

Performance of cement mortars with waste-material addition in microbiological sulphate environment

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Bio-corrosion refers to the corrosion influenced by the presence of microorganisms on the surface of different concrete structures. Sulphate-reducing bacteria (SRB) and sulphur-oxidizing bacteria (SOB) belong to the best studied microorganisms causing bio-corrosion. Concrete sewer pipes, waste water collection systems and treatment plants ensure a suitable environment for the growth and activity of these microorganisms. Sulphur-oxidizing bacteria produce the biogenic sulphuric acid which may cause a significant structural damage to the sewage infrastructure by inducing the deterioration of concrete sewer pipes.

This paper discusses the effects of SOB bacterial activity represented by *Acidithiobacillus thiooxidans* on parameters affecting the durability of cement mortar composites. Two mortar mixtures were used in the experiment: samples with a share of ground granulated blast furnace slag (65 % cement replacement) and the reference samples without any waste addition. The composites were exposed to an aggressive sulphate environment with sulphur-oxidizing bacteria for 60 days. Parameters such as the *pH* of liquid media and the leachability of the basic inorganic compounds from the cementitious matrix due to the aggressive environment were studied. The better durability of cement mortar samples, based on furnace slag addition, against the biogenic sulphate attack was not confirmed.

Key words: bio-corrosion, sulphate acid attack, concrete, blast furnace slag

Introduction

Civil infrastructure systems are critical assets for any country's socioeconomic development. Designing these systems for a particular service lifetime and maintaining them in operation has been recognized as a critical issue worldwide. Deterioration is common in structures located in aggressive environments and subject to, for instance, sulphate attack, chloride penetration and bio-deterioration. Biological processes can accelerate the degradation process by modifying the structural durability [1]. Bacteria are considered the primary colonizers of inanimate surfaces in both natural and man-made environments. Therefore, the majority of microbial-induced corrosion (MIC) investigations have addressed the impact of pure or mixed culture bacterial biofilms on the corrosion behaviour of cement composites. The main types of bacteria associated with concrete corrosion in aquatic habitats are sulphate-reducing bacteria (SRB), sulphur-oxidizing bacteria (SOB), and bacteria secreting organic acids and slime. These organisms typically co-exist in naturally occurring biofilms, forming complex consortia on corroding concrete surfaces [2]. The MIC of a concrete sewer pipe was first observed over a century ago by Olmstead and Hamlin and linked to the activity of

Thiobacillus bacteria in the mid-20th century and later to other bacterial and fungal species [3]. In sewer systems, deteriorations of concrete composites are primarily related to the production of hydrogen sulphide (H_2S) in stagnant zones [4]. The SRB present in the biofilms convert the sulphates in the wastewater to H_2S . The diffusion and turbulence of the wastewater stream then facilitates the release of the H_2S into the sewer atmosphere. There, it is absorbed onto the moist upper surfaces of the concrete pipe where SOB produce sulphuric acid (H_2SO_4) [3]. Eventually, the biogenic sulphuric acid reacts with the free lime ($Ca(OH)_2$) of concrete to form gypsum $CaSO_4 \cdot 2H_2O$. The formation of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) due to the reaction of gypsum with calcium aluminates of portlandite causes another facet of the problem. Ettringite is expansive and causes internal crackings and pitting. Also the thaumasite is formed of the sulphate attack, and it requires sources of sulphate and carbonate. Thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) occurs as a natural mineral, as an alteration product of limestone, although it is rare. The normal cement hydration products, mainly calcium silicate hydrate and calcium hydroxide, are decomposed as a result of both the sulphate attack and carbonation. The formation of the calcium-containing corrosion by-products weakens the structural integrity of the

concrete sewer pipe, which can lead to the eventual collapse of the sewer system [5–7].

This paper presents the results of durability tests evaluated on two mortar mixtures exposed to a sulphate environment with the presence of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans*, considering the leachability of basic inorganic compounds of cement composites and the *pH* of the media.

