

## Sulphur Oxidizing Bacteria as the Causative Factor of Biocorrosion of Concrete

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The start and the course of corrosion is conditioned by many factors which include, in addition to the most studied physical and chemical factors, biological effects like influence of vegetation and microorganisms causing the so called biocorrosion. The majority of studies focusing on microbiology of biocorrosion of concrete have indicated that the autotrophic oxidizing bacteria *Acidithiobacillus thiooxidans* and sulphur reducing bacteria *Desulfovibrio* genera are the causative microorganisms.

This paper aims at study of the biocorrosion degree of concrete samples exposed to the model conditions. Concrete biocorrosion proceeded in a laboratory reactor by sulphur oxidizing bacteria *Acidithiobacillus thiooxidans* exposure during 80 days at constant temperature of 30 °C.

The pH values, Ca and Si ions of concrete samples leachate were measured and evaluated. The pH values were slightly increased. The silicium ions concentrations in leachate increased when compared with the initial concentrations. The formation of gypsum and ettringite was proved by microscopic methods.

### 1. Introduction

Concrete is a worldwide used material in structural applications due to its strength, durability and low cost. Deterioration of concrete will occur when any environmental agent can break the inorganic bonds of the cement binder. Acids, sulfates, ammonium and magnesium salts, alkalies, organic esters, and carbon dioxide can destroy a binder over time (Little and Lee, 1997). The reaction between hydrated cement and aggregate in concrete, or alkali-aggregate reaction, can be divided into two main types: alkali-silica reaction and alkali-carbonate reaction. In alkali-silica reaction, alkalis in the cement paste fraction of concrete react with certain types of reactive silica to form an expansive gel (Winter, 2009).

In alkali – carbonate reaction, aggregate containing dolomite reacts with hydroxyl ions in the paste to form calcium carbonate plus magnesium hydroxide and carbonate ions. One of the often occurred deleterious processes in concrete in relation to alkali carbonate reaction is sulphate attack. Sources of sulphate which can cause sulphate

attack include groundwater, seawater, wastewater (Ghoualem, 2009) oxidation of sulfide minerals in clay adjacent to the concrete, pollution from industrial waste and masonry. Sulphates present in bricks can be gradually released over a long period of time, causing sulphate attack the mortar, especially when sulphates are concentrated due to moisture movement (Winter, 2009).

A special type of sulphate deterioration of concrete materials is biocorrosion - the process caused by presence and activities of microorganisms producing sulphuric acid. The biogenic sulphuric acid is generated by complex mechanisms and various microbial species, particularly ferrous and sulphur oxidizing bacteria genera *Acidithiobacillus*. There are five species of *Acidithiobacillus* sp. that play important roles on corroded and corroding concrete: *T. thioparus*, *T. novellus*, *T. neapolitanus*, *T. intermedius* and *Ac. thiooxidans*. The first four species listed are neutrophilic sulfur-oxidizing microorganisms (NSOM). The last species listed is an acidophilic sulfur-oxidizing microorganism (ASOM) (Nica et al. 2000). Fungi have also recently been found to be involved in the corrosion processes (Gu et al 1998).

The majority of instances of sulphate attack have two main effects on the cement paste: In the first place, sulphate reacts with hydrated aluminate phases, particularly monosulphate phase and any unreacted aluminate producing ettringite. Secondly, calcium hydroxide in the paste supplies calcium to produce the ettringite; when calcium hydroxide becomes scarce, the required calcium for continued ettringite formation is supplied by the C-S-H which becomes partly decalcified. Sulphate attack which can be external or internal causes expansion and cracking, and a general loss of concrete strength, with ettringite often widespread within the cement paste in affected areas (Winter, 2009).

Internal sulphate attack occurs when a source of soluble sulphate is incorporated into the concrete at the time of mixing; an example might be the presence of gypsum particles in the aggregate. External sulphate attack is due to penetration of sulphates into the concrete from outside. This kind of attack is a more common type and typically occurs where water containing dissolved sulphate penetrates into the concrete.

Concrete is typically highly alkaline and has a pH in the range of 11-13. The microorganisms capable of converting hydrogen sulphide to sulphuric acid cannot grow at this elevated pH so fresh concrete is protected from corrosion. The surface of the concrete does not remain basic throughout whole life. CO<sub>2</sub> and H<sub>2</sub>S are both presented in the headspace of sewage collection systems and they both have acidic properties (Roberts et al, 2002). The colonization of the concrete is an excellent example of microbial succession. Once the pH of the concrete surface is reduced to 9 and with sufficient nutrients, moisture and oxygen, some species of sulphur bacteria like *Acidithiobacillus* sp. mentioned above can attack the concrete surface and reproduce (Mori et al, 1992).

This work is a part of the research within the biodeterioration of concrete samples exposed to different kinds of bacteria living in the sewers. This paper presents the particular results of the experiments focused on the concrete biodeterioration influenced by sulphur-oxidizing bacteria under model conditions.

## 2. Material and Methods

The effects of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on various concrete samples in laboratory were investigated during 80 days. The calcium and silicium content in leachate before and after the experiments as well as pH values of leachates during the experiments were evaluated.

