotton swab stick (biolab Zrt., Romania). The swab stick was moistened with sterile physiological solution (8.5 g/L sodium chloride). After sampling, the stick was placed in a glass tube containing 9 mL sterile physiological solution. Subsequently, the glass tube was vortexed (Labinco BV, Breda, Netherlands) for a period of 30 s. Finally, the adenosine triphosphate (ATP) content of the solution was determined with the aid of the BacTiter-Glo Microbial Cell viability assay (Promega, USA) and a Lumac Biocounter M2500 (Lumac, The Netherlands).

Before the start of the assay, an experiment was performed in order to obtain a correlation between the amount of ATP and the number of cells present in solution. The number of cells was quantified by means of a CyAn™ High Performance Flow cytometer (Dakocytomation, Belgium). A volume of 10 μL of bacteria was added to 10 μL of beads (SpectraComp™, Dako, Belgium), 500 μL of phosphate buffered saline and 480 μL of Syto® Live/Dead stain (Molecular Probes, USA).

2.4. Large scale test program

All measurements were performed in triplicate. Figures and tables present the average and standard errors (if indicated).

2.4.1. UV-degradation

Before the start of the chemical and microbiological tests, concrete specimens treated with a coating (EC, PUL and CC) were exposed during 31 days to UV-light, to simulate outdoor exposure to sunlight during storage of the sewer pipes. The specimens were mounted on the apparatus for the chemical tests (see Section 2.4.2). Sylvania G30 lamps were placed 50 cm above the concrete

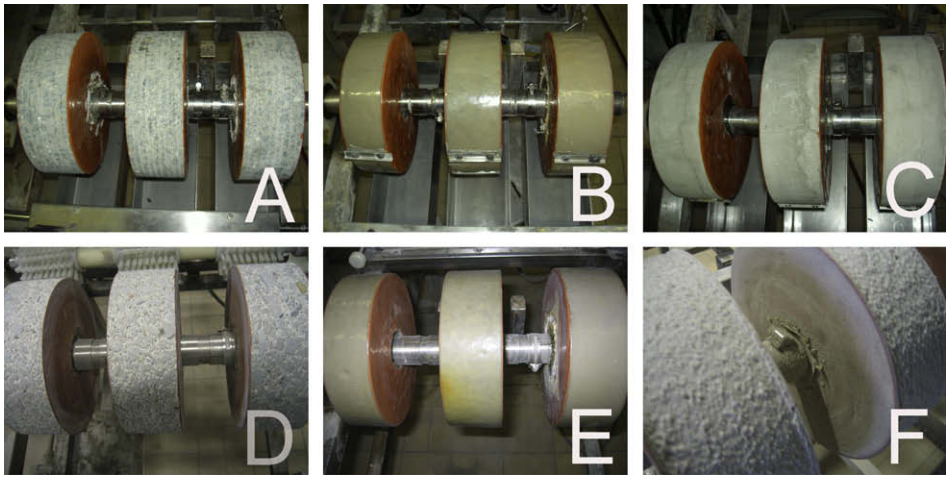

Fig. 1. Overview of the visual aspect of the sewer pipe reference concrete (A) and (D), polyurea lining (B) and (E) and cementitious coating (C) and (F) cylinders mounted on the TAD apparatus, before (A)–(C) and after (D)–(F) 10 cycles of chemical exposure tests. Notice the change in surface roughness for the cementitious coating. See Image D for the position of the brushes.

Table 3
Inhibition of sulfur oxidizing bacteria (SOB) in the biofilm tests after a 24 h contact time with the antimicrobial mortar specimens. The ATP content is a measure of the total bacterial activity.

Series	ATP content (pmol)[a]
RM	1.45 ± 0.32
ZM	0.12 ± 0.03
FM	0.43 ± 0.07

[a] The ATP content of the inoculum amounted to 1.50 pmol.

specimens. The rotation speed of the cylinders on the testing apparatus amounted to 1.04 rotations per hour.

