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Section: Environmental protection

Effectiveness of addition of silica fume as a waste material on durability of cement composites

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Abstract

The papers presents the results of the comparative study of resistance of cement composites with and without addition of silica fume (SF) exposed to the sulphate environment. The concrete samples were exposed to the various liquid media: fresh water, sulphuric acid with pH 3 and 4.2 and magnesium sulphate solution with the concentrations of 3g/L and 10 g/L, respectively. The laboratory experiment proceeded during 270 days under model conditions. A laboratory study was conducted to compare the performance of concrete samples in terms of the concrete deterioration influenced by the leaching of calcium and silicon compounds from the cement matrix. The changes in the elemental concentrations of calcium and silicon in both solid samples and liquid leachates were measured by using X–ray fluorescence method.
Experimental studies confirmed that silica fume based concrete samples were found to have better performance in terms of both silicon and calcium ions leaching. The calcium ions in leachates of concrete samples without silica fume were 1.04 to 1.62 times higher than in leachates of concrete samples with silica fume. Released amount of silicon ions from samples without silica fume addition was 1.03 to 1.47 times higher. The most significant difference between released silicon ions from concrete samples without/with SF was observed for samples exposed to magnesium sulphate solution in opposite to calcium ions where the most significant difference was observed for samples exposed to sulphuric acid. The calculated Si/Ca ratios in leachates varied from 0.404 to 16.267 in dependence on the medium.

Keywords: Silica fume; waste material; durability; concrete.

Nomenclature

SCMs	supplementary cementing materials
SF	silica fume
XRF	X-ray fluorescence analysis

1. Introduction

Concrete is the most widely used construction material because of its availability of raw materials, versatility, economy, strength, and durability. Concrete can be designed to withstand the harshest environmental conditions while taking on the most inspirational and imaginable shapes and forms [1]. Scientist/Engineers and academicians are continuously working for better concrete from strength and durability standpoint with the help of innovative chemical admixtures and supplementary cementing materials (SCMs). In addition, the use of SCMs conserves energy and has environmental benefits because of reduction in carbon dioxide emission as a result of reduction in manufacture of Portland cement [2–4].

Typical examples are fly ash, silica fume (SF), ground granulated blastfurnace slag, metakaolin, rice husk ash and natural pozzolans which can be used incorporated in concrete addition or as partial cement replacement [5–6].

1.1. Silica fume

Silica fume is obtained as a by-product during the manufacturing process of elemental silicon and ferrosilicon alloys [7]. The reduction of high-purity quartz to silicon at temperatures up to 2,000 ^{o}C produces SiO_2 vapours, which oxidizes and condense in the low temperature zone to tiny particles consisting of non-crystalline silica. By-products of the production of

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silicon metal and the ferrosilicon alloys having silicon contents of 75% or more contain 85–95% non-crystalline silica. The by-product of the production of ferrosilicon alloy having 50% silicon has much lower silica content and is less pozzolanic. Therefore, SiO_2 content of the silica fume is related to the type of alloy being produced. Silica fume is also known as micro silica, condensed SF, volatilzed silica or silica dust enhancing the mechanical properties to a great extent [8].

Addition of SF to concrete improves the durability of concrete through reduction in the permeability, refined pore structure, leading to a reduction in the diffusion of harmful ions, reduces calcium hydroxide content which results in a higher resistance to sulphate attack [9-13].

SF particles are extremely small, with more than 95% of the particles finer than 1 μm. SF is composed primarily of pure silica in non-crystalline form (Fig. 1) [8].

Fig. 1. Silica fume [8]

Because of its extreme fineness and very high amorphous silicon dioxide content, silica fume is a very reactive pozzolanic material. As the Portland cement in concrete begins to react chemically, it releases calcium hydroxide. The SF reacts with this calcium hydroxide to form additional binder material called calcium silicate hydrate which is very similar to the calcium silicate hydrate formed from Portland cement. It is an additional binder that gives silica-fume concrete its improved properties. Mechanism of SF in concrete can be studied basically under three roles [8]:

