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A new test procedure for biogenic sulfuric acid corrosion of concrete

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Abstract

A new test method is described for biogenic sulfuric acid corrosion of concrete, more specifically in sewer conditions. The aim of the new test method is the development of an accelerated and reproducible procedure for monitoring the resistance of different types of concrete with regard to biogenic sulfuric acid corrosion. This experimental procedure reflects worst case conditions by providing besides H_2S, also an enrichment of thiobacilli and biologically produced sulfur. By simulating the cyclic processes occurring in sewer pipes, significant differences between concrete mixtures could be detected after 51 days. Concrete modified by a styrene-acrylic ester polymer demonstrated a higher resistance against biogenic sulfuric acid attack.

Introduction

Biogenic sulfuric acid attack (BSA) of concrete sewer pipes, wastewater collection systems, and treatment plants can cause severe damage and has been described in the United States (Islander et al. 1991; Padival et al. 1995), Germany (Sand et al. 1987; Schmidt et al. 1997), Japan (Mori et al. 1991, 1992; Tazawa et al. 1996) and many other places in the world as well. The effects of the corrosive attack of concrete in sewers can be of the order of several mm per year. Moreover, 20% of the total damage of concrete structures in sewer systems seems to be caused by sulfuric acid or sulfate attack (Kaempfer and Berndt 1998). Since the discovery in 1945 of a type of rapid corrosion of a concrete surface by *Thiobacillus* populations (Parker 1945), a lot of effort has been focused on the understanding of the corrosive process (Pomeroy and Parkhurst 1977; Sand and Bock 1984; Nielsen and Hvitved-Jacobsen 1988; Mori et al. 1992; Coleman and Gaudet 1993; Nielsen et al. 1998). It was demonstrated in these tests that the cause of the corrosive action was largely due to metabolic effects of thiobacilli. However, biogenic sulfuric acid corrosion has been studied mainly by using sulfuric acid directly as corrosive agent. Yet, some investigations have shown that even if concrete shows a certain resistance to sulfuric acid, it not always implicates a resistance against BSA (Schmidt et al. 1997).

Some research groups tried to simulate the corrosion processes and investigate not only the pure chemical sulfuric acid attack, but focus on the microbial site of the corrosive processes. For example, in Hamburg, a simulation chamber was built for microbiological corrosion tests in which specific conditions of temperature, nutrients and humidity can be controlled (Sand et al. 1987). The rate of corrosive BSA attack was determined by the loss of weight of the test specimens (cubes of $1.8 \times 1.8 \times 2$ cm) and the pH of the surface water in which the concrete blocks were submerged. Mori et al. (1991, 1992) used also a simulation chamber and in their experiments, the corrosion rate was determined by measuring the decrease of the cross section of the mortar specimens. Schmidt et al. (1997) described another type of simulation reactor developed by the Heidelberger Zement AG. At monthly intervals samples are removed from the reactor in order to determine the cell density at the surface as well as the loss in weight through corrosion.

The main source for biogenic sulfuric acid is the sulfur compound hydrogen sulfide, H_2S. It is produced by sulfate reducing bacteria (SRB, e.g., *Desulfovibrio* sp.). The latter are active under anaerobic conditions and reduce oxidized sulfur compounds to H_2S. These microorganisms, responsible for H_2S formation, live in the sewage, in the mud at the bottom of the pipelines, and in the slime layer (biofilm), coating the surfaces of pipelines above and below the water level. The transformation of H_2S into sulfuric acid occurs after the sorption of H_2S from the sewer atmosphere into the concrete or the biofilm on the surface of the pipelines above the water line under aerobic conditions. Once the H_2S has reached the atmosphere, it may react with oxygen to elemental sulfur, which is deposited on the slimelayer, coating the walls. Sulfur is a substrate for many thiobacilli, such as *Thiobacillus thiooxidans*, *Thiobacillus neapolitanus*, *Thiobacillus intermedius* (Kelly 1982; Trüper 1984; Hazeu et al. 1988), which metabolize it into sulfuric acid. The sulfuric acid produced is aggressive and may attack the inner surface of the concrete pipe and other parts of the treatment and transportation facilities, such as pumping stations, manholes and reservoirs. Ensuing, corrosion products like gypsum and ettringite can be formed (Bock and Sand 1986). These expansive products can lead to increased internal pressure resulting in small cracks. Furthermore, the corroded materials can be removed by the flow of sewage, which also results in the acceleration of corrosion (Mori et al. 1992).

