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Biodeterioration of Ceramic Materials by Biogenic Acids

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ABSTRACT

Microorganisms contribute substantially to the degradation of ceramic materials such as natural stone, concrete, ceramics and glass. Active attack is caused by excreted mineral or organic acids. Passive biodeterior results from excreted hydrophilic slimes of heteropolysaccharides and/or protein (biofilm).

All microorganisms may be of importance in biodeterioration – chemolithotrophic and chemoorganotrophic bacteria, cyanobacteria, algae, fungi and lichens. Recently it has become possible to test the resistance of ceramic materials to microbial attack. Using a simulation apparatus it is possible to demonstrate the interactions between a microorganism and its ceramic substratum. Purely chemical and/or physical testing of materials is not sufficient to determine their resistance to a biologically induced attack. Biogenic sulphuric acid corrosion and nitric acid corrosion simulation experiments have demonstrated differences in the resistance of various concretes, which chemical testing failed to reproduce.

Thus, biotest systems allow selection from many different materials so as to find the most appropriate.

INTRODUCTION

The current definition of ceramic materials includes concrete, natural stone, ceramics and glass. These materials are used mainly for the construction and maintenance of buildings. In the FRG buildings are valued at 5–6 thousand billion DM. About 1% of this sum has to be spent

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each year on maintenance. These expenditures are necessary due to deterioration processes, where physical and chemical attack are combined with biological attack. Usually only the chemical and physical aspects are known, and the biological factors are either unknown or considered to be unimportant. A recent study (DECHEMA-Studie, 1989) indicated that microorganisms participate in at least half of the cases of deterioration. It is known, in the case of concrete (Parker, 1945) that bacteria of the genus *Thiobacillus* are responsible for the destruction of sewage pipelines by sulphuric acid excretion. Recently it was demonstrated in another type of concrete building, a cooling tower of a power plant, that nitrifying bacteria were actively destroying the concrete by excretion of nitric acid (Schiffers *et al.*, 1976). These two examples illustrate the importance of research into the biodeterioration of building materials. Research on the mechanisms of biodeterioration, besides extending basic knowledge, will improve technology and produce more suitable materials for the repair and construction of buildings.

BIOGENIC SULPHURIC ACID CORROSION OF CONCRETE

As early as 1945, Parker showed that thiobacilli are involved in the deterioration of concrete in sewage pipelines. The bacteria use hydrogen sulphide released from the sewage and oxidise it to sulphuric acid. Due to lower sewage temperatures this type of corrosion was thought to be unimportant in Central and Northern Europe. Nevertheless, in the 1970s this type of attack was reported by several authors (Bock & Sand, 1978; Hultman *et al.*, 1978). Before 1969, 40% of the sewage from the City of Hamburg was drained into the river Elbe. In 1969/71, due to legislative requirements to treat all sewage, the City began the construction of pipelines of 3·5 m diameter so that present and future needs would be catered for. When commissioned these pipes were only about one-third full. After 4–6 years of operation serious corrosion was noted at several sites.

Due to the high cost of reconstruction a research project was initiated, with chemists, engineers, microbiologists and state officials working together to establish the mechanisms of this corrosion. It was shown that thiobacilli were present in high numbers at the corrosion sites. The number of *Thiobacillus thiooxidans* was found to be high at sites which were heavily corroded, whereas where less corrosion occurred reduced cell counts were obtained. At sites with negligible corrosion *T. thiooxidans* was not detected. The pH values were in the range 1–2, 3–5, and above 7, respectively. Thus, the cell counts of *T. thiooxidans* could be used as an indicator of the severity of corrosion. As the pH value results from the rate of sulphuric acid generation by bacteria, which is partially buffered by different concrete types, it is unsuitable as an indicator of attack. Cell counts proved to be the optimal tool for evaluation (Milde *et al.*, 1983). The source of hydrogen sulphide, which is the main sulphur compound utilised by thiobacilli in sewage pipelines, is the biological reduction of sulphate under anaerobic conditions, and the biological degradation of proteins. Figure 1 gives an overview of the sulphur cycle in sewage pipelines.

