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Experimental research and prediction of the effect of chemical and biogenic sulfuric acid on different types of commercially produced concrete sewer pipes

N. De Belie[a,*], J. Monteny[a], A. Beeldens[b], E. Vincke[c], D. Van Gemert[b], W. Verstraete[c]

[a]*Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, Technologiepark Zwijnaarde 904, B-9052 Gent, Belgium*
[b]*Reyntjens Laboratory, Department of Civil Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 40, 3001 Heverlee, Gent, Belgium*
[c]*Laboratory of Microbial Ecology and Technology, Ghent University, Coupure links 653, B-9000 Gent, Belgium*

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Abstract

New equipment and procedures for chemical and microbiological tests, simulating biogenic sulfuric acid corrosion in sewerage systems, are presented. Subsequent steps of immersion and drying, combined with mechanical abrasion, were applied to simulate events occurring in sewer systems. Both chemical and microbiological tests showed that the aggregate type had the largest effect on degradation. Concrete with limestone aggregates showed a smaller degradation depth than did the concrete with inert aggregates. The limestone aggregates locally created a buffering environment, protecting the cement paste. This was confirmed by microscopic analysis of the eroded surfaces. The production method of concrete pipes influenced durability through its effect on W/C ratio and water absorption values. In the microbiological tests, HSR Portland cement concrete performed slightly better than did the slag cement concrete. A possible explanation can be a more rapid colonisation by microorganisms of the surface of slag cement samples. A new method for degradation prediction was suggested based on the parameters alkalinity and water absorption (as a measure for concrete porosity).

Keywords: Concrete; Durability; Degradation; Biogenic sulfuric acid; SEM

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1. Introduction

Biogenic sulfuric acid corrosion may cause severe damage to concrete sewer pipes, wastewater collection units and treatment plants. In worst case situations, the degradation is in the order of several millimeters per year. Biogenic sulfuric acid corrosion has been studied since 1945 when Parker [1] discovered that bacteria were involved in the corrosion process. Since then, a lot of effort has been put in the understanding of the corrosion process (among others, Refs. [2–7]). The bacterial and chemical activity in the sewers create a sulfur cycle, which can lead to the bacterial formation of sulfuric acid. When anaerobic conditions occur due to long retention time or slow flow of the sewage, sulfate-reducing bacteria, e.g., *Desulfovibrio*, reduce sulfur-compounds to H_2S. Due to turbulence and pH decrease, H_2S escapes into the sewer atmosphere. The transformation of H_2S into sulfuric acid occurs under aerobic conditions, after the sorption of H_2S from the sewer atmosphere into the concrete or into the biofilm on the surface of the pipelines above the water line. The H_2S may react with oxygen to elemental sulfur, which is deposited on the sewer wall. Sulfur is a substrate for many thiobacilli such as *Thiobacillus thiooxidans*, *Thiobacillus neapolitanus*, and *Thiobacillus intermedius* [8,9]. Those bacteria metabolise the sulfur into sulfuric acid, which causes concrete deterioration.

The sulfuric acid first reacts with the calcium hydroxide (CH) in the concrete to form gypsum ($CaSO_4.2H_2O$). Subsequently, the reaction between gypsum and calcium aluminate hydrate (C_3A) will lead to the formation of ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$). Both products have a larger volume than represented by the initial compounds, which results in cracking. Furthermore, the degraded material can be removed by the sewage flow, which accelerates the corrosion process [6]. When high-sulfate-resistant (HSR) cement is applied, the formation of ettringite is of minor importance due to the limited C_3A content ($\leq 3\%$

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* Corresponding author. Tel.: 32-9-264-5522; fax: +32-9-26458-45.
E-mail address: nele.debelie@UGent.be (N. De Belie).

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in Portland cement, according to Belgian standards). However, the formation of gypsum, together with a direct action of sulfuric acid on the calcium silicate hydrates, may also impair the concrete integrity.

The research performed on the resistance of concrete against this type of corrosion can roughly be divided in three groups: chemical and microbiological tests and tests in situ (reviewed in Ref. [10]). Yet, investigations have shown that a high resistance of a certain concrete type to sulfuric acid in chemical tests does not always implicate a high resistance against biogenic sulfuric acid corrosion [11,12]. In this paper, equipment and procedures developed in our laboratories to examine chemical and biogenic sulfuric acid corrosion are presented. This test equipment was used to study the influence of cement type, production method and aggregate type on the corrosion of different types of concrete sewer pipes, commercially available in Belgium.

In addition, an attempt was made to improve the well-known Pomeroy model for degradation of concrete sewer pipes, using the results of the current experiments. Prediction of deterioration rates can be a valuable tool for the design and management of sewerage systems. As mentioned above, the process of biogenic sulfuric acid corrosion can be divided in two separate parts: (1) the production of H_2S and its release from the water phase and (2) the metabolisation of sulfur to sulfuric acid, which attacks the concrete pipe. Because sulfide generation causes serious problems related to its unpleasant odour (odour thresholds for H_2S in the range of 1–4 ppb by volume) and high toxicity (fatal at gas concentrations within the range of 300–500 ppm by volume in a few minutes), several models have been developed to predict H_2S production in sewers [3,4,7,13–16]. In addition, models have been created to evaluate the second step in the corrosion process [17]. The Pomeroy model describes both steps. Because the first step is not affected by the material properties of the sewer pipes, this part of the model will not be further discussed. The second step of the Pomeroy model is of greater interest for this research because it can be used to calculate the deterioration rate of concrete sewer pipes, based on Eq. (1) [18]:

$$C_r = 11.5k\phi_{sw}1/\mathrm{alk} \qquad (1)$$

where C_r = corrosion rate (mm/yr); k = factor related to the acid formation, based on climate conditions, 0.8 in moderate climates; ϕ_{sw} = sulfide release [g $H_2S/(m^2$ hr]; and alk = alkalinity of the pipe material (g $CaCO_3$/g concrete).

The alkalinity of the pipe material is based on its $CaCO_3$ content and is a measure for its neutralisation capacity. It can be calculated from the experimentally determined content of soluble CaO of the concrete or of its constituents, cement and aggregates, using Eq. (2):

$$\mathrm{Alk} = \frac{(c\mathrm{CaO}_{\mathrm{cement}} + a\mathrm{CaO}_{\mathrm{aggr}})}{d}\frac{100}{56} \qquad (2)$$

where c = cement content (kg cement/m^3 concrete); $\mathrm{CaO}_{\mathrm{cement}}$ = content of soluble CaO in the cement (kg CaO/kg cement); a = aggregate content (kg/m^3 concrete); $\mathrm{CaO}_{\mathrm{aggr}}$ = content of soluble CaO in the aggregates (kg CaO/kg aggregates); and d = concrete density (kg/m^3).

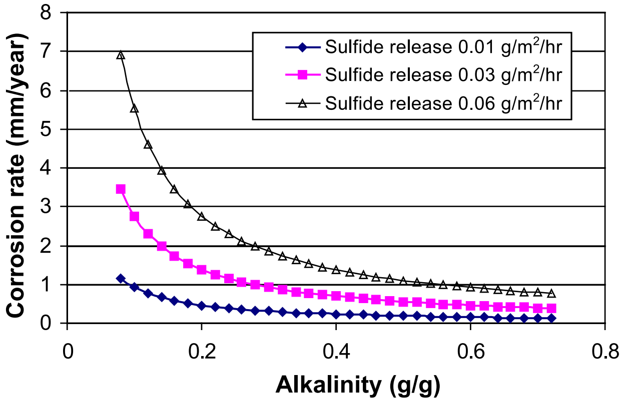

Fig. 1. Rate of concrete corrosion caused by biogenic sulfuric acid vs. alkalinity of concrete calculated for a realistic range of sulfide release values according to the Pomeroy model.

