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Chemical, microbiological, and in situ test methods for biogenic sulfuric acid corrosion of concrete

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Abstract

Biogenic sulfuric acid corrosion is often a problem in sewer environment; it can lead to a fast degradation of the concrete structures. Since the involvement of bacteria in the corrosion process was discovered, considerable microbiological research has been devoted to the understanding of the corrosive process. Mechanical engineers have focused on experiments comparing the resistance of several concrete mixes against biogenic sulfuric acid corrosion. Because of a lack of standardised methods, different test methods have been used, and various parameters have been modified to evaluate the resistance of the materials. The research done on sulfuric acid corrosion of concrete can roughly be divided in three groups: chemical tests, microbial simulation tests, and exposure tests in situ. In this article, an overview of the recent developments in the test methods for biogenic sulfuric acid corrosion and the obtained results are presented. Possible differences between biogenic sulfuric acid corrosion and chemical sulfuric acid corrosion are delineated. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion; Durability; Sulfate attack; Ettringite; Biogenic sulfuric acid

1. Introduction

Biogenic sulfuric acid corrosion is often found in sewers. Several authors have described this problem [1–6]. The bacterial activity in the sewers creates a sulfur cycle, which can lead to the bacterial formation of sulfuric acid. When anaerobic conditions occur due to long residence time or the 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. Once in the atmosphere, it can react with oxygen to elementary sulfur, which is deposited on the sewer wall, where it becomes available as a substrate for oxidising bacteria, *Thiobacilli* sp. [1,7–9]. Those bacteria convert the sulfur into sulfuric acid, which causes corrosion of the concrete.

The sulfuric acid reacts first with the calcium hydroxide (CH) in the concrete to form gypsum. Although the formation of gypsum is associated with an increase in volume by a factor of 1.2–2.2 [10–13], some authors stated that this reaction plays only a secondary role in the corrosion process [11]. Whether or not gypsum formation is expansive is an object of controversy [14,15]. The reaction between gypsum and calcium aluminate hydrate (C_3A) with the formation of ettringite is much more detrimental. The volume of the ettringite mineral is several times greater than the volume of the initial compounds. Some authors report an increase of the volume with a factor 2 [10,13], while others mentions even a factor of 7 [11]. Thus, the formation of ettringite is mainly responsible

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for the large volume expansion, which leads to the increase of internal pressure and deterioration of the concrete matrix.

Biogenic sulfuric acid corrosion has been studied since 1945 when Parker [1] discovered that bacteria were involved in the corrosion process. The research done on the resistance of concrete against this type of corrosion can roughly be divided in three groups: chemical tests, microbiological simulation tests, and tests in situ. Investigations have shown that the high resistance of a certain concrete type to sulfuric acid does not always indicate a high resistance against biogenic sulfuric acid corrosion [16]. The most important part of the experiments on biogenic sulfuric acid corrosion were chemical tests using sulfuric acid as a corrosive agent. Some researchers took the microbiological action into account in simulation tests, which were mainly carried out with different types of simulation chambers. A third kind of investigations on biogenic sulfuric acid corrosion has been done in situ. Sometimes, when a case of biogenic sulfuric acid corrosion is manifested, a case study was performed. Areas that are predisposed to have all the conditions to create biogenic sulfuric acid corrosion were used to investigate the resistance of different materials against corrosion by means of exposure tests.

In many countries at present, due to increased environmental concern and restrictions, a lot of sewers are installed mainly in the form of concrete tubes. It is, therefore, of importance to have a good insight in the phenomena of acid corrosion in these infrastructures. Moreover, concepts to abate such deterioration are warranted.

2. Chemical tests

The chemical resistance of concrete can be tested in different ways:

1. Realistic concentrations of the aggressive acids/salts can be used in combination with a sensitive method to detect deterioration; the latter supplemented with extrapolation method are used to calculate the degradation in the future [17].
2. Accelerated tests can be performed. The degradation rate can be increased by means of higher concentrations of the aggressive medium, higher temperature, larger contact surfaces.

2.1. Close-to-reality investigations

Carrying out the experiments in a realistic way and keeping the factors responsible for the deterioration of unchanged substantiates in this type of investigation the assumption that the deterioration process itself has not changed. Particularly in the case of sulfate corrosion, one must be concerned that accelerating the process could change the attack mechanism. Cohen and Mather [14] warned about the problems that can arise when accelerating the process by, for instance, increasing the sulfate concentration. Regarding sodium sulfate attack, the corrosive mechanism is divided into two parts. At low SO_4^{2-} concentrations (less than 1000 mg SO_4^{2-}/l), deterioration of the concrete is mainly due to the formation of ettringite. On the other hand, at high concentrations, the formation of gypsum is the main cause of deterioration [14,17]. So, the mechanism of attack depends on the concentrations of the SO_4^{2-} ions in the solution. To be able to detect the deterioration or differences in degradation between different test specimens—with methods close to reality within a reasonable time—sensitive methods are needed. Examples include the measurements of the changes in the chemical composition of test specimens and measurements of consumption of acids in function of time.

Rombén [17] determined a relationship between acid consumption and the attack depth of the concrete caused by hydrochloric acid. He measured the amount of acid needed to keep the pH of the solution constant and the amount of Ca released in the solution in function of time. He also determined the Ca content of the concrete. The combination of these data allowed him to estimate the depth of attack in function of time. In this way, he was able to establish a relationship between acid consumption and attack depth.

A disadvantage of this kind of close-to-reality investigation is that only the very first stages of the attack can be measured. To estimate the attack of the concrete at a later stage, an extrapolation of the obtained relationship has to be used. This implicates the risk that new mechanisms of a certain type, which are not noticeable during the time of measurement, arise in a later period of the deterioration. Rombén [17] noted that, in case of sulfuric acid attack, the described method is not useful. The rate of attack in the case of sulfuric acid probably follows certain relationships, which are difficult to extrapolate due to the special mechanism that is characteristic for this acid.