Part of the biological waste water treatment already occurs in the sewage pipeline. The volatile sulphur compounds are dissolved in the sewage. They escape into the sewer atmosphere due to turbulence. This occurs, for example, at sites where pressure pipes with mainly anaerobic sewage end. Hydrogen sulphide is autoxidised in the sewage atmosphere to molecular sulphur, which is deposited on the concrete walls. Thiobacilli grow on the concrete and oxidise sulphur to sulphuric acid. This acid destroys the concrete by reacting with the calcitic binding material. Two other sulphur compounds have been detected on the walls of sewage pipelines: sulphur dioxide and thiosulphate. The source of sulphur dioxide is unknown. It has, however, been shown that *T. thiooxidans* produces SO_2 during the oxidation of molecular sulphur (Sand, 1987) and this process may contribute to the generation of SO_2 in sewage pipelines. Thiosulphate is a reaction product of SO_2 with molecular sulphur and forms a good substrate for thiobacilli.

A strictly controlled simulation apparatus was constructed in order to reproduce the naturally occurring process under conditions which had been optimised for the bacteria. The apparatus (Fig. 2) allowed incubation of up to 32 different concrete samples in an atmosphere with more than

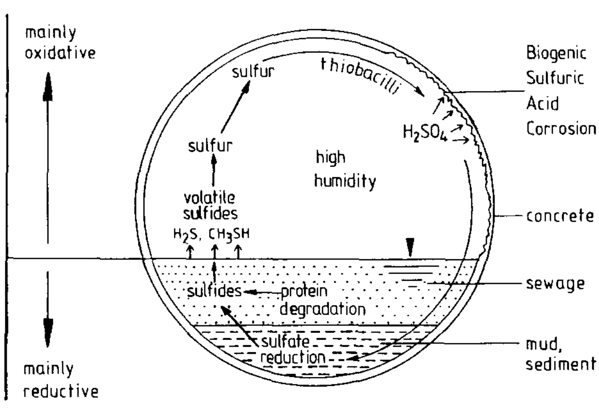

Fig. 1. Sulphur cycle in a partially filled sewage pipeline.

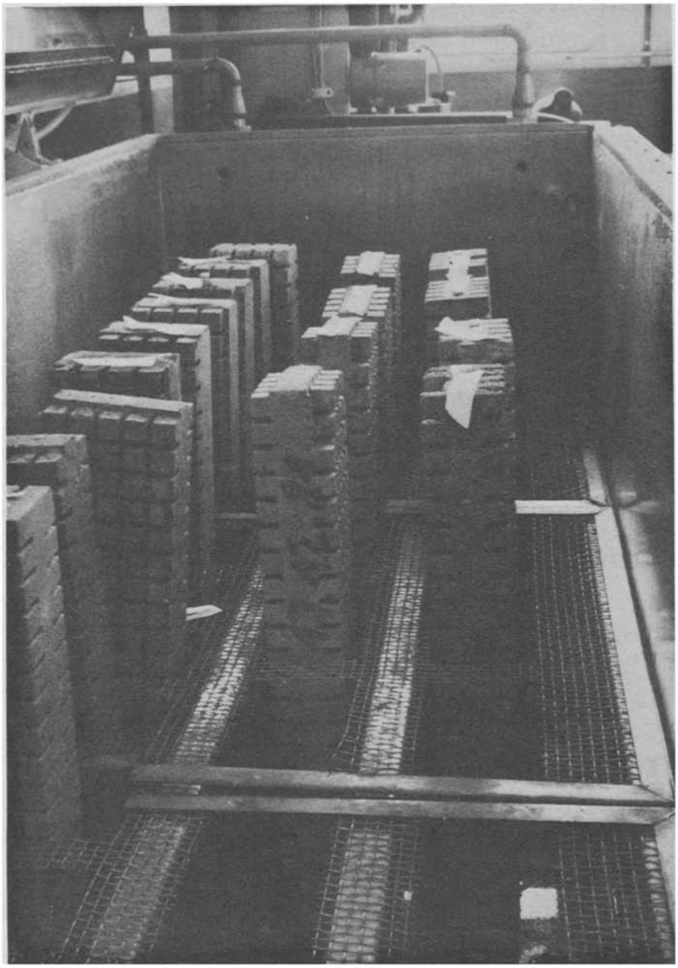

Fig. 2. Presawn concrete test blocks in the simulation chamber for biogenic sulphuric acid corrosion.

95% humidity, 22 mg/m^3 H_2S, and a temperature of 30°C (see Sand, 1987). The H_2S concentration was chosen to avoid any shortage of substrate. It is a concentration which has been measured in the atmosphere of sewage pipelines. The test blocks were standing on end in a waterbath to be humidified. They were presawn to enable monitoring during the experiment. Presawn cubes were broken off and the microorganisms detached by shaking them vigorously in a washing solution† for 2 h, and finally producing a dilution series of the resultant suspension. By a

† Nutrient solution for *T. neapolitanus* without thiosulphate (Sand, 1987; Milde *et al.*, 1983).

three-tube most-probable-number method three types of thiobacilli (*T. intermedius/novellus*, *T. neapolitanus*, *T. thiooxidans*) were counted. Additionally the cell counts of heterotrophs and fungi were monitored. However, they did not influence the corrosion. The determination of the loss of material proved to be, besides the cell counts of *T. thiooxidans*, most valuable.

