

Analysis of Sulphur-Oxidizing Bacteria Attack on Concrete Based On Waste Materials

A. Eštoková, M. Kovalčíková, A. Luptáková, A. Sičáková, M. Ondová

Abstract—Concrete durability as an important engineering property of concrete, determining the service life of concrete structures very significantly, can be threatened and even lost due to the interactions of concrete with external environment. Bio-corrosion process caused by presence and activities of microorganisms producing sulphuric acid is a special type of sulphate deterioration of concrete materials. The effects of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on various concrete samples, based on silica fume and zeolite, were investigated in laboratory during 180 days. A laboratory study was conducted to compare the performance of concrete samples in terms of the concrete deterioration influenced by the leaching of calcium and silicon compounds from the cement matrix. The changes in the elemental concentrations of calcium and silicon in both solid samples and liquid leachates were measured by using X – ray fluorescence method. Experimental studies confirmed the silica fume based concrete samples were found out to have the best performance in terms of both silicon and calcium ions leaching.

Keywords—Bio-corrosion, concrete, leaching, bacteria.

I. INTRODUCTION

DURABILITY of concrete determines the service life of concrete structures very significantly. Due to the interactions of concrete with external influences the durability of concrete may be threatened and even lost under various conditions and factors. Among the threatening factors like freezing and thawing, abrasion, corrosion of steel, chemical attack may deteriorate the concrete significantly [1].

Chemical attack can be classified as: acidic attack, alkali attack, carbonation, chloride attack, leaching and sulphate attack [2]. The topic of durability is even a subject of interest [3] and [4].

The spectrum of aggressive acidic media is wide. Acidic media originate usually from industrial processes, but can even be due to urban activities and natural occurrences. Free

A. Eštoková is with the Technical University of Košice, The Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoškolská 4, 042 00 Košice, Slovak Republic (phone: 00421-55-6024265; e-mail: adriana.estokova@tuke.sk).

M. Kovalčíková is with the Technical University of Košice, The Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoškolská 4, 042 00 Košice, Slovak Republic (e-mail: martina.kovalcikova@tuke.sk).

A. Luptáková is with the Slovak Academy of Science, Institute of Geotechnics, Watsonova 47, 042 00 Košice, Slovak Republic (phone: 00421-949-687-629; e-mail: luptakal@saske.sk).

A. Sičáková is with the Technical University of Košice, The Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoškolská 4, 042 00 Košice, Slovak Republic (phone: 00421-55-6024275; e-mail: alena.sicakova@tuke.sk).

M. Ondová is with the Technical University of Košice, The Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoškolská 4, 042 00 Košice, Slovak Republic (phone: 00421-55-6024125; e-mail: marcela.ondova@tuke.sk).

acids in natural waters occur rarely excepting CO₂ waters and sulphurous and sulphuric acids in peat waters. However, several organic and inorganic acids may occur in sea-water as a consequence of bacteriological activity. Significant quantities of free acids may occur in industrial environment in form of leakage and come in the contact with concrete structures. The source of acid media can even represent air pollution by gaseous carbon dioxide, sulphur dioxide and nitrogen oxides [5]. Soils may contain huminous acids.

The corrosive nature of a sulphuric acid attack has been well documented from both in-situ observations and chemical testing on concrete [6]-[12]. Acidic attack may also occur as a consequence of bacterial activity as mentioned above.

Bio-corrosion as a special type of sulphate deterioration of concrete materials is 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. playing important roles on corroded and corroding concrete: *T. thiooparus*, *T. novellus*, *T. neapolitanus*, *T. intermedius* and *Ac. thiooxidans*. The first four species listed are neutrophilic sulphur-oxidizing microorganisms. The last species listed is an acidophilic sulphur-oxidizing microorganism [13].

Evidence thus far has identified bacterial manifestation of the genus '*Thiobacillus*' as a major contributor to the deterioration process of concrete sewer pipelines [7], [14].