### 2.1. Concrete samples

Concrete samples with addition of 5 % (sample 1) and 10 % (sample 2) of coal fly ash respectively as well as reference samples without coal fly ash addition (sample 3) were used for the experiment. The control samples without bacteria influence (1C, 2C and 3C) were also investigated in the experiment.

Used coal fly ash with volumetric weight of 2381 kg/m<sup>3</sup> originates from black coal's burning process in Košice city heating plant (Tepláreň Košice a.s. TEKŇ). The percentage of basic oxides and total amount of sulphur in coal fly ash used in cement composites was as follow: 36.6 % SiO<sub>2</sub>, 16.06 % Al<sub>2</sub>O<sub>3</sub>, 10.82 % Fe<sub>2</sub>O<sub>3</sub>, 0.65 % TiO<sub>2</sub>, 3.3 % CaO, 1.22 % MgO, 1.41 % K<sub>2</sub>O, 0.27 % MnO, 0.56 % Pb<sub>2</sub>O<sub>3</sub>, 0.09 % S<sub>tot</sub>.

The concrete samples used for the experiments were prepared in accordance with Slovak standard STN EN 206-1 using cement CEM I 42.5 R. The prepared concrete samples were compression tested and categorized as class C30/37. The cubic concrete samples (150x150x150 mm) have been drilled by drilling mechanism STAM in a cylindrical shape with diameter of 32 mm and height of 15 mm. The drilled samples were sterilized in 70% ethanol for 12 hours and dried at 80 °C to constant weight before being used in the cultivation experiments.

### 2.2. Bacteria

Sulfur oxidizing bacteria *Acidithiobacillus thiooxidans* were isolated from the mixed culture obtained from the mine water (the shaft Pech, the locality Smolník, Eastern Slovakia) and the selective nutrient medium 9K was used for the isolation and cultivation of them. The optimal growth temperature was 28 -30°C and pH has been in the range of 2.0 – 3.5.

### 2.3. Experimental conditions

The experiment proceeded under stationary conditions in glass containers at the temperature of 30 °C. The glass containers sterilized before experiment were placed into the thermostat in order to ensure the constant temperature during the experiment. The lower part of each concrete sample (sample 1,2,3) was immersed into a liquid solution consisting of 150 ml of Waksman and Joffe selective medium with 10% inoculums of active bacterial culture. The containers were covered by sterilized foil so that the aerobic conditions were ensured. The manipulation with glass containers (pH measurements, active culture control) was carried out in aseptic box.

The abiotic control samples (1C, 2C, 3C) were treated in the same way but without the presence of bacteria. After 80 days, all investigated concrete samples were picked out, dried in aseptic box at room temperature and afterwards dried at temperature of 80 °C in laboratory drier and stored in exicator.

## 2.4. Methods

The liquid solutions were filtered and analyzed by atomic absorption spectrometry using spectrometer SpectrAA-30 (Varian, Australia) in order to determine the Ca and Si ions concentrations. The detection was carried out by a standard process in acetylene - air flame. pH changes in liquid solutions were evaluated once a week during the experiment by pH meter TIM 854 titration manager. The precipitated compounds were observed by mineralogical stereomicroscope STM 723 ZOOM with the combination of digital camera Olympus – C-770 Ultra Zoom as well as by electron scanning microscopy (SEM) with the equipment Jeol JSM-35CF (Japan). The elemental EDX analyses were carried out on the micro-analytical system LINK AN 10 000 operating in the secondary mode at a potential 25 kV and at various extensions from 90 to 5500.

## 3. Results and Discussion

The changes of calcium and silicium ions concentrations in liquid phase were observed for all samples after 80 days of exposure to *Acidithiobacillus thiooxidans* bacteria. The results of Ca and Si ions concentrations measurements are summarized in Table 1.

Table 1 : Ca and Si ions concentrations in leachate before and after the experiment

Sample	Ca (mg/l)		Si (mg/l)	
	before	after	before	after
1	45.92	33.6	0	4.6
2	45.92	70	0	8.16
3	45.92	100	0	6.49
1C	45.81	12.6	0	11.09
2C	45.81	38	0	17.66
3C	45.81	65	0	0.33

The increase of silicium ions concentrations from zero concentration was observed for all measured leachates after the experiment. The final concentrations of silicium were detected in the range of 4.6 mg/l (reference sample) to 8.16 mg/l (sample with 5 % of coal fly ash) for the samples exposed to bacteria. The higher final concentrations of silicium up to 17.66 mg/l were measured for abiotic control samples (except the sample with 10 % of coal fly ash) in comparison to the samples exposed to *Acidithiobacillus thiooxidans*.

