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Mathematical Investigation of Concrete Corrosion – a Sustainability Study

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Abstract. The issue of sustainability is a major spur to innovation in the flied of civil engineering where the important role is decreasing the detrimental effects on environment and save raw materials and energy. Micro silica is a by-product of the industrial manufacture of ferrosilicon and metallic silicon in high temperature electric arc furnaces and is used as an additive for improving concrete properties. The paper presents the results of chemical corrosion and bio-corrosion tests on concrete samples with 5% addition of microsilica as well as on concrete samples with only Portland cement. Chemical corrosion, simulated by sulphuric acid with pH of 4.2, and bio-corrosion, simulated by sulphur-oxidising bacteria *Acidithiobacillus thiooxidans,* were investigated in terms of basic concrete's elements leachability. Dissolved amounts of Si and Ca due to both chemical attack and biocorrosion were measured in the period of 3 months. The leaching trends were analysed using a mathematical approach for better interpretation of the results. The correlation analysis confirmed the different leaching trends comparing bio-corrosion and chemical corrosion processes. A high dependency was observed between leaching of Ca and Si from concretes prepared with ordinary cement. In case of concrete sample with microsilica addition no correlation was found out.

Keywords: biocorrosion, chemical corrosion, concrete, correlation, microsilica.

Conference topic: Environmental protection.

Introduction

It is well known that microorganisms have detrimental effects on the structures and construction materials with compose them. In aggressive aqueous media as grounds waters, sea waters, agricultural or agro-industrial environments structure made of concrete can suffer deterioration linked to the activity of microorganisms (Bertron 2014; Wells, Melchers 2014; Herisson *et al.* 2013; Alexander *et al.* 2013). Also sewage networks represent a very aggressive environment for cementitious materials. At the same time their relative inaccessibility poses challenges for maintenance and repair (Valis, Pietrucha-Urbanik 2014). The main cause of degradation is the corrosion of concrete due to the in-situ production of sulphuric acid by bacteria (Scrivener, De Biele 2013). Utilization of pozzolanic materials (fly ash, slag, zeolite, metakaolin, microsilica and more) in cement and concrete manufacturing has increased significantly in last decades. In the laboratory study presented by Valipour *et al.* (2013), the effects of substituting cement with 10%, 20% and 30% natural zeolite on concrete durability were compared to the effects of substituting 5%, 10% and 15% metakaolin and 5%, 7.5% and 10% silica fume, along with water-to-cement ratios of 0.35, 0.40, 0.45 and 0.50. Results show that, in general, the zeolite is not as active as silica fume or metakaolin, although it could be used as a substitute for pozzolans because it has better durability characteristics and is economical and environmentally friendly as well. Mostofinejad *et al.* (2016) in its study deals with the durability of concrete containing different additives of micro silica, blast furnace slag and limestone powder as cement replacement with various ratios, exposed to magnesium sulphate with different concentrations. One of the conclusions was that replacing 10% cement by micro-silica reduced the durability in magnesium sulphate. Microsilica is a very fine powder mostly composed of amorphous silicon dioxide. The material is a product of the silicon and ferrosilicon smelting industries. In the early studies in the beginning of 1950s it was documented that microsilica concrete to be as durable as concrete made with sulphate – resisting cement (Fidjestøl, Lewis 1998). Microsilica concrete has improved resistance to sulphate attack probably because it has a finer pore structure and less calcium hydroxide. Used as an admixture, microsilica can improve the properties of both fresh and hardened concrete (Concrete Construction Staff 1985). Microsilica is a mineral that also improves the corrosion protection and strength of concrete by reducing the permeability of the concrete and forming more calcium silicate hydrate (CSH) which provides strength and durability to concrete (Asrar *et al.* 1999). Study of the effect of substitution of micro-silica (SF) and fly ash (FA) on the behavior of composite cement pastes exposed to elevated temperature were presented in paper by Heikal *et al.* (2013). They proved that 5 mass % of silica fume showed the higher values of bulk density than the other pastes and that composite cements with 10% silica fume have good fire resistance up to 450 °C. Paper deals with investigation of concrete chemical corrosion and biocorrosion using mathematical approach. The dependency between leaching basic elements of concrete matrix considering type of aggressive media (sulphuric acid and sulphur-oxidising bacteria) as well as composition of concrete mixture (samples without and with microsilica addition) was calculated. Based on values of correlation coefficient and correlation closeness conclusions were formulated.

