Cement Composites Biodeterioration by *Acidithiobacillus Thiooxidans*

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Abstract: - The focus of this work was to study the biodeterioration of special cement composites by sulfur-oxidizing bacteria *Acidithiobacillus thiooxidans*. The laboratory prepared cement composites that contained the selected additives - silica fume (a secondary raw material) and zeolite (a natural raw material), as partial replacements for the binder. The tests were carried out in laboratory conditions. During the experiments, changes to the pH values and the Ca and Si concentrations were observed in the liquid phases. Based on the achieved results, it can be concluded that concrete composites with partial replacement of the binder by silica fume and zeolite have a higher resistance to biogenic sulfuric acid.

Key-Words: - cement composites, concrete, biodeterioration, biocorrosion, *Acidithiobacillus thiooxidans*, silica fume, zeolite.

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1 Introduction

The biodeterioration of building materials represents a branch of science that focuses on the study of the unwanted changes that are caused by the activity of microorganisms (MO) on building materials, [1]. One of the most used building materials is concrete. This is most commonly in the form of monolithic structures or prefabricated elements. The concrete biodeterioration caused by the biogenic sulphuric acid is known as microbiologically influenced concrete corrosion (MICC) or concrete biocorrosion, [2]. In 1945 was conducted the initial research on the influence of biogenic sulphuric acid on the concrete corrosion process using the bacteria *Acidihiobacillus thiooxidans,* [3].

Additional studies have supplemented and expanded on the knowledge of the biocorrosion process [4], [5]. The sulfuric acid produced by *Acidihiobacillus thiooxidans* (*A. thiooxidans*) reacts with the surface of the concrete converting the cementation material into the main corrosive products of biocorrosion - gypsum or ettringite. Both mentioned products subsequently cause a loss in the strength of the concrete.

Concrete is a composite material. Its main components are cement, gravel aggregate and water. It can contain different additives to improve its properties such as treatability, plasticity, speed of hardening, water permeability, resistance against aggressive environments etc., [6]. Additives are the mineral materials that are added to the concrete during the mixing process. Fly ashes, blast furnace slag, pigments, silica fume and zeolites all belong to this group.

Silica fume is an industrial waste which is formed during the production of crystalline silicon or ferrosilicon in arc furnaces. Silica fumes influence the porous structure of concrete, which then in turn enhances the concrete's hardness and resistance to aggressive environments. The use of these waste products as additives in the concrete decreases their negative impact on the environment. Additionally, they can contribute to improving the resistibility of the prepared concrete composite.

Zeolites are crystalline aluminosilicates which contain alkali and alkaline earth metals. Their use is advantageous from an economic point of view due to their natural abundance and low production costs. The composites which contain zeolite harden faster and have higher values of longstanding strength in comparison with the cement composites based on the blast furnace slag.

The aim of this work was to study the biodeterioration process of cement composites by the bacteria *A. thiooxidans*. The experiments focused on the changes in pH values and Ca and Si concentrations in the liquid phases. These changes were occurring while the composite samples were under the influence of biogenic acid. Cement composites contained a binder which was partially replaced by the chosen additives: silica fume (as the secondary raw material) and zeolite (as a natural raw material).

2 Materials and Methods

2.1 Microorganisms

The sulfur-oxidizing bacteria *A. thiooxidans* used in the experiment was isolated from the acid mine drainage (the Pech shaft, the Smolnik deposit, Eastern Slovakia), [7]. A selective nutrient medium for *A. thiooxidans* (pH 4.0) was applied [8] for the isolation, cultivation, preparation of the active bacterial culture of *A. thiooxidans* and for the biodeterioration experiments.

2.2 Cement Composites Samples

Cement CEM I 42.5 N was used for the preparation of the four studied cement composites samples (S-0, S-Si, S-Si-Z and S-Z). The composition of the samples was prepared with regard to the aggressive environments in accordance with STN EN 206-1. Zeolite and silica fumes were added to improve the durability of concrete according to the appropriate literature, [9]. The composition of the cement composite samples is described in Table 1.

The prepared standardized concrete prisms with dimensions of 100 x 100 x 400 mm were cured for 28 days in an aqueous environment and then cut into small prisms with dimensions of 50 x 50 x 10 mm. The test samples were gently abraded to remove contaminant particles, sterilized in 70 % ethanol for 24 h, and dried at 80 °C to constant weight before use in biodegradation experiments.

