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CONCRETE COMPOSITES RESISTANCE IN SULPHUR ENVIRONMENT

Concrete structures and elements are often exposed to different aggressive environment. It leads to failures, cracking, weathering and deterioration of concrete materials. Under aggressive conditions, the concrete is liable to a corrosive process which is not usually caused by one specific factor but by combination of aggressive media. Sulphur environment is one of the most corrosive factors influencing the concrete durability.

The paper presents the results of the comparative study of the resistance of the Slovak origin zeolite based cement composites and cement composites with addition of silica fume meeting the requirements of aggressive sulphur environment. The five aggressive media were used for concrete resistance study. The leaching of the calcium and silicon ions from concrete specimens, as well as the chemical composition of samples have been studied by using X – ray fluorescence method (XRF).

Key words: concrete, zeolite, silica fume, leaching.

Бетонні конструкції та елементи часто піддаються впливу різних агресивних середовищ. Це призводить до руйнування, тріщиноутворення, вивітрювання і погіршення стану бетонних елементів. У агресивних умовах в бетоні проходять корозійні процеси, який зазвичай не викликані одним конкретним фактором, але поєднанням агресивних середовищ. Сірчане середовища є одним з найбільш корозійних факторів, що впливають на довговічність бетону.

У статті представлені результати порівняльного вивчення опору композитів на основі цементу і цеоліту словацького походження та цементних композитів з додаванням мікрокремнезем в умовах агресивного середовища сірки. П'ять агресивних середовищ були використані для вивчення опору бетону. Вилуговування кальцію та іонів кремнію із зразків бетону, хімічний склад зразків, а також склад фільтрату було вивчено за допомогою рентгено-флуоресцентного методу (XRF).

Ключові слова: бетон, цеоліт, біла сажа, вилуговування.

Introduction

The durability of concrete structures and, consequently, their service life, have improved significantly due to the introduction of pozzolans to the industry; thus, using newly developed pozzolans has become a necessity for the construction of concrete structures, especially in aggressive environments [1]. Blended cements have attracted intensive attention for their ability to enhance the physical and chemical properties of cement-based materials. Among them, materials possessing pozzolanic properties, such as silica fume and zeolite, play a special role. The reactive SiO2 they contain reacts pozzolanically with the portlandite during the hydration of cement to form a stable cementitious compound, calcium silicate hydrate (CSH) [2]. Both materials, when substituted for cement at a level of around 10%, increase the compressive strength, decrease the pore size [3-5] and increase the corrosion resistance to acid solution

[5-6]. Zeolites have been shown to increase the binding properties of cement-based materials for contaminants such as caesium [7]. The presence of zeolite can retard the hydration process, thereby reducing the permeability, sorptivity and diffusivity of concrete because it reduces porosity and improves the transition zone structure between the blended cement paste and the aggregate [8-11]. Addition of silica fume was shown to improve the leaching properties of solidified nuclear wastes [5] and produce more durable cement systems, owing to the changes caused by pozzolanic materials in the amount of the different hydrates, as well as in their chemical composition [2].

A number of studies have compared zeolite to other pozzolanic materials, indicating that the activity of natural zeolite is superior to fly ash but poorer than silica fume [12]. Test results by Ahmadi [13] revealed that the pozzolanic activity of natural zeolite is lower than silica fume but that there is a high rate of lime consumption. Also, the increase of compressive strength in concrete containing natural zeolite was not higher than in silica fume, although this parameter for materials is higher than for the reference concrete. Other studies have been conducted on the effects of natural zeolite on concrete durability. Findings from these studies indicate that using natural zeolite diminishes the formation of alkali– silica reaction (ASR) gel, though not as well as ground granulated blast-furnace slag, and protects the composite material against sulfate attacks by diminishing the formation of ettringite [14], [15], [16]. Moreover, a comparison between the effects of natural zeolite, slag and SF on the prevention of the ASR indicated that natural zeolite operates as effectively as fly ash and better than slag, but not as well as silica fume [17].

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. A laboratory study was conducted to compare the performance of concrete containing zeolite and silica fume in terms of the concrete deterioration influenced by the leaching of calcium and silicon compounds from the cement matrix.

Material and methods

Concrete composites of ordinary CEM I Portland cement with 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.

Concrete samples preparation

Two mixtures of concrete (MSF and MZ) were used for the preparation of concrete samples for the experiment, using cement CEM I 42.5 N. The composition of these mixtures was in accordance with STN EN 206-1 requirements of aggressive environment. 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	
Components	**MSF**	**MZ**
Cement	360 kg	360 kg
Water	200 L	191 L
Zeolite	-	20 kg
Silica fume	20 kg	20 kg
Fr. 0/4 mm	800 kg	750 kg
Fr. 4/8 mm	235 kg	235 kg
Fr. 8/16 mm	740 kg	740 kg
Plasticization additive	3.1 L	3.1 L
w/c ratio	0.49	0.45

The prepared standardized concrete prisms of size 100x100x400 mm were cured 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.