This paper describes a new procedure to test concrete for its potential resistance to biogenic sulfuric acid. The procedure reflects worst case conditions by providing besides H_2S, also consortia of thiobacilli together with biologically produced sulfur. The new set-up consists of a cyclic process of corrosive attack simulating different conditions occurring in sewer systems. The cyclic process consists of a periodical occurrence of the following phenomena: (i) sorption of H_2S in the biofilm and eventually in the concrete surface, (ii) microbial formation of sulfuric acid, (iii) corrosive action of sulfuric acid, (iv) periods with a high loading of the sewer pipe at rainy days which wash the corroded concrete away and (v) dry weather periods exposing the dry concrete again to H_2S emitted by the sewage. In practice, these periods can overlap. Figure 1 gives an overview of the phenomena that the proposed test protocol tries to represent.

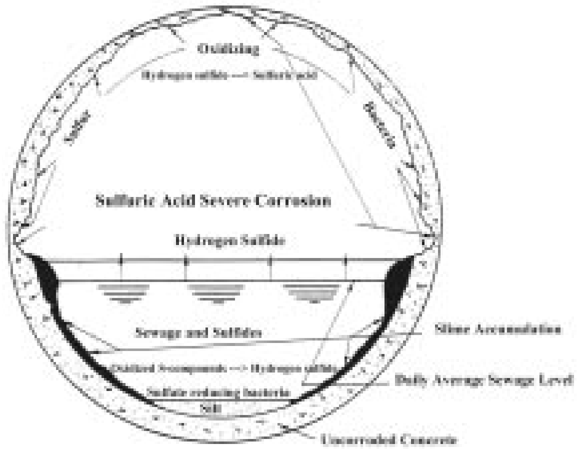

Figure 1. Schematic representation of the S-cycle, occurring in sewer pipes (after De Ceuckelaire 1989).

Materials and methods

Materials

(1) *Concrete samples*
Concrete specimens (size 2 × 2 × 5 cm) were manufactured with two different types of cement, i.e. Portland cement (CEM I 42.5) and blast furnace cement (CEM III 42.5). For each type of cement, specimens were made with and without addition of a polymer, type styrene-acrylic ester. The four different concrete types were tested in the deterioration experiments, each block was separately glued on a glass plate, which functioned as a reference for thickness measurements.

(2) *Bacteria-Biological sulfur*
Biologically produced sulfur is the end-product of the microbiological sulfide oxidation, a process carried out by mixed cultures of *Thiobacillus*-like bacteria. It consists of complex aggregates containing elemental sulfur, biomass and biopolymers and it has a hydrophilic character (Tichy et al. 1994). The biological sulfur particles have been produced in the Laboratory of Microbial Ecology and Technology using a 4.5 L Air Lift reactor and a concentration of 140 g L^{-1} S has been obtained.

The cell numbers of thiobacilli were determined by an MPN-technique using three selective nutrient solutions. *T. intermedius*/*T. novellus* medium was used for moderately acidophilic, facultatively autotrophic thiobacilli. It contained, per L of medium: $Na_2S_2O_3 \cdot 5H_2O$ 10.0 g, K_2HPO_4 4.0 g, KH_2PO_4

1.5 g, $MgSO_4 \cdot 7H_2O$ 0.5 g, $(NH_4)_2SO_4$ 0.3 g, Yeast extract 0.3 g, trace metals solution 10.0 ml and bromothymol blue (internal pH indicator); pH was adjusted to 6.5 (Atlas 1993). *T. neapolitanus* medium of Vishniac and Santer (1957) was used for moderately acidophilic, obligately autotrophic thiobacilli and for *T. thiooxidans*, strongly acidophilic, obligately autotrophic thiobacilli, the slightly changed medium of Vishniac and Santer (1957) was used. The pH was adjusted to 4.5 and bromophenol blue was used as internal pH indicator. The media were sterilized for 15 min at 121 °C. A 10 fold dilution series was inoculated in the different media. The tubes were incubated on a rotary shaker (90-rpm) in the dark at 28 °C for 21 days. Because of the fact that the *T. intermedius*/*T. novellus* medium also supports the growth of the obligately autotrophic thiobacilli, as *T. neapolitanus*, additional plating of the test tubes was done. Each positive tube (showing turbidity and a pH below 4) was streaked on *T. intermedius*/*T. novellus* agar (medium + 2% agar) and incubated for one week at 28 °C. If the colonies were transparent-yellowish, the test was considered positive for *T. intermedius*/*T. novellus*. However if the colonies were white-opaque, *T. neapolitanus* was assumed to be present in the positive colored test tubes (Sand and Bock 1984).