2.2. Accelerated tests

One of the most widely used ways to investigate the chemical resistance of concrete is to carry out accelerated tests in laboratory. The advantage of this method is that the entire life of the specimen in question can be simulated [17]. An acceleration of the process can be achieved in different ways [10,13,14,17,18]. The concentration of the aggressive solution can be increased and/or the reaction surface can be increased by using specimens with large surface area/volume ratio, in the order of 0.5:1 (mm^2/mm^3). In some cases, the process can be accelerated by means of continuous wetting and drying cycles, which increase the crystal pressure. Raising the temperature can also increase the process speed. Cohen and Mather [14] report that, in the case of sulfate attack, increasing the sulfate concentration (>1500 ppm SO_4^{2-}) and increasing the reactive surface are the most practical approaches. Sulfate concentrations higher than the concentrations found in the studied environment should not be used if researchers aim to study the mechanisms of attack because these could be changed. For the same reason, the authors noted that the results obtained in the laboratory under accelerated test conditions by increasing sulfate concentration cannot be used to predict the actual behaviour in the field.

The chemical tests to investigate the resistance of materials against biogenic sulfuric acid corrosion have been mainly performed using sulfate solutions and sulfuric acid solutions. The sulfate solutions used are often sodium- or magnesium sulfate solutions. Although the reaction mechanisms are different in both cases, the results of such tests are often used to obtain an overall impression of the sulfate resistance of the concrete. In the case of sulfate solutions, the type of cation is very important [15] and several authors have focused on its effect. In the case of magnesium sulfate solution, the action of the magnesium ion is of major importance, whereas in the case of a sodium sulfate solution, the action of the sodium ion is less important. The reaction mechanisms are shown in Fig. 1. The general view about the Na_2SO_4 attack is that it is concentrated on the calcium hydroxide [$Ca(OH)_2$] and the hydrated tricalcium aluminate (C_3A), and that it does not attack the calcium silicate hydrates (CSH). Yet, Taylor [19] stated that Na_2SO_4 attacks the calcium silicate hydrates but only when the Ca^{2+} supply by the calcium hydroxide is exhausted. $MgSO_4$ attacks all cement minerals, including calcium silicate hydrates. The decalcification of calcium silicate hydrates is more marked in the case of $MgSO_4$ attack than in case of Na_2SO_4 and leads to the complete destruction of calcium silicate hydrates with the formation of silica gel.

Sulfate solutions are often used because it was believed that the corrosion found in sewers was caused by sulfate attack. In fact, it is not a sulfate attack but a sulfuric acid attack. There is a major difference between these two types of attack [10]. When concrete is attacked by sulfuric acid, there are two important aspects. On one hand, there is the reaction with the sulfate ion; on the other, the action of the hydrogen ion has to be considered. Sulfate attack comprises only one aspect of sulfuric acid attack. Concrete deterioration caused by a sulfuric acid solution was found to be very severe compared to sulfate attack due to the sulfate ion participating in sulfate attack, in addition to the dissolution caused by the hydrogen ion.

Most of the research has been carried out on mortar or cement paste specimens. The results were then extrapolated to concrete. Yet, Cohen and Mather [14] state that cement paste and concrete cannot be compared just like that. Because of the presence of aggregates, a transition zone appears in concrete between the aggregates and the paste. Fig. 2 illustrates gypsum formation in the cement paste near a granulate. Due to the effect of the transition zone, the microstructures of pure paste and paste within the concrete are different. The effects of transition zones extend far beyond the aggregate surface and the individual effects of surfaces in concrete overlap. Therefore, little or no paste in concrete has the same microstructure as pure paste and is not affected. The authors suggest that, when research is done on the sulfate durability of concrete, experiments both on concrete and on paste should be carried out and compared.

2.2.1. Accelerated tests with sodium- or magnesium sulfate

Sulfate resistance of concrete has often been studied using accelerated tests with sodium- or magnesium sulfate solutions. The commonly applied standardized test method ASTM C1012 (1989) [21] also prescribes sodium sulfate to investigate the sulfate resistance.

Various researchers have applied similar test methods [15,22–27]. Mortar specimens with different dimensions are used, varying from prisms of 25 × 25 × 125 mm to prisms of 40 × 40 × 160 mm. The test specimens are immersed in an aggressive solution, often with sodium or magnesium sulfate. The concentrations vary from 5% up to 10%. In most cases, the liquid is replenished at regular intervals, preferably every month or the pH of the solution is maintained at a certain level by automatic titration. The evolution of the deterioration is mostly monitored by

Sodium sulfate corrosion:

$Ca(OH)_2 + Na_2SO_4.10H_2O \rightarrow CaSO_4.2H_2O + 2\ NaOH + 8\ H_2O$

$3CaO.Al_2O_3.12H_2O + 3\ (CaSO_4.2H_2O) + 14\ H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$

$2\ (3CaO.Al_2O_3.12H_2O) + 3\ (Na_2SO_4.10H_2O) \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O + 2\ Al(OH)_3 + 6\ NaOH + 17\ H_2O$

Magnesium sulfate corrosion:

$Ca(OH)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(OH)_2$

$3CaO.Al_2O_3.6H_2O + 3\ MgSO_4 \rightarrow 3\ CaSO_4 + 2\ Al(OH)_3 + 3\ Mg(OH)_2$

$3CaO.2SiO_2.2H_2O + 3\ MgSO_4.7H_2O \rightarrow 3\ (CaSO_4.2H_2O) + 3\ Mg(OH)_2 + 2\ SiO_2$

Sulfuric acid corrosion:

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O$

$3CaO.Al_2O_3.12H_2O + 3\ (CaSO_4.2H_2O) + 14\ H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$

$CaO.SiO_2.2H_2O + H_2SO_4 \rightarrow CaSO_4 + Si(OH)_4 + H_2O$

Fig. 1. Corrosion mechanisms of sodium sulfate, magnesium sulfate, and sulfuric acid (after De Ceukelaire [11] and Lea [20]).