The factor 100/56 is the ratio between the molar masses of $CaCO_3$ and CaO. As an example, Fig. 1 shows the corrosion rate in function of the alkalinity for a range of realistic values for the sulfide release. The chosen minimum and maximum values for alkalinity correspond to a concrete type with inert aggregates (low CaO content) and blastfurnace slag cement, on the one hand, and to a concrete with aggregates with high CaO content and Portland cement. It is clear that, especially in the case of high levels of sulfide release, implying an increased risk on biogenic sulfuric acid corrosion in concrete sewers, the effect of alkalinity becomes important, according to the Pomeroy model.

2. Materials and methods

2.1. Concrete specimens

The concrete specimens tested had a composition that is frequently used by manufacturers of sewer pipes. They were taken from pipes or inspection pits produced using the normal industrial processes. Three parameters were investigated (Table 1): the production method (affecting the W/C ratio and cement content) and the cement and the aggregate types. The different production methods included production using centrifugation (W/C = 0.25, cement content = 420 kg/m^3), immediate form removal (W/C = 0.36–0.40, cement content = 350 kg/m^3), and hardening in the formwork (W/C = 0.43–0.49, cement content = 350 kg/m^3). The cement types used were Portland cement CEM I 42.5 HSR/LA or CEM I 52.5 HSR/LA and blastfurnace slag cement CEM III/B 42.5 HSR/LA. Two types of aggregates were employed: inert (gravel or porphyry) and reactive (limestone). Practical limitations did not allow the inclusion of all factor combinations in the experimental design.

Table 1
Characteristic parameters of the different concrete specimens, compressive strength and water absorption at 28 days

Code	Production method[a]	Cement type	Aggregate type[b]	Compressive strength (N/mm^2)	Water absorption (%)	CaO content (%)
P1-I-G	P1	CEM I 42.5 HSR/LA	G	85.02	3.63	10.75
P1-I-K	P1	CEM I 42.5 HSR/LA	K	84.39	3.60	35.56
P1-III-G	P1	CEM III/B 42.5 HSR/LA	G	58.92	3.86	8.15
P1-III-K	P1	CEM III/B 42.5 HSR/LA	K	71.93	3.32	25.47
P2-I-G	P2	CEM I[c]	G	123.25	2.39	13.90
P1-I52.5-K[d]	P1	CEM I 52.5 HSR/LA	K	67.92	3.65	27.57
P3-III-G[d]	P3	CEM III/B 42.5 HSR/LA	G	56.50	6.18	7.82
P3-I52.5-G[d]	P3	CEM I 52.5 HSR/LA	G	72.72	4.58	8.96

[a] P1: immediate form removal; P2: centrifugation; P3: hardening in the formwork.
[b] G: gravel or porphyry; K: limestone.
[c] More details were not given by the manufacturer.
[d] These concrete specimens were not taken from pipes, but from inspection pits.

Compressive strength was determined at a concrete age of 28 days, according to the Belgian standard NBN B15-220 (1990), on three drilled cores per composition (Table 1). Water absorption was measured according to the Belgian standard NBN B15-215 (1989) on three cylinders of 80-mm diameter and 70-mm height, taken from drilled cores (Table 1). The production method of centrifugation resulted in significantly (P=.05) higher compressive strength and lower water absorption. The highest water absorption was found for elements that had hardened in the formwork. This can be related to the higher W/C factor of these elements. The soluble CaO content of the different concrete types was determined according to the Belgian standard NBN B15-250 (1989). The results shown in Table 1 will be used in the modelling section. Especially the high CaO contents of the limestone aggregates (43–46%), compared with the inert aggregates (1–8%), leads to higher CaO contents for concrete with reactive aggregates. In addition, the higher CaO content of Portland cement (62–64%) compared with slag cement (48–49%) affected the concrete alkalinity.

2.2. New test procedures for chemical and microbiological tests

2.2.1. Chemical test using the apparatus for accelerated degradation testing (TAP)

At the Magnel Laboratory for Concrete Research of Ghent University, an apparatus for accelerated degradation testing (TAP) was developed for investigating the resistance of concrete against chemical attack (Fig. 2). A more detailed description of the used test method is given in Refs. [19,20].

Cylindrical test specimens of 200-mm diameter and 60- to 80-mm height (depending on the pipe thickness) were removed from the produced concrete pipes (Fig. 3). To simulate sulfuric acid attack, three cylinders of each concrete type were subjected to 10 attack cycles consisting of

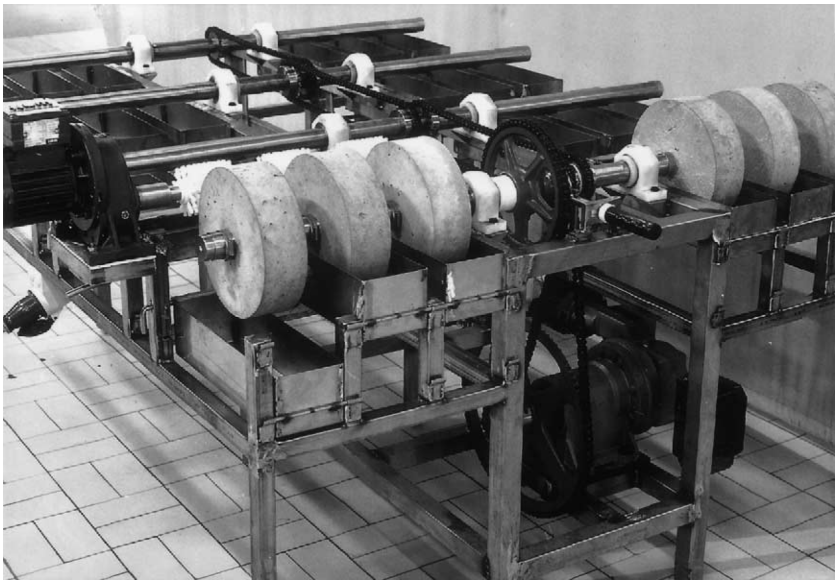

Fig. 2. Apparatus for accelerated degradation testing (TAP).

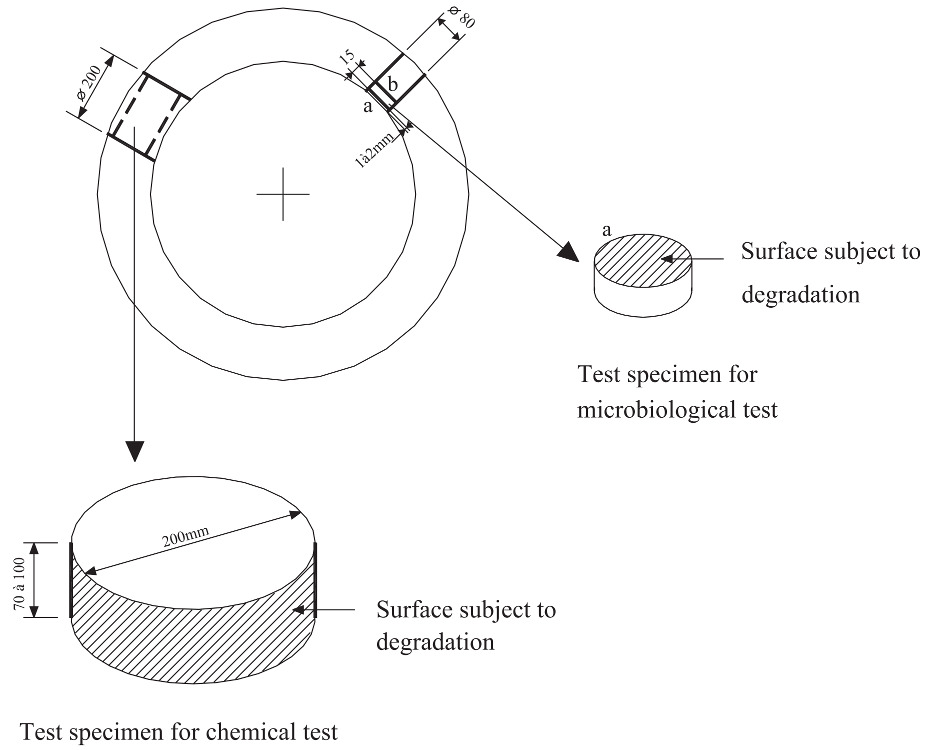

Fig. 3. Schematic representation of the specimens used for chemical and microbiological degradation tests.