Table 1. Composition and labeling of cement composite samples

Components	Cement composites samples (calculation on 0.01 m3)			
	S-0	S-Si	S-Si-Z	S-Z
CEM I 42.5 N (kg)	3.60	3.31	3.02	3.31
Water (L)	1.09	1.22	1.2	1.09
Zeolite (kg)	-	-	0.29	0.29
Silica fume (kg)	-	0.29	0.29	-

S – sample, Si – silica fume, Z – zeolite

2.3 Study of Biodeterioration

The cement composite samples, containing four various compositions (S-0, S-Si, S-Si-Z, and S-Z), were placed into the liquid phase with bacteria *A. thiooxidans* (S-0-At, S-Si-At, S-Si-Z-At, and S-Z-At i.e. biotic conditions) and without bacteria (S-0-R, S-Si-R, S-Si-Z-R, and S-Z-R i.e. reference abiotic conditions). The volume of the bacteria inoculum was 20 %. The volume ratio of the concrete sample to the liquid phase was set to 1:10. The experiments were carried out in glass jars (700 mL) covered by cotton plugs in an aerobic atmosphere at laboratory temperature. Bacterial inoculum was added at 7-day intervals, over a period of 90 days to stimulate the bacteria growth in the presence of the cement composite samples. The experiments without bacteria, which served as a reference abiotic environment, proceeded the same way as the experiment with bacteria. The change of pH, the presence of bacteria as well as the concentrations of calcium and silicon ions released, were measured in leachates after each 7-day period.

2.4 Analytical Methods

The chemical composition of concrete samples and leachates was analyzed before and after the experiments by X-ray fluorescence analysis (XRF). SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10.000 pulses was used for the analysis. The samples were measured for 300 and 180 s at voltage of 25 kV and 50 kV at currents of 0.5 and 1.0 mA under a helium atmosphere by using the standardized method of fundamental parameters. pH changes were measured by pH meter PHM210 (MeterLab, France).

3 Results and Discussion

3.1 The Changes in Calcium Concentration

Figure 1 and Figure 2 show the trend of the leaching of calcium from the studied cement composites throughout the duration of the experiment. All biotic samples have been observed to contain significantly higher concentrations of calcium in the leachates (Figure 1) than in the abiotic samples (Figure 2). The reason for the difference in the leached concentration of calcium has to do with the activity of the present bacterial culture. Bacteria *A. thiooxidans* produced sulphuric acid which caused the Ca to be leached out of the concrete to a higher extent than in the experiments without bacteria. From Figure 1 it is evident that there was a rapid increase in leached calcium which occurred in the presence of bacteria for the first 21 days of the experiment (in the case of S-Si-Z-At until the 57th day). Subsequently, the leaching process stabilized, which is in accordance with the studied literature, [10]. All studied biotic experiment samples record a gradual increase in Ca concentration. In all abiotic experiments, the initial leachability of Ca was from 95 to 80 mg/kg. After an observed gradual decrease, the concentration of Ca stabilized until the end of the experiment, when the concentration of Ca achieved values of 18-25 mg/kg.

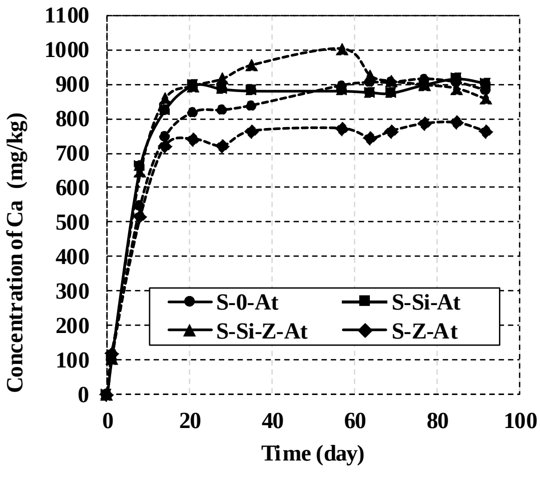

Fig. 1: The changes of Ca concentration – biotic samples. (At – *Acidithiobacillus thiooxidans*)

The concentrations of leached calcium compared to the total calcium in the concrete composite before the experiments are shown in Figure 3. The highest percentage of Ca leachability of 7.03 % was achieved in the biotic sample S-Si-Z-At (silica fume + zeolite). The lowest percentage value 4.07 % of Ca leachability from the biotic samples was observed in sample S-Z-At (zeolite). The range of the percentage of leachability of Ca from the concrete composites without the presence of bacteria was 0.22 - 0.40 %. It is possible to claim that the leachability of Ca under the influence of bacteria was several times higher than in abiotic conditions.