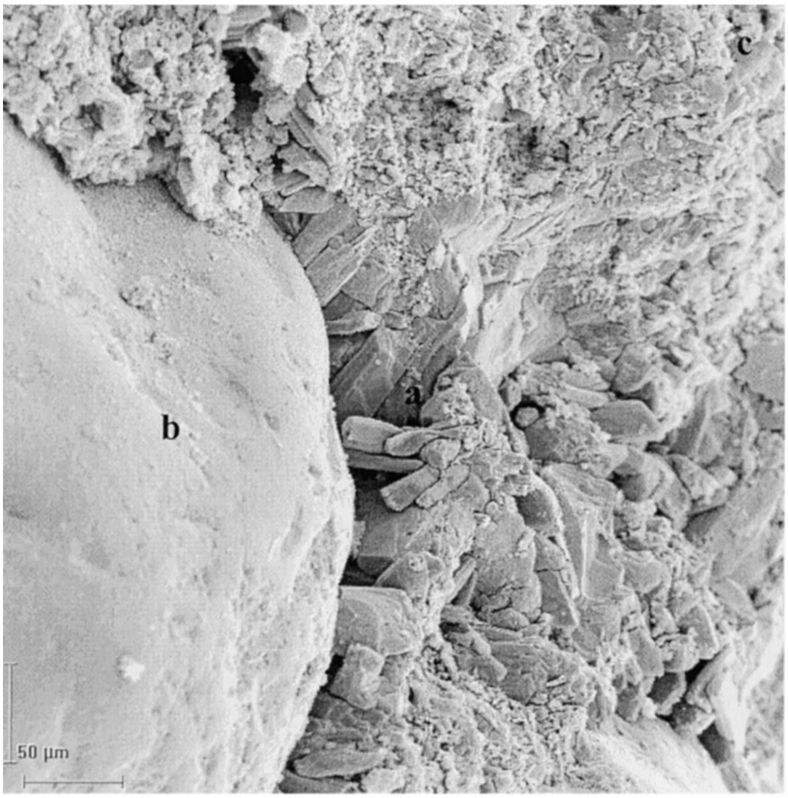

Fig. 2. Scanning electron microphotograph of gypsum crystals in the cement paste near a granulate. Note the many gypsum crystals (a) formed in the cement paste near the granulate (b) on the left. In the right corner, less modified cement paste (c) can be seen.

measurements of the expansion of the specimens. Other parameters such as mass loss, strength loss, and visual inspection often contribute to the evaluation of the performance of the different specimens. Chemical changes are measured through analysis of the liquid. Techniques such as SEM (Fig. 2) and XRD are used to examine the microstructure. In most cases, the experiments are conducted over a period of 1–3 years.

Several researchers found that the expansion of specimens with ordinary Portland cement was greater than the expansion of specimens made with cements blended with blast furnace slag [23,25,28,29]. Gollop and Taylor [29] and Al-Amoudi et al. [23] report that the better resistance of the blended cements was due to a lower amount of calcium hydroxide. Plain cement mortar specimens exposed to sodium sulfate solution showed an expansion of 0.10–0.11%, which was much higher than the expansion of blended cement mortar specimens, which amounted from 0.06% to 0.09% after 360 days of immersion.

In most experiments, highly sulfate-resistant Portland cement shows better resistance to sodium sulfate solutions than ordinary Portland cement [22,30,31]. This is attributed to the lower tricalcium aluminate (C_3A) content of the high sulfate-resisting cement. Nevertheless, Scherer and Fidjestöl [24] found, against all expectations, an inferior behaviour of the highly sulfate-resistant cement compared to normal Portland cement. This was possibly due to the concentration of the sulfate solution used (1500 mg SO_4/l solution). With this concentration, the formation of ettringite is not a dominating factor in the deterioration process: The formation of gypsum is more important and when gypsum is the main cause of deterioration, the tricalcium aluminate (C_3A) content of the cement is of less importance.

The positive effect of the substitution of cement by silica fume have been reported in several investigations [15,19, 20,22,24,25,28,32,33]. Most authors attribute the better performance of cements with silica fume to the decrease of permeability, pore size, and calcium hydroxide content. Although some researchers found a decrease in total pore volume varying from 0% to 20% with a silica fume replacement of 0% to 20%, the refinement of the pore structure of concrete due to the addition of silica fume is of major importance. Dependent on several factors such as the concrete mix composition, the water/cement ratio, the type of cement, and the type of silica fume, a decrease of up to 25% in the volume of the pores larger than 0.025 μm has been measured when silica fume replacements up to 30% are applied. This pore-refinement results in a decrease of the permeability of the specimens up to a factor 10 in the case of a 20% replacement. Where normal hydrated Portland cement paste consists of 20–25% calcium hydroxide, the addition of 30% silica fume can reduce this amount to about 0%, depending on the type of silica fume and the type of cement used. Even when cement is used with a relatively high content of C_3A (10.9%), which would favour the formation of ettringite, a 10% replacement improves the resistance of the specimens more than using a sulfate resisting Portland cement with a low content of C_3A (1.4%) [22].

The addition of fly ash improves the resistance in most cases, although to a smaller degree, than the partial replacement of cement by silica fume [15,23,25,26,34].

A common measure to obtain a high quality concrete, which is relatively resistant to different degradation mechanisms, is to use a low water/cement ratio (< 0.4). This results in the formation of a dense and less permeable cement matrix. However, in the case of sulfate attack, there is no consensus about the effect of the water/cement ratio [34,35]. Most authors advise the use of a low water/cement ratio [25,32], but some authors mention that a greater water/cement ratio (> 0.5) creates more place for the reaction products [24].

2.2.2. Accelerated tests with sulfuric acid

The test method—in the case when sulfuric acid is used as an aggressive liquid—is, in most cases, the same as for sulfates. The test specimens, mostly mortars, are submerged in a sulfuric acid solution. Solutions containing 1–5% sulfuric acid are replenished at regular times, often once a week, or the pH of the solutions is kept at a certain level by titration. The deterioration of specimens is followed up mainly by investigating the mass loss of the specimens. Some researchers also use the change in compressive strength as an indicator for the corrosion. A key difference between the different test procedures is whether or not the test specimens were brushed before weighing.