(3) *Culture media*
Concrete blocks were incubated in a 20 fold diluted aqueous solution of the biological sulfur suspension. The dilution solution contained tapwater and an additional N- and P-source (100 mg L^{-1} $(NH_4)_2SO_4$ and 10 mg L^{-1} K_2HPO_4).

For the control samples, an inactivated suspension was used. It consisted of the basic suspension, inactivated by dosing 1000 mg L^{-1} of a biocide, i.e. glutaraldehyde.

(4) H_2S-atmosphere
The incubation in a H_2S atmosphere occurred in an incubation chamber of 10 L. 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 ca. 250 ppmv.

Methods

(1) *Simulation test*
The corrosion progress was simulated in three cycles, performed at 28 °C. The duration of the experiment was 51 days. One cycle of 17 days consists of the following steps:

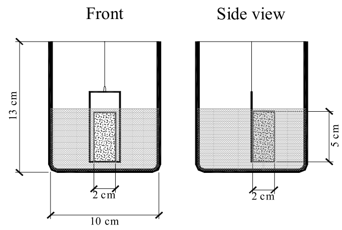

Figure 2. Schematic representation of the experimental set-up in step 2 of the cyclic procedure.

- *Step 1.* H_2S-incubation. The air-dry concrete samples, each glued to a glass plate, were placed in the H_2S incubation chambers of 10 L for 3 days.
- *Step 2.* Incubation of the concrete blocks in solution. Each block was hanging in a separate glass recipient, submerged in 600 ml of the basic suspension of pH 7 (Figure 2). These separate recipients were covered and placed for 10 days on a rotary shaker (90-rpm). A control treatment for each different composition of the concrete consisted of a concrete block hanging in an inactivated suspension. As reference, a recipient containing the suspension without concrete sample was used.
- *Step 3.* Rinsing with Milli-Q water. On rainy days, high flow rates of water can occur in sewer pipes and possible corrosion products and debris can be removed and washed away, which provides a new surface for the corrosive attack. This can cause an acceleration of the deterioration of the concrete surface. Placing the concrete blocks in separate glass recipients, containing Milli-Q water on the rotary shakers for 2 days simulated this. No corrosion occurs when the specimens are placed in distilled water (Mori 1992).
- *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. Drying the concrete samples for 2 days simulates this step.

(2) *Analyses*
The H_2S concentration in the first step was determined by H_2S detector tubes (Scantec NV, Merksem, Belgium).

During step 2, the pH of the suspension was determined daily with a Knick pH-meter (Berlin, Germany) and a Metrohm double electrode (Berchem, Belgium). The sulfate concentration in the suspension was determined according to Standard Methods. Samples were taken on day 4, 7 and 10. Bacterial growth on the concrete surface was examined by Scanning Electron Microscope (SEM type Jeol JSM 840) analysis. The total Ca-concentration of the suspension was determined by a destruction method according to Standard Methods, following detection with a flame atomic spectrometer (Perkin Elmer flame AAS, Überlingen, Germany).

After every cycle, the thickness of the concrete blocks was measured using a Compac 523L dial indicator (Geneva, Switzerland) with accuracy of 0.01 mm. The glass plate was used as reference. The thickness of the concrete block was determined by the mean value of 10 measurements on each concrete sample. For each concrete composition, the mean value of the thickness of two samples was determined.

After 3 cycles, the loss of substance was determined by weighing the cubes after drying in an oven at 60 °C. The latter temperature was chosen to avoid changes in crystal structures of the concrete and interaction of the polymer.

Results

The cyclic test procedure was conducted to evaluate four different types of concrete with regard to resistance against biogenic sulfuric acid attack. The incubation in a H_2S atmosphere during three days was started at an initial gas concentration of 250 ppmv. The H_2S in the incubation chamber gradually decreased, begin and end concentrations of H_2S are given in Table 1. In the reference incubation chamber, without concrete specimens, the H_2S concentration remained at a constant value of 250 ppmv. These results show the sorption of H_2S by the concrete blocks.

The biological sulfur mixture, applied in the second step contained per ml: 2×10^5cells of *T. thiooxidans*, 4×10^5 cells of *T. novellus*/*intermedius* and 1×10^5 cells of *T. neapolitanus*. SEM-analysis showed that after the second step, bacterial cells covered concrete surfaces (Figure 3).

