STUDY OF CONCRETE SAMPLES WITH VARIOUS CONTENTS OF SLAG UNDER SULPHATES ATTACK USING MATHEMATICAL APPROACH

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ABSTRACT

Mineral admixtures are used as a partial replacement for ordinary portland cement, and the progress of sulphate attack can be evaluated by several methods (pH values changes of liquid phases, loss in mass, dynamic modulus, strength, x-ray analysis, mathematical analysis). Leaching of the calcium and silicon ions from the concrete composites of various slag cement replacement (65% and 95% of slag) exposed to two different aggressive sulphate environments (sulphuric acid and magnesium sulphate) was measured by using X-ray fluorescence analysis (XRF). Consequently a statistical analysis of different media´ influence on the concrete samples deterioration was performed. The correlation between the Ca/Si leached-out masses (the same aggressive media) as well as between the concentrations of silicon and calcium each other (different aggressive media) was calculated a presented.

Key words: *concrete corrosion, correlation analysis, magnesium sulphate, sulphuric acid*

1 INTRODUCTION

Sulphate attack can cause severe damage to concrete structures. The most common mitigation strategy against chemical sulphate attack in concrete is reduction of water to cementitious materials ratio and/or use of supplementary cementitious materials [1]. Cement is only one ingredient in the cement paste matrix that binds concrete, and all paste matrix components (such as pozzolans, slags, ground limestone and chemical admixtures), influence concrete performance [2]. Concrete with application of slag aggregates with different percentages of slag in substitution of cement and sand have been found to have better mechanical properties than conventional concrete. Ground granulated blast-furnace slag was found to improve the resistance to physical salt attack [1]. In paper [3] four different concrete mixes were made with sulphur resistant cement. The concretes were tested for compressive strength, transport capacity of sulphates and microstructural properties. An experimental program was proposed in which the concrete samples were submerged in sodium sulphate (Na_2SO_4) solution. The obtained results were compared with reference values of concretes cured in calcium hydroxide. According to the results the concrete with ground granulated blast-furnace slag presented the best behaviour when exposed to sodium sulphate (Na_2SO_4) solution. Same working group consequently studied in [4] four different concrete mixes were made with sulphur resistant cement and mineral admixtures (silica fume, fly ash and blast furnace slag). The concretes were submerged for different period in magnesium sulphate ($MgSO_4$). After that, different tests were carried out to define mechanical and microstructural properties. The results obtained were compared with reference values of concretes cured in calcium hydroxide. According to the results, the concrete with blast furnace slag presented the best behavior front $MgSO_4$.

Concrete composites of slag cement replacement (65% and 95% of slag) were prepared for our leaching experiment. Leaching of the calcium and silicon ions from the concrete composites exposed

to two different aggressive sulphate environments (sulphuric acid and magnesium sulphate) was investigated. Statistical investigation of relation of leaching trend of the same ions from the different liquid media and different ions from the same liquid media was calculated and results are presented in the paper.

2 MATERIAL AND METHODS

Concrete specimens with slag-based additive S65 (65 wt.% of cement replacement) and S95 (95 wt.% of cement replacement) were used in this experiment. For the purpose of simulating the sulphate corrosion, two chemical aggressive solutions were used in accordance with STN 73 1340: solution represented by 0.003 wt. % $MgSO_4$ (initial pH 8.04, $c(SO_4^{2-})$ =3 g/l) and solution represented by 0.003 wt. % H_2SO_4 (pH value 3.00). The experiments were conducted in a glass container closed with aluminum foil with the total volume of 700 ml. Corrosion of the tested concrete samples proceeded during 270 days under laboratory temperature of 23 °C. The samples of cement composites were placed in liquid medium, the volume of which was calculated by determining the volume of applied sample. The ratio of the volumes solid to liquid phases was kept as 1:10. Concentrations of calcium and silicon ions in leachates after were measured using X-ray fluorescence analysis (XRF).

The leaching trend of basic chemical elements of concrete was studied by mathematical approach. For the statistical evaluation, measured leached-out concentrations of Ca and Si (Table 1) were chosen as deterioration parameters.