Durning and Hicks [32] used a 1% and a 5% sulfuric acid solution to subject concrete specimens to 7-day attack cycles. After every cycle, the specimens were brushed and weighed. They investigated the effect of silica fume addition on resistance against sulfuric acid. It was found that, as the amount of silica fume increased (from 0% to 30% by mass of cement), the resistance of the specimens increased also. When a 30% replacement was used, the number of cycles to failure of the specimens in the 1% sulfuric acid solution was already doubled. Yet, in the more concentrated acid solution, there was a noticeably slower increase in the resistance. It took only 1 or 2 cycles more until failure of the specimens was obtained. Durning and Hicks [32] attributed this difference to the decomposition of calcium silicate hydrate in the more concentrated liquid in addition to the reaction with the free calcium hydroxide. In contrast, Yamoto et al. [36] found that the addition of 30% silica fume almost doubled the time to failure of the specimens in a sulfuric acid solution of even 5%. They attribute the increase of resistance for the specimens with silica fume to the decrease of the permeability. It must be noted that these researchers did not brush their specimens. Thus, brushing of specimens, or not, may have an important influence on the results obtained.

Fattuhi and Hughes [37] used the same test procedure and 1% and 3% sulfuric acid solutions. They found that the deterioration of the specimens—measured by means of weight loss—increased with a corresponding increase in cement content. Depending on the acid concentration, increasing the volume fraction of cement from 10% to 17% caused an increase in weight loss with a factor 2 in a 1% sulfuric acid solution and an increase in weight loss with almost a factor 3 in a 3% sulfuric acid solution. They also found a decrease in weight loss due to a decrease in water/cement ratio. When the water/cement ratio was reduced from 0.4 to 0.3, in the case of the 1% sulfuric acid solution, the loss in weight was lowered by nearly 20%. The reduction of the water/cement ratio did not cause any decrease in weight loss in the case of the 3% sulfuric acid solution. In fact, often a combination of two opposite effects took place. Due to a lower water/cement ratio, porosity decreases and corrosion should be lower. Moreover, the relative amount of cement increases and this implicates a higher corrosion. They stated that brushing had a strong influence on the results. At the beginning of the deterioration, an increase in weight is accompanied by volume expansion of the specimens and often, less difference between several concrete types can be found. Due to brushing of the specimens, a larger part of the gypsum formed on the surfaces can be removed so a loss in weight can be measured and a difference between the several concrete types can be found.

Kaempfer [38] and Kaempfer and Berndt [39] investigated the influence of the addition of a styrene acrylic polymer and a styrene butadiene polymer to Portland cement mortar. They used sulfuric acid solutions of different pH values and they measured the penetration depth of the acid. Addition of the polymers reduced the penetration depth with a factor 2–3 compared with specimens without polymers. Styrene acrylic polymer reduced the penetration depth the most. The acid penetrated only 1.1 cm in contrast with the reference mix, which penetrated by about 3.4 cm.

3. Tests using bacteria responsible for the corrosion process

Biogenic sulfuric acid corrosion is often a slow corrosion process (1 mm/year to a maximum of 5 mm/year) [40]. It would require several years to investigate the difference in the durability of various materials. Biogenic sulfuric acid corrosion is a very complex process. It comprises the microbiological aspect of the *Thiobacilli* bacteria, which transform sulfur to sulfuric acid. The action of the sulfuric acid can be seen as a purely chemical aspect that causes the chemical destruction of some components of the concrete. There are also mechanical aspects involved such as the crystal pressure due to growth of for example ettringite and the removal of the corroded concrete layer by sewage flow.

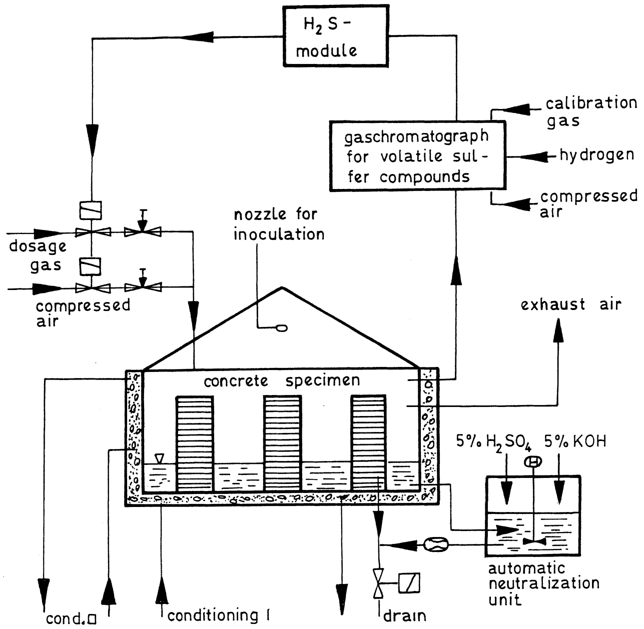

Fig. 3. Scheme of a simulation chamber (Sand et al. [42]).

Because of the complexity of the process due to these different aspects and their interactions, researchers tried to simulate corrosion as it happens in situ. By creating optimum conditions (temperature, nutrients) for the bacteria, which are not always present in situ, the rate of corrosion can be increased.

In Hamburg, a simulation chamber has been built in which a corrosion rate of eight times the one in situ could be reached through the optimisation of the corrosive environment [2,5,41–44]. A scheme of the test apparatus is shown in Fig. 3. In this test, concrete blocks of dimensions 60 × 11 × 7 cm were placed on end with the base standing in 10 cm of water. The water was kept at a temperature of 30°C and a pH of 7.0. The upper part of the test blocks was pre-sawn in small cubes [1, 8 × 1, 8 × 2 cm) to facilitate the sampling. The whole chamber was kept at a constant temperature of 30°C and saturated air humidity. Thiobacilli species were cultivated in a separated fermentor in which sulfur or thiosulfate was used as a substrate for the bacteria. The test blocks were periodically sprayed with the *Thiobacilli* cultures.