Materials and methods

Two sets of mortar samples (R and S) with different mixtures were prepared for the experiment. The R samples represented the reference samples with 100 wt.% of the commonly used Portland cement CEM I 52.5 R. The second set of specimens S was prepared with binder containing 65 wt.% of the granulated blast furnace slag (GBFS) and 35 wt.% of the cement CEM I. The chemical compositions of binders are given in Table 1.

Table 1. The chemical composition of cement CEM I 52.5 R and ground granulated blast furnace slag in wt. %

Component	CEM I, wt. %	GBFS, wt. %
CaO	57.15	39.55
SiO ₂	18.11	38.95
MgO	1.37	10.11
Al ₂ O ₃	4.02	8.33
MnO	-	0.73
SO ₃	1.49	0.57
Fe ₂ O ₃	2.69	0.54
K ₂ O	1.12	0.48
TiO ₂	0.18	0.37
P ₂ O ₅	0.33	0.04
Cl	0.06	0.02

The culture of the sulphur-oxidizing bacteria *A. thiooxidans* was isolated from the acid mine drainage (the Pech shaft, Smolnik locality, Eastern Slovakia). The selective nutrient medium Waksman and Joffe (*pH* 4.0) was used for the preparation of the active bacterial culture as well as for the isolation and cultivation of *Acidithiobacillus thiooxidans* in the presence of the mortar samples [8]. The composition of the nutrient medium is reported in Table 2.

Table 2. The selective nutrient medium by Waksman and Joffe [8]

Chemical compound	Amount, g/L
CaCl ₂ ·6H ₂ O	0.25
(NH ₄) ₂ SO ₄	0.2
K ₂ HPO ₄	3.0
MgSO ₄ ·7H ₂ O	0.5
FeSO ₄ ·7H ₂ O	Trace amount
S ^o	10.0
Distilled water	Up to 1000 mL

Specimens with the dimensions 40×40×160 mm used in the experiment were slightly brushed in order to remove polluting particles, then dried and weighted to a constant mass. In the next step, mortar samples were placed in abiotic and biotic environments, and the effect of *A. thiooxidans* was investigated during 60 days at the temperature of 25 °C. The specimens placed in the solution with bacteria were labelled as R/A and S/A, respectively and the control specimens placed in the nutrient medium without bacteria were labelled as R/C and S/C, respectively.

In the experiment, the chemical composition of mortar samples' leachates and *pH* were investigated every 10 days. The chemical composition of the leachates was analysed by the X-ray fluorescence method (XRF) using the SPECTRO iQ II (Ametek, Germany) with an SDD silicon drift detector with the resolution of 145 eV at 10 000 pulses. The primary beam was polarized by the Bragg crystal and the Highly Ordered Pyrolytic Graphite (HOPG) target. The measurement was performed during 180 s at the voltage of 25 kV and 50 kV and the current of 0.5 and 1.0 mA under the helium atmosphere. The qualitative analysis was based on a standardized method for liquids. The *pH* changes were measured by with a FG2-FiveGo *pH* meter (Mettler-Toledo, Switzerland) [8].

Results and discussion

The development of Ca leaching (Fig. 1, Fig.2) was similar for both specimens, with and without slag, placed in a sulphate environment with *A. thiooxidans* bacteria. A higher concentration of Ca ions in the leachate (782.2 mg/L) was measured for the S/A sample with bacteria when compared with the R/A sample without bacteria (657.8 mg/L). The *pH* value ranged from 3.28 to 4.14 and from 3.59 to 4.68 for the S/A sample and for the R/A reference sample, respectively.

