Sulphate resistance of micro-silica and zeolite with micro-silica contained concrete evaluated by statistical method

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Abstract The use of natural resources and enhancing the use of waste materials as admixture of cement replacement is very important for sustainable development. This paper presents the experimental study of the sulphate attack on concrete prepared according to classic recipe and study of the effectiveness of concrete with 5% of micro-silica cement replacement and 8% of micro-silica and zeolite preplacement in controlling the damage arising from such attack. Ca, Si, Fe and Al ions dissolved from the cement matrix into liquid aggressive medium 0.005 wt. % H_2SO_4 (pH value 3) measured periodically during 270 days under laboratory temperature of 23 °C were determinated by X-ray fluorescence analysis. Statistical method of correlation analysis between the dissolved ions each other according to type of concrete recipes was calculated. Conclusions based on mathematical approach were formulated considering the best concrete mixture for the sulphate resistance point of view.

Keywords: acid corrosion, concrete deterioration, correlation coefficient, supplementary materials

1. Introduction

Mineral admixtures are widely used in cement production as cement replacement material with the aim improve the durability and mechanical properties and also considering the cost effectivity. Investigation of effect of various percentages of slag used as a cement replacement was presented in paper by Praveen *et al*. (2016). The authors used supplementary material as coarse aggregates and studied the mechanical properties of concrete. Mechanical properties of concrete were also studied in Ghafoori *et al*. (2016). Concrete samples prepared with micro-silica and nano-silica were exposed to chemical sulphate attack. Lee at al. (2005) studied sulphate attack on samples with silica fume cement replacement. Tap water was used for comparative study. The authors evaluated microstructure character changes by X-Ray diffraction and by differential scanning calorimetry. Beneficial effect of presence of silica fume on strength loss due to sodium sulphate attack was proven. Yoon *et al*. (2014) in their paper experimentally and statistically investigated the effect of mix-design factors on mechanical properties of high-volume class F fly ash concretes. Ozyildirim and Halstead (1998) investigated two pozzolanic admixtures containing fly ash and silica fume prepared with low water-to cement ration. They reported that the durability and mechanical properties of concrete can be increased by adding micro-silica as partial replacement of cement at low water-cement ratio.

Major compounds of portland cement (tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminoferrite and gypsum) undergoes to hydratation when the water is added to the cement. It affects the properties of the final product. Significate effect on strength has calcium silicates. Other compounds contribute to early strength or strength at later times. Based on these well-known concrete composition knowledges the leaching trends and it dependencies on each other is presented in this part.

2. Material and Methods

2.1. Concrete samples

Three different concrete mixtures were used for a sulphate-resistance experimental investigation. First set of samples, marked as V0, was designed according to a standard recipe, based only on ordinary Portland cement (Povazska cementaren, Slovakia), water, aggregate (Vychodoslovenske stavebne hmoty, Geca, Slovakia) with particle size fractions of 0/4, 4/8, and 8/16 mm, respectively, and plasticizer based on polycarboxylates (Stachema, Bratislava, Slovakia). V1 mixture was a modification of V0 mixture by adding the micro-silica (OFZ Inc., Istebne, Slovakia) in 5% wt. of total binder mass. Micro-silica incorporation resulted in higher water demand of V1 mixture to ensure the same consistency of concretes. Third mixture (V2) consisted of both micro-silica and zeolite addition in the same proportions. 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 mechanical parameters.

Subsequently, the concrete prisms were cut into smaller ones measuring

2.2. Corrosion experiment

Sulphate corrosion was simulated in laboratory by concrete samples exposure to an agressive sulphate solution of H_2SO_4 (pH=3) with concentration of 0.005 wt. %. Sulphuric acid is very damaging to concrete as it combines an acid attack and a sulfate attack. The samples of concrete composites were placed into prepared solutions of sulphuric acid while the volume of liquids was strictly calculated based on the volume of the immersed sample. According to the standards dealing with corrosion of concretes, the ratio of volumes of liquid solutions (400 - 500 mL) to volumes of tested samples were set to 10:1. The experiments were conducted in glass containers covered by aluminum foils. Exposure of the tested concrete samples to liquid aggressive sulphate media proceeded over a period of 270 days under laboratory temperature of 23 °C. The concentrations of dissolved Ca^{2+} , Si^{4+}, Fe^{3+} and Al^{3+} ions in leachates were measured periodically during whole experiment. Calcium, silicon, iron and aluminium leachability was investigated based on the well-known fact that the major compounds of portland cement are tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$), tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$) and gypsum ($CaSO_4.2H_2O$). After hydratation, the concrete main components (C-S-H and C-A-H phases, monosulphate, trisulphate, portlandit etc.) are based on these four elements compounds hydrates. Degradation of the compounds can be manifested by leaching the Ca and Si, Fe and Al. The leached-out amounts of Ca and Si, Fe and Al converted to unit quantities per 1g of concrete sample, represented deterioration parameters in statistical evaluation of concrete´s resistance.