With this chamber, several kinds of experiments have been performed. In one experiment, the relationship between several species of *Thiobacilli* and the corrosion of concrete was investigated [42]. Hydrogen sulfide acted as a substrate for the bacteria and the concentration was maintained at 10 ppmv. The weight loss of the test specimens was determined as a measure for corrosion. During the experiment, the number of cells of different groups of *Thiobacilli* on the concrete surface was counted. The change of the pH of the concrete surface was also monitored. As shown in Fig. 4. the rate of corrosion was dependent on the numbers of *T. thiooxidans*. These organisms depress the pH of the concrete surface to values between 1 and 3. On the surface of very severely corroded test specimens (weight loss up to almost 6%), the cell counts of 5.10^7 cells/cm^2 were measured. Assuming a cell size of Thiobacillus of about 0.5 × 2 μm, this indicates that 50% or more of the surface is directly covered by a layer of the causative bacteria as shown in Fig. 5.

In another experiment, the influence of sulfur source on the corrosion of concrete was investigated [2]. Three different types of sulfur source—hydrogen sulfide, methylmercaptan, and sodiumthiosulfate—were used as a substrate for the bacteria. The concentrations of hydrogen sulfide and methylmercaptan in the air above the water were maintained at 10 ppmv as monitored by gaschromatography. The sodiumthiosulfate was solved in a mineral solution and spread over the concrete blocks. The experiment was monitored by measuring the weight loss of test specimens and the pH of the surface water, in which the blocks were placed. The quantity of the heterotrophic organisms and fungi grown on the concrete surface was also measured. The growth of the bacteria was monitored by measuring the quantity and the composition of the populations found on the concrete surface.

The corrosion—in the case when H_2S gas was used—was about 1.8 times higher than the corrosion measured when thiosulfate was used as a sulfur source. When methylmercaptan was used, no corrosion was found. The reason was that methylmercaptan or other derivated products are not used by *Thiobacilli* as a substrate. The researchers made the hypothesis that eventually, these compounds could be used by aerobic heterotrophic bacteria as a substrate and convert to inorganic sulfur compounds, which in turn can be used by *Thiobacilli.*

Even when the timespan—the length of time deemed necessary to investigate the resistance of concrete against biogenic sulfuric acid—was decreased in the simulation chamber described above by up to eight times in comparison with an in situ situation, the investigation still took about 1 year. Another simulation system has been built by the Research, Development and Consulting Department of Heidelberger Zement, in which timespans of 3–5 months are sufficient to investigate the resistance of several concrete

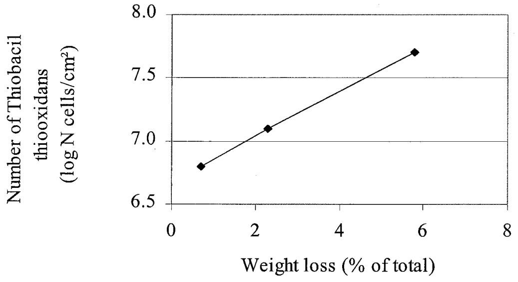

Fig. 4. The relationship between biodegradation of concrete and number of *T. thiooxidans* (after Sand et al. [42]).

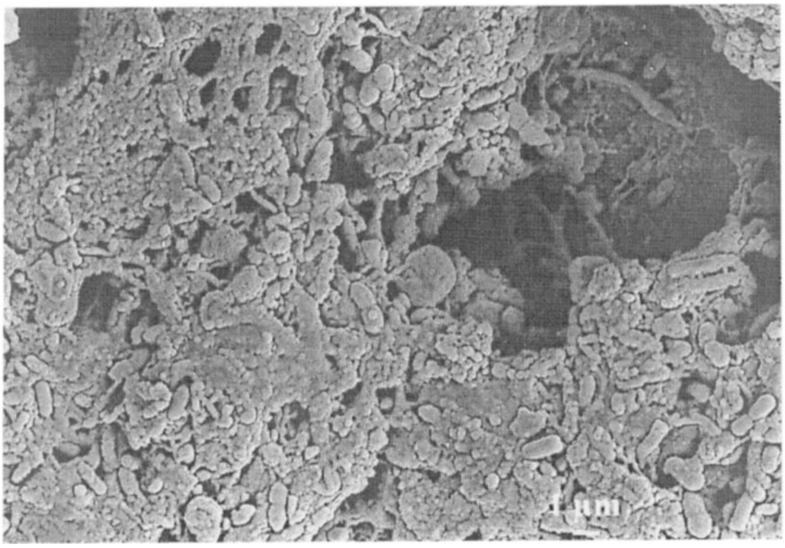

Fig. 5. Concrete surface covered with Thiobacilli (SEM-analysis, 4000 ×). The thiobacilli (1- to 3 µm-sized rods) form a dense layer on the concrete.

types against biogenic sulfuric acid [16,45]. The test system (Fig. 6 [45]) is separated in two parts: a growth and a reaction part. In the growth part, a 25-l fermentor, *T. thiooxidans* is cultivated at optimal conditions. The reaction part consists of a glass bio-reactor where the test specimens are stored. A warm and humid environment was sustained in the reactor. In contrast with the other test system, the test specimens were, in this case, mortar briquettes with dimensions of 10 × 10 × 60 mm. These specimens were flooded periodically for 5 min by an aliquot of the fermentor content followed by a 1-h interruption. The experiment was followed up by measuring the weight loss of the test specimens and by determining the cell density on the surface of the specimens. The difference between high alumina cement and ordinary Portland cement and the influence of the type of aggregates on the resistance to corrosion was investigated. All aggregates were tested using high alumina cement mortar.