The product of their metabolism results in sulphuric acid being formed which attacks the cement matrix of the concrete causing loss of strength and cohesion. *Thiobacillus* however, plays only a part of a much broader and complicated corrosion process. In the often anaerobic conditions which develop in raw sewage influent, sulphate reducing bacteria convert sulphates into sulphides such as hydrogen sulphide (H₂S) gas. In favourable conditions this diffuses into the atmosphere and, in the presence of oxygen, is further reduced to elemental sulphur or partially reduced sulphur compounds. In turn, they provide the catalyst necessary for the aerobic *Thiobacillus* bacteria to begin producing sulphuric acid. Sulphuric acid has been identified as a corrosive agent not only in corroding sewers but also in wastewater treatment plants [15], [16].

An attack by sulphuric acid however is a combined acid-sulphate reaction with the hydrogen ion causing a dissolution effect, coupled with corrosive role played by the sulphate ion [17], [8].

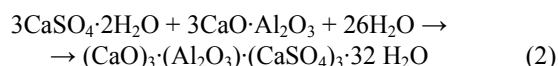
When sulphuric acid reacts with a cement matrix, the first step involves a reaction between the acid and the calcium

hydroxide (Ca(OH)₂) forming calcium sulphate according to the following equation:



This is subsequently hydrated to form gypsum (CaSO₄·2H₂O), the appearance of which on the surface of concrete pipes takes the form of a white, mushy substance which has no cohesive properties and has, “the consistency of cottage cheese” [18].

In the continuing attack, the gypsum would react with the calcium aluminate hydrate (C₃A) to form ettringite, an expansive product:



According to Skalny et al. [8], the ettringite can be located in deeper sections of concrete as long as the pH is high enough for it to form and the gypsum can migrate into these regions. The evidence gathered by Davis et al. [18] in their analysis of piping, however, showed that little ettringite was discovered in the corroding front and that the thermodynamics of the conversion to gypsum may be so fast that ettringite is a short-lived intermediate.

This paper presents the particular results of the experiments focused on the concrete bio-deterioration influenced by sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on various concrete samples based on waste material (silica fume and zeolite) investigated under laboratory conditions.

II. MATERIAL AND METHODS

The effects of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on various concrete samples in laboratory were investigated during 180 days.

A. Concrete Samples

Three mixtures of concrete (mixture 0, 1 and 2) 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:

- slightly aggressive chemical environment -exposure class XA1 (mixture 0 and 1 with concrete strength class of C 25/30);
- moderately aggressive chemical environment -exposure class XA2 (mixture 2 with concrete strength class of C 30/37).

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 of concrete samples with appropriate w/c ratio for concrete with above mentioned specifications is given in Table I. Zeolite and silica fume were added in order to improve the durability of concrete according to literature knowledge [19].

TABLE I
MIX PROPORTIONS OF THREE DIFFERENT CONCRETE MIXTURES

Components	Concrete mixture (1m ³)		
	0	1	2
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
Plasticizer	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 100 x 100 x 400mm were cured for 28 days in water environment and afterwards cut into small prisms with dimensions of 50 x 50 x 10mm. The test specimens were slightly brushed in order to remove polluting particles, sterilized in 70% ethanol for 24 hours and dried at 80°C to constant weight before use in the cultivation experiments.

B. Microorganisms

Bacterial culture of sulphur-oxidising bacteria – *Acidithiobacillus thiooxidans*, isolated from the acid mine drainage (the shaft Pech, the locality Smolnik, Eastern Slovakia) was used in the experiment. Selective nutrient medium Waksman and Joffe (pH 4.0) was applied [20] for the preparation of the active bacterial culture, as well as for the isolation and cultivation of *Acidiacidithiobacillus thiooxidans* in presence of the concrete samples. Composition of selected nutrient medium is described in Table II.

TABLE II
THE SELECTIVE NUTRIENT MEDIUM BY WAKSMAN AND JOFFE [20]

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

Concrete samples of three various compositions (S0, S1, S2) has been placed into the activated bacteria liquid medium and in the cultivating medium without bacteria as well (K0, K1, K2). The volume ratio of concrete 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.