2.4.2. Chemical exposure tests

The chemical tests were performed on the Testing apparatus for Accelerated Degradation testing (TAD) developed at the Magnel Laboratory for Concrete Research of Ghent University [32]. Three cylinders of each series were subjected to 10 cycles consisting of an alternated immersion (1.04 rotations per hour) in a 0.5% sulfuric acid solution, followed by drying by air and brushing at the end of each cycle, simulating the events occurring in sewer systems (see [32] for a more detailed description). During the 7 days immersion period, in which the specimens were submerged for one third of the time, the pH of the sulfuric acid solution was measured daily. The corrosion of the specimens was measured using distance measurements with laser sensors. Measurements were made before and after brushing to separate the purely chemical (mainly expansion) and mechanical (material loss) effects. Brushing was performed by means of rotary brushes (394 rpm) that were mounted on the TAD apparatus after each immersion period. The brushes were positioned in such a way that they made contact with the outer surface of the concrete cylinder (Fig. 1). Upon complete rotation of the cylinders (one time forward and one time backward), a uniform removal of loose particles was obtained. The average change of the radius is presented as the average of 12 profiles (three cylinders × four profiles per cylinder). From these profiles, the surface roughness was calculated by means of the R_a value (based on the ISO 4287 norm), for which a reference length of 50 mm was taken.

2.4.3. Microbiological simulation tests

The resistance of the different treatments towards biogenic sulfuric acid corrosion was measured by a test procedure developed at the Laboratory of Microbial Ecology and Technology of Ghent University [31,33]. Two series of tests were performed separated in time. The first (sewer pipe RC, CC, EC, PUL and WGC) and second (laboratory RC, FC and ZC) test series consisted of eight and four cycles, respectively, of accelerated testing. Each cycle consists of four steps: (1) H_2S-incubation in a vessel containing about 200 ppm H_2S for 2 days; (2) submersion in a vessel containing 1.5 L of mixed cultures of SOB obtained from a sewer pipe biofilm [31] (medium composition: 10 g/L elemental sulfur, 3 g/L KH_2PO_4, 0.1 /L NH_4Cl, 0.1 g/L $MgCl{\cdot}6H_2O$ and 0.14 g/L $CaCl{\cdot}2H_2O$) for 10 days; (3) submersion in a vessel containing distilled water for 2 days and (4) drying at room temperature for 1 day. The vessels in the second and third step were placed on a rotary shaker at 90 rpm. During the second step of every cycle, the pH was measured at a regular basis. The corrosion of the specimens was measured using the automated laser measurement system (ALM). This system consists of a laser sensor that is mounted on a table and is able to move in a horizontal plane by means of two computer-driven stepping motors. Measurement of the distance from the sensor to the specimen that is placed on the table is based upon optical triangulation. The change of the thickness is presented as the average thickness of three specimens (seven profiles per specimen; the distance between each profile amounted to 1 cm). The weight loss was determined by weighing the samples after drying in an oven at 45 °C until a constant weight was achieved (a weight change of less than 0.1% between two measurements at 24 h intervals), before and after the test procedure.

2.4.4. Bonding strength

The bonding strength (NBN-EN 1542) of the PUL and EC coatings was determined after eight cycles of microbiological tests. Reference samples (not subjected to any chemical or microbiological tests) were only available for the EC. For this test, cores with 50 mm diameter were drilled out of the cylindrical specimens. Metal fixtures were glued on top (coatings) and bottom (concrete) of these cores using rapid setting epoxy. The cores were subjected afterwards to a tensile load using an Amsler hydraulic testing machine.

3. Results and discussion

3.1. Incubation test

The addition of antimicrobial compounds in the mortar mixture resulted in a significant decrease of the bacterial activity, as observed from ATP measurements (Table 3). While the inhibition was limited in case of the antimicrobial fibers, a 12-fold decrease of ATP content was obtained after 24 h for the mortar specimens with antimicrobial zeolites. ATP is used as primary energy currency for all bacteria, which makes it very suitable for the quantification of active biomass [34]. ATP measurements were used in this research to obtain a rapid indication of the biocidal activity, as they only require 5 min, whereas determination of cell survival of *Thiobacillus* by plate counting requires 7 days. However, as the presence of free ATP from dead cells might give an overestimation of the active biomass [35], in future experiments, the actual decrease in cell numbers will be additionally determined by means of plate counting.