- Pore-size Refinement and Matrix Densification.
- The presence of silica fume in the Portland cement concrete mixes causes considerable reduction in the volume of large pores at all ages. It basically acts as filler due to its fineness and because of which it fits into spaces between grains in the same way that sand fills the spaces between particles of coarse aggregates and cement grains fill the spaces between fine aggregates grains.
- Reaction with Free-Lime (From Hydration of Cement) CH crystals in Portland cement pastes are a source of weakness because cracks can easily propagate through or within these crystals without any significant resistance affecting the strength, durability and other properties of concrete. SF which is siliceous and aluminious material reacts with CH resulting reduction in CH content in addition to forming strength contributing cementitious products which in other words can be termed as ''Pozzolanic Reaction''.
- Cement Paste–Aggregate Interfacial Refinement.
- In concrete the characteristics of the transition zone between the aggregate particles and cement paste plays a significant role in the cement-aggregate bond. SF fume addition influences the thickness of transition phase in mortars and the degree of the orientation of the CH crystals in it. The thickness compared with mortar containing only ordinary Portland cement decreases and reduction in degree of orientation of CH crystals in transition phase with the addition of silica fume. Hence mechanical properties and durability is improved because of the enhancement in interfacial or bond strength. Mechanism behind is not only connected to chemical formation of C–S–H (i.e. pozzolanic reaction) at interface, but also to the microstructure modification (i.e. CH) orientation, porosity and transition zone thickness) as well [8].

Several authors have studied experimentally the effectiveness of addition of SF as a waste material on durability of cement composites under different environmental conditions.

According to ACI Committee 234 [14], the effect of SF on sulphate resistance is due more to the reduction in permeability than to dilution of the C_3A content because of the relatively low doses of silica fume used in practice.

Sellevold and Nilsen [15] reported field studies of concretes with and without 15% SF. After 20 years exposure to ground water containing 4 g/L sulphate and 2.5–7.0 pH, the performance of the silica fume concrete was found equal to that of the concretes made with sulphate-resisting Portland cement, even though the water/cementitious materials ratio was higher for silica fume concrete (0.62) than for control (0.50).

Cohen and Bentur [16] studied the effect of 15% SF replacement of Types I and V Portland cement on the resistance to sulphate attack in magnesium and sodium sulphate solutions. The water-cementitious materials ratio was 0.3. In the sodium sulphate solutions, the silica fume concrete specimens were resistant to sulphate attack. In the magnesium sulphate solutions, all the specimens expanded, with the Type I cement specimens (with or without silica fume) expanding more than Type V cement specimens (with or without silica fume). Since specimens were thin (6 mm), the authors attributed the effect of SF on sulphate resistance more to chemical effects than to reduced permeability.

In this paper, the resistance of concrete based on SF as added cementitious material has been investigated in various sulphate environment. A laboratory study was conducted to compare the performance of concrete containing SF in terms of the concrete deterioration influenced by leaching of calcium and silicon compounds from the cement matrix.

2. Material and methods

2.1. Concrete samples

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

Two mixtures of concrete (MA and MSF) 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 in accordance with STN EN 206-1. Mix proportions with appropriate water to cement ratio w/c for concrete with above mentioned specifications are in Table 1.

Table 1: Mix proportions of two different concrete mixtures.

	Components							
Mixture	Cement	Water	Silica fume	Fr. 0/4 mm	Fr. 4/8 mm	Fr. 8/16 mm	Plasticizer	w/c ratio
MSF	360 kg	200 L	20 kg	800 kg	235 kg	740 kg	3.1 L	0.49
MA	360 kg	170 L	-	825 kg	235 kg	740 kg	3.1 L	0.47

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 prepared concrete samples were exposed to the various liquid media:

- 1 - sulphuric acid with pH of 3 (samples MSF1 and MA1),
- 2 - sulphuric acid with pH of 4.2 (samples MSF2 and MA2),
- 3 - magnesium sulphate solution with SO42- concentrations of 10g/L (samples MSF3 and MA3),
- 4 - magnesium sulphate solution with SO42- concentrations of 3g/L (samples MSF4 and MA4) and
- 5 - fresh water with pH of 7.2 (samples MSF5 and MA5).

The ratio of concrete sample volume to liquid phase was set to 1:10. pH value of sulphuric acid solutions was kept on constant level of 3 and 4.2, respectively. The exposition of concrete samples to various liquid media proceeded during 270 days at laboratory temperature of 23 °C. Once a 7-day period, the change in pH as well as the released concentration of calcium and silicon were measured in leachates.