To stimulate the bacteria grow in presence of S0, S1, and S2 samples bacterial inoculum was added once a 7-day interval, over a period of 180 days. The used inoculum consisted of bacteria *Acidithiobacillus thiooxidans* (20 % vol.) and liquid selective culture medium (80 % vol.) pH value of liquids was kept on optimal level for bacteria grow of 4.0 during experiment.

The experiment without bacteria representing reference a-biotic environment proceeded the same way as the experiment with bacteria except that the used inoculum does not content

bacterial culture.

After each 7-day immersion period, the change in pH, the presence of bacteria as well as the concentrations of calcium and silicon ions released was 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. 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 III in oxides form.

TABLE III
THE CHEMICAL ANALYSIS OF TESTED CONCRETE SAMPLES

Oxides	Mixture		
	0 (%)	1 (%)	2 (%)
Na ₂ O	0.11	0.11	0.11
MgO	3.04	2.73	2.38
Al ₂ O ₃	5.21	5.39	5.25
SiO ₂	30.16	45.63	39.82
P ₂ O ₅	0.10	0.09	0.09
SO ₃	2.89	2.72	2.81
Cl	0.02	0.02	0.01
K ₂ O	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 ₂ O ₃	4.04	3.75	4.63

According to Sand et al. [21], 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 IV presents measured Si concentrations in the liquid phases of samples during 180 days of the experiment.

TABLE IV
THE CONCENTRATIONS OF SI IONS IN LEACHATES DURING 180 DAYS OF THE EXPERIMENT

Days	Si ions (mg/L)					
	30	60	90	120	150	180
S0	555.9	1249	1908	605.7	6382	1830
K0	568.8	606.8	678.3	402.6	449.3	460
S1	564.9	1142	1932	615.4	2584	2171
K1	647.1	528.4	672.2	304.8	313.2	403.2
S2	1858	2923	3363	995.5	4016	5370
K2	873.1	897.5	904.1	304.9	536.4	573.9

Ca concentrations in the liquid phases of samples during 180-day experiment are presented in Table V.

TABLE V
THE CONCENTRATIONS OF CA IONS IN LEACHATES DURING 180 DAYS OF THE EXPERIMENT

Days	Ca ions (mg/L)					
	30	60	90	120	150	180
S0	355.3	787.6	1142	728.8	3577	2511
K0	77.1	131.2	633.4	38.8	4051	355.5
S1	483.9	833.7	1099	743.3	1906	1829
K1	87.8	71.7	55.4	27.3	66.5	26.2
S2	667.8	651.4	705.1	453.3	693.2	868.5
K2	107.7	69.9	689.8	22	3502	856

Masses of silicon ions released corresponding to 1 g of concrete samples are illustrated in Figs. 1-3. The leaching of silicon ions was much intensive for concrete samples affected with bacteria *Acidithiobacillus thiooxidans* comparing to reference samples during 180 days of the experiment as it can be seen in Figs. 1-3.

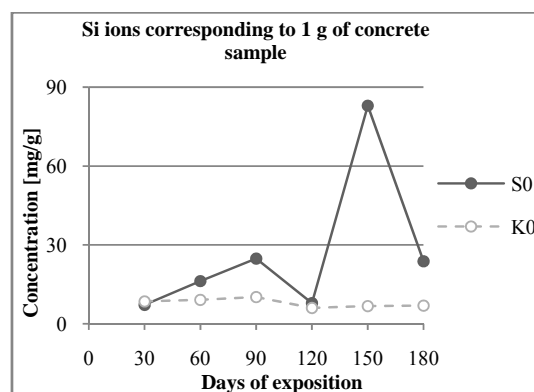


Fig. 1 Silicon ions released corresponding to 1 g of concrete samples S0 and K0

The maximum of Si ions concentrations (82.9 mg/g) was measured in leachate of sample S0 after 150 days of exposition. The concentration of Si ions released in leachates was observed to be lower for reference sample K0 compared to the sample exposed to bacteria S0 during the experiment except for sample K0 after 30 days of exposition (Fig. 1).