3.2. Chemical exposure tests

3.2.1. Change in pH

The evolution of the pH in the sulfuric acid solutions of the different treatments versus the number of cycles is given in Fig. 2. The CC was the only treatment that showed significant different final pH values (2.10–3.29) compared to the RC (0.99–1.10) for

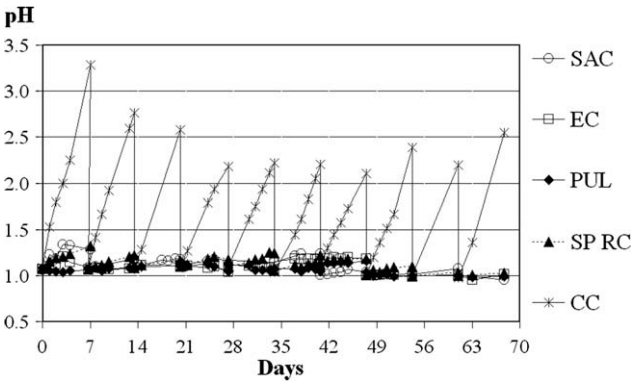

Fig. 2. Evolution of the pH of the sulfuric acid solutions in which the different specimens were submerged during the chemical test cycles. As a result of the neutralization of the acid by dissolution of the cement matrix, a large increase in pH was noticed for the cementitious coating (CC). See Table 4 for explanation of the codes.

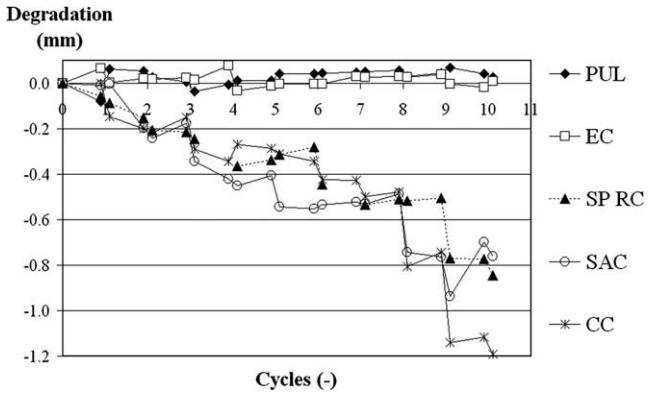

Fig. 3. Evolution of the radius of the concrete specimens from the different treatments versus the number of chemical test cycles. Negative values indicate a loss of material. See Table 4 for explanation of the codes.

all the test cycles. In the case of the CC treatment, a large increase of the pH was noticed. This is attributed to the neutralization of the acid by the dissolution of the cementitious coating. The limited increase of the pH of the RC and WGC is a result of the use of inert aggregates and High Sulphate Resistance (HSR) cement.

3.2.2. Change in radius of the concrete cylinders

The average change of the radius of the cylinders in function of the number of cycles is given in Fig. 3. The alternating increase and decrease of the radius corresponds to the expansion of the concrete as a result of product formation (mainly gypsum, since HSR cement was used) during immersion and subsequent material loss due to brushing. A decrease of the radius during the immersion period can be attributed to the loss of adhesion from the expanded parts [33]. The largest decrease in radius was noticed for the CC. For this treatment, a degradation depth of 1.2 mm was observed after 10 cycles of the chemical test. The WGC showed a similar material loss as the RC. As a result of their chemical resistance, no significant changes could be observed for the EC and PUL. Changes in the visual appearance of the concrete cylinders due to the chemical exposure tests can be seen in Fig. 1.

3.2.3. Change in surface roughness of the concrete cylinders

The evolution of the surface roughness of the concrete cylinders as a function of the number of cycles is shown in Fig. 4. The two values per cycle represent the measurements before and after brushing. While the differences in initial R_a values were rather small, large differences could be noticed after 10 cycles. The EC and PUL were the only treatments where no change of the surface roughness could be observed. The differences in degradation pattern between the CC treatment and the RC and WGC can be attributed to the presence of inert porphyry aggregates. The removal of cement paste, in-between these relatively large aggregates of the RC and WGC, resulted in increased R_a values. The CC treatment contains, however, only small sand aggregates and shows, therefore, a small change in R_a values.