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) using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses. 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

The percentage of the major elements which the concrete samples were consisted of before the experiment is illustrated in Table 2 in oxides form.

Table 2: Basic components of the studied materials (% mass)

Sample	Oxides (% mass)								
	CaO	SiO_2	Al_2O_3	Fe_2O_3	P_2O_6	MgO	MnO	K_2O	SO_3
MSF	26.17	45.63	5.39	3.748	0.094	2.727	0.364	0.794	2.718
MA	31.27	30.16	5.21	4.037	0.096	3.040	0.375	0.766	2.889

Measured Si and Ca ions concentration in liquid media of samples during the 270 days of the experiments are illustrated in Figures 2–4.

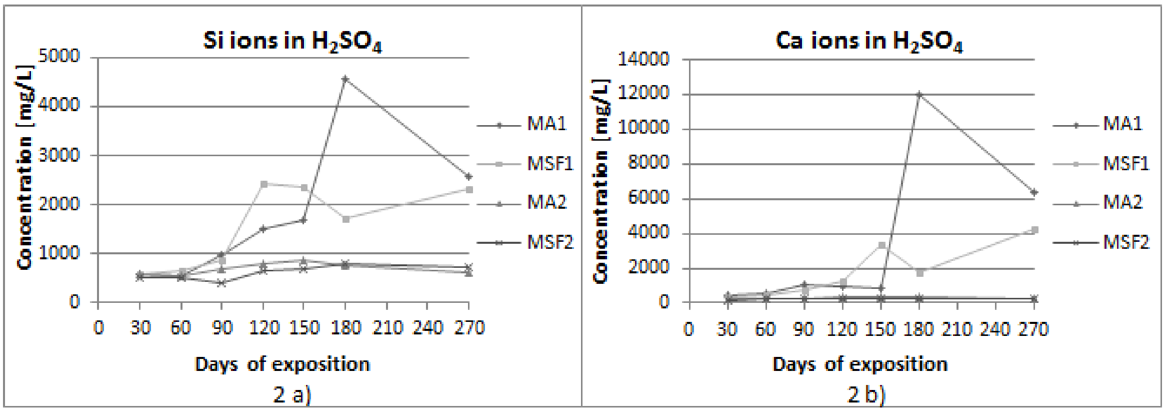

Fig. 2. Silicon (2a) and calcium (2b) ions released into sulphuric acid environment during the experiment

The concentrations of ions in sulphuric acid environment ranged from 388.1 to 4555 mg/L and from 302.1 to 12 040 mg/L for Si and Ca, respectively during the experiment with the strong peak after 180 days of the experiment beginning. The concentrations of both ions in sulphuric acid with pH of 4.2 reached lower values compared to sulphuric acid with pH of 3. Thus sulphuric acid with pH of 3 has been confirmed to be more aggressive environment in terms of both ions releasing when comparing to sulphuric acid with pH of 4.2, as assumed. This corresponds to the other authors results [18–19].

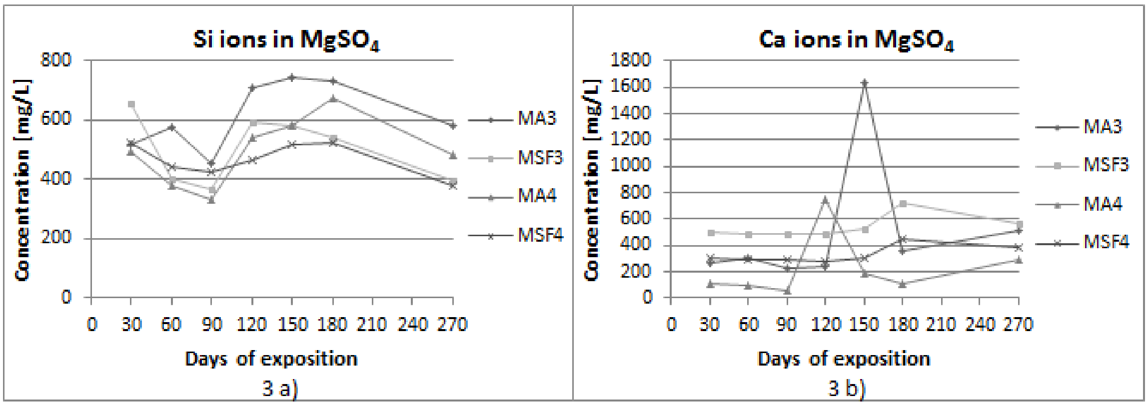

Fig. 3. Silicon (3a) and calcium (3b) ions released into magnesium sulphate solution during the experiment

The concentrations of measured ions in magnesium sulphate environment ranged from 332.9 to 745.7 mg/L and from 57.1 to 1634 mg/L for Si and Ca, respectively. Similarly as for sulphuric acid, more concentrated magnesium sulphate solution was confirmed to have more significant influence to silicon and calcium ions releasing.