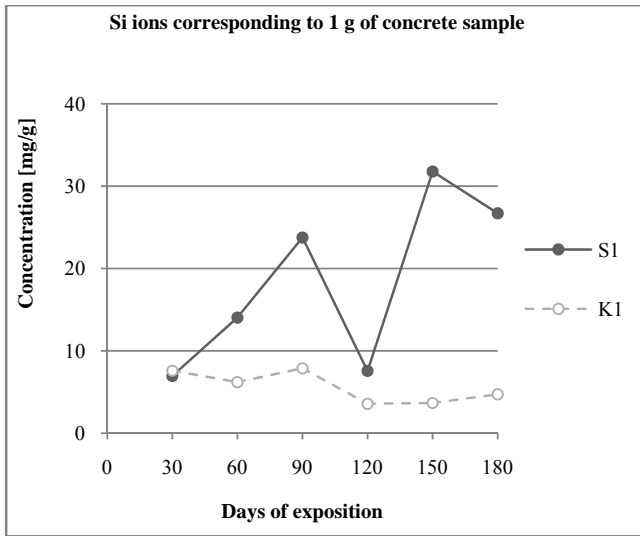


Fig. 2 Silicon ions released corresponding to 1 g of concrete samples S1 and K1

Similarly, the maximum of Si ions concentration (31.8 mg/g) was measured in leachate of sample S1 after 150 days of exposition. The concentration of released Si ions in leachates was observed to be lower for reference sample K1 compared to the sample exposed to bacteria S1 during the experiment except for sample K1 after 30 days of exposition (Fig. 2).

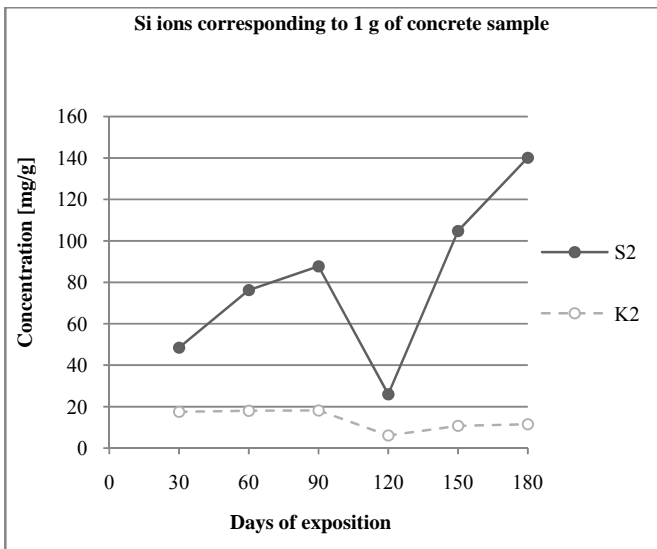


Fig. 3 Silicon ions released corresponding to 1 g of concrete samples S2 and K2

The concrete sample K2 was found to have better leaching performance of silicon ions during 180 days of exposition. The highest concentration of silicon ions (140.1 mg/g) was measured in leachate of sample S2 after 180 days of exposition (Fig. 3).

Leaching trend of measured calcium ions in the liquid phases of samples during 180-day experiments is illustrated in Figs. 4–6.