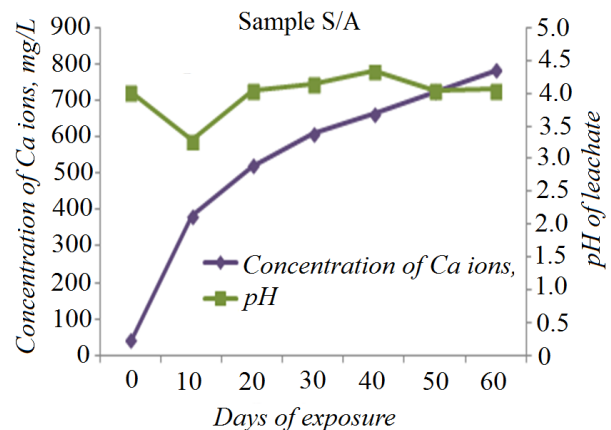


Fig. 1. The leached-out amount of Ca and the leachate *pH* of the S/A sample with a furnace slag in bacterial media during the 60-day experiment

For the reference samples S/C and R/C, the leaching of Ca ions in the abiotic solution proved a different trend as shown in Fig. 3 and Fig. 4. The highest measured concentration of Ca ions for the S/C sample was 75.7 mg/L

and for the R/C sample 71.4 mg/L. The *pH* ranged from 6.81 to 7.84 for the S/C sample and from 7.03 to 8.14 for the reference sample R/C.

The findings revealed the leaching of Ca ions to be noticeably higher for samples placed in the biotic sulphate environment with bacteria as compared with the control samples placed in the abiotic environment as reported in [9].

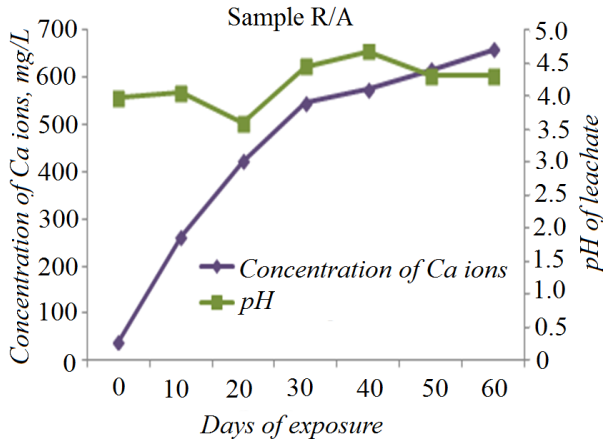


Fig. 2. The leached-out amount of Ca and the *pH* of the leachate of the R/A reference sample with bacteria during the 60-day experiment

The decreasing trend of Ca concentrations in the leachate (Fig. 3 and Fig. 4) may be caused by chemical reactions of leached-out Ca ions in the solution, followed by the precipitation of the calcium-based compounds on the surface of the sample as mentioned in [10].

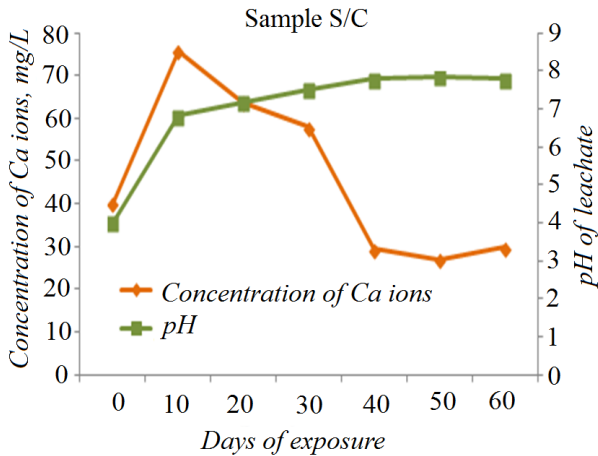


Fig. 3. The concentration of Ca ions and the *pH* of GBFS sample with bacteria *A. thiooxidans* S/C during the 60-day experiment