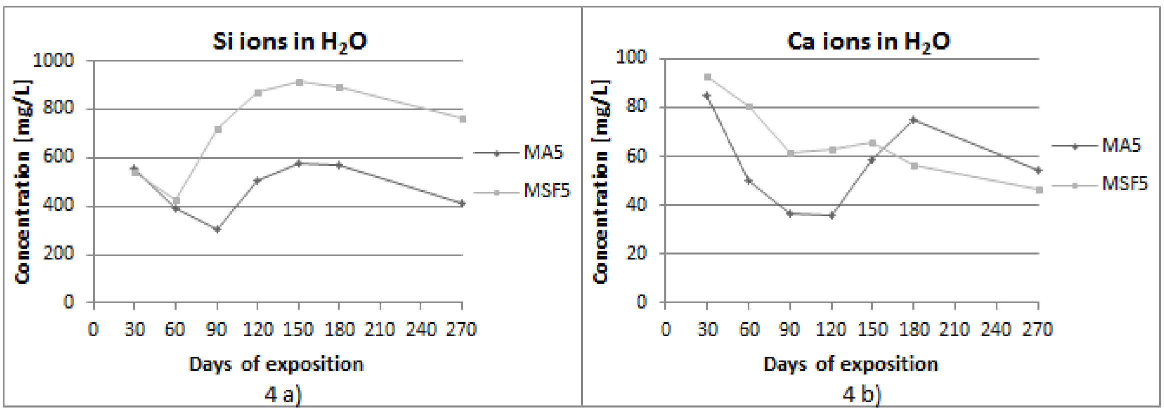

Fig. 4. Silicon (4a) and calcium (4b) ions released into water environment during the experiment

As it is seen in Fig. 4a, the minimum concentration of silicon ions released into water environment has been measured of 304.1 mg/L while maximum concentration reached value of 891.9 mg/L. Calcium concentration in water ranged 35.5 to 93 mg/L.

Considering the samples composition - with/without silica fume addition, maximum of silicon ions concentration released from concrete samples without SF was measured in leachate of sample MA1 (4555 mg/L) after 180 days of exposition, the minimum of silicon ions concentration in leachate of sample MA5 (304.1 mg/L) after 90 days of exposition as it is seen in Figures 2a and 4a. The concentrations of Si ions in liquid leachates of samples with SF reached the values from 366.6 mg/L (in leachate of sample MSF3 after 90 days of exposition) to 2417 mg/L (in leachate of sample MSF1 after 120 days of exposition).

The calcium ions in leachates of samples without SF ranged from 35.5 mg/L (in leachate of sample MA5 after 120 days of exposition to fresh water) to 12040 mg/L (in leachate of sample MA1 after 180 days of exposition to H_2SO_4 with pH of 3) as it can be seen in Fig. 2b. The highest concentration of released Ca ions in leachates of concrete samples with SF was noticed in leachate of sample MSF1 (4285 mg/L) after 270 days of exposition.

Masses of released ions of silicon (mg) after the experiment (270 days) corresponding to 1 g of concrete sample are presented in Figure 5.