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 used media are summarized in Table 2.

Table 2

Characterization of samples

Sample	Liquid medium	Characteristics of medium
MSF1	H_2SO_4	pH 3
MSF2	H_2SO_4	pH 4.2
MSF3	$MgSO_4$	10 g/L of SO_4^{2-}
MSF4	$MgSO_4$	3 g/L of SO_4^{2-}
MSF5	fresh water	pH 7.2
MZ1	H_2SO_4	pH 3
MZ2	H_2SO_4	pH 4.2
MZ3	$MgSO_4$	10 g/L of SO_4^{2-}
MZ4	$MgSO_4$	3 g/L of SO_4^{2-}
MZ5	fresh water	pH 7.2

The volume ratio of concrete sample and liquid phase was set to 1:10 at the beginning of the experiment. The exposition of concrete samples proceeded during 63 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. pH value of sulphuric acid solutions was kept on constant level of 3 and 4.2, respectively.

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, respectively 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).

Results

The percentage of the major elements which the concrete samples were consisted of before the experiment is illustrated in Table 3 in oxidic form.

Table 3

Chemical analysis of tested concrete samples

(% mass)	MSF	MZ
Na_2O	0.11	0.11
MgO	2.727	2.383
Al_2O_3	5.385	5.252
SiO_2	45.63	39.82
P_2O_5	0.0941	0.0911
SO_3	2.718	2.804
Cl	0.0187	0.0132
K_2O	0.7941	0.7512
CaO	26.17	25.12
TiO_2	0.2583	0.2692
MnO	0.3642	0.3747
Fe_2O_3	3.748	4.632

The concentrations of silicon and calcium ions released into the water and acid environment from the cement composites during 63 day exposition are summarized in Table 4 and 5.

Table 4

Leaching of silicon ions from tested concrete samples

	Si ions (mg/L)									
	MSF1	**MSF2**	**MSF3**	**MSF4**	**MSF5**	**MZ1**	**MZ2**	**MZ3**	**MZ4**	**MZ5**
7	569.2	542.4	514.4	519.2	569	536.9	504.5	588.1	610.3	557.6
14	448.2	454.1	442.7	457.8	422.7	482.2	502.2	527.4	469.6	447.7
21	570.1	500.4	492.2	542.7	527.3	684.3	728	558.2	728.8	514.1
28	684.5	533.4	495.7	505.5	534.4	623.1	661.7	492.6	531.7	537
35	587.4	517.5	660.2	522.6	538	848.4	943.3	759.7	730.3	606.5
42	449.3	467.3	337.3	296.7	352.2	486.3	540.5	317	338.4	296.3
49	456.6	329	318.1	299.9	395.9	483.8	702.1	310.6	367	361.8
56	638.3	433.9	402.7	360.7	359.1	843.7	1827	330.8	479.1	403.6
63	640.6	510.7	401.9	443.9	428.5	710	1214	480.9	529.8	622.5

The concentration of released Si ions in $MgSO_4$ with the concentrations of 3 g/L of SO_4^{2-} was observed to be lower for concrete sample MSF4 compared to the sample MZ5 during 63 days of exposition. The highest concentrations of silicon ions (1827 mg/L) were measured in leachate of sample MZ2 (Table 4). The silicon releasing to the all aggressive environments was higher for samples of type MZ except sample MZ1 after 7 and 28 days of exposition, sample MZ2 after 7 days of exposition, sample MZ3 after 28, 42-56 days of exposition and sample MZ5 after 7, 21, 42, 49 days of exposition as presented in Table 4.