an alternated immersion in a 0.5% sulfuric acid solution (initial pH 0.9–1.0), drying by air and brushing. The subsequent steps simulate certain events in sewer systems (Table 2). For each cycle, fresh solution was used.

During the alternated immersion step, the cylinders, fixed on horizontal axes, turned with a speed of 1 rph through separate recipients containing the sulfuric acid solution. Each point of the outer circumference was submersed during 1/3 of the rotation time. The pH of the solution was measured daily. After each 5-day cycle, the cylinders were dried in air and brushed with rotary brushes to remove weakly adhering concrete particles. The corrosion of the specimens was measured using contactless distance measurements with laser sensors, providing six measurements/mm along the concrete surface. After every cycle, the same four profiles along the circumference of the cylinders were scanned. The average change of the radius for one concrete type is presented as the average over 12 profiles (3 cylinders × 4 profiles per cylinder). The measurements were performed before, as well as after, brushing to determine the change of the radius due to chemical reaction during immersion, as well as the change of the radius due to brushing.

Table 2
Different steps of each cycle of the chemical and microbiological test procedure

Cyclic process in sewers	Chemical test with TAP	Microbiological test
H_2S release and uptake in biofilm and concrete		H_2S incubation
Formation of sulfuric acid, concrete deterioration; wetting/drying by fluctuation of the wastewater level	Cyclic immersion in sulfuric acid solution; chemical attack	Incubation of the concrete blocks in medium with Thiobacilli; sulfuric acid production and attack
Removal of material (heavy rainfall, high flow rates, pumping, turbulence, etc.)	Abrasion by brushing	Continuous shaking on a rotary shaker; rinsing with water
Availability of new surface for sulfuric acid attack, dry weather situation with low wastewater level	Drying in air	Drying at 28 °C

The measurements with the laser were also used to calculate the change in the surface roughness of the concrete cylinders. In sewer systems, a rough surface can result in an easier colonisation by the sulfide oxidising bacteria. The surface roughness was expressed by means of the R_a value, based on the British standard BS 1134, which, in turn, refers to ISO/R 468 surface roughness. The R_a value is defined as the arithmetical average value of the departure of the profile above and below the centre line throughout the prescribed sample length. A sample length of 50 mm was used, and presented values are again averages of R_a values for different profiles and cylinders.

2.2.2. Microbiological tests

To take into account the action of the Thiobacilli bacteria in the corrosion process, a simple and reproducible test method was developed at the Laboratory of Microbial

Ecology and Technology of Ghent University. The test procedure described earlier for small concrete samples (size 20 × 20 × 50 mm; [21]) was scaled up to obtain more representative results for concrete with large aggregates. The samples were cylinders of 80-mm diameter and 15-mm height, taken some millimeters below the inner surface of the concrete pipes (Fig. 3). Each test specimen was glued on a plastic plate of 120 × 90 mm. The samples were incubated in a 20-fold diluted aqueous solution of a biological sulfur suspension. The dilution solution contained tap water and an additional N and P source [100 mg l^{-1} $(NH_4)_2SO_4$ and 10 mg l^{-1} K_2HPO_4]. Biologically produced sulfur is the end product of the microbiological sulfide oxidation, a process carried out by mixed cultures of *Thiobacillus* bacteria. It consists of complex aggregates containing elemental sulfur, biomass and biopolymers [21]. For the control samples, the basic suspension was inactivated by dosing 1000 mg l^{-1} of the biocide glutaraldehyde. The corrosion progress was simulated in four cycles of 17 days, performed at 28 °C (Table 2). One cycle consisted of the following steps:

- Step 1: H_2S incubation. The air-dry concrete samples were placed in H_2S incubation chambers of 10 l for 3 days. The gas concentration was generated by 100 ml of a 4% Na_2S solution and 100 ml of a 1.5 N HCl solution. The initial gas concentration was approximately 250 ppmv.
- Step 2: Incubation in solution. Each concrete block was hanging in a separate glass recipient, submerged in 600 ml of the culture medium of pH 7. These separate recipients were covered and placed for 10 days on a rotary shaker (90 rpm). As a control treatment, a sample of each concrete composition was hanging in an inactivated suspension.
- Step 3: Rinsing. On rainy days, high flow rates of water can occur in sewer pipes, and corrosion products can be washed away, which provides a new surface for the attack. Placing the concrete blocks in separate glass recipients, containing Milli-Q water on the rotary shakers, for 2 days simulated this.
- Step 4: Drying. After periods of high loading, dry periods follow, in which H_2S can penetrate into the surface layers of the concrete and new reaction products can be formed. This was simulated by drying the concrete samples for 2 days.

During Step 2, the pH of the suspension was determined daily. The sulfate concentration in the suspension was determined according to standard methods. The total Ca concentration of the suspension during Steps 2 and 3 was determined by decomposition according to standard methods, following detection with a flame atomic spectrometer. After every cycle, the thickness of the concrete blocks was measured, using a measurement table with an accurate laser sensor developed in the Magnel Laboratory for Concrete Research. The laser could be moved in the horizontal $X-Y$ plane by a motor and measured the vertical (Z) distance to the objects on the measurement table. For each concrete sample, surface profiles were measured in the X direction for six different Y positions (3.3 measurements/mm). After every attack cycle, the plastic plates with concrete samples were put on the same position on the measurement table using a template. Values presented are averages over the six different profiles of three test specimens per concrete type. The surface roughness was determined as described for the chemical tests. Before the exposure, each specimen was dried at 60 °C until it reached a constant weight. After four attack cycles, the loss of substance was determined by weighing the samples after drying in an oven at 60 °C.

2.3. Microscopic investigation of the attacked samples

A study of the morphology of the concrete specimens was made by means of microscopic investigation. The eroded surface, as well as cross-sections, of the samples submitted to the microbiological test was used for SEM analysis (JEOL JSM-6400) in the SEI mode. Additionally, thin sections were studied with an optical microscope with normal and polarized light. The thin sections were made from the eroded surface and from a cross-section of the samples submitted to the microbiological test.

3. Results

3.1. Chemical tests with sulfuric acid

3.1.1. Change in pH

The changes in pH of the sulfuric acid solution during the attack cycles were limited. During the first cycle, the pH increased from 0.9 to 1.6 maximum. For the subsequent cycles, the increase was even limited to 0.4 units. No systematic differences between the concrete types could be noticed during successive cycles.