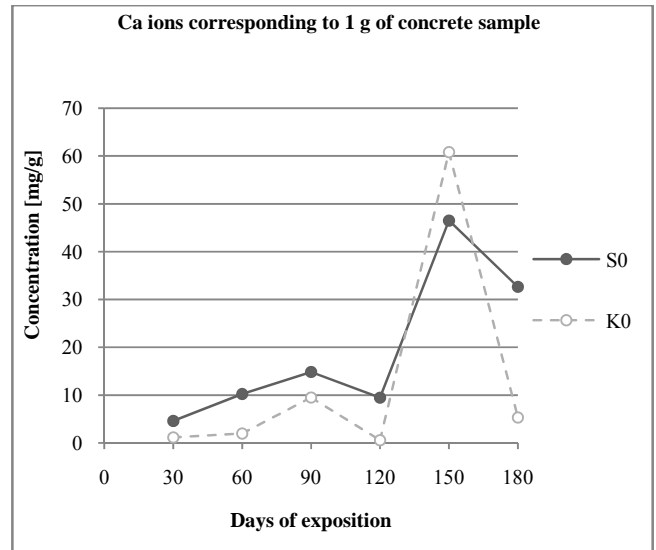


Fig. 4 Calcium ions released corresponding to 1 g of concrete samples S0 and K0

The highest concentrations of released calcium ions (46.5 mg/g) were observed in leachate of sample K0 (Fig. 4). The concrete samples K0 was found to have better leaching performance of calcium ions than sample S0 except period after 150 days of exposition.

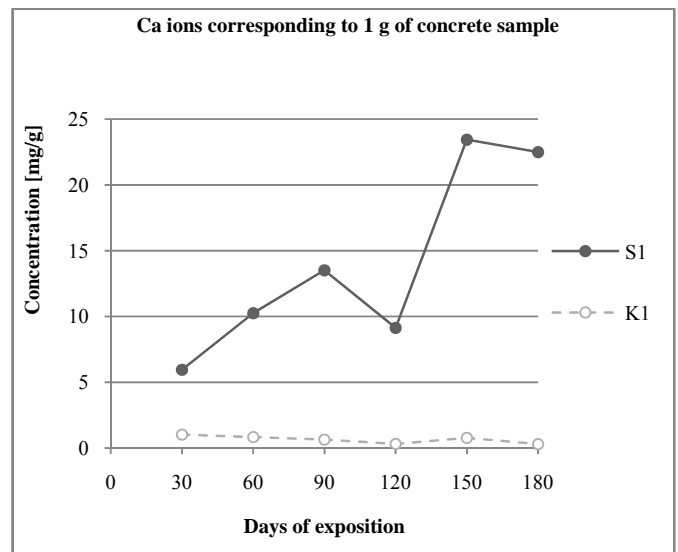


Fig. 5 Calcium ions released corresponding to 1 g of concrete samples S1 and K1

The most intensive leaching of calcium ions calculated to 1 g of concrete sample during 180 days of exposition was observed for concrete sample S1 exposed to bacteria. The maximum of Ca ions concentration (23.4 mg/g) was measured in leachate of sample S1 after 150 days of exposition (Fig. 5).

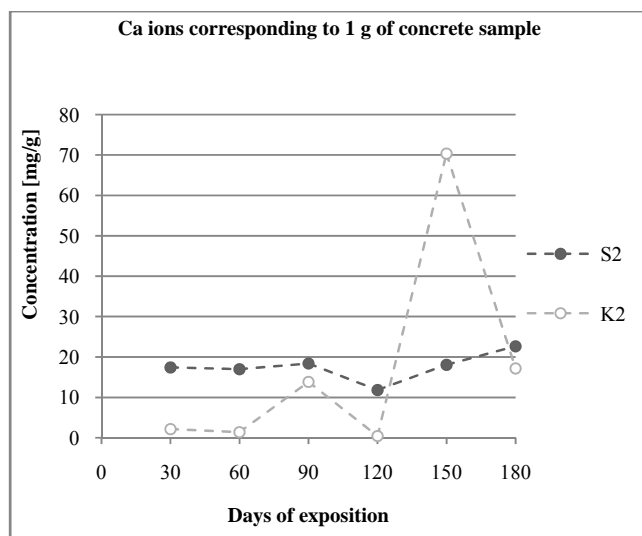


Fig. 6 Calcium ions released corresponding to 1 g of concrete samples S2 and K2

The highest concentrations of released calcium ions (70.4 mg/g) were observed in leachate of sample K2 (Fig. 6). The concrete sample K2 was found to have better leaching performance of calcium ions during 180 days of exposition except period after 150 days of exposition.

