Influence of Biogenic Acid on Concrete Materials

Alena LUPTÁKOVÁ[1)], Vlasta Ondrejka HARBUĽÁKOVÁ[2], Adriana EŠTOKOVÁ[2)], Jana JENČÁROVÁ[1)], Miloslav LUPTÁK[3)]

[1)] Slovak Academy of Sciences, Institute of Geotechnics, Watsonova 45, 040 01 Košice, Slovak Republic; email: luptakal@saske.sk
[2)] Technical University of Košice, Civil Engineering Faculty, Vysokoškolská 4, 040 01 Košice, Slovak Republic
[3)] Technical University of Košice, Faculty of Materials, Metallurgy and Recycling, Letná 9, 042 00 Košice, Slovak Republic

http://doi.org/10.29227/IM-2019-01-19

Submission date: *11-07-2018* | Review date: *02-04-2019*

Abstract

Microbial sulphur cycle in sewers evocate the serious problem in the area concrete corrosion, health related aspects and odour. These problems are primarily related to the release of bacterially produced hydrogen sulphide from wastewater to the atmosphere during sewage transports that dissolves in the condensate on the sewer crown. In the event sulphur-oxidizing bacteria oxidize the dissolved hydrogen sulphide and other sulphur compounds to sulphuric acid, which corrodes the concrete. The concrete gradually expands causing cracks and ruptures, loss of strength and overall decay of concrete.

The paper is focused on the investigation of the concrete specimens surface biodegradation study. From the viewpoint of concrete materials biodeterioration, mainly the bacteria sulphur- and sulphide-oxidising bacteria and sulphate-reducing bacteria are important and interesting. The role of bacteria mentioned above has been linked to the generation of the biogenic sulphuric acid resulting in corrosion process by dissolution of calcium containing minerals from the concrete matrices. The penetration of the corrosion was manifested by structural changes of concrete samples. The surface structure changes were by stereomicroscopy and atomic force microscopy (AFM) investigated.

Keywords: bacterially produced hydrogen sulphide, sulphuretum, biogenic sulphuric acid, concrete, AFM

Introduction

Corrosion in sewer systems by biologically produced sulphuric acid is a worldwide phenomenon and is considered to have a great economic impact (Sand, 1997). It is a consequence of a cyclic process caused by bacterial sulphur metabolism. Two types of bacterial metabolism sulphur compounds are involved in the cycle of sulphur in the environment. One is an anaerobic process in which anaerobic bacteria produce hydrogen sulphide. The other is an aerobic process in which the hydrogen sulphide is oxidised to elemental sulphur or sulphuric acid by aerobic bacteria. This biological cyclic process exists as a natural way for the cycling of sulphur compounds in the environment and may also exist in sewage collection systems. The bacterial population of this biological sulphur cycle is called "sulphuretum".

It involved mainly the sulphate-reducing bacteria (SRB) and sulphur- and sulphide-oxidising bacteria (SOB).

SRB are a unique and ubiquitous group of prokaryotic microorganisms (MO), found in a variety of anaerobic environmental niches such as soil, mud and sediments of freshwaters (rivers, lakes), thermal or no-thermal sulphur springs, sewage, mining waters from sulphide deposits, waters from deposits of mineral oil and natural gas and gastrointestinal tract of man and animals (Odom and Rivers Singleton, 1993). The most studied SRB are bacteria Desulfovibrio desulfuricans. The basic metabolic process of SRB is the anaerobic reduction of sulphates to hydrogen sulphide in which organic substrate (lactate, malate, etc.) or gaseous hydrogen is the electron donor and sulphate is the electron acceptor. Hydrogen sulphide consequently in the water reacts with the metals cations and forms the metallic sulphates of low solubility. It is the positive aspect of SRB, which is used in the area of treatment AMD (Tabak et al., 2003). In the case of sewage overcharge hydrogen sulphide enters the sewer atmosphere by volatilisation and dissolves in the condensate on the sewer crown. In addition hydrogen sulphide has reached the atmosphere it may react with oxygen to elemental sulphur, which is deposited the slime layer coating the walls. Hydrogen sulphide and sulphur are substrates for many SOB such as *Acidithiobacillus* thiooxidans, *Acidithiobacillus* neapolitanus and *Acidithiobacillus* intermedius. They will metabolise the hydrogen sulphide and sulphur to sulphuric acid, which corrodes the concrete.