3.1.2. Change in radius of the concrete cylinders

In Fig. 4, the average change of the radius of the cylinders during the chemical test is shown versus the number of measurements for the different concrete types. The alternating increase and decrease of the radius corresponds to the alternating expansion of the concrete due to the immersion and formation of reaction products and subsequent material loss due to brushing. Eventually, a decrease of the radius could also occur during the period of immersion of the cylinders due to the loss of adhesion of the expanded parts.

The resulting change in radius after 10 attack cycles was relatively limited for all concrete types (maximum − 0.4 mm). An analysis of variance was carried out, with the three parameters, production method, cement type and aggregate type, as the independent variables and the change in radius as the dependent variable. Significant differences were analysed with a Student–Newman–Keuls test (P=.05). During the first five cycles, only the aggregate type had a significant

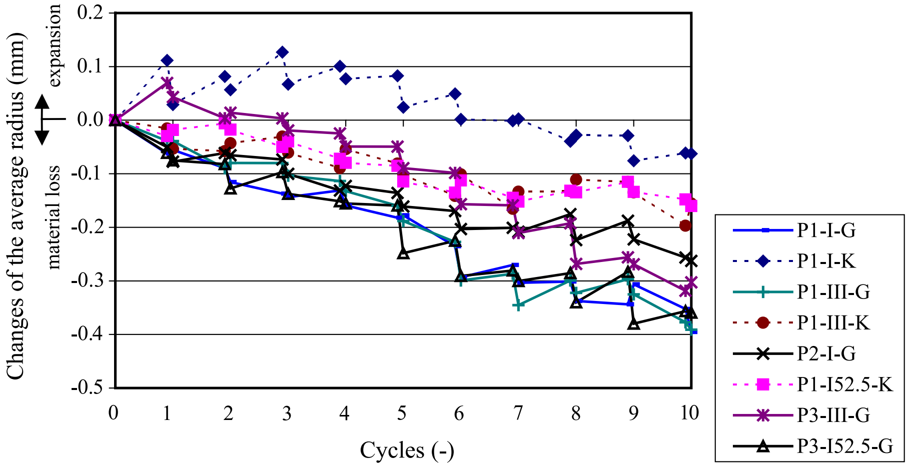

Fig. 4. Average change in the radius of the cylinders during the chemical test vs. the number of attack cycles for the different concrete types.

effect on the concrete degradation: The compositions with limestone showed a significantly smaller decrease in radius than did the compositions with inert aggregates. For Cycles 6 to 10, the influence of the production method became more pronounced. The change in radius was significantly more limited for the concrete pipes produced through centrifuging or immediate form removal, compared with the concrete hardened in the formwork. Yet, the aggregate type stayed the most dominant factor.

The effects of the alternated immersion and of the mechanical abrasion by brushing were also separated to obtain a clear view on the degradation process. This helps to distinguish between, for instance, a concrete type that undergoes large expansion, followed by an equally large material loss by brushing, and a concrete type that shows little expansion and material loss. When only the absolute change in radius is considered, both concrete types would show a limited change, while the first one is, in fact, considerably more prone to degradation. For the current experiments, no significant differences between concrete types were found when only the effect of the alternated immersion was considered. Regarding the effect of the mechanical abrasion, the same significant differences were found, as mentioned higher for the resulting change in radius after 10 cycles. Concrete types P1-III-K and P1-I52.5-K showed the highest resistance to brushing.

3.1.3. Change in surface roughness of the concrete cylinders

The average surface roughness of the concrete cylinders versus the number of attack cycles is shown in Fig. 5. Again, the two values per cycle present the measurements before and after brushing. The differences in initial R_a value (shown under Cycle 0) were relatively small. Yet, clear differences were recorded after 10 cycles. Analysis of variance proved that the parameter aggregate type had the largest effect. Concrete with limestone showed a significantly smoother surface than did the concrete with gravel or porphyry. This logically results from the fact that the limestone is also

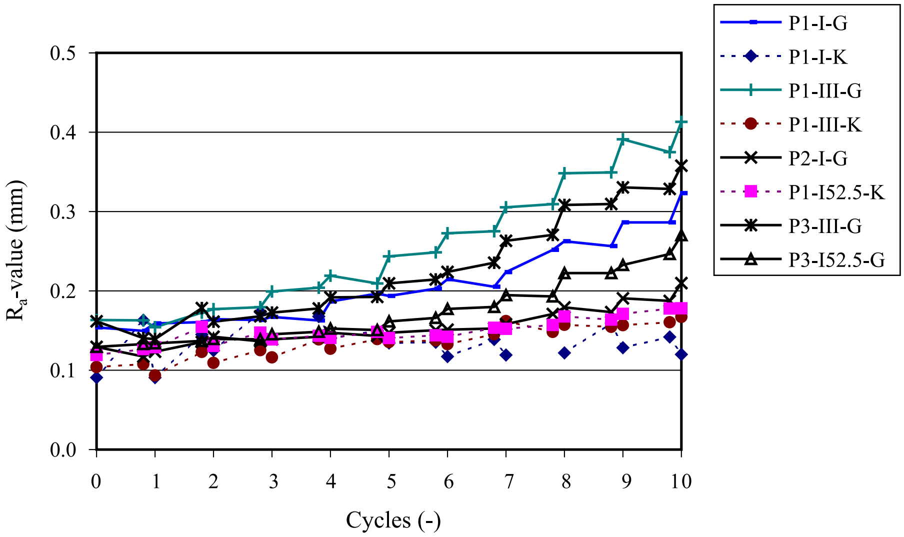

Fig. 5. Average surface roughness of the concrete cylinders during the chemical test vs. the number of attack cycles.

degraded by the sulfuric acid solution, whereas for the concrete with inert aggregates, the cement paste is removed in between the aggregates until the degradation of the matrix is sufficiently large for the aggregates to be detached. The production methods of centrifugation or immediate form removal resulted in lower roughness than the concrete hardened in the form. Of the two cement types, the use of Portland cement induced a smaller roughness.

3.2. Microbiological tests with biogenic sulfuric acid

3.2.1. Change in pH and sulfate and calcium concentration of the solution

During the second step of each cycle, the pH of the solution decreased for all concrete types, rapidly from about 8.0 to 3.0, after 3 days and continued to drop to pH 1.0 on Day 10. At the same time, the sulfate concentration increased from almost 0 to 2–4 g SO_4^{2-}/l solution, proving the production of sulfuric acid by the microorganisms. In a control treatment, in which concrete blocks were suspended in the solution, inactivated by means of glutaraldehyde, no change in sulfate concentration could be determined, while the pH increased slowly to about 9.0 due to the high alkalinity of the concrete specimens. ANOVA analysis could not reveal significant differences (P=.05) in the overall pH and sulfate profiles of the different concrete types.

The average calcium loss during Steps 2 and 3 of each cycle indicated, as expected, that more calcium was released by the samples with limestone aggregates, compared with the samples with inert aggregates. Although the Portland cement samples had a higher content of free lime in comparison with slag cement samples, they did not show a higher calcium loss.

3.2.2. Change in thickness

The change in thickness versus the number of cycles is presented in Fig. 6. Analysis of variance showed that the aggregate type had the largest effect on thickness change, followed by cement type and production method. As for the chemical tests, the inclusion of limestone aggregates decreased the degradation. The use of Portland cement resulted in smaller degradation depths than the use of slag cement did. Concerning the production method, immediate form removal, centrifugation and hardening in the form can be mentioned in increasing order of degradation.