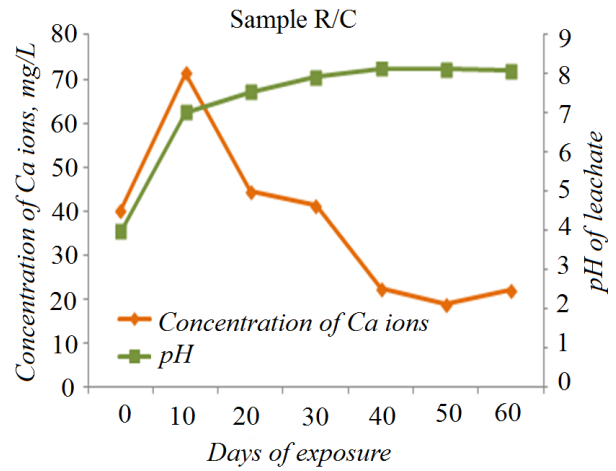


Fig. 4. The concentration of Ca ions and the *pH* of the reference sample R/C in a liquid medium without bacteria during the 60-day experiment

This correlated with the fact that a weak coating was found on the surface of specimens (Fig. 5). The result of the precipitation was a reduction of calcium concentration in the solution.

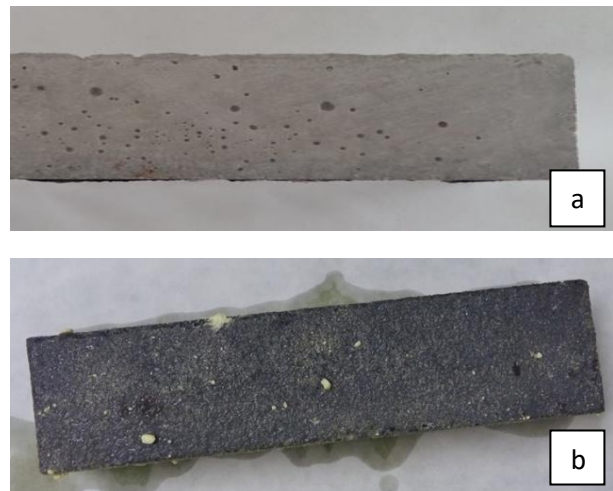


Fig. 5. The surface of a sample before (a) and after (b) immersion in the bacterial medium with *A. thiooxidans* after 60 days

The formation of the new compounds on the mortar surface was manifested also by changes in the weight of samples after the experiments as illustrated in Table 3.

Table 3. Changes in the weight of samples after 60 days: (+) – increase, (-) – decrease

Sample	Input weight, g	Weight change of specimens after the experiment	
		g/cm ²	%
R/A	574.35	- 1.978	- 0.79
R/C		+ 2.027	+ 1.65
S/A	573.82	+ 2.019	+ 1.39
S/C		+ 2.030	+ 1.89

The increase in weight was observed for both samples without bacteria exposure (R/C and S/C), but for the

sample with slag addition S/A under the bacterial attack as well. The increase in the weight of the samples without bacteria was found to be more intensive as compared with the samples under bacterial exposure. An increase in the weight of the specimens may be linked with the leaching process, whereas a decrease should indicate the formation of new sulphate-based compounds or the deposition of a layer of calcium carbonate on the surface of the samples.

To compare the samples with and without addition of GBFS regarding the calcium leaching, the leaching percentage was calculated. The percentage of leached-out calcium was calculated by dividing the maximum leached-out mass during the experiment $[Ca]_{max}$, measured in the leachate, by the total content of calcium in a concrete sample, measured by XRF prior to the experiment $c(Ca)_{total}$.

$$LP(Ca) = \frac{[Ca]_{max}}{c(Ca)_{total}} \times 100.$$

As shown in Table 4, the highest percentage of calcium leaching was found for the samples which contained GBFS (S/A and S/C samples), opposed to a reference sample with no addition of waste material (R/A and R/C samples).

