Microbial corrosion of concrete

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Summary. Sulphuric-acid-producing thiobacilli cause severe corrosion of concrete walls in sewage pipelines. The bacteria excrete sulphuric acid, which degrades carbonaceous binding material. Nitrifying organisms have been found in high cell numbers on historical sandstone buildings as well as on concrete buildings. The nitric acid, which is excreted by these organisms as metabolic end-product, also causes severe corrosion. The microorganisms are able to metabolize inorganic substances like ammonia and NO originating from air pollution.
The natural process was remodelled by means of simulation experiments. It became evident that mineral-acid-producing bacteria play an important role in biodeterioration of building materials.
Key words. Nitrifying bacteria; ammonia; nitric acid; nitrous acid; thiobacilli; H_2S; sulphur; sulphuric acid; sewage; concrete; sandstone; bricks; biodeterioration.

Introduction

In recent years it has become obvious that microorganisms are an important factor in the deterioration of ceramic materials[6]. These materials consist of concrete, natural stone, ceramics, and glass. The aggressive components, important for deterioration of ceramic materials, are mainly of an acidic nature. Organisms like green algae, fungi, chemoorganotrophic bacteria, cyanobacteria, and lithoautotrophic bacteria were found regularly on buildings of concrete as well as of standstone or of bricks[2,4]. Chemoorganotrophic microorganisms may cause damage by an excretion of organic acids like oxalic acid or glucuronic acid. These acids degrade the carbonaceous binding material of the stone. Furthermore, many microorganisms excrete organic exopolymers – slimes – which fill up the pores of stones and keep the water fixed to the stone. In a dry environment the availability of water is the most important factor for the survival of microorganisms. In addition, the water contributes to the weakening of the stone texture together with thermal stress like the freezing-thawing process.

Lithoautotrophic bacteria excrete their metabolic end-products, sulphuric acid or nitric acid, which react and degrade the carbonaceous binding material.

An important group of aerobically-living bacteria involved in corrosion of ceramic materials are the autotrophic thiobacilli, which utilize reduced sulphur compounds in the presence of air and form sulphuric acid. These bacteria are able to grow with sulphur as the only energy source and CO_2 as the only carbon source.

Thiobacilli could not be detected on buildings above the surface because their substrates – sulphur compounds – are lacking[2]. However, these environments support the growth of so-called nitrifying bacteria. These bacteria were isolated from numerous buildings[5]. The nitrifying bacteria are divided into two large groups, which are not related to each other. The first group consists of the ammonia oxidizers, which oxidize ammonia to nitrite. The second group is composed of nitrite oxidizing bacteria, which oxidize nitrous to nitric acid. The nitrifying bacteria have been isolated from such extreme habitats as the inner wall of a cooling tower, where they were responsible for a degradation of the surface layer of the concrete walls[3]. They were also isolated from surface layers of sandstone as well as from the inside of stones. Nitrifiers belong to the natural flora of soil and play an important role in the nitrogen cycle by oxidizing ammonia via nitrous to nitric acid.

Degradation of concrete by biogenic acids

Biogenic sulphuric acid corrosion

Within 4–6 years after the commencement of operation serious corrosion problems were noted in pipelines of the Hamburg sewage system[1]. Although coated with a thin layer of epoxy resin, the concrete matrix had been partially destroyed to a depth of 6 cm and more. The pH values of the surfaces ranged between 1 and 2, and up to 50% of the corroded wall material consisted of gypsum. It was observed that thiobacilli grew to high cell numbers on the walls of the sewage pipelines, the pH value decreased on the concrete surface to the above-mentioned values, and corrosion was severe. In wastewater H_2S is produced by anaerobic processes like sulphate reduction. Air oxidizes reduced sulphur compounds like H_2S to molecular sulphur, which is deposited on the surface of the walls of the sewage pipelines[12]. Thiobacilli oxidize sulphur to sulphuric acid, which reacts and destroys the alcaline binding material of concrete. The attack starts from the surface. Carbonaceous material reacts with the sulphuric acid. The granular texture is lost. Quartz, glauconite, remaining calcite, and dolomite are formed together with gypsum. This results in a deterioration of the concrete in a characteristical way. The microorganisms responsible for a generation of volatile sulphur compounds have been isolated from wastewater and have been characterized:

– protein-decomposing microorganisms produce H_2S, methylmercaptan, and other volatile sulphur compounds under aerobic as well as under anaerobic conditions;
– sulphate-reducing bacteria produce H_2S under strict anaerobic conditions.