In the case of reinforced concrete elements, not only the average degradation depth, but also the maximum local degradation depth is important. This gives an indication of the present protection of the reinforcement against corrosion. For each concrete type, the third measured profile of one sample, randomly selected from the three replicates, was analysed more in detail. Histograms were made of the distribution of distances between the profile measured after four cycles and a regression line drawn through the profile measured initially (Fig. 7). This figure should be interpreted as follows: for example, the largest bar in the histogram for P1-I-G indicates that 16% of single values measured with the laser sensor corresponded to a (rounded) degradation depth of 0.45 mm. Degradation depths of 0.5 and 0.4 mm occurred with a frequency of 12% and 11%, respectively. The maximum local degradation depth amounted to 0.85 mm, a value reached for less than 1% of the measurements considered. It should be taken into account that some pits of about 1.7 mm depth were already initially present in sample P3-III-G, whereas all other samples showed maximum initial deviations from the regression line of 0.3 mm. From the histograms, it appears that P2-I-G is characterised by a very uniform degradation; for 65% of the measured points, the depth varied between 0.7 and 0.9 mm. For all other concrete types, there was a much larger variation. This effect can be explained by the production method of centrifugation, causing an unequal distribution of large aggregates in the matrix. At the inner side of the concrete pipes, almost no coarse aggregates were present, which

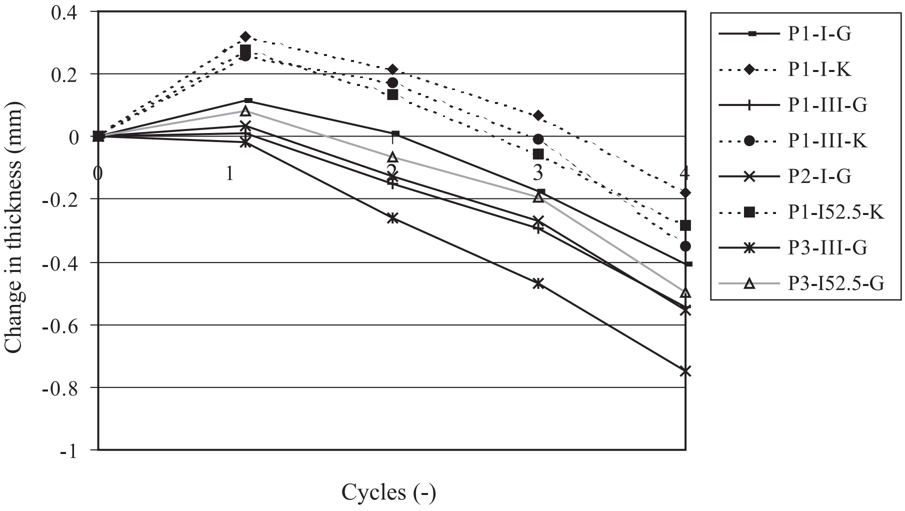

Fig. 6. Average change in the thickness of concrete samples during the microbiological test vs. the number of attack cycles.

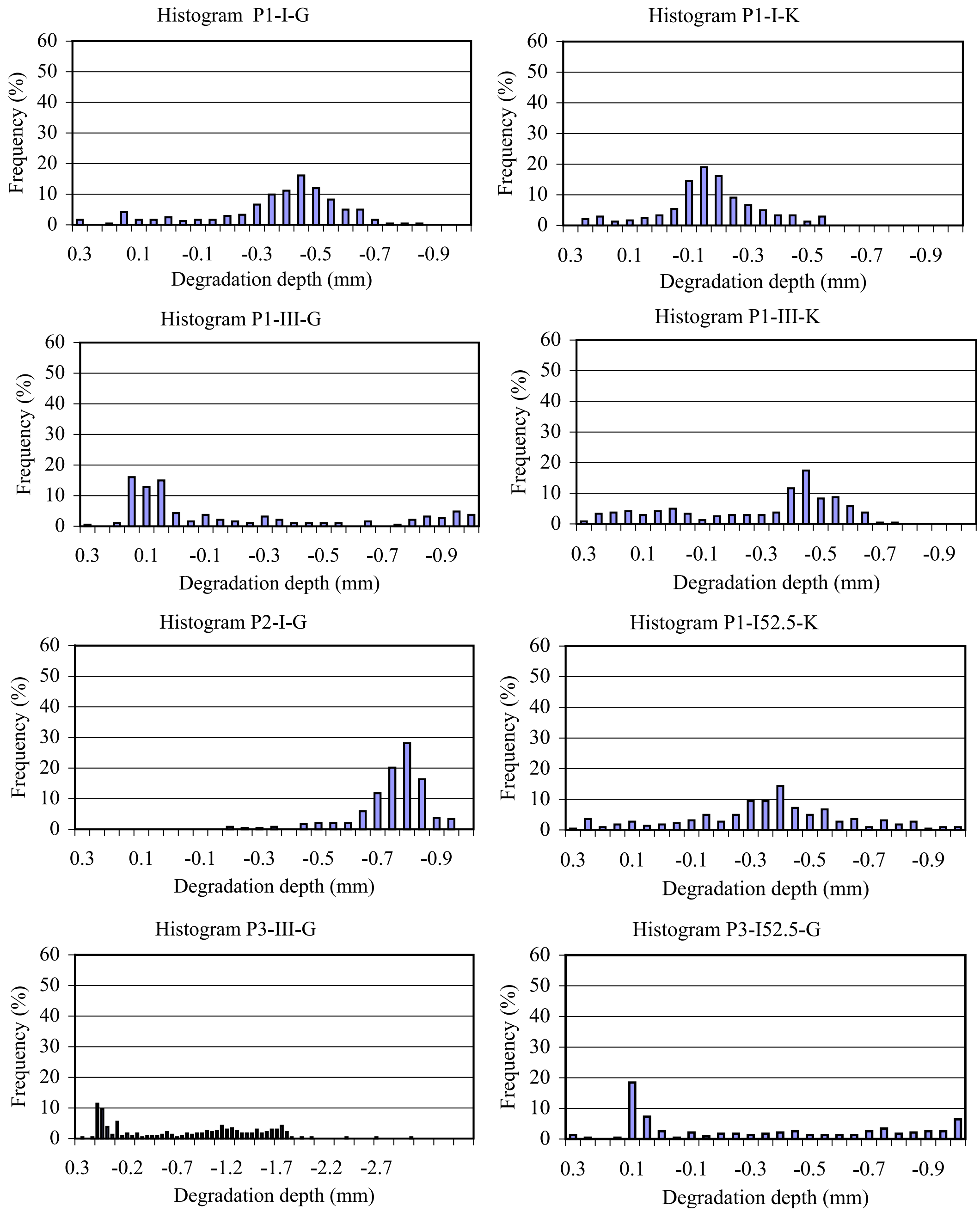

Fig. 7. Histograms of the distribution of distances between a profile measured after four cycles and a regression line drawn through the profile measured initially.

implied that the surface in contact with the biological suspension consisted nearly completely of cement paste. Fig. 8 shows a sample of the centrifuged concrete and of concrete produced by immediate form removal. The deepest pits, up to 2 mm, were measured for concrete P3-III-G. Concrete types P1-III-G, P3-III-G and P3-I52.5-G were, at several locations, degraded to a depth of 1 mm or more. Despite the homogeneous deterioration of P2-I-G, the average degradation depth was larger than the depth of local pits in P1-I-G, P1-I-K, P1-III-K and P1-I52.5-K. Concrete P1-I-K performed best, with a maximum depth of local pits of 0.6 mm.