Table 4. Leaching percentage of calcium

Sample	LP(Ca), %
R/A	1.82
S/A	3.03
R/C	0.19
S/C	0.29

The concentration of silicon ions in the leachate had an irregular course compared to the trends of Ca ions concentration. As shown in Fig. 6, the highest concentration of Si ions for the S/A slag sample immersed in the bacterial culture was measured as 476.4 mg/L after 50 days of the experiment, whereas for the reference sample R/A in the biotic sulphate solution was 798.2 mg/L after 10 days of the experiment (Fig. 7).

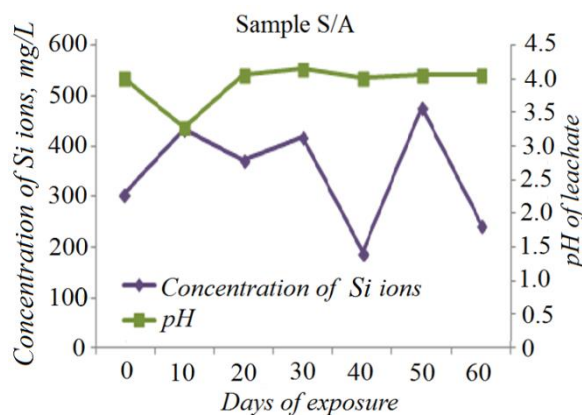


Fig. 6. The concentration of Si ions and the pH of the slag sample S/A with bacteria during the 60-day experiment

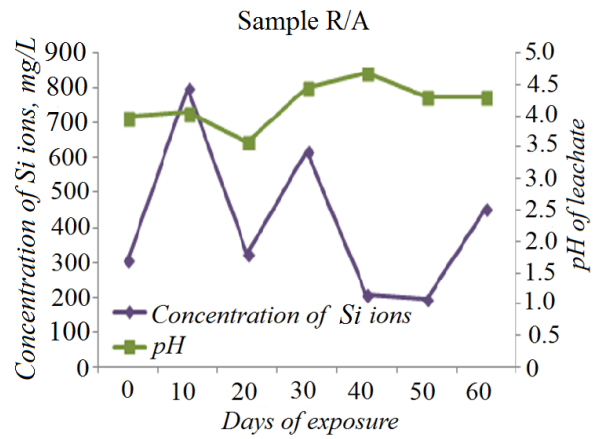


Fig. 7. The concentration of Si ions and the pH of the reference sample R/A immersed in a liquid medium with bacteria during the 60-day experiment

Changes in the concentrations of Si ions for the control samples (S/C and R/C) in the sulphate environment without bacteria are shown in Fig. 8 and Fig. 9. The highest concentration of Si ions for the S/C sample was 609.7 mg/L and for the R/C sample 401.0 mg/L. At the 10th day of the experiment, the concentrations of silicon ions were for both samples the highest, and they decreased during the experiment.

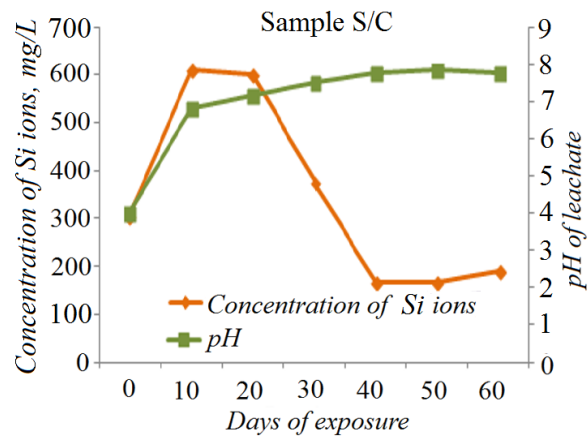


Fig. 8. The concentration of Si ions and the pH of a sample with GBFS without bacteria S/C during the 60-day experiment

