The Study of Zeolite Based Cement Composites in Aggressive Environment

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The exposition of concrete and cement composites to the aggressive environment is resulting in damages in the structures before the expected service life. Prolonging the service life of concrete composites through enhancing the mechanical and durability properties has gained great importance in recent years. It is possible to achieve environmental and economical benefits with the utilization of pozzolanic mineral additives in cement production. The use of zeolite as partial replacement of Portland cement prevents alkali-silica reaction by decreasing the alkaline ion concentration in the pore solution in concrete via ion exchange, adsorption and pozzolanic reaction, therefore the formation of alkali silicate gel is eliminated and the interface is improved.

The papers presents the results of the comparative study of the resistance of the Slovak origin zeolite based cement composites and cement composites of ordinary CEM I Portland cement exposed to the sulphate environment. The various aggressive media was used for the experiment: sulphuric acid with pH 3 and 4.2 and magnesium sulphate solution with the concentrations of 3g/L and 10g/L. The laboratory experiment proceeded during 90 days under model conditions.

The mass changes of samples as well as the changes in the elemental concentrations of calcium and silicon in liquid leachates were observed. The leaching of the calcium and silicon from concrete specimens has been studied by using X – ray fluorescence method (XRF). The pH values of leachates increased to the alkali region for all leachates as expected. Surprisingly, higher leaching ratio of calcium and silicone ranged 1.29 - 8.18 and 2.32 -20.44 for Si and Ca, was confirmed in case of the zeolite based cement composites when comparing to the ordinary cement composites.

1. Introduction

Considering the deteriorating state of the infrastructure worldwide and the limited resources available for repair and rehabilitation of constructed facilities, it is imperative to find effective and economical techniques and materials to revive the aging infrastructure.

Today, concrete is the most widely used man-made construction material in the world due to its low price, appropriate mechanical and durability characteristics as well as ease of being formed into various shapes and sizes (Mehta, 1992). Despite these advantages, environmental problems are arising from the manufacture of Portland cement as a component of concrete (Eštoková, 2012). The cement industry alone is estimated to be responsible for about 7% of all CO_2 generated (Damtoft, et al., 2008). Therefore, reducing the cement consumption is considered a solution towards sustainable development. In addition, prolonging the service life of cement and concrete composites through enhancing the mechanical and durability properties has gained great importance in recent years (Najimi, 2012).

In recent studies, various types of materials such as silica fumes, fly ash, coal bottom ash and zeolites have been investigated as Portland cement replacement materials or admixtures to reach these goals (Kula, et al., 2001) and more recently by Canpolat, et al. (2004).

Natural zeolite as porous aluminosilicates containing large quantities of reactive SiO_2 and Al_2O_3 are natural pozzolans (Breek, 1974). Similar to other pozzolanic materials, zeolite substitution can improve the strength of concrete by the pozzolanic reaction with $Ca(OH)_2$. The porous structure of natural zeolite holds

water which can increase curing time and increase strength during curing. In general, natural zeolite contributes to the strength of concrete better than the strength of cement (Negis, 1999). Zeolites also have much higher cation exchange capacities than other natural pozzolans and these limits, or totally prevents the alkali-silica reaction (Canpolat, et al., 2004) and following undesirable expansion due to alkali–aggregate formation. Zeolites can be used to replace up to 40 % of the cement in Portland cement concrete to make lightweight concrete with specific properties. Since cement clinker manufacture requires a lot of energy and produces massive amounts of carbon dioxide, the use of zeolite in concrete leads not only to prolonging of concrete materials lifetime but to significant energy savings and reductions in CO_2 emissions as well. The use of 10 t of zeolite saves approximately 1 t of fuel.

Also other mineral admixtures such as fly ash, ground granulated blast furnace slag and silica fume are widely used in concrete to improve the workability and strength or to reduce the costs (Zhong-he Shui, 2010). With increased environmental awareness and its potential hazardous effects, utilization of industrial byproducts has become an attractive alternative to disposal. One such by-product is silica fume, which is a byproduct of the smelting process in the silicon and ferrosilicon industry (Siddique, 2011). It is well known that, this product has several advantages such as high ultimate strength, high sulfate resistance and low heat of hydration when used in Portland cement concrete. These advantages derived from high specific surface and pozzolanic activity of silica fume particles (Sezer, 2012). The addition of silica fume has proved to improve both the compressive strength and durability of concrete. Also, the presence of this admixture has been shown effective in increasing the electrical resistivity and the durability of concrete exposed to aggressive conditions like chloride containing environments (Dotto, et al., 2004).