SOB occurs in the sewage but predominantly represents autochthonous bacterial culture of sulphide deposits where it takes part on sulphide minerals oxidation and acid mine drainage (AMD) production (Johnson, 1995). The positive aspect of SOB in the environment and industry is bacterial leaching of sulphidic minerals and its concentrates and different wastes with the high content of sulphur compounds (Rawlings, 1997).

The general mechanism for the biogenic sulphuric acid caused corrosion of sewer systems was described many authors (King and Miller, 1971; Sand, 1997; Roberts et al., 2002 and others). The model depicting of biocorrosion of concrete pipes attributed to sulphuretum is given in Figure 1.

During the transport of raw sewage from the top of the sewage collection system to the treatment plants, the organisms in the sewage start to degrade the abundant organic compounds present in the raw sewage. This often results in a depletion of O_2 from the sewage. This result in the creation of anaerobic or anoxic conditions that allow the growth of SRB which grow only in the absence of O_2 and obtain energy by utilising small organic compounds or H_2 as energy sources and transferring the electrons produced to sulphate, thus reducing it to hydrogen

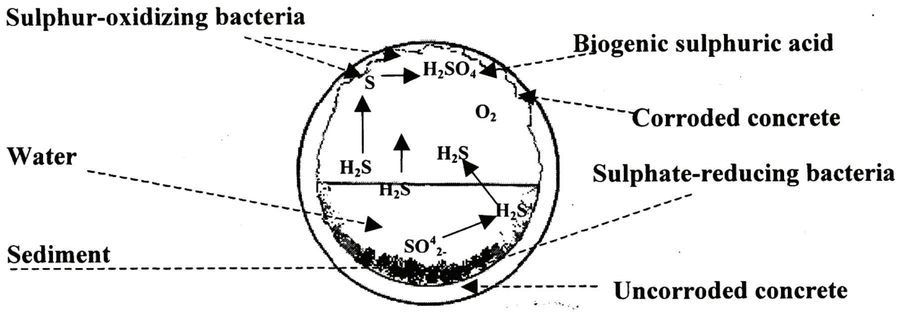

Fig. 1. Schematic representation of the sulphur-cycle occurring in sewer pipes [King and Miller, 1971 (adapted)]
Rys. 1. Schematyczne przedstawienie cyklu siarkowego występującego w rurach kanalizacyjnych [King and Miller, 1971 (dostosowany)]

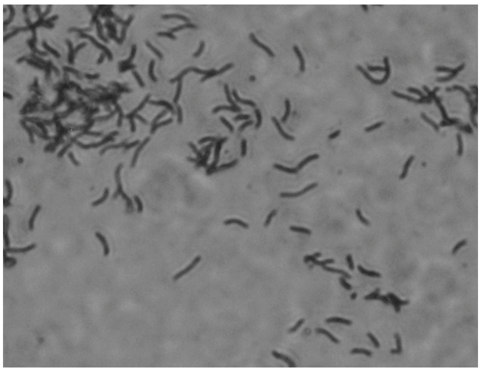

Fig. 2. Bacteria Desulfovibrio desulfuricans, isolated from the potable mineral water (Gajdovka spring, Slovakia)
Ryc. 2. Bakterie wyizolowane z pitnej wody mineralnej (źródło Gajdovka, Słowacja)

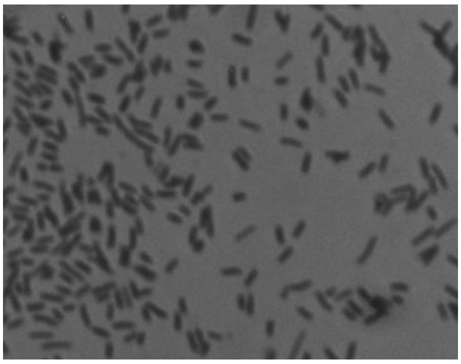

Fig. 3. Bacteria *Acidithiobacillus* thiooxidans, isolated from AMD from the shaft Pech (the old mine Smolník, Slovakia)
Ryc. 3. Bakterie *Acidithiobacillus tiooksydans*, wyizolowane z kwaśnego odcieku (AMD) z szybu Pech (stara kopalnia Smolník, Słowacja)

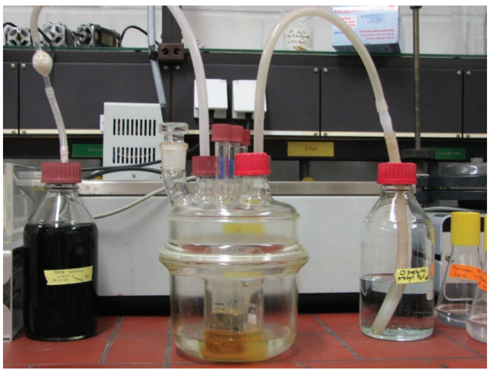

Fig. 4. The laboratory experimental system apparatus
Rys. 4. Laboratoryjne urządzenia pomiarowe