Thiobacilli oxidize hydrogen sulphide to sulphuric acid under aerobic conditions. Thiosulphate, which has been detected in sewage pipelines too, is also degraded by thiobacilli. Volatile organic sulphides were not degraded by thiobacilli found in the Hamburg sewage system. Only in mixed cultures including methylotrophs organic sulphides may be of importance[9,10].

Several species of thiobacilli were detected and identified: *Thiobacillus thiooxidans, T. intermedius, T. novellus, and T. neapolitanus*[7].

The process of corrosion in newly built concrete pipelines was found in a succession of these species of thiobacilli. Thus, the high alcaline pH value of concrete was impaired. On the concrete wall at first weakly acidophilic species like *T. intermedius* and *T. neapolitanus* together with other bacteria and fungi started to grow. By their activity the pH value of the originally alcaline surface decreased. At pH values below 5 *T. thiooxidans* started to grow and produce high amounts of sulphuric acid. Other microorganisms were inhibited by the sulphuric acid. Thus, *T. thiooxidans* grew in a self-produced ecological niche. If enough substrate (molecular sulphur and/or sulphur compounds like thiosulphate) was provided, pH values as low as 0 were measurable. A positive correlation between the cell number of *T. thiooxidans* and the grade of corrosion could be noted. Therefore, *T. thiooxidans* can be considered as the key organism – marker – for biogenic sulphuric acid corrosion[7]. Under the assumption that the substrate of the thiobacilli like sulphur is available and the building materials are wet concrete will be degraded up to a depth of several cm per year.

Other lithoautotrophic bacteria like the nitric-acid-producing nitrifying bacteria were detected in wastewater systems too. They oxidize ammonia via nitrous to nitric acid. However, in sewage systems they may be neglected because of their failure to grow at acidic pH values lower than 5.

Nitrification-induced corrosion

Nitrifying organisms are important for corrosion of concrete buildings as well as of buildings of sandstone. They severely degrade building stones by their production of nitric acid. In the case of public buildings and monuments thiobacilli are usually not important because their substrate is lacking[2].

Nitrifying bacteria grow on the surface and within the pores of stones in the form of a biofilm. There, they can survive freezing, thawing, and dryness. The biofilm is composed primarily of heteropolysaccharides secreted by the organisms. Together with salts like sodium nitrate they rapidly accumulate water from the atmosphere and release it with delay even under conditions of low humidity[11]. How do nitrifying bacteria infect buildings? It seems most likely that these bacteria, which stick to the surface of dust particles, are deposited on buildings immediately prior to or during rain or thunderstorms. Since the bacteria are very sensitive to light, they have to be moved rapidly from the surface to the inner part of the stone by water transport. Capillar water transport is responsible for bacterial movement in porous stone material.

The substrates for bacteria growing on and in stones are either naturally and/or anthropogenically produced. Ammonia, the substrate for ammonia-oxidizing bacteria, is emitted into the atmosphere from protein degradation mainly originating from manure of livestock breeding. In addition ammonia originates from intensive agriculture, as well as from technical processes for desulphurization of flue gas from power stations. Volatile ammonia reacts with acidic air pollutants like SO_2 and NO_x to ammonium sulphite/-sulphate and ammonium nitrite/-nitrate. Furthermore, ammonia can react with volatile hydrochloric acid – produced and emitted for example in incineratory plants – to ammonium chloride. All these ammonia compounds are hygroscopic, adsorb water vapour, and form a hydrate cover. They will be deposited as dust particles on surfaces of buildings, where they are used for bacterial metabolism.

It can be summarized that ammonia in addition to SO_2 and NO_x has to be regarded as an important air pollutant. These airborne pollutants are responsible for the biogenic degradation of ceramic building materials. Experiments demonstrated that nitrous and nitric acid produced from ammonia are the corrosive agents. Furthermore, it was proven that the conversion of SO_2 to sulphite and subsequently to sulphate is catalysed by nitrous acid[2]. The overall process can be called nitrification-induced corrosion[5].