3.3. Microbiological simulation tests

3.3.1. Change in pH

The evolution of the pH during the second step of each cycle is shown in Figs. 5 and 6 for the first and second tests series, respectively. As a result of the conversion of elemental sulfur to sulfuric acid by cultures of SOB, a decrease of the pH could be observed 3–4 days after inoculation. The pH continued to decrease to a value around one (Fig. 5) or two (Fig. 6) after 10 days of testing.

Contrary to the chemical tests, for which a different pH pattern was obtained for the cementitious coating compared to the other treatments, no global differences could be seen in the evolution of the pH of the microbial solutions for the different treatments of the first series. This could be attributed to the fact that the rate and extent of the biogenic sulfuric acid production (proton production) was much higher than the rate and extent of the dissolution of the cement matrix (proton consumption). The relatively limited consumption of protons due to the dissolution of the cement matrix could be further explained by the fact that only a limited area of concrete was exposed to the solution in comparison with the chemical tests. The observed differences in final pH values between the two series are probably a result of the variance in microbial activity of different inoculum cultures (experiments were performed separated in time). From Fig. 6 it is clear that the presence of antimicrobial compounds in the concrete mixture did not result in a decrease of the bacterial activity, as no differences could be observed between the pH of the solutions in which control or antimicrobial concrete specimens had been immersed. A decrease of bacterial activity would have resulted in a decreased sulfuric acid production, and hence, higher pH values of the solution in which the specimens were immersed.

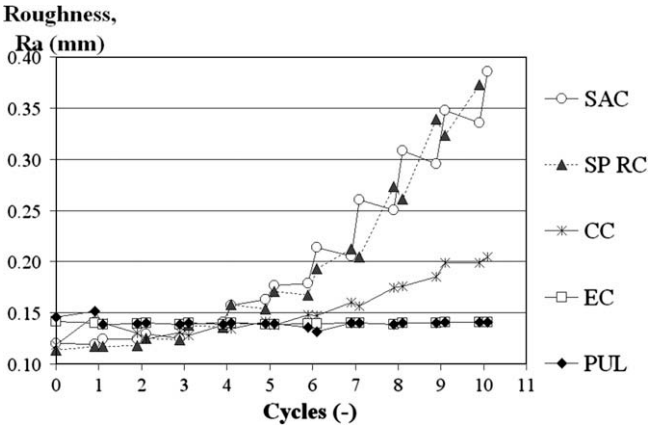

Fig. 4. Evolution of the surface roughness of the concrete specimens from the different treatments versus the number of chemical test cycles. The removal of cement paste in-between the large aggregates of the silicate admixture concrete (SAC) and sewer pipe reference concrete (SP RC) resulted in a large increase of roughness. See Table 4 for explanation of the codes.

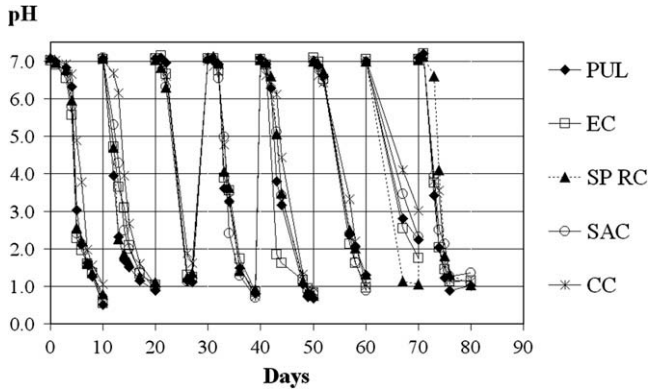

Fig. 5. Evolution of the pH of the bacterial solutions in which the specimens from the first microbiological test series were submerged. The pH decreased as a result of the conversion of elemental sulfur to sulfuric acid. See Table 4 for explanation of the codes.