Material and Methods

Two mixtures were prepared for mathematical evaluation of concrete's corrosion. Reference mixture consisted of Portland cement (Povazska cementaren, Slovakia), water, aggregate (Vychodoslovenske stavebne hmoty, Geca, Slovakia) with particle size fraction 0/4 mm, 4/8 mm, and 8/16 mm and plasticizer Stachement 2353 based on polycarboxylates (Stachema, Bratislal, Slovakia). Microsilica-based mixture contained, in addition, 5% wt. of microsilica (OFZ a.s., Istebne, Slovakia) what resulted in higher water demand of mixture to ensure the same consistency of concretes. After hardening, standardized concrete prisms with dimensions 100 x 100 x 400 mm^3 were cured for 28 days in a water environment prior to testing the required mechanical parameters. Subsequently, the concrete prisms were cut into smaller ones measuring 50 x 50 x 10 mm for corrosion examination. The test specimens were slightly brushed in order to remove any spare surface particles, sterilized in 70% ethanol for 24 hours and dried at 105ºC to a constant mass before use in the corrosion experiments.

The simulating experiment of chemical acidic corrosion was based on exposure the samples to solution of H_2SO_4 with pH of 4.0 (concentration of 0.0005 wt. % H_2SO_4). Concentrated medium of activated bacteria *Acidithiobacillus thiooxidans* were used for simulation of the bio-corrosion of concrete. The concentrated medium consisted of bacteria *Acidithiobacillus thiooxidans* inoculum (20 vol. %) and a Waksman and Joffe nutrient medium with a pH 4.0 (80 vol. %). Sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* were isolated from the mixed culture which originated from the local mine water source (the shaft Pech, the locality Smolník, Eastern Slovakia). The selective nutrient medium with pH value of 4.0 for isolation and cultivation of bacteria was prepared according to Waksman and Joffe (1992). Both types of samples were exposed to the aggressive environments (Table 1) for 270 days by immersing the samples to liquid media mentioned above. The volumes of liquid media were ten times larger than the volume of solid phases. The laboratory corrosion experiment proceeded in covered glass containers at a temperature of 23 °C. The 6 mL of bacterial mixture was inoculated into bio-solutions at 7-day intervals over a period of 270 days. The pH value of H_2SO_4 solutions was kept at a constant level of 4.0 to be comparable to bio-solutions. Dissolved concentrations of Ca^{2+} and Si^{4+} in leachates were measured periodically, once a week, over a whole testing period. The dissolved masses of calcium and silicon were used as input data in a correlation analysis.

Table 1. Characterization of corrosion environments and concrete samples

Type of corrosion testing	Labelling	Samples binder	Labelling
Chemical corrosion, simulated by H_2SO_4 solution with pH = 4.0	CHEM	Portland cement only	S0
Bio-corrosion simulated by bacterial culture of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans*	BIO	Portland cement + 5 wt. % addition of microsilica	S5

X-ray fluorescence analysis (XRF) using SPECTRO iQ II equipment (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses was utilized to measuring the concentrations of Ca and Si in leachates. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite – HOPG target. The samples measuring proceeded 300 and 180 s at voltage of 25 kV and current of 0.5 mA and of 50 kV and 1.0 mA. The sample was flushed with helium. A calibration method of fundamental parameters for concrete leachates was used to convert the measured intensities to concentrations of elements.

A statistical method was used for evaluation of the trend of chemical elements leaching as well for description of a relation among the selected parameters. Information about two dimensional statistical data set gives a correlation coefficient R_{xy} (Kreyszig 2011) and its calculation is presented in our previous paper (Ondrejka Harbuľáková *et al.* 2015). The calculated R_{xy} values are from the interval $<–1,1>$. If $R_{xy} = 1$, the correlation is full linear, if $R_{xy} = –1$, then the correlation is inversely linear and if $R_{xy} = 0$, the pairs of values are fully independent. Than degree of the correlative closeness is defined as: medium, if $0.3 \leq | R_{xy} | < 0.5$; significant, if $0.5 \leq | R_{xy} | < 0.7$; high, if $0.7 \leq | R_{xy} | < 0.9$; and very high, if $0.9 \leq | R_{xy} |$.