The pH measurements during the second step of the cyclic procedure are given in Figure 4. The pH of the solution decreased rapidly from pH 7.0 to pH 3.0 after 2 days for the four types of concrete and continued to drop to pH 1.0 on day 10. The pH of the reference, the solution without a concrete block,

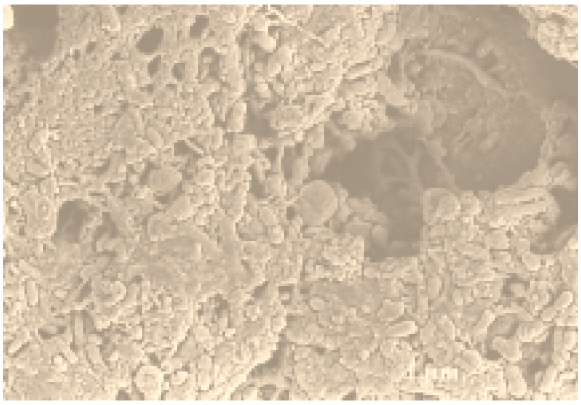

Figure 3. Concrete surface after exposure to biological sulfur mixture (SEM-analysis, 4000x). The bacterial cells (1 to 3 μm-sized rods, probably thiobacilli) form a dense layer on the concrete.

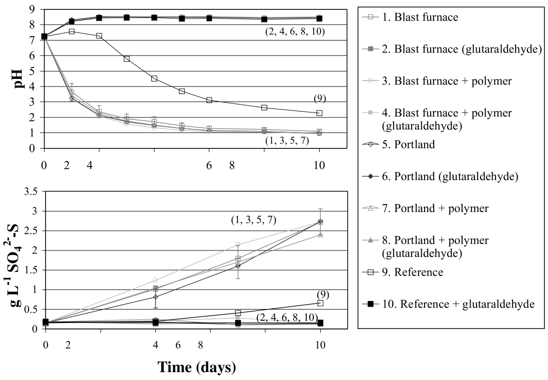

Figure 4. Profiles of pH measurements and sulfate concentrations of the solution, wherein the different types of concrete samples were hanging, during the second step of the first cycle.

decreased less rapidly in the beginning and after 10 days, a constant pH of 2.2 was reached. Additional tests (data not shown) indicated that this was due to a smaller stirring (no concrete block hanging in the solution), which has as a consequence less mass transfer and aeration of the suspension. The control samples, i.e. concrete blocks in inactivated solution, showed a small increase of pH. This can be explained by the inactivation of the microorganisms (no acid production) and the alkalinity of the concrete samples hanging in the solution.

Additional indications of the biological activity are the profiles of the sulfate concentrations in the solution (Figure 4). For the control samples, i.e. bacterial solutions with addition of glutaraldehyde, the sulfate concentrations started with 0.2 g L^{-1} SO_4^{2-}-S and remained constant. However, for the active systems, the sulfate concentration increased after 10 days towards a

Table 1. Begin and end concentrations of H_2S in the gas phase of the incubation chambers in the first step of the three cycles.

	Begin concentration (ppmv)	End concentration (ppmv)		
		Cycle 1	Cycle 2	Cycle 3
Reference	250	250	250	250
Incubation chamber 1	250	<0.1	1	1.7
Incubation chamber 2	250	1.5	4	0.6

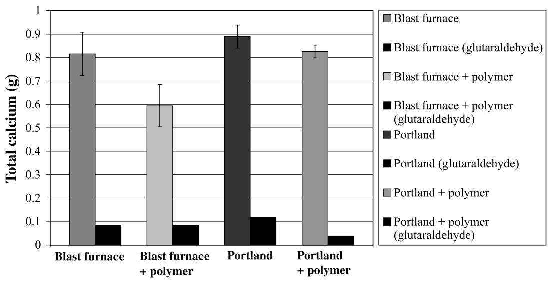

Figure 5. Total amount of Ca released out of the concrete samples during the three cycles.

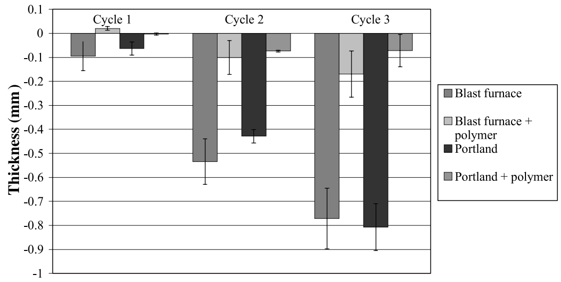

Figure 6. Overview on the thickness measurements of the concrete blocks during the 3 cycles.

concentration of 2.7 g L^{-1} SO_4^{2-}-S. For the reference solution, there was a smaller increase of the sulfate concentration, probably caused by a smaller activity due to a lower mixing in the recipient. Figure 4 is only presenting the profiles of pH measurements and sulfate concentrations for cycle 1; the profiles for cycle 2 and 3 are comparable with the profiles for cycle 1 (data not shown). The largest deviation on the mean value for pH and sulfate values is shown.