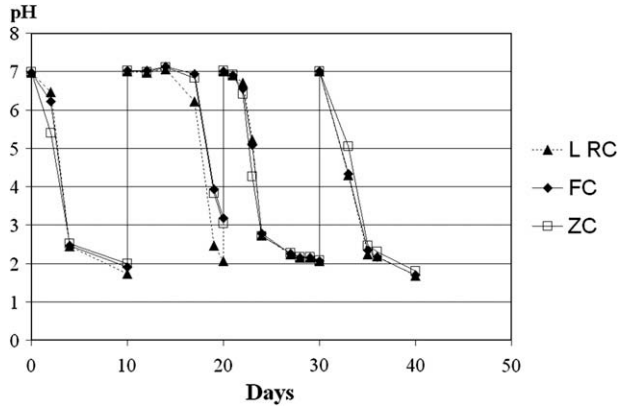

Fig. 6. Evolution of the pH of the bacterial solutions in which the specimens from the second microbiological test series were submerged. The addition of antimicrobial compounds did not result in a decrease of the biogenic sulfuric acid production. See Table 4 for explanation of the codes.

3.3.2. Change in thickness of the concrete cylinders

The change in thickness versus the number of cycles for the first test series is presented in Fig. 7. When chemical (Fig. 3) and microbiological (Fig. 7) test methods are compared, the following can be noticed: (1) Each treatment showed a similar pattern of effectiveness in the two tests: the best protection was obtained with the EC and PUL, followed by the WGC and RC, which showed a similar resistance towards corrosion, while the largest loss of material was noticed for the CC; (2) The microbiological tests were more aggressive to concrete: in the case of the CC, the chemical tests resulted in a maximum degradation depth of 1.2 mm after 10 cycles of 7 days in acid solution, while the microbiological tests resulted in a maximum degradation depth of 4 mm after four cycles of 10 days in a biological suspension. The faster degradation in the microbiological test procedure can be partially attributed to the continuous shaking of the samples, resulting in an immediate removal of material [33]. The latter is also responsible for the observed differences in magnitude of degradation between the CC and other tests series among the microbiological and chemical tests. While shaking in the microbiological tests resulted in both the removal of small aggregates and cement paste of the CC, degradation of the cement paste of the SP RC and L RC and WGC series was not sufficient for the removal of the large aggregates. On the other hand, removal of material in the chemical test series occurred mainly as a result of the mechanical action of the brushes on the expanded layer at the end of each cycle. The formation of gypsum and other expansive products might have limited the penetration of sulfuric acid in the underlying layers, thus limiting the size of the corroded zone. As a result, the difference in magnitude of degradation between the CC and other series in the chemical tests was much less pronounced compared to the microbiological tests.

Fig. 8 presents the change in thickness versus the number of cycles for the antimicrobial concrete test series. The presence of antimicrobial admixtures did not result in an improved resistance towards corrosion under the given test conditions. From Figs. 3 and 7 it can be noticed that the decrease in thickness was very limited for the antimicrobial test series compared to the first test series. A decrease of 0.25 and 0.67 mm was noticed for the laboratory RC (Fig. 8) and SP RC (Fig. 7), respectively, after four cycles of microbiological tests. This might be attributed to differences in microbial activity between the two test series, as could be noticed from the pH measurements (Figs. 5 and 6). Furthermore, the curing regime might have played some role in the limited material loss of the second test series [33]. The L RC underwent carefully controlled curing (28 days at >90% R.H.) while the SP RC from the first test series was obtained from commercially produced sewer pipes.

3.3.3. Weight loss

The weight loss (Table 4) confirms the findings from the pH evolution and the thickness measurements. The largest amount of weight loss was observed for the CC. The WGC and SP RC showed lower and similar weight losses, while the EC and PUL remained relatively unaffected. The L RC from the antimicrobial test series had a weight loss of about half of the SP RC from the first test series. This is somewhat in contrast with the observed changes in thickness, for which the loss of material of the L RC was about one sixth of that of the SP RC. The latter could be attributed to the fact that the sides of the laboratory specimens were not coated, and thus were exposed to the sulfuric acid. No differences in weight loss could be observed between the L RC and the series with antimicrobial compounds.

From the visual observations (Fig. 9), it can be seen that the weight loss of the SAC is mainly attributable to the attack of the cement paste. The degradation of the latter after eight cycles (first test series) was not sufficient for the larger aggregates to be detached. Similar observations were made for the SP RC, L RC, ZC and FC.