A test using this apparatus, takes from 9 to 12 months. Concrete test blocks of known and unknown composition with and without protection by resins or impregnations are introduced. Over 3 months 10^{13} cells of *T. neapolitanus*, *T. intermedius*, *T. novellus* and *T. thiooxidans* are grown in the laboratory, harvested, and finally sprayed as an aerosol into the breeding chamber. A part of the aerosol settles on the test blocks. At the end of the inoculation period about 10^8 cells of each species are present per cm^2. All strains have originally been isolated from samples of corroded sewer walls. During the whole of the experiment the supply of H_2S is maintained. Figure 2 shows test blocks in the simulation chamber and Fig. 3 gives the results for a concrete block with low resistance to the biogenic attack. In agreement with the results of the field study the cell count of *T. thiooxidans* proved to be an indicator of the degree of corrosion. The loss of substance varied from 1% for concrete types with high resistance up to 100%, i.e. total degradation. An important result was the finding that chemical testing (with diluted sulphuric acid) did not demonstrate the differences in resistance of various concretes to the sulphuric acid attack.

Nine experiments have been done. It was shown that hydrogen

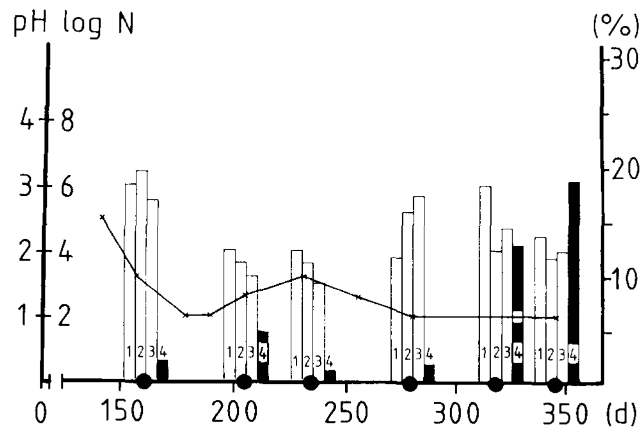

Fig. 3. Results of a simulation experiment with a block of low resistance to biogenic sulphuric acid corrosion: 1, cell count of *T. intermedius/nouvellus*; 2, cell count of *T. neapolitanus*; 3, cell count of *T. thiooxidans*; 4, loss of substance; ×, pH value in the surface water.

sulphide is the most important sulphur compound. With this compound cell counts of *T. thiooxidans* ranged up to $10^8/cm^2$ with pH values in the surface water between 1 and 2. Loss of material from the blocks was noted and in one experiment gave a medium value of 3·3%. With thiosulphate or a reduced H_2S concentration (2 instead of 22 mg/m^3) a reduced cell count of 10^5–10^7 was measured (pH 2–3) and a reduced loss of substance (1·8%). Methylmercaptan as a representative of the organic sulphides in the sewer atmosphere (20 mg/m^3) did not affect the biogenic sulphuric acid corrosion. *T. thiooxidans* was not detectable on the test blocks, the pH values remained at about 5–7, and there was no weight loss.

Finally the rate of corrosion in the apparatus was compared with test blocks incubated in a sewage pipeline. The site had been carefully chosen in order to find a place with highly corrosive conditions. After several years corrosion was measurable on the sewer site test blocks and the acceleration factor using the simulator was found to be eight fold. Thus, one test in the simulation chamber is equivalent to 8 years in operation. The apparatus is now used for the testing of materials and enables us to select the appropriate materials and techniques for use in sewage pipelines and plants (Emmel *et al.*, 1988).