In Figure 5, the total amounts of Ca released in the suspension during the three cycles are presented. The amount of Ca released out of polymer modified concrete samples was significantly lower than for the concrete samples without polymer. A comparison between the two different concrete types, blast furnace and Portland cement is difficult to make due to a different Ca-content. The control samples showed a small release of Ca.

The thickness measurements of the concrete samples after the three cycles are given in Figure 6. For the control samples no significant change, swelling or loss of material could be noticed (data not shown). This is as expected, because no bacterial activity and consequently no sulfate production, was seen in the solution. For the concrete blocks incubated in the active solution, differences in thickness between the different types of concrete were observed. For the concrete compositions without addition of a polymer, a loss of thickness of 0.75–0.8 mm was measured after 3 cycles. The concrete samples with polymer showed a higher resistance: the loss of material was in the order of 0.1–0.15 mm after three cycles. No significant difference could be seen between the Portland and the blast furnace cement. Upon prolonged exposure, a gradual loss of material can be seen. During the first 2 cycles, the Portland cement showed a smaller loss, but after three cycles the loss of thickness between Portland and blast furnace cement reached the same level. As an average, this cyclic treatment gave rise to a corrosion rate of at least 5.7 mm/year of the unprotected concrete.

The weight measurements before and after the three cycles are shown in Figure 7. For the polymer compositions, a weight loss of 2.8–3.2 g (5–6%) was seen, for the concrete blocks without polymers a weight loss of 5–6 g (9-11%) was determined.

Discussion

Biogenic sulfuric acid corrosion is often a slow corrosion process, a corrosion rate of 5 mm a year was described by Mori et al. (1991). Moreover, it often takes some years before the corrosion processes start. For example, Sand (1987) did some field ex-

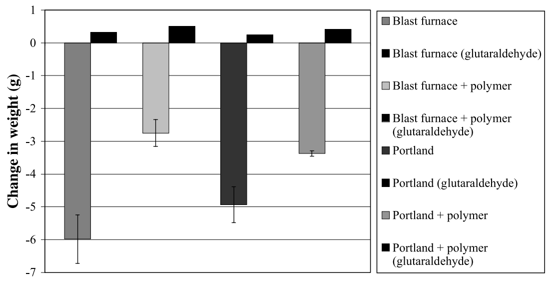

Figure 7. Weight measurements after three cycles.

periments and the first signs of corrosion were only measurable after 6 years of incubation. So, to investigate differences in durability and resistance against the corrosive attack between different materials and compositions, often long experimental periods are necessary. To avoid these long periods, scientists have been searching for simulation experiments, in which the corrosive attack could be accelerated (Sand et al. 1984, 1987; Mori et al. 1992; Schmidt et al. 1997). Sand et al. (1984, 1987) performed some experiments over a period of 270 days. The severely corroded test blocks were characterized with a mass loss of 5.8%, while a loss of 0.7% was seen for the test blocks with slight corrosion. Schmidt et al. (1997) stated that time spans of 3 to 5 months were enough to investigate the resistance of several concrete types against biogenic sulfuric acid attack. In these experiments the corrosion rate was determined by measuring the weight loss of the test specimens. The specimens that showed a higher resistance, were characterized by a 3 to 4% loss of weight; while the severely damaged concrete blocks were characterized by a loss of weight of 18 to 31% after 5 months of testing. Another investigation on laboratory scale was carried out by Mori et al. (1992); the duration of the experiments was 6 months. The corrosion rate was determined by measuring the thickness of the concrete samples. The maximum corrosion rate of the specimens exposed to sewage was 6 mm/year, approx. 20 mm above the liquid level.