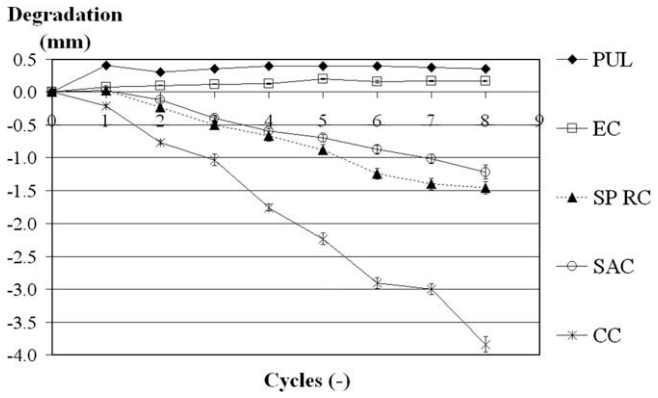

Fig. 7. Evolution of the thickness of the concrete specimens from the first series of treatments versus the number of microbiological test cycles. The largest deterioration was obtained with the cementitious coating. See Table 4 for explanation of the codes.

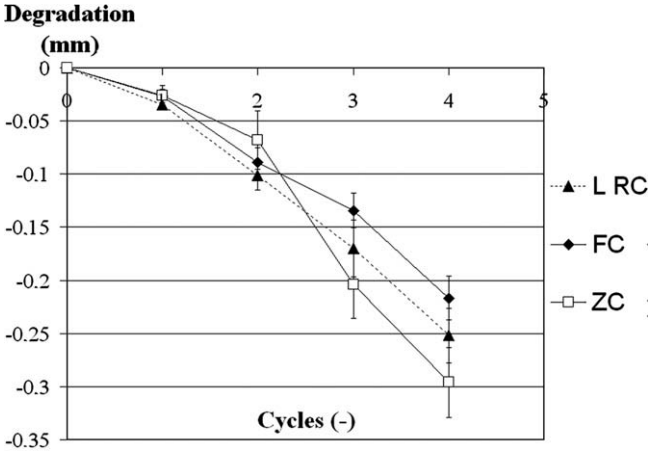

Fig. 8. Evolution of the thickness of the concrete specimens from the second series of treatments versus the number of microbiological test cycles. The concrete types with antimicrobial admixtures showed a similar loss of material as the reference concrete. See Table 4 for explanation of the codes.

Table 4
Weight loss of the concrete specimens after four or eight cycles of microbiological tests.

Series	Code	Weight loss (g)
Sewer pipe reference concrete	SP RC	18.72 ± 1.01
Silicate admixture concrete	SAC	18.91 ± 0.53
Cementitious coating	CC	39.44 ± 1.02
Polyurethane lining	PUL	1.65 ± 1.20
Epoxy coating	EC	1.93 ± 0.41
Laboratory reference concrete	L RC	9.91 ± 0.57
Silver–copper zeolites concrete	ZC	9.47 ± 0.89
Antimicrobial fibers concrete	FC	9.19 ± 0.44

3.4. Bonding strength

The bonding strength of the EC significantly decreased from 5.95 ± 0.15 MPa to 4.81 ± 0.24 MPa (19%) as a result of eight cycles of microbiological tests. The bonding strength of the PUL could not be obtained, as drilling of the specimens resulted in the release of the majority of the lining. The loss of bonding strength could possibly be attributed due to the penetration of sulfuric acid by surface defects of the coating and subsequent reaction with the underlying concrete.

4. General discussion

While a 2–12-fold decrease of SOB was observed for the antimicrobial mortar mixtures from the incubation experiments, no improved resistance towards degradation could be seen from the microbiological simulation tests. Whereas these accelerated simulation tests have provided a rapid test method for the evaluation of different surface treatments or innovative concrete formulations towards BSA of concrete, the relevance of this kind of test procedure for antimicrobial concrete formulations is less evident. First of all, in the case of inorganic systems, the inhibition is primarily a result of the contact between bacteria and the antimicrobial components in the surface. As the specimens were submerged in a rather large liquid volume (1.5 L), the contact surface area of the specimens was probably too low to exert a substantial biocidal effect on the majority of the bacteria present in solution. Second, the relatively large amount of liquid might have resulted in a dilution of the antimicrobial component below the minimal inhibitory concentration (MIC). This is of major importance for organic systems. In contrast to inorganic systems that are based on metal ions that are stabilized, organic systems consist of small molecules that are incompatible with a polymer matrix, and therefore, slowly diffuse to the surface and surroundings [36]. Furthermore, as the tests were performed on sawn surfaces, the amount of cement paste at the surface (and thus biocides present in it) might have been too low to exert any significant influence. These findings necessitate the development of a new test procedure for the evaluation of antimicrobial concrete admixtures.