In this paper, the resistance of concrete based on natural zeolite (Slovak origin) and silica fume as added cementitious materials has been investigated in sulphate environment.

2. Material and methods

Concrete composites of ordinary CEM I Portland cement with and without natural pozzolans exposed to the various liquid media were investigated in terms of the concrete deterioration influenced by the leaching of calcium and silicon compounds from the cement matrix.

2.1 Concrete samples preparation

Two mixtures of concrete (MZ and MA) 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 specifications in accordance with STN EN 206-1: concrete of strength class C 25/30 and exposure class XA1: Slightly aggressive chemical environment (mixture MA) and concrete of strength class C 30/37 and exposure class XA2: Moderately aggressive chemical environment (mixture MZ). Mix proportion with appropriate water to cement ratio w/c for concrete with above mentioned specifications is in Table 1.

Table 1: Mix proportions of two different concrete mixtures.

Mixture	Cement	Water	Zeolite	Silica fume	Fr. 0/4 mm	Fr. 4/8 mm	Fr. 8/16 mm	Plasticizer	w/c ratio
					Components				
MZ	360 kg	191 L	20 kg	20 kg	750 kg	235 kg	740 kg	3.1 L	0.45
MA	360 kg	170 L	-	-	825 kg	235 kg	740 kg	2.6 L	0.55

The prepared standardized concrete prisms of size 100x100x400 mm were hardened 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, cleaned, dried and weighted.

2.2 Laboratory experiments

The concrete samples were exposed to the various liquid media: fresh water, sulphuric acid and magnesium sulphate solution. The characteristics of concrete samples and media are summarized in Table 2.

The volume ratio of concrete sample to liquid phase was set to 1:10 at the beginning of the experiment. The exposition of concrete samples proceeded during 90 days at laboratory temperature of 23 °C. After each 7 day-immersion period, the change in pH as well as the released concentration of calcium and silicon were measured in leachates. The pH value of sulphuric acid solutions was kept on constant level of 3 and 4.2.

The deterioration of the concrete specimens was also quantified by changes in weight of the specimens. The change in concrete samples weight was measured as the difference between the original weight before and final weight after the experiment.

Table 2: Characterization of samples

Sample		Liquid medium	Characteristics of medium
MZ1	MA1	H_2SO_4	pH 3
MZ2	MA2	H_2SO_4	pH 4.2
MZ3	MA3	$MgSO_4$	10 g/L of SO_4^{2-}
MZ4	MA4	$MgSO_4$	3 g/L of SO_4^{2-}
MZ5	MA5	fresh water	pH 7.2

2.3 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 pellets and concrete leachates. pH changes were measured by pH meter FG2- FiveGo (Mettler-Toledo, Switzerland).

3. Results

Leaching trend of silicon and calcium ions in H_2SO_4 solutions with pH of 3 and 4.2 during 90 day-experiments is illustrated in Figures 1 A) and 1 B).
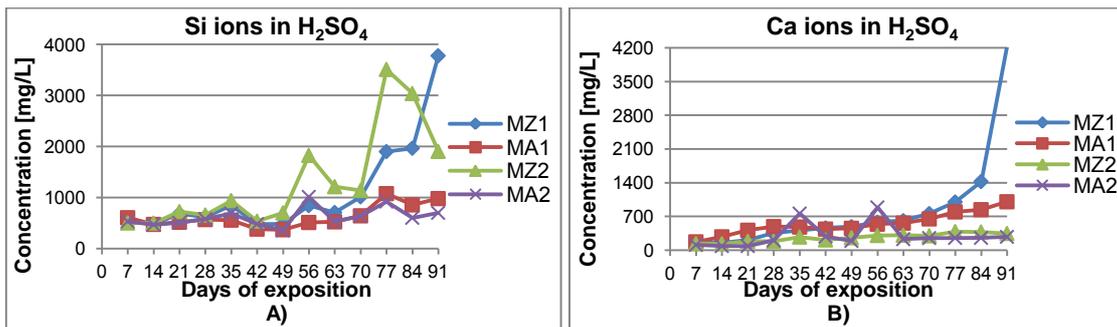