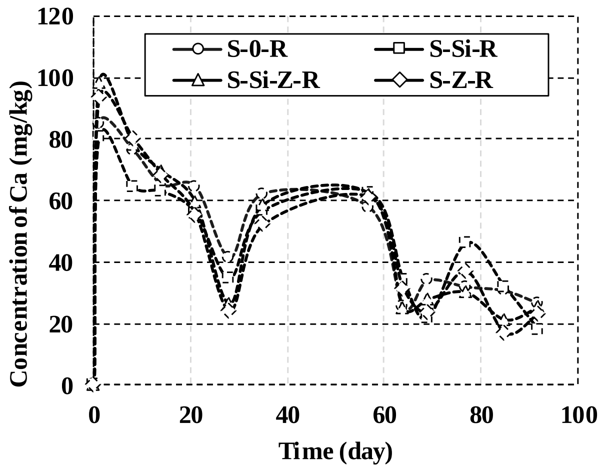

Fig. 2: The changes of Ca concentration – abiotic samples. (R – reference abiotic conditions)

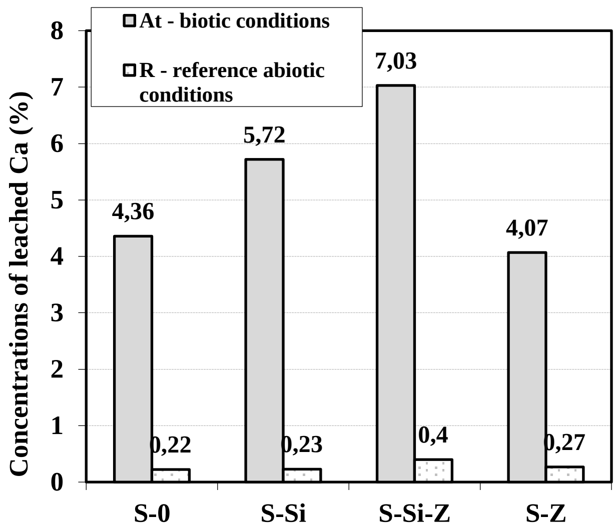

Fig. 3 Concentrations of leached Ca compared to total calcium concentration in the concrete composite

3.2 The Changes in Silica Concentration

Figure 4 and Figure 5 display the changes in the leachability of silica during the whole experiment. The highest increase of the Si concentration in the liquid phase for biotic, as well as abiotic samples, was observed after eight days. Subsequently, the concentration of Si increased, later gradually decreased, and finally decreased considerably at the end of the experiment. This is most likely due to Si precipitation. The final concentration of Si in all samples was in the range of 500 - 590 mg/kg. The largest recorded difference between the highest and lowest detected Si concentrations was in sample S-Z-At (zeolite). The highest concentrations were measured on the 8th day and the lowest on the 90th day. This fact can be explained by the properties of the applied zeolite. Zeolite belongs to a group of inorganic materials that contains a large amount of active SiO_2 and Al_2O_3, which has the potential to react with $Ca(OH)_2$ released by the hydration of Portland concrete, [11].

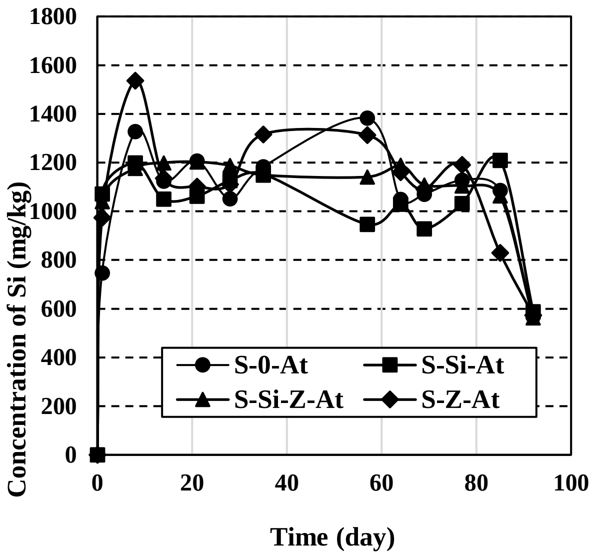

Fig. 4: The changes of Si concentration – biotic samples. (At – *Acidithiobacillus thiooxidans*)