BIOGENIC NITRIC ACID CORROSION

Two groups of bacteria, which are known as nitrifying bacteria, oxidise ammonia via nitrous to nitric acid. This acid reacts with calcitic binding material of concrete or natural stone in an analogous way to sulphuric acid. The end product, calcium nitrate, is readily water soluble (in contrast to calcium sulphate) and is lost from the matrix of the stone. It either remains within the stone, thus adding a salt to the pore water, or is washed away. The first group of bacteria oxidise ammonia via hydroxylamine and an unidentified compound to nitrous acid. The second group oxidise nitrous acid. The first group are represented by *Nitrosomonas*, *Nitrosovibrio*, etc., and the second by the genus *Nitrobacter*. Thiobacilli are responsible for the degradation of the parts of buildings below ground and nitrifying bacteria for those above ground. Nitrifying bacteria are involved in the deterioration of Cologne Cathedral, Regensburg Cathedral, the Old Pinakothek of Munich, and cooling towers of power plants (Schiffers *et al.*, 1976, Kirstein *et al.*, 1986). Many other buildings are attacked by these bacteria too. Especially susceptible are those materials which contain calcareous binding material. The attack is a reaction between acid and base, but the products also contribute to the biodeterioration. As they are hygroscopic they remain in part within the pore system of the stone and retain water. During freezing and thawing this water causes deterioration of the stone. Also it absorbs gases from the atmosphere, e.g. SO_2 and NO_x, which in turn react with the binding materials. Furthermore, it has been shown that these bacteria grow as biofilms within the stone (Bock, 1987). These biofilms enhance the processes described above. Work by Meincke *et al.* (1989) has shown that natural stone is an environment of its own.

The most abundant ammonia oxidisers belong to the genus *Nitrosovibrio*, which had formerly been isolated from Wales and acid tea soils of Sri Lanka. It appears that a hitherto unknown species of *Nitrobacter* is growing within natural stone. Often the ammonia and the nitrite oxidisers grow as separate colonies (Bock, 1987). Due to their susceptibility to ultraviolet light nitrifying bacteria survive only within the stone. Thus, only part of the surface is colonised under natural conditions. As a result, sometimes the end product of the ammonia oxidisers is detectable in high concentrations.

The nutrients utilised by these bacteria are mainly of anthropogenic origin (Fig. 4). Intensive livestock breeding as well as soil fertilisation give rise to large amounts of ammonia, which escape into the atmosphere. The ammonia then reacts in part with acidic compounds such as SO_2, NO_x, chlorides and acetate forming hygroscopic salts, which adsorb water vapour. They are transported as aerosol droplets and may be deposited on buildings. Nitrifying bacteria present on the surface of the building oxidise the ammonia compounds to nitric acid. This leads, in the case of concrete, to a loss of the binding material revealing the quartz components (known as washed concrete). In natural stone the

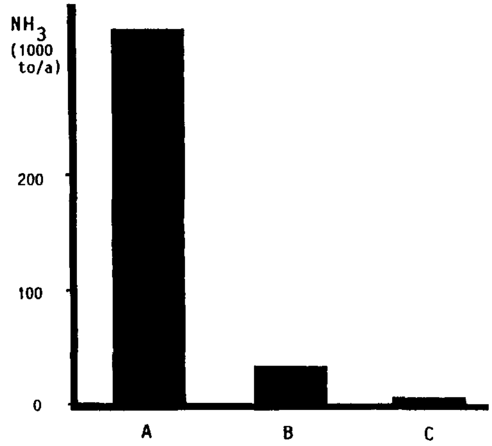

Fig. 4. Sources of ammonia emission in FRG: A, livestock; B, fertilizer; C, industry.

pore system is enlarged, the water content increased, finally resulting in either a sandy surface or a flaking of the natural stone.

Again this type of attack was reproduced by a simulation chamber. Details are given by Bock *et al.* (1989). The system is comparable to the chamber used for biogenic sulphuric acid corrosion. After inoculation with nitrifying bacteria, isolated from corroded cooling towers, a set of concrete test blocks was colonised by the bacteria. The cell counts ranged around $10^7/cm^2$. The pH value of the surface water decreased from 8·5 to 5. About 3% of the material was lost after 12 months exposure. The apparatus therefore may also be used to evaluate the resistance of ceramic materials and methods of protection against biogenic nitric acid corrosion.

A new simulation apparatus (Bock & Krumbein, 1989), allows the differentiation between chemical attack on concrete and natural stone and combined chemical and biological attack.

CORROSION BY ORGANIC ACIDS

Detailed information on biodeterioration of stone by other organisms is given in the DECHEMA report and other publications (Eckhardt, 1978; Rose, 1981; Krumbein, 1988; Bock & Krumbein, 1989; DECHEMA, 1989).

CONCLUSION

It has been shown that microorganisms are important in the deterioration of ceramic materials. The impact of microorganisms on these materials can only be determined by the use of simulation equipment. This can also lead to an improved material/protection, which will effectively reduce the costs of maintenance. Realistic results cannot be obtained by purely physical and/or chemical testing of the materials' resistance.

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