The hypothesis that thiobacilli and nitrifying organisms are responsible for the biogenic degradation of concrete was proven by simulation experiments. Biogenic corrosion of concrete was remodelled in strictly controlled breeding chambers under biologically optimized conditions.

Simulation of biogenically induced corrosion

Nitrifying organisms as well as thiobacilli destroy building materials made of concrete by production of mineral acids. The impact of microorganisms was proven by simulation of the natural process in strictly controlled breeding chambers. The experiments fulfilled the classical postulates of Robert Koch. Microorganisms were isolated from degraded stones. Pure cultures were characterized. With these pure cultures concrete specimens, which were placed into breeding chambers, were inoculated either with strains of thiobacilli or nitrifiers. The chamber conditions were optimized for the microorganisms regarding temperature, humidity, and substrate. The process of biodeterioration of ceramic materials, which will take a long time under natural conditions, was accelerated significantly under these conditions.

In the H_2S breeding chamber, where the conditions of a sewage system were simulated, biogenically induced corrosion occurred 9 months after inoculation of the concrete specimen. This exposure time corresponds to an exposure of more than 5 years in a sewage system. After this time of simulation an average loss of substance of 3.5% per concrete specimen could be noted. These investigations allow the test of different types of concrete for their resistance to biogenic sulphuric acid attack. It was possible to differentiate between suitable and non-suitable concrete types[8].

The simulation experiments demonstrated that an active thiobacilli population was living on the surface of the concrete specimen. *T. thiooxidans* dominated the flora and outnumbered other thiobacilli by a factor of about 10. The thiobacilli grew with sulphur that had been generated by chemical autoxidation reactions from H_2S. Throughout the simulation experiments an excess of sulphur was noted on the concrete specimens. The decline of the pH value that took place on the concrete surface was the first indication of the start of the corrosion process. Due to different buffer capacities of the concrete types and varying amounts of sulphuric acid produced by thiobacilli, the final pH value of the concrete surfaces differed significantly. Therefore the pH value may not be an adequate tool to quantify the corrosion process. The cell number of *T. thiooxidans* proved to be the most accurate standard for a precise quantification of corrosion. Concrete specimens, which were not inoculated and kept under sterile conditions, showed no corrosion under the conditions tested.

Similar results were obtained by simulating the biogenic nitric acid corrosion[3]. Different concrete specimens were placed into a breeding chamber, inoculated with nitrifying organisms, and the substrate ammonium sulphate was supplied discontinuously in form of an aerosol. Five months after inoculation cell numbers of 1×10^7 cells/g stone were measured. The flora consisted of equal parts of ammonia and of nitrite oxidizers. Cell numbers of heterotrophic bacteria and fungi amounted to 1×10^7 cells/g stone. The water draining from the stones decreased in pH value within 6 months from pH 10 to pH 6. After 24 months a slow increase of the pH value was noted. It can be concluded that nitrifying organisms acidified the concrete surface by production of nitric acid. By this acid carbonaceous binding material was converted to soluble calcium nitrate. As long as the acidification of bacteria is balanced by the alcaline material of the stone the pH value remains the same. When the buffering capacity is used up, a decrease of the pH value will be measurable. The nitric acid produced by nitrifying bacteria amounted to 14 ml concentrated nitric acid (65%) per concrete block (0.5 m^2 surface) and year. The loss of substance amounted to about 3%. Severe corrosion could be noted on the concrete surface, which in some cases looked like washed concrete.

Conclusions

Microorganisms may contribute substantially to the degradation of ceramic materials. Microorganisms can only play an important role in deterioration if they are supplied with substrate. The metabolism of thiobacilli and nitrifiers results in the excretion of sulphuric or nitric acid and/or slime, which may change the resistance of inorganic materials. The substrate may originate from exogenous or endogenous sources. Exogenous sources may be ground water, sewage, waste materials etc., whereas endogenous sources may originate from the deposited material itself. Thus, to ensure the stability of nuclear wastes embedded in concrete, it has to be avoided that microorganisms are supplied with substrate.

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