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Effect of Acidithiobacillus thiooxidans on different types of concrete mixtures

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***Abstract*— Durability of a material is its ability to last for a long time without any significant deterioration. Microorganisms that produce sulphuric acid accelerate the deterioration of concrete structures in a process termed "Microbially Induced Concrete Corrosion". The effects of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on various concrete samples in laboratory were investigated during 90 days. The calcium and silicium contents in leachates during the experiments were evaluated using X – ray fluorescence method (XRF). Disruption and damages of the concrete surface, the samples' weight-loss and the calcium release were observed after the experiments.**

***Keywords*—concrete, bacteria, biodenoration, calcium, silicon, leaching**

I. Introduction

Durability of a material means its ability to last for a long time without any significant deterioration. Existing evidence [1, 2, 3] has shown that in many concrete structures exposed to aggressive aqueous environments corrosion problems are present. Microorganisms that produce sulphuric acid accelerate the deterioration of concrete structures in a process termed "Microbially Induced Concrete Corrosion" (MICC) [4]. The theory describing MICC has been under development since 1900, when Olmstead and Hamlin first mentioned it in the literature [5]. Deterioration of concrete can be caused by the adverse performance of the aggregate, paste or reinforcement and due to chemical and physical causes. Among the various other factors affecting durability of concrete, water to binder ratio (w/b) is one of the parameter having the largest influence on it. This affects the porosity and permeability of the paste. Permeability of the paste is closely related to interconnectivity of pores. Inter connected capillary pores greatly influence the rate at which water and aggressive agents penetrate into pores of concrete. Ingress of harmful chemicals is responsible for concrete deterioration. Several materials including fly ash, silica fume, zeolite, metakaoline, wollastonite etc. which are either industrial wastes or naturally occurring minerals, have been investigated for making durable concrete material [6].

The aim of this work is the study of the concrete biodeterioration by the bacteria genus *Acidithiobacillus* in laboratory by sulfuretum simulation.

II. Material and Methods

The effects of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on various concrete samples in laboratory were investigated during 90 days.

A. *Concrete samples*

Three mixtures of concrete (A0, A1 and A2) were used for the preparation of concrete samples for the experiment, using cement CEM I 42.5 N. The composition of these mixtures was prepared considering two aggressive environments in accordance with STN EN 206-1: 1) Slightly aggressive chemical environment (exposure class XA1) - mixtures A0 and A1 with concrete of strength class C 25/30 and 2) Moderately aggressive chemical environment (exposure class XA2) - mixture A2 with concrete of strength class C 30/37. Zeolite and silica fume were added in order to improve the durability of concrete according to literature knowledge [7].

Quality of concrete, mainly strength and durability, strongly depends on the water amount. Therefore in the EN 206-1, the recommendations in terms of water-cement ratio (w/c) are given for each environmental exposure and strength class. Mix proportion with appropriate w/c ratio for concrete with above mentioned specifications is shown in Table 1.

TABLE I. MIX PROPORTIONS OF THREE DIFFERENT CONCRETE MIXTURES

Components	**Concrete mixture**		
	A0	***A1***	***A2***
Cement	360 kg	360 kg	360 kg
Water	170 L	200 L	191 L
Zeolite	-	-	20 kg
Silica fume	-	20 kg	20 kg
Fr. 0/4 mm	825 kg	800 kg	750 kg
Fr. 4/8 mm	235 kg	235 kg	235 kg
Fr. 8/16 mm	740 kg	740 kg	740 kg
Plasticization additive	3.1 L	3.1 L	3.1 L
w/c ratio	0.47	0.49	0.45

The prepared standardized concrete prisms of size 100x100x400 mm were cured for 28 days in water environment and afterwards cut into small prisms with dimensions of 50x50x10 mm. The test specimens were slightly brushed in order to remove polluting particles, sterilized in 70% ethanol for 24 hours and dried at 80^{o}C to constant weight before use in the cultivation experiments.