As can be seen from the individual data for Ca ions in Table 1, both the decrease and the marginal increase were observed in investigated leachates. The increase of calcium concentration in leachates is probably related to the cement matrix degradation and calcium compounds release. The concentration of calcium ions in leachates increased in relationship with the added amount of coal fly ash in concrete samples (33.6 mg/l, 70 mg/l, 100 mg/l). Higher amount of calcium released into the solution was detected in case of sample 2 with 10 % of coal fly ash. On the other hand, biocorrosion of the concrete sample 3 as well as corrosion of samples 1C and 3C led to a significant

decrease of calcium concentration in leachates. This decrease may result in surface compounds being formed by reactions of calcium compounds with sulphuric acid. Considerable changes of pH were observed after 80 days of *Acidithiobacillus thiooxidans* influence. The measured pH values are illustrated in Table 2.

Table 2 : pH values of leachate during the experiment

sample	day 0	day 7	day 14	day 21	day 28	day 35	day 49	day 56	day 63	day 80
1	2.98	3.17	3.66	4.17	4.29	3.03	3.12	2.84	2.77	3.09
2	2.98	3.12	2.93	3.01	2.77	2.43	2.66	2.38	2.08	2.59
3	2.98	2.81	2.98	2.92	2.82	2.90	3.56	3.22	3.09	3.11
1C	3.94	4.96	6.16	6.27	6.10	6.03	6.17	6.21	6.20	6.18
2C	3.94	5.84	6.13	6.27	6.22	6.18	6.13	6.08	6.12	6.23
3C	3.94	3.73	3.68	3.16	2.85	3.94	5.05	5.07	4.70	4.76

The pH values of samples 1,2 and 3 exposed to bacteria varied from the initial value of 2.98 to 4.29 during the experiment. The slight rise of pH is caused by alkali compounds release due to cement matrix degradation. The further rise of pH is probably compensated by reaction of mentioned alkali compounds with biogenic sulphuric acid produced by *Ac. thiooxidans*. pH values of abiotic control samples (1C and 2C) reach the values slightly higher than 6 after two weeks and consequently no changes until the end of the experiment were observed as it is seen in Table 2.

The precipitation of sulphate compounds forming on the surface of concrete samples was observed by stereomicroscopy (Figure 1) and electron microscopy.

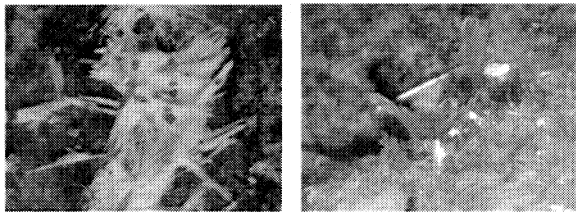


Figure 1: The precipitated surface products (magnification 20x4.5)

The presence of gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Figure 2a) and ettringite  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$  (Figure 2b) as surface precipitate product was confirmed by EDX.

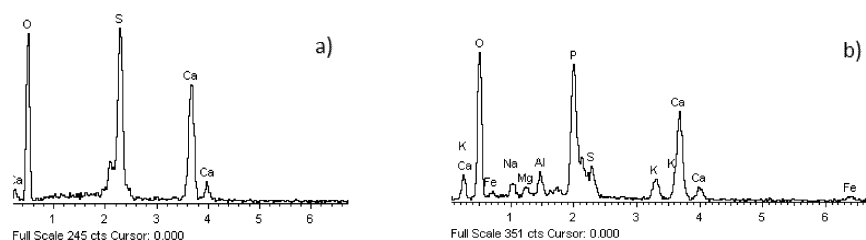


Figure 2: EDX analysis – gypsum (a) and ettringite (b)

#### 4. Conclusions

The effects of *Acidithiobacillus thiooxidans* on three types of concrete samples were investigated under model conditions. There was a slight increase in the the pH values of liquid phases. The silicium ions concentrations in leachate increased when compared with the initial concentrations. The formation of gypsum and ettringite was proved by microscopic methods. The samples with coal fly ash replacement seem to be more resistant against aggressive environment than expected. For relevant conclusions more detailed investigation is in progress.

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#### References

- Ghoualem H., 2009, Assesment of Wastewater and treatment by the Lagoon Process, Chemical Engineering Transaction, 17, 391-396.
- Gu J.-D., Ford T.E., Berke N.S. and Mitchell R., 1998, Biodeterioration of concrete by the fungus *Fusarium*. International Biodeterioration & Biodegradation, 41, 101–109.
- Little B.J and Lee J. S., 2007, Microbiologically influenced corrosion, John Wiley & Sons, Inc., Hoboken, New Jersey.
- Mori T., Nonaka T., Tazaki K., Koga M., Hikosaka Y. and Noda S., 1992, Interactions of nutrients, moisture, and pH on microbial corrosion of concrete sewer pipes, Water Research, 26, 29–37.
- Nica D., Davis J.L., Kirby L., Zuo G. and Roberts D.J., 2000, Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers, International Biodeterioration & Biodegradation, 46, 61–68.
- Roberts D.J., Nica D., Zuo G. and Davis J.L., 2002, Quantifying microbially induced deterioration of concrete: initial studies, International Biodeterioration & Biodegradation, 49, 227 – 234.
- Winter N., 2009, Understanding Cement, WHD Microanalysis Consultants Ltd, United Kingdom.