3.2.3. Weight loss

Fig. 9 shows the average weight loss of all concrete types after four cycles. ANOVA analysis indicated that for the parameter weight loss, the cement type explained most of the variance, followed by production process and aggregate type. Concrete with slag cement lost more weight than did concrete with Portland cement. Regarding the production method, immediate form removal, centrifugation and hardening in the form can be mentioned in order of increasing weight loss. The aggregate type had only little effect, with limestone samples showing a higher weight loss than did the samples with inert aggregates.

Fig. 8. A sample of the centrifuged concrete P2-I-G (left) and of concrete P3-I52.5-G (right) produced by hardening in the form after four cycles of the microbiological test.

3.2.4. Change in surface roughness

The change in R_a value versus the number of cycles is presented in Fig. 10. Composition P1-I52.5-K showed a significantly larger initial surface roughness than did the other concrete types, caused by the presence of relatively large pits in two of the three replicates. Analysis of variance on the roughness increase gave about the same results as for the chemical tests. The aggregate type had the largest effect on R_a, with a more limited roughness increase for concrete with limestone aggregates. Concrete produced by centrifugation was the smoothest, followed by concrete produced by immediate form removal and by hardening in the form. The use of Portland cement resulted in a lower roughness than the use of slag cement did.

3.3. Microscopic analysis of samples submitted to the microbiological test

The SEM analysis of the eroded surface of the specimens confirmed the difference between the concrete samples prepared with inert aggregates and those with limestone aggregates (extensively described in Ref. [22]). In the former case, the cement matrix is redrawn between the aggregates, as can be seen in Fig. 11, for composition P1-I-G. Remarkable is that due to the continuous aggregate size distribution, the aggregates are kept well in place. However, if the attack continues, a sudden increase in deterioration rate may occur due to the release of the larger aggregates. In the case of the reactive aggregates, the surface is smoother

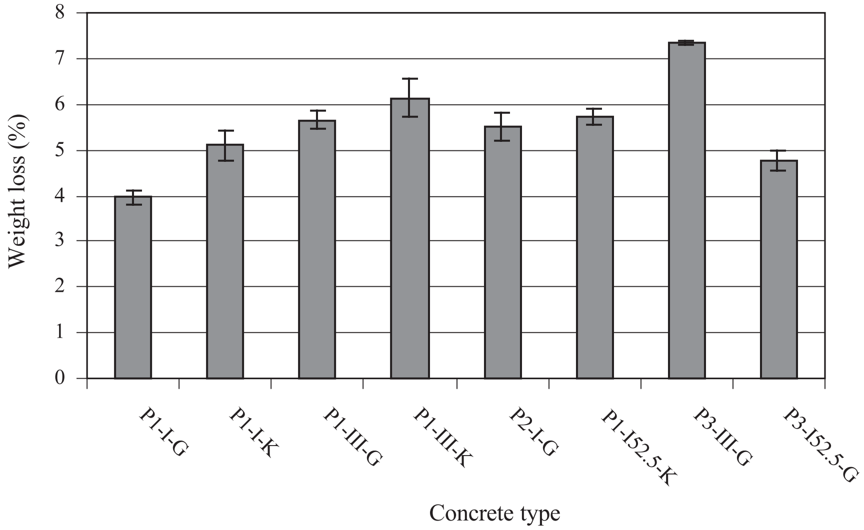

Fig. 9. Average weight loss of all concrete types after four cycles of the microbiological test procedure.

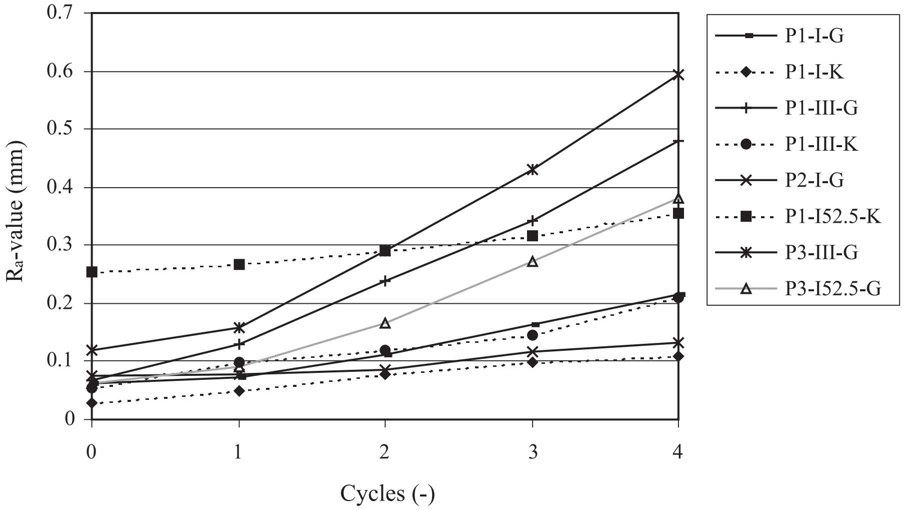

Fig. 10. Change in R_a value of concrete samples during the microbiological test vs. the number of attack cycles.

because the large limestone aggregates are deteriorated layer by layer, and the eroded surface of the aggregates is at the same depth as the surrounding matrix. In the case of inert aggregates, the deterioration rate will increase after each cycle because of an increase in the release of large aggregates and an increase in area of the cement matrix subject to acid, whereas in the case of the reactive aggregates, the deterioration rate will remain more constant during each cycle. An investigation of the thin sections also clearly indicated the decalcification of the cement matrix. The attacked matrix was first transformed into an amorphous gel, prior to the total deterioration, by changing completely into gypsum crystals.

3.4. Extension of the Pomeroy model

A reasonable correlation (correlation coefficient r=.75) was found between the concrete degradation (change in thickness), obtained after four cycles of the microbiological test (Fig. 6), and the inverse of the concrete alkalinity calculated from the CaO content of the concrete (Table 1). This relation was suggested by Pomeroy (Eq. (1), with k and ϕ_{sw} being constant). Indeed, in our tests, the concrete types with higher alkalinity [containing limestone aggregates and (less important) Portland cement] showed a higher resistance to biogenic sulfuric acid. Thus, the parameter alkalinity was reasonably well suited to estimate concrete resistance; however, it was not able to explain all the important influences. For instance, the Pomeroy model does not account for the important effect of concrete porosity on deterioration. This effect can be seen in the experimental results, when different production methods (implying different W/C ratios and water absorption values) are compared. For example, concrete types P1-III-G and P3-III-G had a comparable alkalinity (0.15 and 0.14 g $CaCO_3$/g concrete, respectively). Yet, the degradation of P3-III-G was significantly higher (0.75 mm compared with 0.54 mm for P1-III-G). Consulting Table 1, it can be noticed

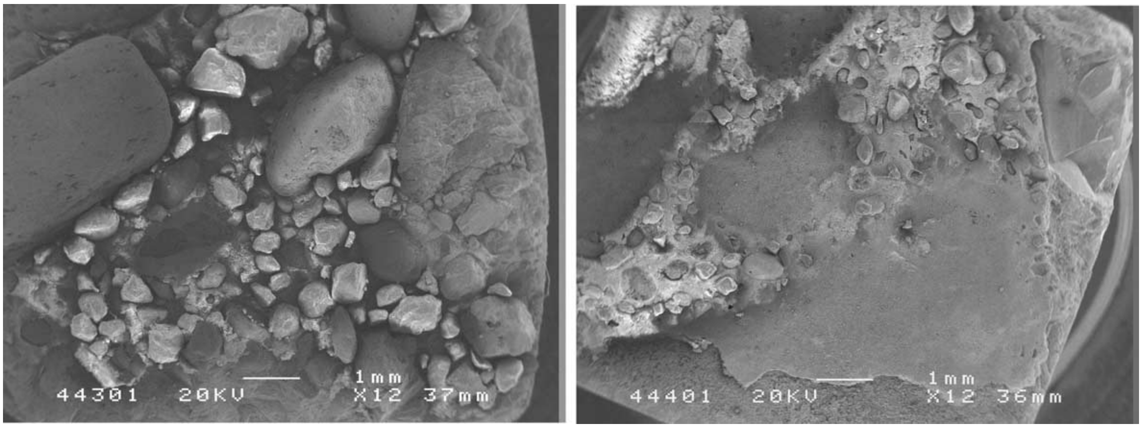

Fig. 11. Eroded surface of specimens P1-I-G (left) and P1-I-K (right) submitted to the microbiological test.

that P3-III-G had a considerably higher water absorption than P1-III-G did. Because water absorption can be considered as a measure of concrete porosity, it was suggested to include it as a parameter in the Pomeroy model.