Figure 1: Concentrations of A) Si ions and B) Ca ions in H_2SO_4 solution

The maximum of Si ions concentrations (3778 mg/L) was measured in leachate of sample MZ1 (sulphuric acid with pH 3.2) as it is seen in Figure 1 A). The concrete samples of type MA were found to have better leaching performance of silicon ions in both aggressive environments of H_2SO_4 than concrete samples of type MZ (comparing MZ1 to MA1 and MZ2 to MA2). The highest concentrations of calcium ions (4234 mg/L) were observed in H_2SO_4 solution with pH 3.2 (Figure 1 B).

Measured concentrations of silicon and calcium ions in $MgSO_4$ solutions with the concentrations of 3 g/L and 10 g/L, during the experiment are illustrated in Figures 2 A) and 2 B).
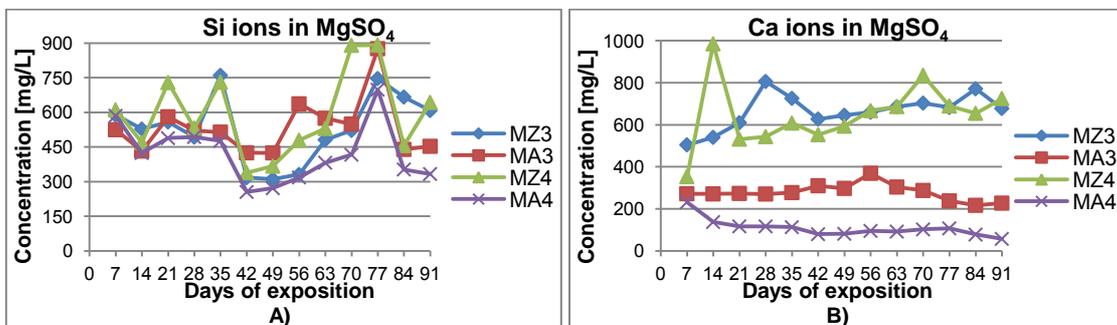

Figure 2: Concentrations of A) Si ions and B) Ca ions in $MgSO_4$ solution

The concrete sample MZ3 was found to have better performance of silicon ions leaching during period of 42 – 77 d in aggressive environments of $MgSO_4$ with the concentrations of 10 g/L than concrete sample MA3. The silicon releasing to $MgSO_4$ environment (concentrations of 3 g/L) was higher for sample MZ4 compared to the sample MA4. The concrete samples of type MA were found to have better performance in leaching trend of Ca ions in both aggressive environments of $MgSO_4$ than concrete samples of type MZ (comparing MZ3 to MA3 and MZ4 to MA4). The maximum of Ca ions concentrations (985.4 mg/L) was measured in leachate of sample MZ4 ($MgSO_4$ with concentration of 3 g/L) as it is seen in Figure 2 B. Slightly concentrations changes were measured in $MgSO_4$ solutions for concrete samples of type MA.

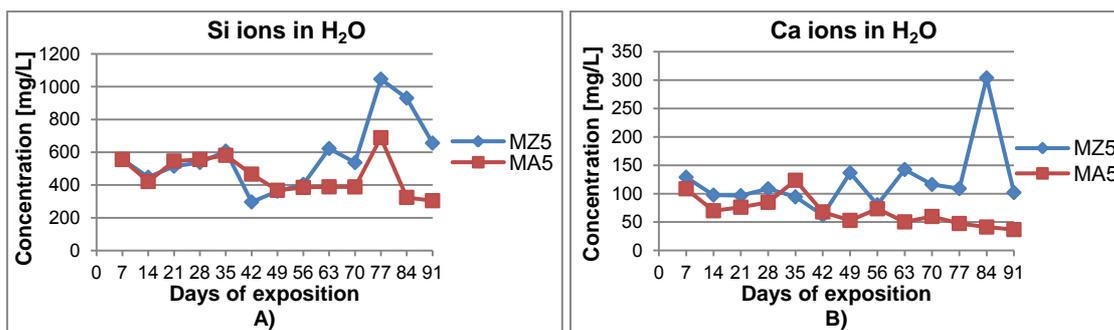The leaching of silicon and calcium ions to water environment is presented in Figures 3 A) and B).