The calculated ratios of ions released comparing concrete sample affected by bacteria and sample in a-biotic environment (S/K) are illustrated in Table VI.

TABLE VI
RATIOS OF IONS CONCENTRATIONS IN LEACHATES FOR SAMPLES AFFECTED BY BACTERIA AND SAMPLES IN A-BIOTIC ENVIRONMENT (S/K)

Ca		Si			
S0/K0	S1/K1	S2/K2	S0/K0	S1/K1	S2/K2
7.1	69.8	1.1	4.0	5.4	9.4

According to Table VI, leaching of calcium ions in presence of bacteria was observed to be 1.1 to 69.8 times higher than in a-biotic environment. Similar trend was confirmed for silicon ions leaching by 4.0–9.4 times higher concentrations of silicon released under bacterial influence.

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

TABLE VII
CHANGES IN WEIGHT AFTER THE 180-DAY EXPERIMENT

Sample	Before experiment (g)	Weight		Weight change (%)
		After 90-day experiment (g)	After 180-day experiment (g)	
S0	76.912	76.8758	77.0906	+ 0.2
K0	66.6197	66.9929	67.6122	+ 1.5
S1	81.3056	81.194	81.498	+ 0.2
K1	85.2934	85.7272	86.1295	+ 0.9
S2	38.3324	38.4348	38.539	+ 0.5
K2	49.7765	50.1009	50.2788	+ 1.0

The increase in weight was noticed for all tested concrete specimens. The percentage of weight increase varied from 0.2 % (S0 and S1 samples) to 1.5 % (sample K0). The increase in

weight of concrete samples is probably caused by precipitation of new formed compounds on the surface of samples [22].

IV. CONCLUSION

This paper presented the results of the investigation of sulphate attack on concrete samples caused by effect of sulphur - oxidising bacteria represented by *Acidithiobacillus Thiooxidans*.

Experimental studies confirmed:

- bacteria *Acidithiobacillus thiooxidans* caused massive calcium and silicon release from the concrete matrices into the solution;
- leaching of calcium ions in presence of bacteria was observed to be 1.1 to 69.8 times higher than in a-biotic environment;
- leaching of silicon ions has been measured to be 4.0 – 9.4 times higher under bacterial influence;
- increase in weight was observed for all concrete samples;
- silica fume based concrete samples were found to have the best performance in terms of both silicon and calcium ions leaching.

ACKNOWLEDGMENT

This research has been carried out within the Grant No. 2/0166/11 and No. 1/0481/13 of the Slovak Grant Agency for Science.

REFERENCES

- [1] V. Zivica, A. Bajza, "Acidic attack of cement based materials - a review: Part 1. Principle of acidic attack" in *Construction and Building Materials*, vol. 15, issue 8, 2001, pp. 331–340.
- [2] ACI Committee 201. *Quid to durable concrete*, American Concrete Institute, Report of ACI Committee, ACI 201.2R-77, DETER, Detroit, 1982, p. 37
- [3] Comite Euro-International du Beton. 'Durability of Concrete Structures: State-of-Art Report'. Bulletin d'Information, No.148, Paris, 1982, p. 328.
- [4] Comite Euro-International du Beton. 'Durable Concrete Structures: CEB Design Guide', Bulletin d'Information, No. 182, Lausanne, 1989, p. 268.
- [5] C.R. Ecob, E.S. King, "Aggressive underground environment: factors affecting durability of structure and specification of appropriate protective systems" in *Proc. of the Int. Conf. University of Dundee*, 1990, pp. 507–517.
- [6] J. Monteny, E. Vincke, A. Beeldens, N. De Belie, L. Taerwe, D. Van Gemert, W. Verstraete, "Chemical, microbiological, and in situ test methods for biogenic sulfuric acid corrosion of concrete", in *Cement and Concrete Research*, 2000, vol. 30, no. 4, pp. 623-634.
- [7] T. Mori, T. Nonaka, K. Tazaki, M. Koga, Y. Hikosaka, S. Noda, "Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes", in *Water Research*, 1992, vol. 26, no. 1, pp.29-37.
- [8] J. Skalny, J. Marchand, I. Odler, "Sulfate attack on concrete", London, Spon Press, 2002, ch. 4.
- [9] Z.T. Chang, X.J. Song, R. Munn, M. Marosszeky, "Using limestone aggregates and different cements for enhancing resistance of concrete to sulfuric acid attack", in *Cement and Concrete Research*, 2005, vol. 35, no.8, pp.1486-1494.
- [10] M.T. Bassuoni, M.L. Nehdi, "Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction", in *Cement and Concrete Research*, 2007, vol. 37, no. 7, pp.1070-1084.
- [11] Building Research Establishment. BRE Special Digest 1, Concrete in aggressive ground. Part 2: Specifying the concrete and additional protective measures. 2nd Edition; 2003.
- [12] J. Hill, E.A. Byars, J.H. Sharp, C.J. Lynsdale, J.C. Cripps, Q. Zhou, "An experimental study of combined acid and sulfate attack of concrete", in *Cement and Concrete Composites*, 2003, vol. 25, no. 8, pp. 997-1003.