Different equations containing the parameters alkalinity and water absorption and one to four coefficients were tested. Logically, the inclusion of more coefficients allowed to improve the correlation. However, because the fitted curve is only based on the very limited number of eight data points, the use of more coefficients will induce the risk to create less robust equations. Therefore, the robustness was checked using leave-one-out cross validation. This implies that for each data point, the difference between the experimental value and the value estimated from an equation based on a reduced data set (all data except for the selected data point) was calculated. This was successively done for all different data points. The root-mean square error of prediction was then determined according to Eq. 3:

$$\mathrm{RMSEP} = \sqrt{\frac{\sum (x_{ie} - x_{ip})^2}{n}} \tag{3}$$

with x_{ie} = experimental value for concrete degradation after four cycles of the microbiological test (mm); x_{ip} = predicted value based on the equation (mm); and n = number of data points (eight).

Finally, an equation with two coefficients was selected as having a high correlation coefficient combined with preservation of the robustness (Eq. (4)):

$$C = \frac{c_1}{\mathrm{alk}} + c_2 W \tag{4}$$

with C = degradation depth after four cycles of the microbiological test (mm); alk = alkalinity (g/g); W = water absorption (%); and c_1, c_2 = model coefficients.

For the data set considered, the obtained values for the coefficients were $c_1 = -0.064$ and $c_2 = -0.039$. This equation had a correlation coefficient r=.84 compared with r=.75 for the Pomeroy model, and the robustness was preserved, as was proved by the RMSEP of 20% compared with 22% for the Pomeroy model. Of course, the values for the coefficients c_1 and c_2 will change when a different data set is used, but the procedure outlined above confirms the validity of the overall shape of Eq. (4). The relation between the degradation depth and the parameters alkalinity and water absorption is visually presented in Fig. 12. To relate this equation to the abovementioned example of concrete types P1-III-G and P3-III-G, the inclusion of the parameter water absorption in the model allows to better predict the higher degradation depth of P3-III-G. The high water absorption of this concrete type, pointing to an inferior quality, was the basic reason for the faster deterioration of these samples.

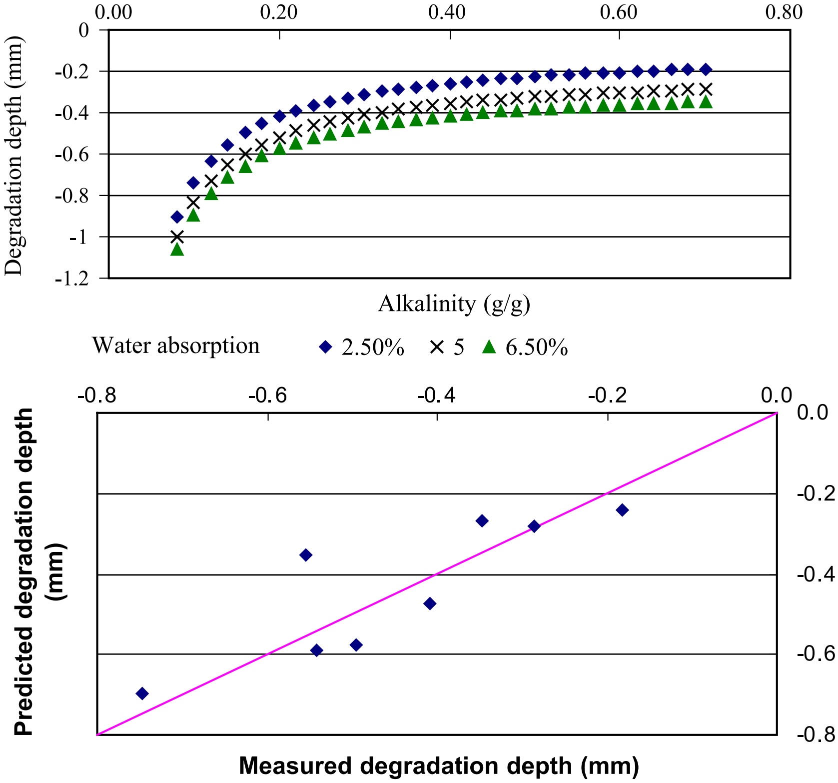

Fig. 12. Relation between concrete degradation depth and the parameters alkalinity and water absorption in the prediction model (top) and relation between measured and predicted values of degradation depth (bottom).

4. Discussion

When chemical and microbiological test methods were compared, it can be noticed that the microbiological tests were more aggressive to concrete: The chemical tests resulted in a maximum degradation depth of 0.4 mm after 10 cycles of 5 days in acid solution, while the microbiological tests resulted in a maximum degradation depth of 0.8 mm after 4 cycles of 10 days in the biological suspension. This difference, however, is due to the different experimental procedure and not to the origin of the acid. Concrete degradation by chemical and biogenic sulfuric acid using exactly the same sample size and test procedure were compared in Ref. [23]. This was realised by performing a chemical test, mimicking the microbiological test described earlier. During the second step of every cycle of the microbiological test procedure, pH and sulfate concentrations were measured and based on these profiles, sulfuric acid was dosed in the chemical test procedure to obtain the same values. These data showed that for Portland cement samples, thickness and weight losses were more than twice as high for the chemically treated concrete samples in comparison with the microbiologically treated samples. The continuous shaking of the samples during this procedure, resulting in the immediate removal of the deteriorated material, may be one of the important causes of the faster degradation in this procedure compared with the TAP procedure.

The aggregate type appeared to influence the concrete degradation to the largest extent. The concrete with limestone aggregates showed a more limited decrease in radius or thickness than did the concrete with inert aggregates. Because the decrease in radius or thickness is an average value for cement paste and aggregates, and considering that the inert aggregates are unaffected by the sulfuric acid, it is clear that the cement paste of concrete with inert aggregates is significantly faster degraded. Apparently, the limestone aggregates exert a protective action at the level of the cement paste by neutralisation of the acid. However, this more pronounced neutralisation was not noticed in the pH change of the acid solution. It can therefore be suggested that the effect is more local and that a microenvironment with higher pH is created near the concrete surface. The dissolution of the limestone aggregates thus prevents that the acid reaction is concentrated on the cement matrix [24].