The specimens with high alumina cement (3–4% loss of weight) showed better resistance against severe sulfuric acid attack than ordinary Portland cement specimens (18–31% loss of weight). These values were obtained after 5 months of testing. After 1 month, it was already possible to make a difference between the two mortars. In comparison with the type of cement, the influence of the aggregate that was used (high alumina cement-clinker, quartz and broken traprock) was very small.

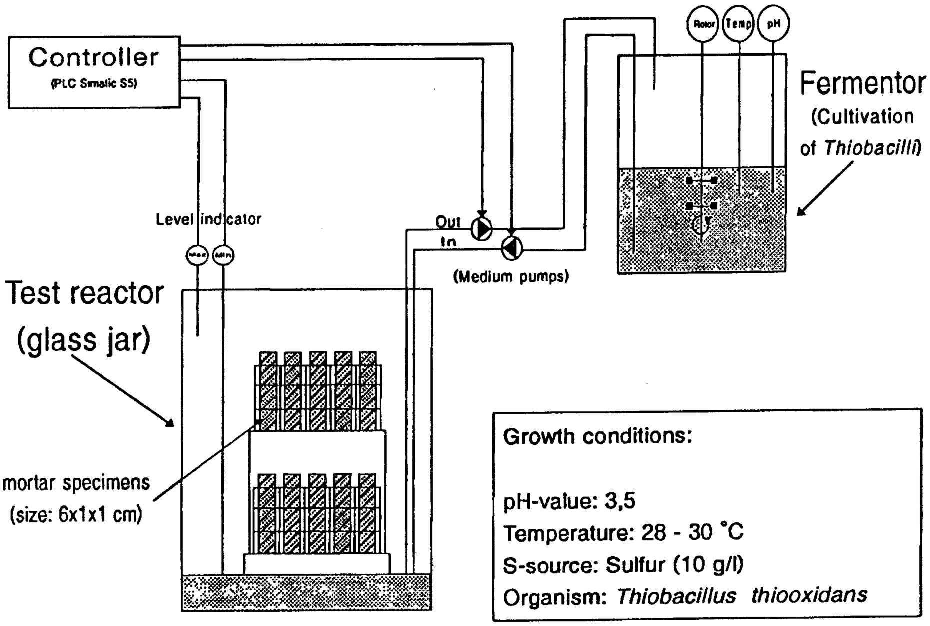

Fig. 6. Test system for biogenic sulfuric acid corrosion (Hormann et al. [45]).

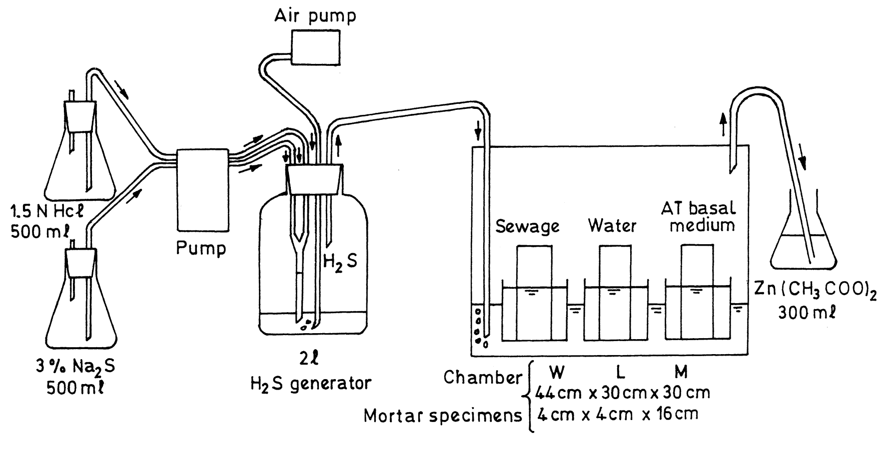

Fig. 7. Simulation chamber used by Mori et al. [46].

Another investigation, which used a simulation chamber, was carried out by Mori et al. [46]. They investigated the effects of nutrients on the corrosion of concrete. Their simulation chamber is shown in Fig. 7.

In comparison with other researchers, they worked with a very high concentration of H_2S (400 ppmv) in the chamber. This was in accordance with measurements in heavily corroded sewer pipes. The test specimens were mortar samples of size 4 × 4 × 16 cm. They were placed in sewage, a special culture medium (a solution containing all the nutrients and minerals needed by the bacteria but without thiosulfate) or distilled water. The experiment lasted for 6 months and during the first 2 months, the test specimens were inoculated with *T. thiooxidans* every 2 weeks. The corrosion rate was determined by measuring the reduction in cross-section of the specimens. Using a scanning electron microscope, the corroded samples were investigated. The number of *T. thiooxidans* was determined by plate counting of the bacteria.

Mori et al. [46] found a corrosion rate of 6.1 mm/year when the specimens were submerged in the sewage and 3.8 mm/year for the specimens placed in the basal medium. The most severe corrosion occurred approximately 20 mm above the liquid level. This confirmed their statement that the greatest corrosion occurs close to the liquid level because this location provides a constant supply of moisture and nutrients. No corrosion was measured for the specimens submerged in distilled water. They concluded that nutrients and oxygen must be present to cause a maximum corrosion rate.

These researchers simulated the corrosion process in a second way [46]. They used a demonstration plant in which the conditions to cause biogenic sulfuric acid corrosion were created. As shown in Fig. 8, it consisted of a pipe with a diameter of 15 cm and a length of 20 m. The temperature in the system ranged from 12°C to 30°C and the H_2S concentration ranged from 25 to 300 ppmv. They used the same test specimens as those in the simulation chamber. After 6 months, the mortars started to corrode just above the sewage level. Corrosion rates of 3.8–7.6 mm/year were measured. The corrosion pattern obtained was identical to the one found in sewage pipes. Corrosion reached its maximum level just above the sewage level. Further, above the sewage, corrosion diminished. The material situated under the sewage level was not corroded.