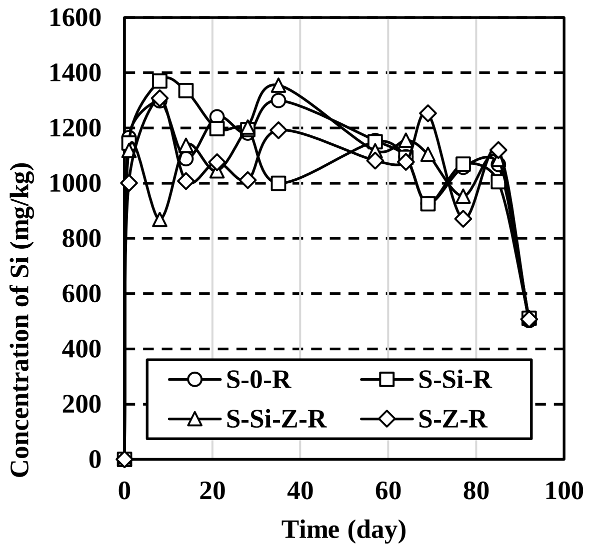

Fig. 5: The changes of Si concentration – abiotic samples. (R – reference abiotic conditions)

Figure 6 displays the concentrations of leached Si compared to total Si concentration in all studied concrete composite samples after the experiment was completed (At - biotic conditions, R - abiotic conditions). The highest percentage of Si leachability was in abiotic sample S-0 (reference sample without the replacement) with a value of 6.5 %, whereas the lowest percentage was found in biotic sample S-Si (silica) with a value of 4.71 %.

Figure 4, Figure 5 and Figure 6 refer to the fact that the applied nutrient medium had a fundamental influence on the Si leachability. The presence of bacteria most likely did not have a fundamental influence on the leachability of Si.

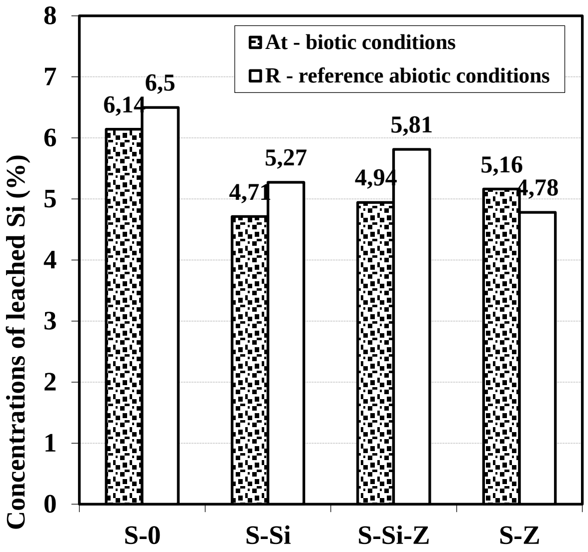

Fig. 6: Concentrations of leached Si compared to total silica concentration in the concrete composite

4 Conclusion

This contribution is focused on the study of the influence of bacterially produced sulphuric acid on concrete composites, which had their binder partially replaced by chosen additives (silica fume as the secondary raw material and zeolite as the natural raw material). The leachability of Ca and Si was observed in particular, and the following results were achieved:

- Substantially higher concentrations of Ca were measured in all the biotic samples than in the abiotic samples. This is a result of the production of sulphuric acid by the used bacteria *A. thiooxidans*, which caused the leaching of Ca from the concrete;
- The highest percentage of Ca leachability of 7.03 % was observed in sample S-Si-Z-At (silica fume + zeolite). Sample S-Z-At (zeolite) had the lowest value of Ca leachability at 4.07 %;

- The leachability of Ca under the influence of bacteria was several times higher than in abiotic conditions;
- The concentration of Si in leachates for all studied samples (for biotic, as well as for abiotic), after experiments were completed, was in the range of 500 - 590 mg/kg. The achieved results can most likely be explained by understanding the properties of the applied zeolite. Zeolite belongs to the aluminosilicate group of minerals with a large amount of active SiO_2 and Al_2O_3, which has the potential to react with $Ca(OH)_2$ released by the hydration of Portland concrete;
- The applied nutrient medium had a fundamental influence on the leachability of Si. The presence of bacteria most likely had no influence.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- Alena Luptakova has organized and executed the experiments.
- Adriana Estokova processed and evaluated the results.
- Miloslav Luptak executed the experiments.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.