Medium/ Ions	H_2SO_4				$MgSO_4$			
	Ca mg/L		Si mg/L		Ca mg/L		Si mg/L	
Days	S65	S95	S65	S95	S65	S95	S65	S95
7	72.9	56.8	414	403	169	181	407	443
14	140.1	146.4	359	335	223	228	292	408
21	168.5	184.5	334	373	283	275	383	441
28	197.7	211.6	457	391	364	316	617	826
35	225.5	243.6	372	446	372	345	526	395
42	265.7	272.3	501	439	391	376	363	379
49	317.9	301.9	439	447	443	414	413	344
56	349.2	357	480	477	479	444	387	393
63	433.8	370.3	625	381	522	477	457	584
70	421.6	407.3	363	345	568	545	242	346
77	470.2	434.8	459	155	588	575	395	188
84	474.7	473.9	352	435	625	599	432	237
91	504.8	489.5	301	402	604	628	347	276
120	566.6	568.7	438	771	680	588	588	465
150	541.3	643.6	389	370	687	547	314	260
180	646.2	615.2	577	620	625	616	446	197
270	635.4	719.3	255	222	643	622	186	245

Tab. 1 Leached-out amounts of calcium and silicon measured during 270 days

A statistical relationship between deterioration parameters was analysed as dependency between leached-out concentrations of silicon and calcium each other in relation to the slag percentage in concrete.

In statistics, dependence refers to any statistical relationship between two random variables or two sets of data. Correlation refers to any of a broad class of statistical relationships involving dependence. Descriptive statistics is the discipline of quantitatively describing the main features of a collection of data [5]. Increase of the absolute value of the correlation coefficient (R_{xy}) is proportional to linear correlation. Information about two dimensional statistical data set gives correlation coefficient R_{xy} as is shown in *Eq*(1).

$$R_{xy} = \frac{n\sum_{i=1}^{n} x_i y_i - (\sum_{i=1}^{n} x_i)(\sum_{i=1}^{n} y_i)}{\sqrt{\left[n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i^2\right)^2\right]\left[n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i^2\right)^2\right]}}$$

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: 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 $0.9 \leq |R_{xy}|$.

Correlation coefficient was for the purposes of our assessment obtained by the function "Pearson" in Microsoft Excel.

3 RESULTS AND DISCUSSION

Dependency between leached-out amounts of calcium and silicon each other according to the different percentage content of slag is presented in Table 2.

Solution	Correlated parameters	R_{xy}
H_2SO_4	Ca (S65/S95)	0.98
	Si (S65/S95)	0.34
$MgSO_4$	Ca (S65/S95)	0.97
	Si (S65/S95)	0.50

Tab. 2 Correlation coefficients of dependency of leached concentration of selected chemical elements

As it shown in Table 2, the correlation closeness of Ca leaching in both sulphuric acid and magnesium sulphate was calculated as very high ($0.9 \leq |R_{xy}|$) while only a medium correlation was found for Si ions ($0.3 \leq |R_{xy}| < 0.5$). The calculated correlations closeness confirmed the hypothesis that the leaching mechanism of calcium was quite similar for the samples with different percentage content of slag. This can be concluded for both aggressive media. On the contrary, there was not found a similar trend in silicon leaching regarding the composition of concretes during the aggressive exposure. This fact was confirmed for both sulphuric acid and magnesium sulphate solution.

Based on these findings, correlations between individual ions leached-out from the concrete matrix each other for the same type of sample were determined and are presented in Table 3.

Solution	Correlated parameters	R_{xy}
H_2SO_4	Ca/Si (S65)	0.04
	Ca/Si (S95)	0.15
$MgSO_4$	Ca/Si (S65)	-0.10
	Ca/Si (S95)	-0.56

Tab. 3 The correlation coefficients of dependency between leached-out masses of elements each other

As shown in Table 3, a weak or a very slight correlation was calculated for leaching Ca/Si from both 65% and 95 % slag addition in concrete samples exposed to sulphuric acid and similar situation (no dependency, but inverse) was calculated for Ca/Si dependency of sample with 65% slag addition. Inversely significant dependency was found out for Ca/Si leaching trend in case of sample with 95% of slag cement replacement (R_{xy}= -0.56).

4 CONCLUSION

Based on the correlation analysis of the leached-out masses of the main cement matrix´s elements it can be concluded:

- similar leaching mechanisms of calcium in case of the samples with different percentage content of slag exposed to sulphuric acid and magnesium sulphate attack was confirmed,
- a significant difference was observed in correlation coefficients for Ca/Si leaching from samples with 65% cement replacement by slag (0.15) and Ca/Si leaching from samples with 95% cement replacement (0.56) exposed to magnesium sulphate,
- almost no correlation was calculated for Ca/Si leaching for both samples (65% and 95 % slag addition in concrete) exposed to sulphuric acid.

In the next study, the correlation analysis of the leached-out masses of others main cement matrix´s elements (Al, Fe, Mn, Cu) of corrosion experiment in relation to different percentage of slag addition to concrete as well as comparison with concrete prepared according to classic recipe will be analysed.

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