Results and Discussion

Quantities of leached Si^{4+} and Ca^{2+} from samples without microsilica addition (S0) and samples with 5% addition of microsilica (S5) exposed to chemical corrosion (aggressive medium: sulphuric acid) measured over a period of 270 days are given in Table 2. The results of the calcium and silicon quantities leached from samples exposed to biocorrosion are presented in Table 3. The leached-out masses in both tables (Table 2 and 3) correspond to 1 g of concrete specimen and have been consequently used as input data in the correlation analysis.

Table 2. Quantities of leached-out Ca^{2+} and Si^{4+} from samples exposed to chemical corrosion

Interval of exposure (days)	CHEM			
	Ca (mg/g)		Si (mg/g)	
	S0	S5	S0	S5
0	0	0	0	0
7	0.40	0.47	2.28	2.28
14	0.30	0.36	2.01	1.91
21	1.23	3.68	2.16	2.10
28	0.66	0.86	2.47	2.24
35	0.99	3.20	2.94	2.17
42	0.93	1.19	2.05	1.96
49	0.94	0.81	1.53	1.38
56	3.40	3.74	4.33	1.82
63	1.45	0.97	2.28	2.15
70	1.57	1.07	2.72	2.04
77	1.58	1.07	3.93	3.23
84	1.56	1.08	2.58	1.83
91	1.57	1.17	2.99	1.63
120	1.85	1.34	3.42	2.77
150	1.82	1.45	3.69	2.87
180	2.05	1.64	3.16	3.33
270	1.13	1.17	2.63	3.01

Table 3. Quantities of leached-out Ca^{2+} and Si^{4+} from samples exposed to biocorrosion

Interval of exposure (days)	BIO			
	Ca (mg/g)		Si (mg/g)	
	S0	S5	S0	S5
0	0.72	0.87	0	0
7	1.34	2.13	6.19	5.02
14	0.66	1.40	3.05	3.22
21	1.12	2.25	3.23	4.75
28	1.48	2.02	2.31	2.36
35	1.94	2.57	4.03	4.77
42	2.27	2.80	4.29	6.31
49	2.69	3.23	3.33	5.21
56	3.28	3.49	5.20	4.78
63	3.93	4.22	4.91	8.47
70	4.75	4.22	7.94	8.08
77	4.24	4.86	6.04	13.75
84	67.36	17.10	9.23	7.08
91	5.32	6.77	4.60	10.37
120	3.03	3.11	2.52	2.57
150	14.88	7.97	26.55	10.81
180	10.45	7.65	7.61	9.08
270	2.99	2.98	4.57	4.77

Since the cultivation medium by Waksmann and Joffe contained calcium chloride hexahydrate, the input concentration of calcium in bio-solution is not equal 0 (Table 2). Comparing the effects of chemical and biocorrosion, based on the leaching results of main cement matrix components, it was observed that higher portions of ions have been dissolved due to bacterial influence than due to chemical corrosion. As mentioned, the correlation analysis and calculation of correlation closeness were performing according to data presented in Table 2 and 3.

Mathematical evaluation started with investigation of mutual relationship between the leachability of particular elements (calcium and silicon) depending on type of concrete sample, for chemical corrosion and biocorrosion, separately. Calculated correlation coefficients as well as the degree of correlation closeness are presented in Table 4.

Table 4. Correlation results of calcium and silicon leaching trends

CHEM				BIO			
Ion/Sample	Relationship	R_{xy}	Closeness degree	Ion/Sample	Relationship	R_{xy}	Closeness degree
Ca	S0/S5	0.54	significant	Ca	S0/S5	0.94	very high
Si	S0/S5	0.49	medium	Si	S0/S5	0.52	significant
S0	Ca/Si	0.81	high	S0	Ca/Si	0.34	medium
S5	Ca/Si	0.20	no correlation	S5	Ca/Si	0.47	medium

Evaluating the leaching of calcium in dependence on the composition of concrete samples, it can be concluded that a very high correlation having a correlation coefficient 0.94 was found in bio-solutions. That means the type of concrete sample does not play a dominant role in Ca compounds dissolving and consequent behavior in a leachate. A calcium leaching trend from reference sample (S0) corresponds to the leaching trend from microsilica-based sample (S5). Lower but still significant closeness (R_{xy} = 0.54) was observed for calcium leaching due to chemical sulphate exposure. This point to the differences in calcium compounds dissolving when compared reference sample and microsilica-based samples. Senhadji *et al.* (2014) attributed the effect of silica fume on sulphate resistance more to chemical effects than reduced permeability, while investigating the resistance of concrete to decomposition in $MgSO_4$ and Na_2SO_4 solutions.