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B. *Microorganisms*

In the experiment the bacterial culture of sulphur-oxidising bacteria – *Acidithiobacillus thiooxidans*, isolated from the acid mine drainage (the shaft Pech, the locality Smolnik, Eastern Slovakia) was used. For the preparation of the active bacterial culture, as well as for the isolation and cultivation of *Acidiacidithiobacillus thiooxidans* in the presence of the concrete samples the selective nutrient medium Waksman and Joffe (pH 4.0) was used [8]. Its composition is described in Table 2.

TABLE II. THE SELECTIVE NUTRIENT MEDIUM BY WAKSMAN AND JOFFE

Chemical compound	**Amount**
$CaCl_2.6H_2O$	0.25 g/L
$(NH_4)_2SO_4$	0.2 g/L
K_2HPO_4	3.0 g/L
$MgSO_4.7H_2O$	0.5 g/L
$FeSO_4.7H_2O$	Trace amount
S°	10.0 g/L
Distilled water	Up to 1000 mL

First set of concrete samples (SA0, SA1 and SA2) was placed in the medium of activated bacteria. The volume ratio of solid sample to the liquid phase was set to 1:10. Experiments carried out in covered glass jars (700 ml) in an aerobic atmosphere at laboratory temperature using liquid selective culture medium inoculated at 7 day intervals with bacteria *Acidithiobacillus thiooxidans*. The 20 % vol. inoculum of bacteria *Acidithiobacillus thiooxidans* relative to the total of the liquid phase was used. pH value of samples was kept on optimal level of 4.0.

The second set of concrete specimens - reference samples (KA0, KA1 and KA2) placed in the cultivating medium without bacteria were used as abiotic controls. The experiment proceeded under same conditions as were those for the first set of samples.

After each 7 day-immersion period, the change in pH, the presence of bacteria as well as the released concentration of calcium and silicon ions were measured in leachates. The deterioration of the concrete specimens was also quantified by changes in weight of the specimens.

C. *Analytical methods*

The chemical composition of both concrete samples and leachates were 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 primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The samples were measured during 300 and 180 s at voltage of 25 kV and 50 kV at current of 0.5 and 1.0 mA under helium atmosphere by using the standardized method of fundamental parameters for leachates. pH changes were measured by pH meter FG2-FiveGo (Mettler-Toledo, Switzerland). The change in concrete samples weight was measured as the difference between the original weight before and final weight after the experiment.

III. Results

The percentage of the major components which the concrete samples were consisted of before the experiment is illustrated in Table 3 in oxides form.

TABLE III. THE CHEMICAL ANALYSIS OF TESTED CONCRETE SAMPLES

Oxides	**Mixture**		
	A0 (%)	***A1 (%)***	***A2 (%)***
Na_2O	0.11	0.11	0.11
MgO	3.04	2.73	2.38
Al_2O_3	5.21	5.39	5.25
SiO_2	30.16	45.63	39.82
P_2O_5	0.10	0.09	0.09
SO_3	2.89	2.72	2.81
Cl	0.02	0.02	0.01
K_2O	0.77	0.79	0.75
CaO	31.27	26.17	25.12
TiO_2	0.27	0.26	0.27
MnO	0.37	0.36	0.37
Fe_2O_3	4.04	3.75	4.63

According to Sand et al. [9], the biogenic acids cause the dissolution of calcium containing minerals from the concrete matrices. Consequently, Ca as well as the Si concentrations were measured during the experiments in the liquid phase. Table 4 presents measured Si and Ca concentrations in the liquid phases of samples during the 90 days of experiments.

TABLE IV. THE CONCENTRATIONS OF SI AND CA IONS IN LEACHATES AFTER 30, 60 AND 90 DAYS OF EXPERIMENT

	Si (mg/L)			**Ca (mg/L)**		
Days	***30***	***60***	***90***	***30***	***60***	***90***
SA0	555.9	1249	1908	355.3	787.6	1142
KA0	568.8	606.8	678.3	77.1	131.2	633.4
SA1	564.9	1142	1932	483.9	833.7	1099
KA1	647.1	528.4	672.2	87.8	71.7	55.4
SA2	1858	2923	3363	667.8	651.4	705.1
KA2	873.1	897.5	904.1	107.7	69.9	689.8

As it is seen (Tab. 4) bacteria *Acidithiobacillus thiooxidans* caused more significant calcium and silicon release from the concrete matrices into the solution when compared to reference leachates. Comparing the releasing of calcium and silicon influenced by bacteria, higher concentrations of silicon ions have been measured in leachates.