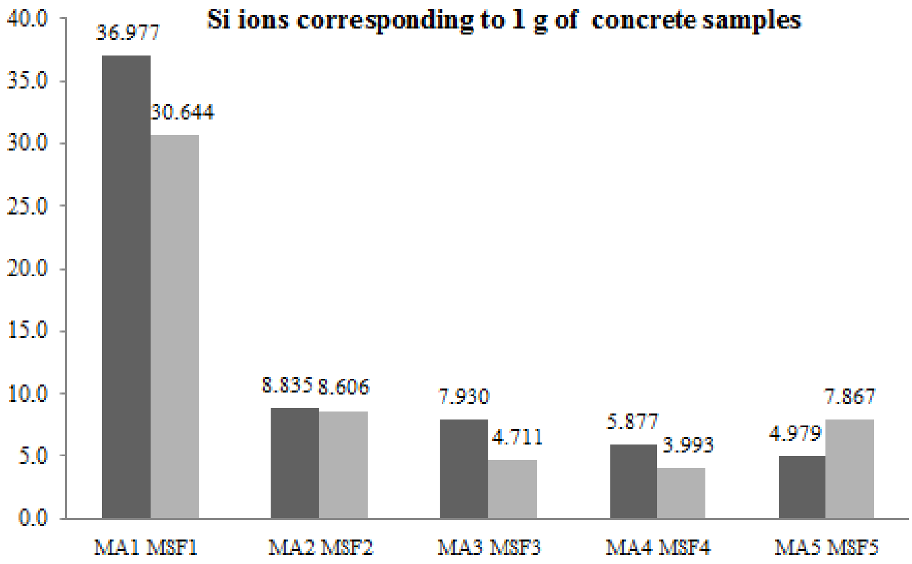

Fig. 5. Comparison of released Si ions after 270 days of exposition (mg/g)

Comparing the concrete samples with and without SF, more significant releasing of Si ions was noticed from all samples without SF except for samples exposed to water (Fig. 6). Released amount of silicon from samples without SF addition was 1.21, 1.03, 1.68 and 1.47 times higher for sulphuric acid with pH of 3 and 4.2 and magnesium sulphate solution with SO_4^{2-} concentrations of 10 and 3 g/L, respectively. As assumed, samples with addition of SF were confirmed to be more resistant in aggressive environment compared to samples without SF. This finding corresponds to the results of other researchers [15, 16]. The most significant difference between released silicon ions from concrete samples without /with SF was observed for samples exposed to magnesium sulphate solution (media 3 and 4).

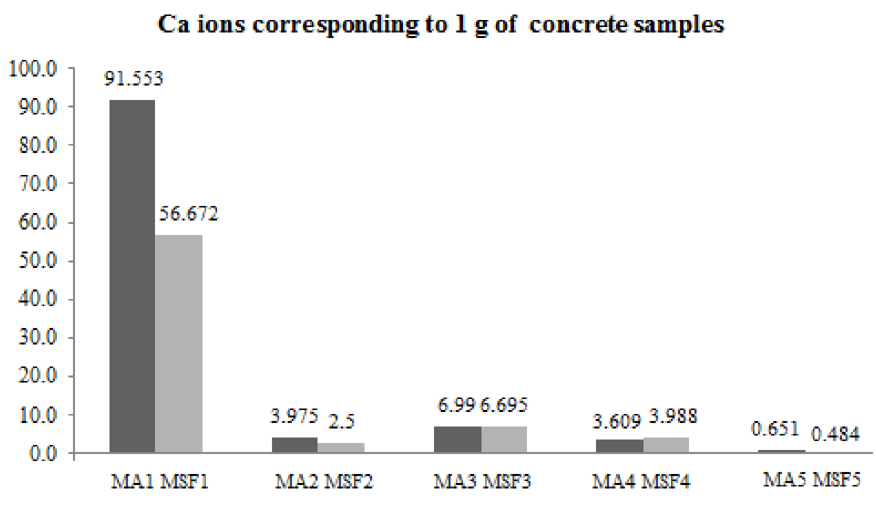

Fig. 6. Comparison of released Ca ions after 270 days of exposition (mg/g)

Calculated concentrations of calcium ions (mg) released from concrete samples after 270 days of experiment corresponding to 1 g of concrete sample are illustrated in Figure 6.

Similarly, the concentration of released Ca ions in leachates was observed to be lower for samples with SF addition except for sample MSF4 (magnesium sulphate solution with SO_4^{2-} concentrations of 3g/L) as it can be seen in Figure 2. The calcium ions in leachates of concrete samples without SF were 1.62, 1.59, 1.04, 1.35 times higher than in leachates of concrete samples with SF. On the other hand, Hekal *et al.* [17] reported that partial replacement of Portland cement by SF (10–15%) did not show a significant improvement in sulphate resistance of hardened cement pastes. Opposed to silicon ions, the most difference between released calcium ions from concrete samples without /with SF was observed for samples exposed to sulphuric acid (media 1 and 2).