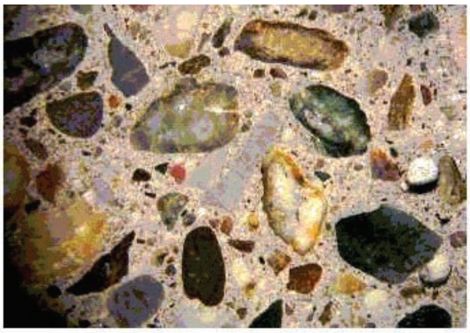

Fig. 5a. Smooth surface filling among aggregates before experiment Magnification of image 20 x 4.5
Rys. 5a. Wypełnienie powierzchni wśród agregatów przed eksperymentem. Powiększenie obrazu 20 x 4,5

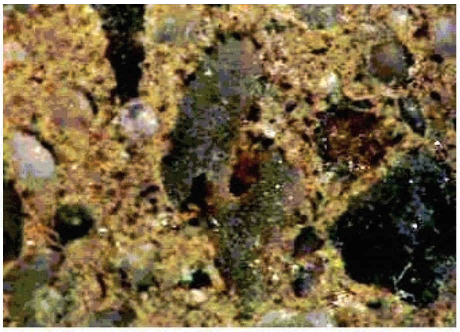

Fig. 5b. Considerable biodeterioration of concrete sample surface after 90 days. Magnification of image 20 x 4.5
Rys. 5b. Biodeterioracja powierzchni próbki betonu po 90 dniach. Powiększenie obrazu 20 x 4,5

sulphide. Well SRB grow in anaerobic conditions of the sediment and water that collects in the bottom of concrete pipes and hydrogen sulphide is produced. The sulphide produced eventually partitions into HS- and H_2S. H_2S is a gas and evolves into the headspace of the sewer pipes, reaching the crown of the pipe. The crown of the pipe is exposed to an aerobic environment that supports the growth of SOB.

The biodeterioration genesis has three stages: infection – creation of the permanent contact between MO and material; incubation – the period from the infection until the symptoms of biodegradation are visible or start causing a considerable technical damage to the material; manifestation – symptoms of biodegradation are clearly visible representing a technically significant damage to the material (Wasserbauer, 2000). The concrete deterioration after application of individual bacterial culture on the concrete samples by sulphuretum simulating was studied in our previous works (Harbulakova et al., 2008a,b). The changes of the concrete samples weight, the change of the pH and increased content of calcium and silicon in liquid phase were observed. The penetration of the corrosion is manifested by structural changes of concrete samples. The surface structure changes of corroded specimens can be investigated by many methods. The atomic force microscopy (AFM) can be used to image features with dimensions at the atomic scale up to approximately 100 μm and it reveals the surface topography with direct depth information (Denkhaus et al., 2006).

This paper is focused on the concrete surface structure changes study by microscopy methods.

Materials and methods

Bacteria and grow conditions

In the experiment, sulphate-reducing bacteria (SRB – Fig. 2) genera Desulfovibrio sp. and sulphur-oxidising bacteria (SOB – Fig. 3) genera *Acidithiobacillus* thiooxidans were used. SRB were isolated from the potable mineral water (Gajdovka spring, Košice, Slovakia) using Postgate's medium E and SOB were isolated from the acid mine water (the shaft Pech, Smolník, Slovakia) using the selective nutrient medium S according Waksman´s and Joffe´s by the plate dilution method.

Samples preparation

The original concrete specimens from real conditions were used for experiment. Concrete samples were tested according to the European Standards STN EN 206-1(2004): Concrete. The concrete were assessed on compression strength and categorized as class C 25/30. Concrete samples drilled by diamond apparatus were cut in triangle form with 5 cm in width and 1 cm thickness. Before experiments samples were sterilized in 70% ethanol and dried in an oven at 60ºC to constant weight.

Concrete biocorrosion

Concrete samples were put into reactor (Fig. 4) and inserted into two containers: the first was filled by acid mine drainage (AMD) and the second by distillate water (DV). The reactor was interconnected with the two flasks. One was filled by bacterial cultures SRB for the H_2S production. The second flask was filled by cadmium acetate solution for the H_2S capture. During 90 days concrete samples were every 7 days inoculated by SOB and was realized the change of nutrient medium for SRB cultivation too.