Very similar findings were found for silicon leaching regarding the type of concrete samples. Correlation coefficients, relating to both chemical and biocorrosion, have been calculated to be very close (0.49 and 0.52, respectively) to the calcium one. The lower is the calculated correlation coefficient the more significant is the chemical composition of concrete. Therefore, the type of concrete sample and thus a chemical composition of concretes can be considered as significant factor in silicon leaching and its behavior in liquid medium.

When investigating the dependence of calcium on silicon leaching, as seen in Table 4, a high correlation (R_{xy} = 0.81) was found for reference sample (S0) deterioration due to chemical corrosion. This fact confirmed the similarity in leachability and subsequent performance of both ions in leachants in case of exposure the concrete with ordinary Portland cement to chemical environment. On the contrary, no correlation was observed for dependence of calcium on silicon leaching from microsilica-based sample (S5). This confirmed a significance of differences in chemical composition of samples regarding the basic components leaching, as assumed. However, Hekal, Kishar and Mostafa (2002) found out that even up to 15% replacement of Portland cement by microsilica did not improve significantly the sulfate resistance of cement pastes. As for bio-corrosion, a different leaching mechanism or subsequent performance in leachants was found for calcium and silicon.

After these findings, the correlation analysis was used to evaluate a relationship between the types of corrosion each other (chemical versus bio-corrosion). Based on the leached-out Ca^{2+} and Si^{4+} quantities, correlation coefficients and correlation degree of closeness are reported in Table 5.

Table 5. Correlation results for corrosion types

	S0		S5	
Ions	Ca(CHEM)/Ca(BIO)	Si(CHEM)/Si(BIO)	Ca(CHEM)/Ca(BIO)	Si(CHEM)/Si(BIO)
R_{xy}	0.19	0.35	–0.02	0.18
closeness degree	no correlation	medium	no correlation	no correlation

Is it seen from Table 5, based on the calculated correlation coefficients, a very low or no correlation exists between leaching processes and/or subsequent performance of ions in liquid media when considering chemical corrosion and biocorrosion. That fact confirmed knowledge about different leaching processes (Estokova *et al.* 2016) during simulation chemical corrosion in laboratory conditions and bio-corrosion processes under bacteria influence. The different trend was observed for both concrete types – samples with microsilica content and concrete samples with only ordinary Portland cement as well.

Conclusion

Correlation analysis was used to help to interpretation the results of concrete composites corrosion testing. The finding revealed that:

– Biocorrosion is more effective, in negative meaning, than chemical corrosion;
– Different leaching mechanisms and behavior of dissolved ions was found comparing bio-corrosion and chemical corrosion;
– Type of concrete sample was confirmed as significant parameter in silicon leaching and its behavior in liquid medium due to both chemical and bio-corrosions;
– However, the type of concrete sample and the chemical composition was not confirmed to be a dominant factor in Ca compounds dissolving due to chemical corrosion.

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References

Alexander, M.; Bertron, A.; De Belie, N. 2013. *Performance of cement-based materials in aggressive aqueous environments*. RILEM TC 211-PAE: Springer, Berlin. https://doi.org/10.1007/978-94-007-5413-3

Asrar, N.; Malik, A. U.; Ahmad, S.; Fadi, S.; Mujahid, F. S. 1999. Corrosion protection performance of microsilica added concretes in NaCl and seawater environments, *Construction and Building Materials* 13(4): 213–219. https://doi.org/10.1016/S0950-0618(99)00016-1

Bertron, A. 2014. Understanding interaction between cementitious materials and microorganisms: a key to sustainable and safe concrete structures in various contexts, *Materials and Structures* 47(1): 1787–1806. https://doi.org/10.1617/s11527-014-0433-1