Figure 3: Concentrations of A) Si ions and B) Ca ions in H_2O

The concentration of released Si ions in water environment was observed to be higher for concrete samples MZ5 compared to the sample MA5 except the period between 21 - 28 and 42 - 49 d of exposition. The highest concentrations of calcium ions (304 mg/L) were measured in leachate of sample MZ5 (Figure 3 B). The calcium releasing to water environment was higher for samples MZ5 except the period between 35 - 42 d of exposition as presented in Figure 3 B). Mass of released ions of silicon and calcium corresponding to 1 g of concrete sample is illustrated in Tables 3 and 4.

The leaching of silicon ions calculated to 1 g of concrete sample was higher for concrete samples of type MZ compared to the samples MA except sample MA3 after 56 d of exposition and sample MA5 after 42 d of exposition as it can be seen in Table 3.

Table 3: Released ions of silicon corresponding to 1 g of concrete sample

	Si (mg)									
d	MZ1	MA1	MZ2	MA2	MZ3	MA3	MZ4	MA4	MZ5	MA5
7	18.30	8.73	15.34	7.68	13.82	7.17	13.37	7.14	9.07	6.65
14	16.43	6.85	15.27	6.78	12.39	5.91	10.29	5.17	7.28	5.05
21	23.32	7.45	22.13	7.29	13.12	7.93	15.97	5.96	8.36	6.54
28	21.24	8.21	20.12	8.33	11.58	7.12	11.65	6.02	8.73	6.65
35	28.92	8.05	28.68	9.90	17.85	7.03	16.00	5.81	9.86	6.96
42	16.57	5.52	16.43	6.91	7.45	5.80	7.41	3.11	4.82	5.59
49	16.49	5.36	21.35	5.14	7.30	5.80	8.04	3.31	5.88	4.40
56	28.76	7.39	55.55	14.57	7.77	8.70	10.50	3.88	6.56	4.61
63	24.20	7.57	36.91	7.67	11.30	7.85	11.61	4.66	10.12	4.66
70	34.66	9.26	34.72	9.16	12.26	7.50	19.50	5.08	8.73	4.65
77	64.83	15.50	106.72	13.23	17.54	11.96	19.53	8.52	17.01	8.25
84	67.08	12.33	92.40	8.67	15.65	6.00	9.99	4.30	15.12	3.88
91	128.77	14.11	57.95	10.07	14.28	6.19	14.08	4.06	10.66	3.64

The mass of calcium ions released corresponding to 1 g of concrete sample of concrete samples was measured much higher for MZ type samples than for MA samples except for sample MA2 after 35 and 56 days of exposition (Table 4).

Table 4: Released ions of calcium corresponding to 1 g of concrete sample.

d	MZ1	MA1	MZ2	MA2	Ca (mg) MZ3	MA3	MZ4	MA4	MZ5	MA5
7	5.66	2.50	4.18	1.59	11.86	3.71	7.74	2.82	2.10	1.30
14	5.25	4.01	4.11	1.24	12.70	3.70	21.59	1.67	1.59	0.84
21	7.24	5.97	5.62	1.25	14.34	3.73	11.65	1.42	1.57	0.91
28	12.28	7.05	5.66	2.93	18.95	3.70	11.91	1.42	1.77	1.02
35	14.08	6.92	8.34	10.92	17.06	3.79	13.32	1.38	1.53	1.48
42	15.77	6.31	6.49	4.06	14.75	4.24	12.12	0.97	1.01	0.81
49	16.70	6.55	7.89	2.76	15.17	4.06	13.00	0.99	2.22	0.63
56	19.83	7.77	9.31	12.74	15.51	5.04	14.62	1.16	1.31	0.88
63	20.94	8.09	9.47	3.29	16.12	4.15	15.05	1.12	2.32	0.60
70	25.95	9.34	9.09	3.64	16.53	3.93	18.30	1.24	1.89	0.72
77	34.15	11.43	11.78	3.66	16.04	3.25	15.11	1.31	1.77	0.57
84	48.57	12.10	11.54	3.68	18.13	2.96	14.34	0.95	4.94	0.49
91	144.31	14.45	10.60	3.99	15.93	3.10	15.88	0.70	1.66	0.44