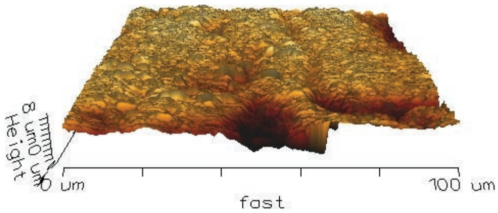

Fig. 6. Surface of concrete sample before experiment
Rys. 6. Powierzchnia próbki betonu przed eksperymentem

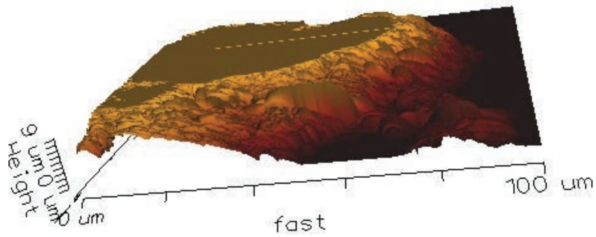

Fig. 7a. AMD immersed part of concrete sample
Rys. 7a. Część próbki betonu zanurzona w kwaśnym odcieku kopalnianym (AMD)

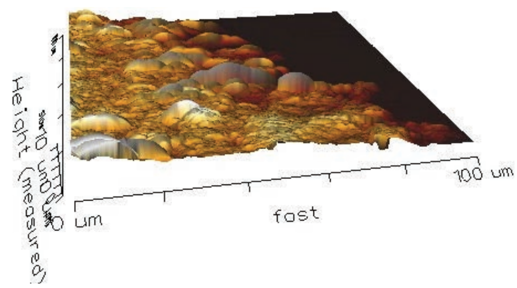

Fig. 7b. AMD not immersed part of concrete sample
Rys. 7b. Część próbki betonu nie zanurzona w kwaśnym odcieku kopalnianym (AMD)

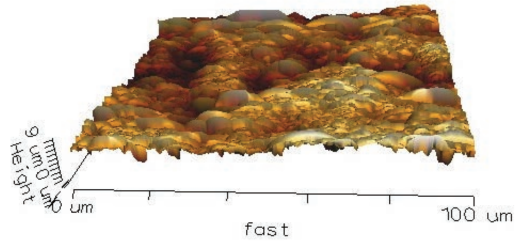

Fig. 8a. Immersed part of concrete sample taken out from DW
Rys. 8a. Zanurzona część próbki betonu pobranej z wody destylowanej (DW)

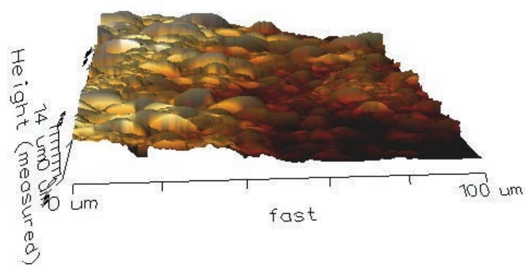

Fig. 8b. Non immersed part of concrete sample taken out from DW
Rys. 8b. Nie zanurzona część próbki betonu pobrana z DW

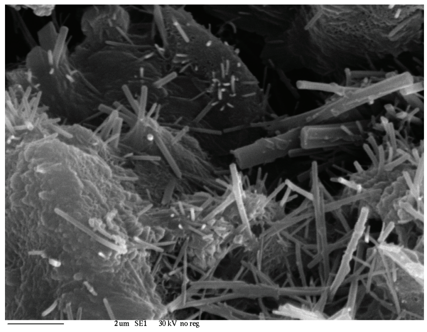

Fig. 9. Image of ettringit crystals precipitated on the concrete sample surface immersed into AMD captured by SEM
Rys. 9. Obraz kryształów etringitu wytrąconych na powierzchni próbki betonu zanurzonej w AMD zarejestrowanej przez SEM

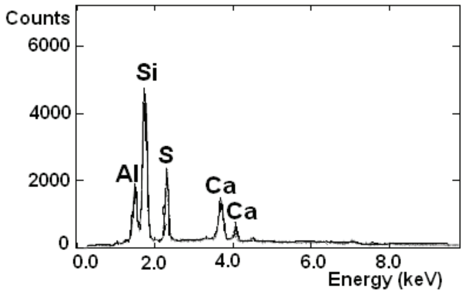

Fig. 10. EDS qualitative ettringite analysis
Rys. 10. Analiza jakościowa EDS etringitu