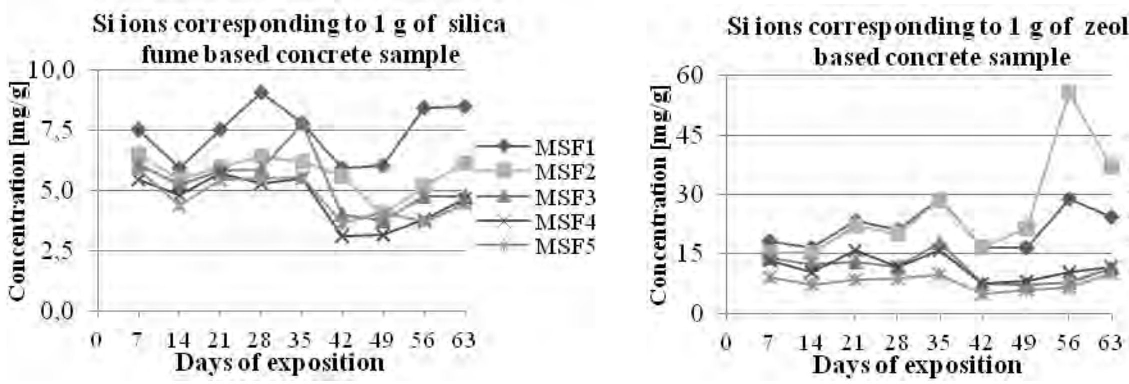
Table5

Leaching of calcium ions from tested concrete samples

	Ca ions (mg/L)									
	MSF1	**MSF2**	**MSF3**	**MSF4**	**MSF5**	**MZ1**	**MZ2**	**MZ3**	**MZ4**	**MZ5**
7	117.6	115.7	388.1	220.4	127.8	166.1	137.4	504.6	353.3	128.9
14	86.8	72.2	388.5	485.5	108.2	154	135.1	540.2	985.4	97.5
21	135.2	98.8	428.7	261.5	93.7	212.4	184.8	610.2	531.6	96.6
28	297.1	113.7	463.6	274.2	92.7	360.4	186.2	806.2	543.8	108.7
35	302.1	156.8	500.4	303.8	93	413	274.2	725.8	608.1	94.3
42	296.5	310.6	455.1	271.9	63.8	462.8	213.4	627.4	553.2	62.1
49	346.2	168.4	469.6	281.8	71.2	489.9	259.4	645.4	593.4	136.7
56	391.8	206.3	491.2	291.1	129.5	581.7	306.3	660	667.4	80.5
63	450.4	212.8	483.9	289.9	80.5	614.5	311.4	685.8	686.7	142.5

The maximum of Ca ions concentrations (985.4 mg/L) was measured in leachate of sample MZ4 ($MgSO_4$ with the concentrations of 3 g/L of SO_4^{2-}) after 14 days of exposition as it is seen in Table 5. The concrete samples of type MSF were found to have better leaching performance of calcium ions in all aggressive environments than concrete samples of type MZ (comparing MSF1 to MZ1, MSF2 to MZ2, etc.), except samples: MZ2 after 42 days of exposition and sample MZ5 after 14, 42 and 56 days of exposition as it can be seen in Table 5.

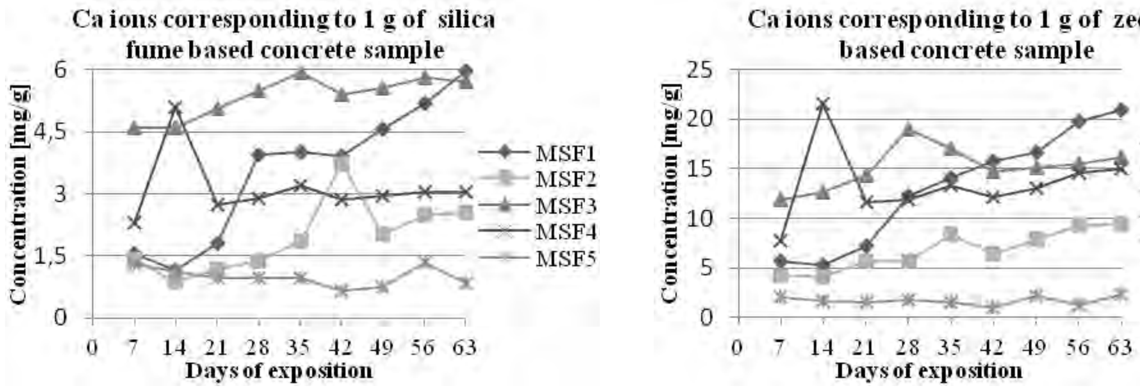
Mass of released ions of silicon and calcium corresponding to 1 g of concrete sample is illustrated in Figure 1 and 2.



a *b*

Fig. 1. Released ions of silicon corresponding to 1 g of concrete sample

The leaching of silicon ions calculated to 1 g of concrete sample was much higher for concrete samples of type MZ compared to the samples MSF as it can be seen in Figu re 1 a) and b).



a *b*

Fig. 2. Released ions of calcium corresponding to 1 g of concrete sample

The mass of calcium ions released corresponding to 1 g of concrete samples was measured much higher for MZ type samples than for MSF samples except for sample MZ5 after 56 days of exposition (Figure 2b).

Conclusion

Natural pozzolans (zeolite and silica fume) based concrete samples were investigated in various sulphate environments. 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. The higher resistance of zeolite based concrete samples was not confirmed.

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