The newly proposed test procedure consists of 3 cycles of 17 days. Each cycle is a sequence of H_2S incubation, sulfuric acid formation, removal of loose material and drying. By simulating the cyclic process of sewer environments, statistically significant differences between concrete compositions can be observed after three cycles or 51 days. Weight measurements were done after the third cycle, because changes in weight (increase or decrease) are in the beginning very difficult to relate to the resistance of the concrete samples. An increase in weight can possibly be due to the formation of corrosion products. This goes together with swelling of the concrete and an increased internal pressure in the concrete. The pressure results in small cracks and eventually, loss of material and decrease in weight. As for the thickness measurements, a difference could be seen between the concrete compositions with and without polymer addition. However these differences are smaller compared with the differences seen in the thickness measurements. The smaller differences in weight compared to thickness can possibly be explained by the formation of reaction products with different molecular weights. The weight losses are of the same magnitude as obtained by other researchers. No difference between Portland and blast furnace cement specimens could be seen in the cyclic procedure. These date agree with those presented by Ehrich et al. (1999). In these experiments a rather low resistance of the ordinary Portland and blast furnace cement was observed in comparison with calcium aluminates. The changes in thickness are also comparable with the changes in thickness measured in the laboratory scale experiments in sewage water after 50 days by Mori et al. (1991). In contrast to other tests where the most severe corroded point of the specimens was used, our results represent the thickness as a mean value of 10 measurements on the concrete block. This gives a more balanced appreciation of the corrosion of the surface. An advantage of this method is the measurement of weight losses as well as thickness measurements; in this way additional information can be obtained. The experimental period of 51 days is a rather short period compared to other test protocols. Yet the overall procedure provides statistically valid data. Another parameter to reflect the usefulness of a test procedure is the acceleration rate of the biogenic sulfuric acid attack of the test procedure compared to the attack in sewer systems. Different values were given in literature, acceleration rates varying between 8–24 times (Ehrich et al. 1999). However, this parameter is rather difficult to compare. Mori et al. (1991) determined corrosion rates of 4.3–4.7 mm per year in the sewer pipes of Ohmuta station (Japan). In Belgium, severely corroded sewer pipes were observed in the district of Bruges; after six years the concrete pipes were deteriorated to a depth of 2.3–3.1 cm. These data demonstrate the difficulty to compare the corrosion rate of an experimental set-up with the corrosion rate in situ. Literature shows that differences in atmospheric content and thiobacilli species on concrete surfaces occur in corroded sewer systems all over the world (Milde et al. 1983). Some important parameters for biogenic sulfuric acid attack are sewage characteristics, aerobic/anaerobic conditions, temperature and turbulence in the sewage flow, caused by among others connection of local lines into large interceptors, changes in velocity and sewage flow levels.

The procedure simulates worst case situations. The succession of dry H_2S, wet bio-S and cleaning is somewhat arbitrary but effective. The incubation of the concrete specimens in an atmosphere containing H_2S, in the absence of thiobacilli, results in the deposition of substantial amounts of elemental sulfur (formed by chemical oxidation) on the concrete surface. Elemental sulfur is known as a good substrate for thiobacilli, by which it is transformed into sulfuric acid and consequently causes concrete corrosion. By using bio-S in this experiment, there is an abundance of the bacteria responsible for sulfuric acid formation and accessibility to nutrients necessary for their activity. The thickness of the concrete samples was measured using a measuring apparatus (dial indicator) with an accuracy of 0.01 mm. The concrete blocks were glued on an inert glass plate as reference value. The value for each composition is the mean value of the thickness of two samples. By using the reference value and by taking the mean value of ten thickness measurements for every concrete sample, this method is reliable. In this test procedure, concrete specimens were preferred above mortar specimens, because of possible influences of the polymer on the aggregate-cement paste interface.

A variety of test conditions can potentially be optimized, but the purpose of the new test procedure was to obtain an aggressive worst case situation giving adequate measurements of pH decrease, SO_4^{2-}-formation, loss of material and weight loss in a rather short period. A further optimization of the cyclic procedure is necessary to come to a comparison between the experimental procedure and experiments in situ. By this, an useful instrument would be obtained to evaluate the biogenic sulfuric acid resistance of different concrete compositions as an accurate reflection of the difference in resistance of concrete in sewer conditions.

Further work is also necessary with respect to the stoechiometry of the biological conversions.

Conclusion

The test procedure can be used as a straightforward inexpensive method for monitoring the resistance of different types of concrete against biogenic sulfuric acid. The procedure simulates worst case situations by providing H_2S penetration in the concrete surface, supplementation with sulfur enriched active thiobacilli and furthermore by regularly providing a new accessible surface for corrosive attack. The procedure yields interpretable data in a period of 51 days (3 cycles).

Acknowledgments

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