Concrete Construction Staff. 1985. *How microsilica improves concrete* [online], [cited 13 January 2017]. Available from Internet: http://www.concreteconstruction.net/how-to/materials/how-microsilica-improves-concrete_o

Estokova, A.; Kovalcikova, M.; Luptakova, A.; Prascakova, M. 2016. Testing silica fume-based concrete composites under chemical and microbiological sulfate attacks, *Materials* 9(5): 324. https://doi.org/10.3390/ma9050324

Fidjestøl, P.; Lewis, R. 1998. Microsilica as an addition, in *Lea's Chemistry of Cement and Concrete*. 4th ed. Elsevier Limited. https://doi.org/10.1016/B978-075066256-7/50024-2

Hekal, E. E.; Kishar, E.; Mostafa, H. 2002. Magnesium sulfate attack on hardened blended cement pastes under different circumstances, *Cement and Concrete Research* 32: 1421–1427. https://doi.org/10.1016/S0008-8846(02)00801-3

Heikal, M.; El-Didamony, H.; Sokkaryc, T. M.; Ahmed, I. A. 2013. Behavior of composite cement pastes containing microsilica and fly ash at elevated temperature, *Construction and Building Materials* 38: 1180–1190. https://doi.org/10.1016/j.conbuildmat.2012.09.069

Herisson, J.; van Hullebusch, E. D.; Moletta-Denat, M.; Taquet, P.; Chaussadent, T. 2013 Toward an accelerated biodeterioration test to understand the behavior of Portland and calcium aluminate cementitious materials in sewer networks, *International Biodeteriorioration* & *Biodegradradation* 84: 236–243. https://doi.org/10.1016/j.ibiod.2012.03.007

Kreyszig, E. 2011. *Advanced engineering mathematics*. 10th ed. (Eds.). United States of America: John Wiley and sons.

Mostofinejad, D.; Nosouhian, F.; Nazari-Monfared, H. 2016. Influence of magnesium sulphate concentration on durability of concrete containing micro-silica, slag and limestone powder using durability index, *Construction and Building Materials* 117: 107–120. https://doi.org/10.1016/j.conbuildmat.2016.04.091

Ondrejka Harbuľáková, V.; Purcz, P.; Estokova, A.; Luptrakova, A.; Repka, M. 2015. Using a statistical method for the concrete deterioration assessment in sulphate environment 2015, *Chemical Engineering Transaction* 43: 2221–2226.

Scrivener, K. L.; De Biele, N. 2013. Bacteriogenic sulfuric acid attack of cementitious materials in sewage system, Chapter 12, in M. G. Alexander, A. Bertron, N. De Belie (Eds.). *Performance of cement-based materials in aggressive aqueous environment*. University of Cape Town, South Africa: Springer. https://doi.org/10.1007/978-94-007-5413-3_12

Senhadji, Y.; Escadeillas, G.; Mouli, M.; Khelafi, H.; Benosman, A. S. 2014. Influence of natural pozzolan, silica fume and limestone fine on strength, acid resistance and microstructure of mortar, *Powder Technology* 254: 314–323. https://doi.org/10.1016/j.powtec.2014.01.046

Valipour, M.; Pargar, F.; Shekarchi, M.; Khani, S. 2013. Comparing a natural pozzolans, zeolite, to metakaolin and silica fume in terms of their effect on the durability characteristics of concrete: a laboratory study, *Construction and Building Materials* 41: 879–888. https://doi.org/10.1016/j.conbuildmat.2012.11.054

Valis, D.; Pietrucha-Urbanik, K. 2014. Utilization of diffusion processes and fuzzy logic for vulnerability assessment, *Eksploatacja i Niezawodnosc – Maintenance and Reliability* 16(1): 48–55.

Waksman, S. A; Joffe, J. S. 1922. Microorganisms concerned in the oxidation of Sulfur in the soil II: Thiobacillus Thiooxidans, a New Sulfur-oxidizing Organism Isolated from the Soil, *Journal of Bacteriology* 7(2): 239–256.

Wells, T.; Melchers, R. E. 2014. An observation-based model for corrosion of concrete sewers under aggressive conditions, *Cement and Concrete Research* 61–62: 1–10. https://doi.org/10.1016/j.cemconres.2014.03.013