- [13] D. Nica, J.L. Davis, L. Kirby, G. Zuo, D.J. Roberts, "Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers", in *International Biodeterioration & Biodegradation*, 2000, vol. 46, pp. 61-68.
- [14] C.D. Parker, "The isolation of a species of bacterium associated with the corrosion of concrete exposed to atmospheres containing hydrogen sulfide", in *Australian Journal of Experimental Biology & Medical Science*, 1945, vol. 23, pp. 81-90.
- [15] A.F. Idriss, S.C. Negi, J.C. Jofriet, G.L. Hayward, "Corrosion of steel reinforcement in mortar specimens exposed to hydrogen sulfide, Part 1: Impressed voltage and electrochemical potential tests", in *Journal of Agricultural Engineering Research*, 2001, vol. 79, no. 3, pp.223-230.
- [16] E. Vincke, S. Verstichel, J. Monteny, W. Verstraete, "A new test procedure for biogenic sulfuric acid corrosion of concrete", in *Biodegradation*, 1999, vol. 10, no. 6, pp. 421-428.
- [17] E.K. Attiogbe, S.H. Rizkalla, "Response of concrete to sulfuric acid attack", in *ACI Materials Journal*, 1988, vol. 84, no. 6, pp. 481-488.
- [18] J.L. Davis, D. Nica, K. Shields, D.J. Roberts, "Analysis of concrete from corroded sewer pipe", in *International Biodeterioration and Biodegradation*, 1998, vol. 42, no. 1, pp. 75-84.
- [19] J. Yajun, J.H. Cahyadi, "Effects of densified silica fume on microstructure and compressive strength of blended cement pastes", in *Cement and Concrete Research*, 2003, vol. 33, pp. 1543-1548.
- [20] G.I. Karavajko, G. Rossi, A.D. Agate, S.N. Groudev, Z.A. Avakyan, *Biogeotechnology of metals*, Centre of projects GKNT, Moscow, 1988.
- [21] W. Sand, T. Dumas, S. Marcdargent, "Accelerated biogenic sulfuric-acid corrosion test for evaluating the performance of calcium-aluminate based concrete in sewage applications" in *Microbiologically Influences Corrosion Testing*, Eds. J.R. Kearns and B. J. Little, American Society for Testing and Materials, Philadelphia, Pennsylvania, USA, 1994, pp. 234-249.
- [22] A. Estokova, V. Ondrejka Harbulakova, A. Luptakova, M. Prascakova, N. Stevulova, "Sulphur oxidizing bacteria as the causative factor of biocorrosion of concrete", in *Chemical Engineering Transactions : Selected Papers of ICheaP-10*, 2011, vol. 24, p. 1-6. - ISBN 978-88-95608-15-0, ISSN 1974-9791.