Mass of released ions of silicon and calcium corresponding to 1 g of concrete sample is illustrated in Figure 1 and 2. The leaching of silicon ions calculated to 1 g of concrete sample was much intensive for concrete samples affected with bacteria *Acidithiobacillus thiooxidans* comparing to reference samples after 60 and 90 days of the experiment as it can be seen in Figure 1.

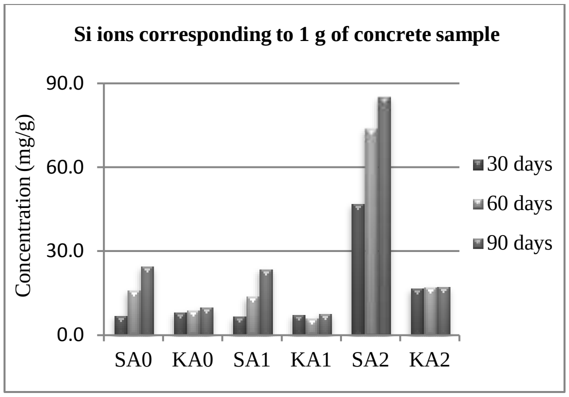

Figure 1. Released ions of silicon corresponding to 1 g of concrete sample

The maximum of Si ions concentrations (85.51 mg/g) was measured in leachate of sample SA2 after 90 days of exposition.

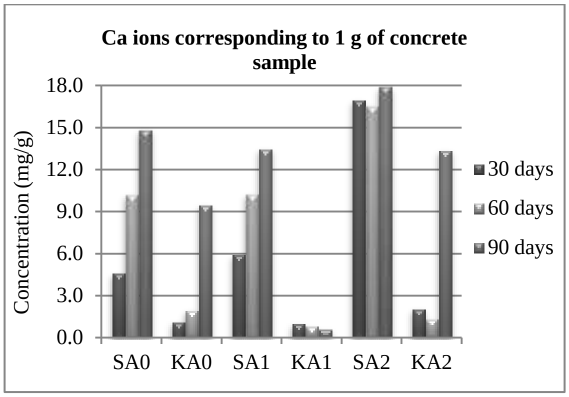

Figure 2. Released ions of calcium corresponding to 1 g of concrete sample

Similarly, the concentration of released Ca ions in leachates was observed to be lower for reference samples (KA0, KA1 and KA2) compared to the samples exposed to bacteria (SA0, SA1 and SA2) during the experiment (Fig. 2).

Table 5 presented measured concentrations of released ions of silicon and calcium corresponding to 1 g of concrete sample after 90 days of the experiment.

TABLE V. SILICON AND CALCIUM CORRESPONDING TO 1 G OF CONCRETE SAMPLE AFTER 90 DAYS OF EXPERIMENT

Sample	***SA0***	***SA1***	***SA2***
Si ions (mg/g)	24.81	23.76	85.51
Ca ions (mg/g)	14.85	13.52	17.93

The maximum concentration of Si ions released (85.51 mg/g) have been measured for sample SA2 after 90 days of experiment as it is seen in Table 5. The concentrations of released Si ions for samples SA0 and SA1 have been more than 3 times lower.

In like manner as in case of Si, the highest concentrations of released Ca ions have been measured for sample SA2 (17.93 mg/g), the lowest ones for sample SA1 (13.52 mg/g) – Table 5.

The highest amounts of both silicon and calcium ions released have been found out in case of sample SA2 (with zeolite addition), what is in contrast as expected. Zeolite based concrete samples were expected to be more resistant as concrete samples without zeolites.

The concrete sample SA1 (with silica fume addition) was found to have the best performance in terms of both silicon and calcium ions leaching during the experiment.

pH changes measured during 90 days are given in Figure 3, 4 and 5.