However, the incubation test procedure presented in this paper already gave an indication of the potential inhibitory activity of antimicrobial compounds in mortar and concrete, as could be observed from the ATP measurements. In contrast to several studies on BSA corrosion which use fully grown pure cultures of thiobacilli [28], mixed cultures of SOB were used in this research. From the results of this research it could be concluded that the biocidal effect towards SOB was limited in the case of the antimicrobial fibers. The silver–copper zeolites provided a better performance. Further experiments are required to corroborate the biocidal effect against several SOB species. More specifically, the inhibitory effect of higher concentrations of silver–copper zeolites in the mortar matrix should be investigated.

Okabe et al. [6], reported on the impact of pioneer organisms on the initial pH decrease to allow the establishment of suitable growth conditions for SOB species. Among these species, mainly heterotrophic, halotolerant and neutrophilic bacteria were present. In future experiments, it will be of interest to investigate the influence of the antimicrobial compounds on the colonization of these pioneer microorganisms. Moreover, in an adapted incubation test, sulfur could be provided as gaseous H_2S, in order to prevent possible reactions of the metal and sulfur ions. The use of small scale specimens, as in the incubation test, allows working with small set-ups. These small set-ups can be easily stored under a fume hood without exposing researchers to toxic concentrations of H_2S.

5. Conclusions

In this research, the effectiveness of different surface treatments and admixtures towards biogenic sulfuric acid corrosion of concrete was tested by means of accelerated chemical and microbiological simulation tests.

The best protective performance was obtained with an epoxy coating. No degradation of the surface treated concrete could be observed after eight and 10 cycles of microbiological and chemical tests, respectively. The strongest degradation was observed for the cementitious coating. The addition of hydrous silicates or antimi-

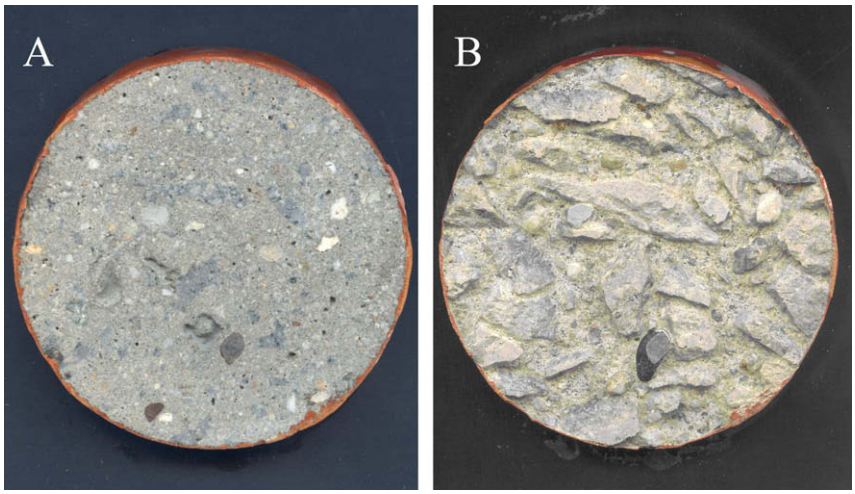

Fig. 9. A sample of the silicate admixture concrete (SAC) before (A) and after (B) eight cycles of the microbiological test. A loss of cement paste is clearly visible, while the aggregates remain relatively unaffected.

crobial compounds failed to give an improved performance towards degradation under the given test procedures. Finally, a biofilm approach as a novel test method for the evaluation of antimicrobial concretes was proposed.

From the findings in this research, it was concluded to apply the epoxy coating and polyurea lining in a sewer system in the near future. The in-situ performance of the treatment will be monitored on a regular basis.

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