Whereas cement matrix is assumed to release the studied elements, the amounts of silicon and calcium ions released from 1 g of cement matrix have been calculated and compared after 60 and 90 d of exposition (Figures 4 A) and B).
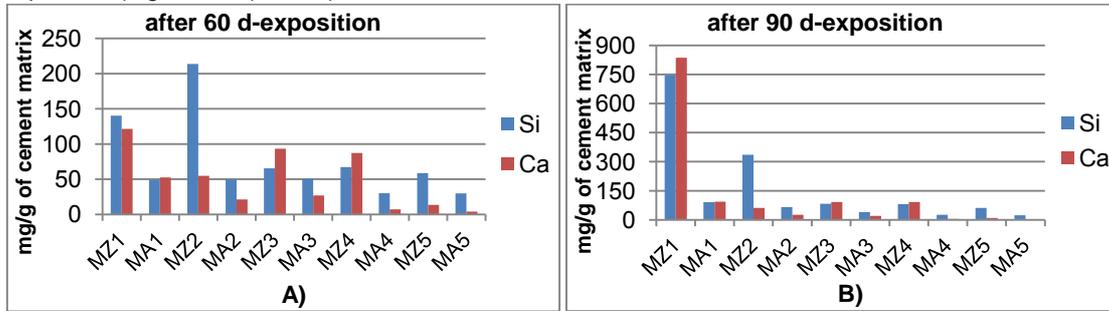

Figure 4: Si and Ca released from 1 g of cement matrix after A) 60 and B) 90 days of exposition

Comparing MZ and MA samples much higher released amounts of both calcium and silicon ions were found out in case of MZ samples, what is on the contrary as expected because of higher resistance of zeolite and silica fume based concrete samples. Calculated ratios of released silicon and calcium ions after 60 and 90 d of exposition are summarised in Table 5. MZ/MA ratios ranged 1.29 - 8.18 and 2.32 - 20.44 for Si and Ca, what means the releasing of ions was measured to be higher for all MZ samples after 60 and 90-day exposition.

Table 5: Zeolite and non-zeolite based samples ratio of ions released from 1 g of cement matrix

	Si		Ca	
MZ/MA ratio	60 d	90 d	60 d	90 d
MZ1/MA1	2.86	8.18	2.32	8.94
MZ2/MA2	4.31	5.15	2.57	2.38
MZ3/MA3	1.29	2.06	3.47	4.59
MZ4/MA4	2.23	3.10	12.10	20.44
MZ5/MA5	1.96	2.64	3.44	3.43

The results of changes in weight after the 90-day experiment are given in Figure 5.

Figure 5: Changes in weight after the 90-day experiment

The decrease in weight was noticed for all tested concrete specimens. The percentage of weight losses varied from 0.81 % (sample MA3) to 2.18 % (sample MZ1). Comparing the weight losses of MZ type and MA type samples in equivalent media (MZ1 to MA1; MZ2 to MA2; MZ3 to MA3 etc.)

4. Conclusions

Natural pozzolans (zeolite and silica fume) based concrete samples (MZ) were investigated in various sulphate environment and compared to the ordinary concrete ones (MA). The study was aimed at confirmation the importance of zeolite and silica fume additives in order to prolonging the lifetime of concrete and that the environment deterioration reduction. Surprisingly, the higher resistance of zeolite and silica fume based concrete samples was not confirmed. Concluding results:

- Mass of calcium and silicon ions released (corresponding to 1 g of concrete as well as to 1 g of cement matrix) was measured much higher for MZ type samples than for MA samples;
- The releasing of ions was measured to be higher for all MZ samples after 60 and 90-day exposition;
- MZ/MA ratios ranged 1.29 - 8.18 and 2.32 -20.44 for Si and Ca;
- Percentage of samples weight losses varied from 0.81 to 2.18 %. There were found out higher weight decreases for all samples of type MZ when compared to MA samples.

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