Methods

The disruption and damages of the concrete surface under sulphuric acid affect were investigated by stereomicroscopy, atomic force microscopy (AFM) and electron microscopy. Mineralogical stereomicroscope STM 723 ZOOM with the combination of digital camera Olympus – C-770 Ultra Zoom was used for upper (not immersed) part concrete samples study because of noticeable changes in structure of concrete. AFM (JPK Instruments, Germany) was used for both (immersed and not immersed) parts of concrete samples investigation. A NanoWizardII contant mode AFM was used to image the surface of concrete samples. For AFM imaging, silicon cantilever CSC 37 B (Micromash Estonia) with force constant 0.3 N/m, resonance frequency 37 Hz was used. Set point was 750 mV. Each AFM image consists of 512 by 512 pixels. The qualitative analyses of precipitates onto samples surface were investigated by scanning electron microscopy and energy depressive spectrometry (EDS) analysis.

Results and discussion

The considerable changes of concrete samples structure were observed by stereomicroscopy. Fig. 5a illustrates a surface of concrete specimen before experiment and Fig. 5b shows the visible surface changes after 90 days sulphuretum simulation.

For detailed study of concrete samples surface changes AFM method was used. In Fig. 6 the surface of concrete sample before experiment is shown. The surface is quite smooth, with the low roughness. After 90 days the both parts (immersed and non immersed) of concrete samples surface were by AFM observed. The differences between surface changes of lower (immersed) and upper (non immersed) parts of concrete samples were observed. The Fig. 7a and 7b represents the image of samples taken from AMD. On both figures is visible that the roughness increased and some aggregates were fallen out of concrete surface. The images of concrete samples surface taken out from deionised water are presented on Fig. 8a and 8b.

During the experiment the pH values of leachate were increasing up 7.03 (AMD) and 7.2 (DI water) because of calcium releasing. Depends on pH the lath-shaped crystals of ettringit ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) were on the surface observed by scanning electron microscopy and energy depressive spectrometry (EDS) analysis as shown on Fig. 9 and 10. The ettringite is secondarily produced under alkaline conditions after exposure to sulphate (Mori et al., 1992).

Conclusion

Experimental studies confirmed that visible changes of concrete samples surface structure were observed. Significant changes were observed mainly for concrete sample inserted in AMD because of sulphuric acid corrosion influence. More considerable structure changes were detected in not immersed part of both concrete samples because of direct microorganism application on the samples surface and absence of appropriate conditions for microorganisms grow (esspecially pH) in the liquid phase.

Crystals participated on concrete surface was identified as ettringite. According to literature (Mori et al., 1992) in range pH > 3 under strong alkaline conditions during hydratation, ettringite is formed in the corroded area.

Acknowledgements

This work has been supported by Grant Agency of Slovak Republic (project No. 2/0145/15). I also thank University of Duisburg-Essen, Biofilm Centre, Aquatic Biotechnology, Dusburg, Germany especially group of prof. Wolfgang Sand for opportunity to work with AFM.

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Wpływ kwasu biogennego na materiały betonowe

Cykl mikrobiologiczny siarki w wywołuje poważne problemy związane z korozją betonu a także dotyczące aspektów zdrowotnych i zapachu. Problemy te związane są przede wszystkim z uwalnianiem wytwarzanego przez bakterie siarkowodoru ze ścieków do atmosfery podczas transportu ścieków, który rozpuszcza się w kondensacie w instalacji kanalizacyjnej. W takim przypadku bakterie utleniające siarkę utleniają rozpuszczony siarkowodór i inne związki siarki do kwasu siarkowego, który powoduje korozję betonu. Beton stopniowo rozszerza się, powodując pęknięcia , utratę wytrzymałości i ogólny rozkład betonu.

Praca koncentruje się na badaniu badania biodegradacji powierzchni próbek betonu. Z punktu widzenia biodeterioracji właściwych materiałów, ważne są bakterie, głównie bakterie utleniające siarkę i siarczki oraz bakterie redukujące siarczany. Rola bakterii wspomnianych powyżej została powiązana z wytwarzaniem biogennego kwasu siarkowego, powodując proces korozji poprzez rozpuszczanie minerałów zawierających wapń z betonowych matryc. Penetracja korozji objawiła się zmianami strukturalnymi próbek betonu. Zmiany struktury powierzchni były badane za pomocą stereomikroskopii i mikroskopii sił atomowych (AFM).

Słowa kluczowe: wytwarzany przez siarkowodór, siarczek, biogenny kwas siarkowy, beton, AFM