The calculated silicon/calcium ions ratios in liquid leachates after the experiment (270 days) ranged from 0.404 – 7.654 for the samples without SF addition and from 0.541 – 16.267 for the samples with SF addition. Analysing the Si/Ca ratios, the releasing of calcium ions comparing to silicon ions dominated in sulphuric acid environment of pH of 3 for both samples without and with silica fume as well as in magnesium sulphate solution with SO_4^{2-} concentrations of 10 mg/L what is manifested by the Si/Ca ratios lower than 1 (Figure 7). Silicon ions releasing dominated in all other media for both types of samples.

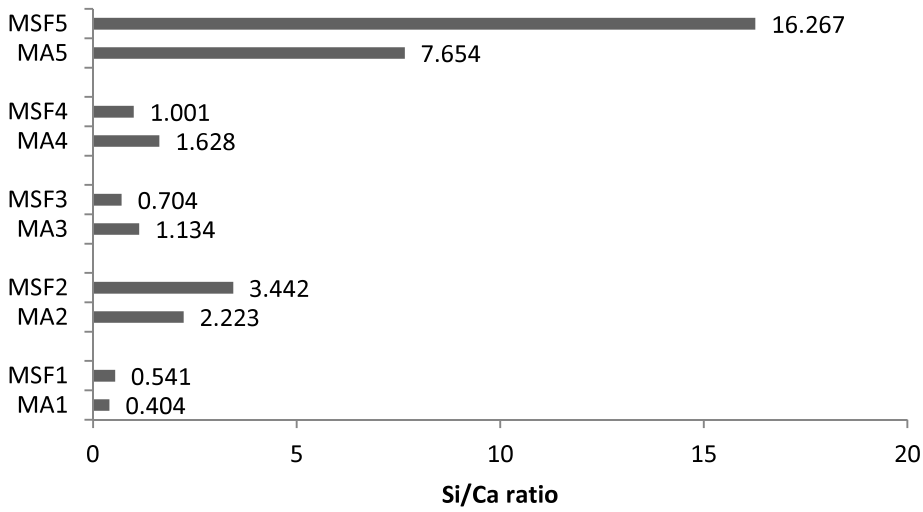

Fig. 7. Comparison of Si/Ca ratios of samples without/with silica fume

Regarding to the equivalent ratios for samples without/with silica fume addition illustrated in Figure 7, much intensive releasing of silicon ions was observed after the exposition of silica fume based samples to water environment compared to non-silica fume samples (16.3 versus 7.7). Similar trend was observed for both sulphate acid environments (with pH of 3 and 4.2). On the contrary, less intensive releasing of silicon ions has been found out for silica fume based samples in both magnesium sulphate environments.

4. Conclusion

The study was aimed at confirmation the importance of silica fume additives as a waste material in order to prolonging the lifetime of concrete and the environment deterioration reduction. Silica fume based concrete samples were investigated in various sulphate environments. Summarizing the results:

- sulphuric acid with pH of 3 has been confirmed to have the most significant influence to silicon and calcium ions releasing, as assumed;
- more concentrated magnesium sulphate solution was confirmed to be more aggressive in terms of both ions releasing;
- more significant releasing of Si ions was noticed from all samples without SF except for samples exposed to water;
- released amount of silicon from samples without SF addition was 1.21, 1.03, 1.68 and 1.47 times higher than from SF based samples for sulphuric acid with pH of 3 and 4.2 and magnesium sulphate solution with SO_4^{2-} concentrations of 10 and 3 g/L, respectively;
- the concentration of released Ca ions in leachates was observed to be lower for all samples with SF addition except for one sample;
- calcium ions in leachates of concrete samples without SF were 1.62, 1.59, 1.04, 1.35 times higher than in leachates of concrete samples with SF;
- different leaching behaviour of silicon and calcium was observed;

- releasing of calcium ions comparing to silicon ions dominated in sulphuric acid environment of pH of 3 for both samples without and with silica fume as well as in magnesium sulphate solution with SO_4^{2-} concentrations of 10 mg/L for silica fume based sample ;
- silicon ions releasing dominated in water environment, sulphuric acid environment of pH of 4.2 for both of samples.

Concluding the results, the higher resistance of silica fume based concrete samples has been confirmed.

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