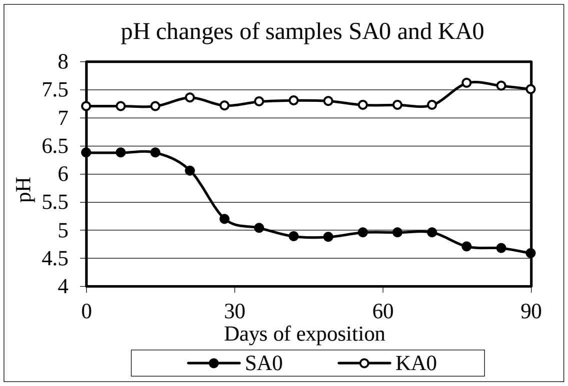

Figure 3. pH changes of samples SA0 and KA0

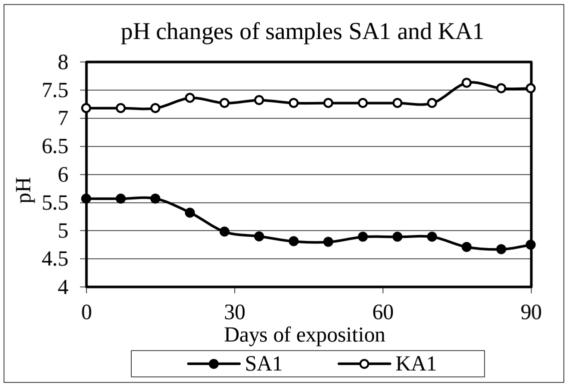

Figure 4. pH changes of samples SA1 and KA1

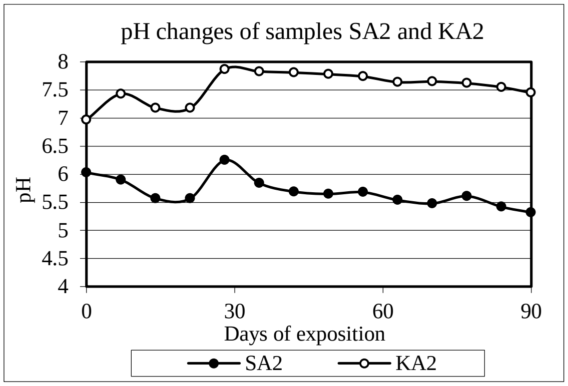

Figure 5. pH changes of samples SA2 and KA2

The values of pH ranged from 4.59 to 6.38 for concrete samples SA0 to SA2. pH value of samples mentioned above was set to the optimal level of 4.0 after each 7 day-interval. The values of pH for reference samples (KA0, KA1 and KA2) ranged from 6.97 to 7.81. The increase in pH values was caused by leaching of alkali compounds of calcium and silicon from cement matrix.

The results of changes in weight of investigated concrete samples after the experiments are given in Table 5.

TABLE VI. CHANGES IN WEIGHT AFTER THE 90-DAY EXPERIMENT

Sample	Weight		
	Before experiment (g)	***After experiment (g)***	***Weight change (%)***
SA0	76.912	76.8758	- 0.047
KA0	66.6197	66.9929	+ 0.560
SA1	81.3056	81.194	- 0.137
KA1	85.2934	85.7272	+ 0.509
SA2	38.3324	38.4348	+ 0.267
KA2	49.7765	50.1009	+ 0.652

The decrease in weight was noticed for concrete specimens SA0 (0.05 %) and SA1 (0.14 %). The percentage of weight increases for the samples varied from 0.267 % (sample SA2) to 0.560 % (sample KA0). The increase in weight of concrete samples is probably caused by precipitation of new formed compounds on the surface of samples [10].

IV. Conclusion

The deterioration of concrete can occur for many reasons. In many cases, it is due to the influence of synergistic effect of several factors. Experimental studies confirmed:

- bacteria *Acidithiobacillus thiooxidans* caused calcium and silicon release from the concrete matrices into the solution;
- the higher resistance of zeolite based concrete samples was not confirmed;
- silica fume based concrete samples were found to have the best performance in terms of both silicon and calcium ions leaching corresponding to 1 g of concrete;
- both weight loss and increase were observed for concrete samples.

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