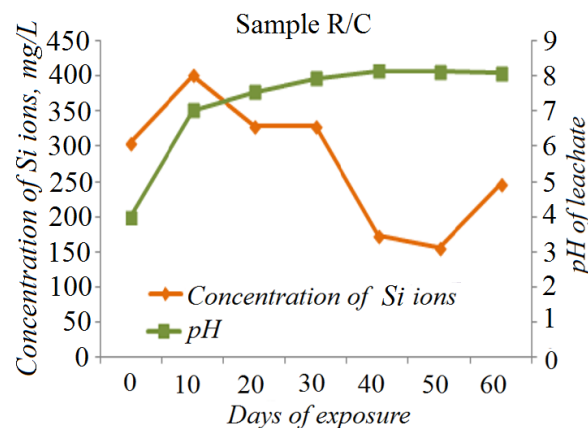


Fig. 9. The concentration of Si ions and the pH of the reference sample in media without bacteria R/C during the 60-day experiment

The decrease in silicon concentrations in leachates during the experiment is probably connected with the same processes as discussed for calcium.

The percentage of silicon leaching was calculated similarly as in the case of calcium as follows:

$$LP(Si) = \frac{[Si]_{max}}{c(Si)_{total}} \times 100$$

where $[Si]_{max}$ was the maximum of Si concentration measured in the leachate during the experiment, and $c(Si)_{total}$ was the total content of silicon in the concrete sample, measured by XRF prior to the experiment.

The highest percentage of silicone leaching was observed for the reference sample R/A placed in the medium with bacteria, as opposed to control samples where a better leaching performance was observed for a sample with the addition of slag S/C, placed in the solution without *A. thiooxidans* as illustrated in Table 5.

Table 5. Leaching of Si ions in the solution

Sample	LP(Si), %
R/A	1.41
S/A	0.72
R/C	0.71
S/C	0.92

Conclusions

The work has presented partial results of bio-corrosion caused by bacteria *A. thiooxidans*. Mortar specimens with 65 wt.% of granulated blast furnace slag didn't prove any better leaching properties towards the biogenic sulphuric acid attack. Similar results have been observed in our previous work where the small-sized concrete samples with GBFS have been studied. To make a definite conclusion regarding the ability of slag addition to improve the durability of cement mortars, a further study is needed.

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CEMENTO SKIEDINIŲ SU ATLIEKŲ PRIEDU SAVYBIŲ TYRIMAS MIKROBIOLOGINĖJE SULFATINĖJE APLINKOJE

S a n t r a u k a

Biokorozija – tai korozija, kurią sukelia ant skirtingų struktūrų betonų paviršiaus esantys mikroorganizmai. Sulfatus mažinančios bakterijos (SRB) ir sierą oksiduojančios bakterijos (SOB) yra labiausiai ištirti biokoroziją sukeliantys mikroorganizmai. Tinkama aplinka šioms bakterijoms augti ir veikti yra betoniniai kanalizacijos vamzdžiai, nuotekų surinkimo sistemos ir valymo įrenginiai. Sierą oksiduojančios bakterijos išskiria biogeninę sieros rūgštį, kuri gali smarkiai pažeisti betoninius kanalizacijos vamzdžius.

Straipsnyje aptariama sierą oksiduojančių bakterijų *Acidithiobacillus thiooxidans* įtaka kompozicinių cemento skiedinių ilgaamžiškumo parametrui. Eksperimentuota su dviem skiedinių mišiniais: tirti bandiniai, kuriuose 65 % cemento pakeista granuliuotu aukštakrosnių šlaku, ir kontroliniai bandiniai be atliekų priedo. Bandiniai 60 parų buvo laikomi agresyvioje sulfatų aplinkoje su SOB bakterijomis. Buvo nustatytas skystosios terpės *pH* ir pagrindinių cemento matricos junginių išsiplovimas dėl agresyvios aplinkos. Didėnis cemento skiedinio bandinių su šlako priedu atsparumas biogeninei sulfatinei korozijai nepatvirtintas.

Reikšminiai žodžiai: biokorozija, sieros rūgšties poveikis, betonas, aukštakrosnių šlakas.