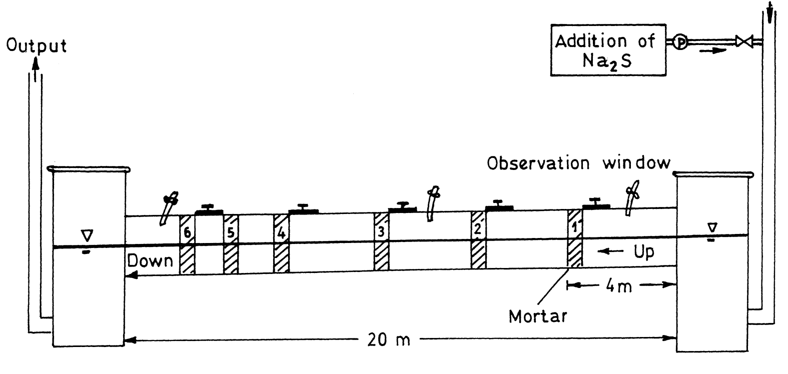

Fig. 8. Demonstration plant for studying biogenic sulfuric acid corrosion (Mori et al. [46]).

As part of a wide-ranging project to investigate deterioration of concrete caused by metabolites of aerobic micro-organisms, Tazawa et al. [47,48] performed some experiments with sulfide-producing and sulfur-oxidizing bacteria. These bacteria were isolated from an underground structure in which biological deterioration occurred. The test mortar specimens were completely immersed in culture bottles with 300 ml of ordinary liquid medium. After the bottles were sterilised, bacteria were inoculated. Two types of hydrogen sulfide-producing bacteria were used (*Xanthomonas* sp., the other type of bacteria could not be identified) and one type of sulfur-oxidizing bacteria (*T. intermedius*). The Thiobacillus species were inoculated 9 days after the inoculation of hydrogen sulfide-producing bacteria. The experiments were monitored by measuring the pH, the calcium concentration, the changes in dissolved hydrogen sulfide concentration, and changes in sulfate concentration of the culture medium. Growth curves of the micro-organisms were measured by light absorbance of the medium. They also investigated the calcium content of the surface area and the internal area of the mortar specimens. The authors first thought that the deterioration of the concrete was caused by sulfuric acid. However, they found only little gypsum on the surface of the specimens and only little change of the concentration of sulfate ions in the culture medium. Therefore, they assumed that other factors must cause the concrete deterioration. They analysed the compositions and the concentrations of the metabolites of the micro-organisms in the culture medium. The analyses were performed before the inoculation of the hydrogen sulfide-producing bacteria, during the logarithmic growth phase, and during the stationary growth phase of the latter. Hence, the metabolites of the sulfur-oxidizing bacteria were not taken into account. It was found that considerable amounts of acetic acid (85.6 ppm after 3 h), propionic acid (55.0 ppm after 3 h), and carbonic acid (343 ppm after 1 day) were generated. With these results, they carried out some new tests in which they used a synthetic solution containing compositions of metabolites of the micro-organisms. The authors concluded that the deterioration of concrete was mainly caused by carbonic acid (HCO_3^-, CO_3^{2-}) and organic acids (acetic acid, propionic acid) produced by the bacteria. High levels of bicarbonate and carbonic acid (HCO_3^-, H_2CO_3), excreted by respiration of the bacteria decomposes cement hydrates, producing calcium carbonate, silica gel and alumina gel. The calcium carbonate (solubility in water: 6.86 mg/l) is easily soluble in the presence of organic acids, produced by the bacteria. Calcium in cement hydrates is dissociated in the form of calcium ions in pore solutions of concrete, and is leached out of the concrete. As this process is repeated, the deterioration of concrete proceeds.

It was thought that the entire deterioration of the underground structure was caused mainly by organic acids and carbonic acid, which are common metabolites of all micro-organisms. Additional external factors, which contribute to the deterioration process, were the production of sulfuric acid and hydrogen sulfide by oxidation and reduction reactions of bacteria. The sulfuric acid then reacts with cement hydrates producing ettringite. This complex salt can be decomposed by carbonic or bicarbonic acid and organic acids produced by bacteria. By repetition of production and decomposition, the concrete becomes porous and weak.

4. In situ tests and observations

For durability problems, simulation tests are never completely satisfactory. It is difficult to reproduce all natural conditions and interactions under artificial conditions in a laboratory. In fact, the only way to study the real process of biogenic sulfuric acid corrosion, while taking into account all factors and interactions, are in situ exposure tests and observations.

To investigate the resistance of different concrete mixes, some researchers have performed in situ tests. In most cases, mortar or concrete samples were placed in sewer pipes in which biogenic sulfuric acid corrosion occurred. The samples were followed up for a few years. The large amount of parameters involved in the corrosion process and the great diversity in the sampled sites and used concrete mixes make it difficult to compare the results of the different studies. Therefore, the description of this topic will be limited to the most important results and to the comparison of the different test procedures.

Mori et al. [46] used a heavily corroded sewer pipe to expose mortar specimens to biogenic sulfuric acid. The mortar specimens were made with Portland cement and a water/cement ratio of 0.65. The test samples measured 40 × 40 × 160 mm. The atmospheric concentration of hydrogen sulfide in the pipe ranged from 5 to 400 ppmv and the temperature ranged from 10°C to 30°C. The mortar specimens were placed in a manhole for 8 months. They measured a corrosion rate of 5.7 mm/year.