2.3. X-ray fluorescence analysis

X-ray fluorescence analysis (XRF) was used to analyze the concentrations of dissolved ions in leachates. The resolution of SDD silicon drift detector on equipment SPECTRO iQ II (Ametek, Germany) was 145 eV at 10 000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite – HOPG target. The parameters of samples´ measurement were as follows: time - 180 s, voltage - 25 kV and 50 kV, current - 0.5 and 1.0 mA, respectively. The measurement was conducted under inert helium atmosphere. The concentrations of Ca, Si, Fe and Al in solutions were calculated according to the calibration method for concrete leachates.

2.4. Statistical evaluation

A statistical method was used for evaluation of deleterious process and to determine 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} (Kreyzig, 2011) and its calculation is presented in our previous paper (Ondrejka Harbuľáková, 2015). Software Excel 2010 by Microsoft was used for its calculation. 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 $0.9 \leq |R_{xy}|$.

3. Results and Discussion

The results of the leached-out amounts of main concrete components (Ca, Si, Fe and Al) in sulphuric acid are given in Tables 1, 2 and 3.

Table 1. Concentrations of studied elements measured in V0 samples solutions

	Ca	**Si**	**Fe**	**Al**
Day	mg/g			
14	1.19	2.03	0.04	0.74
21	1.77	2.21	0.04	1.08
28	2.09	2.43	0.04	0.82
35	2.05	2.39	0.08	0.78
42	1.87	1.64	0.05	0.32
49	1.94	1.59	0.04	0.70
56	2.30	2.19	0.05	0.61
63	2.40	2.24	0.06	0.44
70	2.77	2.74	0.04	0.25
77	3.39	4.59	0.05	0.46
84	3.58	3.65	0.05	0.35
91	4.28	4.18	0.03	0.21
180	51.23	19.38	0.04	0.91
270	27.12	10.10	0.04	0.14

Table 2. Concentrations of studied elements measured in V1 samples solutions

	Ca	Si	Fe	Al
Day	mg/g			
14	0.36	1.88	0.05	0.55
21	0.57	2.40	0.06	0.79
28	1.25	2.88	0.04	0.93
35	1.27	2.47	0.05	0.73
42	1.25	1.89	0.04	0.44
49	1.45	1.91	0.04	0.64
56	1.65	2.68	0.05	0.60
63	1.89	2.69	0.03	0.64
70	2.25	3.02	0.04	0.31
77	2.62	4.61	0.03	0.29
84	2.66	2.93	0.03	0.35
91	3.11	3.70	0.04	0.12

180	7.56	7.23	0.07	1.86
270	18.00	9.74	0.26	1.53

Table 3. Concentrations of studied elements measured in V2 samples solutions

	Ca	**Si**	**Fe**	**Al**
Day	mg/g			
14	0.65	2.02	0.04	0.52
21	0.89	2.86	0.04	0.82
28	1.51	2.61	0.04	0.93
35	1.73	3.55	0.06	0.58
42	1.94	2.04	0.06	0.38
49	2.05	2.03	0.04	0.50
56	2.45	3.53	0.04	0.45
63	2.57	2.97	0.05	0.40
70	3.19	4.26	0.02	0.30
77	4.19	7.96	0.03	0.28
84	5.96	8.24	0.04	0.16
91	17.72	15.81	0.03	0.13
180	132.59	20.76	0.98	2.38
270	17.37	10.30	0.11	2.24

The presented results were applied as input data for the statistical analysis with the aim of better understanding to the deterioration of concrete samples under sulphate and acidic attacks, based on the concentrations of ions (calcium, silicon, aluminium and iron) dissolved into the liquid phase of sulphuric acid. The calculated correlation coefficients (R_{xy}) of calcium leaching trends regarding the composition of concrete mixture are presented in Table 4 while the correlation coefficients for silicon are in Table 5.