For the microbiological tests, the weight loss was determined as an additional parameter to judge degradation. Although the aggregate type had only little effect, limestone samples showed a higher weight loss than did the samples with inert aggregates. This seems to contradict the thickness measurements. Nevertheless, this effect can be explained by taking the density of the concrete constituents into account. For the concrete with limestone aggregates, the removed material consisted of “concrete” (= aggregates + cement mortar) with a density of about 2400 kg/m^3. For the concrete with inert aggregates, on the contrary, the removed material consisted, in this stage, only of cement mortar with a density of around 2000 kg/m^3. This partly explains why limestone concrete with a lower average attack depth can still figure a higher weight loss. This effect will probably disappear when the degradation process proceeds and large

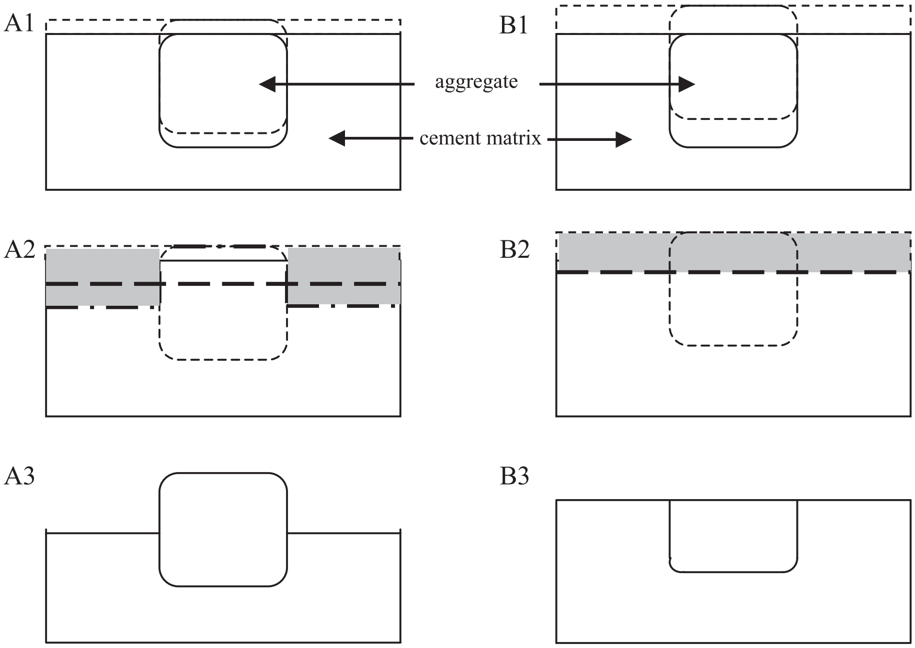

Fig. 13. Schematic representation of the degradation by (biogenic) sulfuric acid for concrete with inert (A) or limestone (B) aggregates. The degradation can be regarded as a combination of the expansion (Step 1) and the removal of degraded concrete (indicated in grey, in Step 2). The bold, dashed lines represent the average degradation, and the dashed, dotted line the real profile as measured with the laser sensors (in Panel B2, both lines coincide). The result is shown in Step 3. This figure illustrates how a more limited thickness change of limestone concrete can be combined with a higher weight loss.

aggregates are removed from the matrix. However, even this effect cannot explain completely the large differences between the thickness and weight results. This could suggest that concrete with limestone aggregates undergoes a somewhat larger expansion than does concrete with inert aggregates. The different degradation process of concrete with inert and limestone aggregates respectively, is illustrated schematically in Fig. 13A and B.

Concrete types produced by centrifugation or immediate form removal showed a higher resistance than did those hardened in the form. This was most probably due to the higher W/C ratio of the latter and the corresponding higher water absorption.

The influence of the cement type was limited, especially in the chemical tests. Concrete types P1-III-K and P1-I52.5-K both had a high resistance and were produced with different cement types. Yet, in previous chemical experiments on concrete produced in the laboratory, the use of slag cement resulted in a higher resistance than did the use of HSR Portland cement [25]. This might be due to the fact that the laboratory concrete underwent ideal curing (28 days at >90% relative humidity), while for the current experiments, the concrete samples were taken from pipes produced according to the normal commercial production methods. After the normal factory curing, they were stored in a climate chamber at 20 °C and 60% relative humidity, to simulate possible outside conditions. It is well known that slag cement concrete is more sensitive to good and prolonged curing conditions than Portland cement concrete. However, the better performance of Portland cement concrete in the microbiological tests did correspond to results of previous experiments. Live/Dead analysis in Ref. [23] during the microbiological tests showed a more rapid colonisation by microorganisms of the surface of slag cement samples.

By the inclusion of, porosity-related, water absorption values, a better prediction of average degradation depths could be obtained, compared with the Pomeroy model, which uses the alkalinity as only material parameter. The authors agree that the proposed equation was only validated on a limited amount of research results and that it has to be checked in future experiments. However, because it is founded on a physical basis, namely, that concrete porosity has an effect on degradation, it is believed that this equation will also be able to better describe future test results.

5. Conclusion

A summary of the test results is given in Table 3.

The aggregate type influenced the concrete degradation to the largest extent both in tests with chemical and with microbiologically produced sulfuric acid. The concrete with limestone aggregates showed a more limited decrease in radius or thickness than did the concrete with inert aggregates. The results suggest that the limestone aggregates locally at the level of the mortar matrix create a protective microenvironment by neutralisation of the acid.

Concrete types produced by centrifugation or immediate form removal showed a higher resistance than those hardened in the form. This was ascribed to the lower W/C ratio of the former specimens and the corresponding lower water absorption values.

In contrast to previous chemical experiments on concrete produced in the laboratory, the influence of the cement type was limited. Furthermore, where previous experiments showed that slag cement concrete had a higher resistance, the current measurements were more to the advantage of the HSR Portland cement. This might be

Table 3
Summary of results from chemical and microbiological tests

Concrete types in order of increasing					
Degradation depth		R_a value		Weight loss	Depth local pits
Chemical	Microbiological	Chemical	Microbiological	Microbiological	Microbiological
P1-I-K	P1-I-K	P1-I-K	P2-I-G	P1-I-G	P1-I-K
P1-I52.5-K	P1-I52.5-K	P1-III-K	P1-I-K	P3-I52.5-G	P1-I52.5-K
P1-III-K	P1-III-K	P1-I52.5-K	P1-I52.5-K	P1-I-K	P1-III-K
P2-I-G	P1-I-G	P2-I-G	P1-III-K	P2-I-G	P1-I-G
P3-III-G	P3-I52.5-G	P3-I52.5-G	P1-I-G	P1-III-G	P2-I-G
P1-III-G	P1-III-G	P1-I-G	P3-I52.5-G	P1-I52.5-K	P1-III-G
P3-I52.5-G	P2-I-G	P3-III-G	P1-III-G	P1-III-K	P3-I52.5-G
P1-I-G	P3-III-G	P1-III-G	P3-III-G	P3-III-G	P3-III-G
Global results of statistical analysis, parameters in order of decreasing importance					
G>K	G>K	G>K	G>K	III>I	
P3>P1,P2	III>I	P3>P1,P2	P3>P1>P2	P3>P1>P2	
I ≈ III	P3>P2>P1	III>I	III>I	K>G	

P1: immediate form removal. P2: centrifugation. P3: hardening in the formwork. I: CEM I (Portland cement). III: CEM III/B (blastfurnace slag cement). G: gravel or porphyry. K: limestone.

due to the limited curing of commercially produced precast concrete elements.

Both in the current and previous investigations, Portland cement concrete performed better in the microbiological tests. A possible explanation can be a more rapid colonisation by microorganisms of the surface of slag cement samples.

An improvement of the Pomeroy model was suggested, in which water absorption (as a measure for porosity) was added as an important parameter related to concrete degradation, next to the parameter alkalinity. With this equation, a better correlation between measured and predicted values for degradation depth was obtained, while the statistical calculations of RMSEP showed that the robustness of the estimation was not impaired.

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