From 1988 till 1991, in situ experiments were performed in Rotterdam (the Netherlands) [49,50]. Samples of four different concrete mixes were exposed to biogenic sulfuric acid corrosion in 10 different locations. Three of the four mixes were made in the laboratory and had a water/cement ratio of 0.32 and a cement content of 400 kg/m^3. The only difference between the three mixes was the type of cement: blast furnace cement, Portland cement or Portland fly ash cement. To investigate the difference between concrete made in the laboratory and concrete made in a factory, the fourth set of test samples was sawn out of a concrete pipe made in factory. The concrete pipe was made with blast furnace cement, a water/cement ratio of 0.32 and a cement content of 400 kg/m^3. The test samples measured 140 × 45 × 45 mm and were placed in a basket, which was placed in a manhole just above the dry weather sewage level. After 3.5, 23, and 35 months, the test specimens were examined. The degradation of the test specimens was followed by measuring the porosity, the flexural strength, the density, the mass loss, the neutralisation depth, and by visual inspection. The neutralisation depth was determined with phenolftaleine. The mass loss (in fact, the reduction of the cross-section) and the neutralisation depth were expressed in mm. The sum of these two parameters was called the degradation of the sample, expressed in mm. The different exposure locations were characterised by measuring the pH, the temperature, the oxygen content, and the sulfide concentration of the sewage.

After 3.5 months, a small increase in mass was measured for some samples. This was probably due to the uptake of water. It seems that the exposure time of 3.5 months was too short to find a difference between the different samples. After 23 months, the samples with Portland cement showed the lowest degradation rate of 0.8 mm/year (measured as the sum of the loss in material and the neutralization depth). The samples with blast furnace cement showed an average degradation rate of 1.0 mm/year. The largest degradation rate of 1.3 mm/year was found for samples with Portland fly ash cement. But the degradation products of the samples with Portland cement and with Portland fly ash cement were less coherent and fell earlier than the degradation products of the samples with blast furnace cement. After 35 months of exposure, the samples with blast furnace cement showed less mass loss than the other samples. These samples had an average mass loss of 0.4 mm/year. When the neutralisation depth was also taken into account, there was no difference between all samples made in the laboratory (1.0 mm/year). The samples of the concrete pipe made in a factory generally showed a slightly better resistance (0.8 mm/year) than the samples made in the laboratory.

5. Differences between biogenic sulfuric acid and chemical sulfuric acid attack

Although most researchers, except for Tazawa et al. [47,48], agree that attack in sewers is mainly caused by sulfuric acid produced by S-oxidising bacteria, large differences are found between purely chemical tests with H_2SO_4 and tests involving microbially produced H_2SO_4. The bacteria play a distinctive role. Even more important is the relationship between the bacteria and the substratum. The latter influences the activity of the bacteria, which, in turn, affects the amount of sulfuric acid formed. In all instances, gypsum and ettringite are the main corrosive products. Yet, the ratio of the latter products could be one of the differences between the two types of degradation. A soft and pulpy layer with an increased porosity is formed on the eroded surface. In the case of chemical corrosion by sulfuric acid, the formation of this layer constitutes an extra barrier for further attack. The sulfuric acid must penetrate through this layer before it reaches new "un-attacked" concrete. In the case of biologically produced sulfuric acid, the soft layer creates excellent conditions for the growth of the bacteria. Due to increased porosity, the bacteria penetrate into the layer and the formation of more sulfuric acid can occur near the "un-attacked concrete". Due to the gypsum layer, the humidity of the environment stays high and it protects the bacteria against dry conditions. Brushing the specimens has the opposite effect relative to the two types of attack. For chemical degradation, it creates new "un-attacked" concrete and removes the extra barrier. Brushing the specimens disturbs the microbiological balance and retards corrosion. Once the gypsum layer is too large, it may be that the oxygen content at the site of the "un-attacked" concrete is too low for the growth of the aerobic bacteria. In this case, brushing should increase the degradation rate.

6. Research needs

Although a lot of research has been performed on the issue of biogenic sulfuric acid corrosion of concrete, more research should be performed focusing on the relationship between the substratum—in this case, concrete—and the bacteria responsible for the production of the sulfuric acid. The role of gypsum as a growth matrix and provider of moisture and potentially other nutrients to the bacteria deserves an in-depth study. Because no correlation has yet been found between the resistance against biogenic sulfuric acid corrosion and the resistance against purely chemical sulfuric acid, parallel investigations should be carried out comparing the sulfuric acid and biogenic sulfuric acid corrosion process. For the chemical part of the corrosion process, sulfuric acid must be used and not a sulfate solution such as sodium- or magnesium sulfate. In previous studies, parameters such as weight loss, reduction in compressive strength, and change in dynamic modulus were often measured. Yet, change in the dimensions of the specimens, penetration rate, and depth of the acid and/or the bacteria are also important parameters and need to be taken into account. Biogenic sulfuric acid corrosion is conceived to start at the surface of the concrete and to progress inward while one layer after the other is attacked. Because of the superficial character of the corrosion process, accelerated tests should be performed using test specimens with a large surface/volume ratio. The process should better not be accelerated by increasing the concentration of the aggressive solution because of the different mechanisms, which occur at different sulfuric acid levels. Concentrations in the order of those found in sewers, i.e. 9000 mg SO_4^{2-}/l, should be used. Different concrete compositions and protection systems have been investigated and some of them lead to enhanced concrete resistance. Nevertheless, there is still a need for further development of more resistant types of concrete and for liquids that can be applied to exposed concrete surfaces to abate the putative sulfuric acid attack.

7. Conclusions concerning resistance of different concrete compositions

Based on the chemical tests, it seems that the addition of silica fume increases the resistance of concrete against chemical attack, especially in the case of sulfuric acid. The results are not confirmed by tests in simulation chambers for biogenic sulfuric acid. Also, the addition of polymers to the concrete composition had a potential to increase the chemical resistance against sulfuric acid and maybe, against biogenic sulfuric acid, but no research has yet been performed using bacteria. Blast furnace cement had a better resistance compared to Portland cement in all kinds of investigations. Taking into account that only few concrete compositions were tested in simulation chambers or in situ tests, high alumina cements seem to give the best results concerning biogenic sulfuric acid corrosion. The formed reaction products are found in bacteriological tests as well as in chemical tests with sulfuric acid—mainly gypsum and ettringite. The formation of these products is of great importance to the further evolution of the corrosion process. They can either increase the reaction rate or slow down the whole corrosion process by blocking the pores for further attack.

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