Table 4. Pearson´s correlation analysis of Ca leachability

	Ca		
	V0	V1	V2
V0	1	-	-
V1	0.69	1	-
V2	0.93	0.38	1

A high correlation coefficient was calculated for leaching trends of calcium from V0 and V2 samples during the sulphate exposure (Table 4). This points to the very similar deterioration process when compared concrete samples with ordinary Portland cement and concrete samples with a combination of cement-micro-silica-zeolite. On the contrary, the weak correlation between V1 and V2 samples could evoke a big difference in deterioration mechanisms of the concrete samples.

Table 5. Pearson´s correlation analysis of Ca leachability

	Si		
	V0	V1	V2
V0	1	-	-
V1	0.84	1	-
V2	0.84	0.69	1

As seen in Table 5, based on the correlation coefficients reported, the different V1 and V2 leaching rate were found similarly as for calcium for silicon as well. The correlation coefficients calculated for iron and aluminium leachability due to sulphuric acid for all three types of concrete mixture are presented in Tables 6 and 7, respectively.

Table 6. Pearson´s correlation analysis of Fe leachability

	Fe		
	V0	V1	V2
V0	1	-	-
V1	-0.16	1	-
V2	-0.07	0.13	1

Table 7. Pearson´s correlation analysis of Al leachability

	Al		
	V0	V1	V2
V0	1	-	-
V1	0.35	1	-
V2	0.21	0.97	1

Very low correlation values were calculated for iron leaching rates (Table 6). It can be concluded that no correlation exist for any pair of concrete mixture, so the trend of iron leaching is very different from concrete mixture to mixture. Based on one recipe it cannot be predicted the durability and resistance of the others. For aluminium, the trend seems to be similar, except “very high” correlation between mixtures with addition of micro-silica and micro-silica-zeolite (Table 7). In addition, every concrete mixture was investigated separately. Correlation coefficients were established leaching trend between pair of basic chemical compounds of concrete (Ca/Si, Ca/Fe, Ca/Al and Fe/Al).

Table 8. Pearson´s correlation analysis between the elements each other

		R_{xy}
V0	Ca/Si	0.99
	Fe/Al	0.25
	Ca/Al	0.10
	Ca/Fe	-0.17
V1	Ca/Si	0.95
	Fe/Al	0.63
	Ca/Al	0.66
	Ca/Fe	0.93
V2	Ca/Si	0.81
	Fe/Al	0.25
	Ca/Al	0.71

Ca/Fe	0.99

Correlation between Ca/Si was found “very high” (V0, V1) or “high” (V2), so the dissolution trend is under way in similar trend (Table 8). The similar trend can be explained according to the chemical mechanism of the acidic attack. Sulfuric acid reacts with calcium hydroxide by forming calcium sulfate according to the Eq. 1.

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \quad (1)$$

When is of fine grain size, calcium sulfate can easily dissolving in water. Generally, the acidic attack results in water soluble calcium compounds which are leached away. In addition, sulfuric acid may also cause the decomposition of calcium silicate hydrates (C-S-H) and transformation the C-S-H into amorphous hydrous silica.

$$xCaO \cdot SiO_2 \cdot aq + xH_2SO_4 + xH_2O \rightarrow xCaSO_4 \cdot 2H_2O + SiO_2 \cdot aq \quad (2)$$

A relatively high correlations were found also for the leached-out quantities of Ca/Al and Ca/Fe regarding the concrete samples with micro-silica (V1) and micro-silica-zeolite (V2) - Table 8. The correlation could be linked with the dissolution of Afm and Aft phases under low pH, caused by acid attack, and production of gypsum and aluminium sulphate . This correlation was not confirmed in case of ordinary Portland cement – based concretes (V0 samples).

Different behaviour can be seen for Fe/Al in mixtures V0 and V2 where no correlation was found (R_{xy}=0.25). “Significant” correlation was between Fe/Al leaching from the concrete samples containing micro-silica addition (V1).

4. Conclusion

Analysing the leached-out quantities of main components of concretes of various compositions (ordinary Portland cement – based concretes, concretes with addition of micro-silica, and combination of micro-silica-zeolite) using the correlation analysis, we can conclude:

- ✓ The differences in dissolving rates of Ca, Si, Al and Fe have been found regarding the composition of concretes.
- ✓ Based only on the correlation analysis, no definite conclusions about the differences in durability of studied concretes with various compositions can be concluded.

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