

# Study of sulphate corrosion simulations on concrete composites

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**Abstract** — The paper is focused on the investigation of the influence of aggressive sulphate environment on the concrete material. The concrete specimens with coal fly ash addition as well as without coal fly ash were studied. The aggressive environment was represented by sulphuric acid and aluminium sulphate solution. Water environment was also used as reference medium. The experiments proceeded during the five 7-days cycles. The pH values and chemical composition of leachates were measured and evaluated after each cycle. Concrete specimens visual changes as well as the weight changes were observed at the end of experiments. The higher resistance of concrete samples with the addition of 5% and 10% of coal fly ash to the aggressive environment wasn't confirmed.

**Keywords** — aggressive environment, aluminium sulphate, coal fly ash, concrete corrosion, sulphuric acid, X-ray fluorescence spectrometry

## I. INTRODUCTION

**I**N the last decades several concrete structures have shown severe durability problems. Existing evidence [1, 2, 3] has shown that in many concrete structures exposed to aggressive aqueous environments corrosion problems are present. Especially in places like sewage, underground and hydraulic structures, chemical plants, industrial structures, liquid-containing structures, agricultural structures or marine environments, where these problems are very well visible. In [4] various hull construction materials were analyzed and the results showed that the corrosive effect increased with water

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content, and that the influence of chloride and sulphate concentration, and to a lesser extent, particle size distribution, is dependent on the quantity of moisture. Additives and admixtures are used to improve the properties of the concrete [5]. Coal fly ash (hereafter referred to as “fly ash”) is a naturally-occurring product of the coal combustion process. It is nearly identical in composition to volcanic ash. When mixed with calcium hydroxide, it has many of the same properties as cement. Replacing a portion of the cement with fly ash creates a cement material that, when used as an input with aggregates, water and other compounds, produces a concrete mix that is well-suited to road, airport runway and bridge construction. Fly ash concrete has a number of very significant, well-documented benefits that make it a mixture of choice for many state and local transportation departments and transportation engineers. It is more durable, yet less expensive than other traditional portland cement blends. Fly ash concrete has also been praised for its environmental benefits as a “green” building material—putting to use an energy production byproduct that reduces the demand for carbon-intensive portland cement and requires less water in the hydration process [6]. According to [7] developing a sustainable application for fly ash in agriculture should reduce the need for its disposal in landfill, while saving farmers at least 30% the cost associated with treating the soil using lime. Using fly ash to replace portland cement in concrete not only provides the benefit of recycling fly ash, but also reduces emissions and energy that would have been used to make the higher volume of cement [6].

On the other hand new concrete types have been developed over the last years, such as high and ultra strength concrete, self compacting concrete, high volume fly ash concrete, etc. Using of suitable test methods and analysis of basic characteristics of tested material is necessary for better understanding of solving problem and can be very helpful in cases of durability prediction. Existing test methods can be classified in different ways. In most cases, the classification is as following [8]: a) according to the type of aggressive species, b) according to the aggressive environment, c) according to the scale of the test methods, d) according to the combination with mechanical action or not, d) according to parameters to accelerate degradation in simulation tests, e) according to the way of measuring the degradation of specimens, f) other important points to be considered (effect of age of test specimens). While a fly ash content of less than 25% of the total cementitious content is used in concrete, high volumes of

fly ash (HVFA) are not commonly used due to perceived lower early-age strengths [9]. The objectives of this research was to demonstrate, using maturity based modeling, that the beneficial effects of high in-place hydration effects observed in structural elements may be able to compensate for the slower rate strength gain of class F fly ash concrete.

In this paper the influence of  $H_2SO_4$ ,  $Al_2(SO_4)_3$  and distilled water as a comparative medium on the concrete composites with/without coal fly ash replacement were studied and consequently evaluated. Previous investigations of fly ash exploitability as a partial cement replacement (max. 15 %) into the concrete cover of pavement were previously published in [10]. The analysis of the resistance of the cement composites with coal fly ash replacement against biological attack was also investigated in [11,12]. Other studies of these samples were aimed on economic calculation of the financial benefits of partial fly ash utilization in concrete road with orientation to building companies [13].

In this paper there was studied the chemical composition of concrete samples (solid material) as well as chemical composition of liquid phase of leachates before and after experiment of sulphate corrosion simulation by the X-Ray fluorescence analysis. The same method is usually used not only in the field of concrete buildings materials, but also in case of marbles, ceramics, metal oxides (pigments of works of art and building materials) and pieces of authentic sculptures for determination of several physicochemical quantities, which enables the physicochemical characterization of the heterogeneous surfaces of the solids as it was measured in [14]. Except this method the visual and weight changes as well as the pH values of different kinds of corrosive media were evaluated.

## II. MATERIAL AND METHOD

Experimental part was aimed on study and evaluation of chemical impact and leaching due to aluminium sulphate/sulphuric acid/distilled water influence on concrete samples (with/without coal fly ash replacement). This simulation took place on 9 concrete specimens prepared using different mixtures. Concrete cylinder samples (Fig. 1) of a 32 mm diameter and 15 mm height formed as a drilled core from concrete cube (150x150x150 mm) using drilling mechanism STAM were used for experiment.



Fig. 1: Concrete samples prepared for corrosion experiment

The cylinder specimens were rid of impurity. The composites

without the coal fly ash were prepared according to the classics recipe; in the other cement composites cement was replaced for 5% respectively 10% coal fly ash.

This observation was under way in model conditions and selected liquid media presents 3 models of corrosion:

- distilled water (pH values <5.5 – 6.3>) - corrosion caused by leaching,
- 0.5% solution of  $H_2SO_4$  (pH values <0.9 – 1.0>) - acid corrosion,
- 0.5% solution of  $Al_2(SO_4)_3$  (pH values <0.9 – 1.0>) - sulphate corrosion.

### A. Liquid media

Distilled water of pH 6.25 used in the experiment was prepared using ELGA – PURELA OPTION apparatus in the Laboratory of Institute of Geotechnics, Slovak Academy of Science in Košice. The solution of 0.5 M  $H_2SO_4$  was prepared by dissolving of 98%  $H_2SO_4$  of analytical grade in distilled water. The solution of 0.5 M  $Al_2(SO_4)_3$  was prepared dissolving 171,1 g  $Al_2(SO_4)_3$  and added to 1000 ml. Simulation of leaching process in concrete was made by inserting the concrete specimens into the distilled water, acidic corrosion were simulated using 0.5%  $H_2SO_4$  solution and sulphate corrosion were simulated using 0.5%  $Al_2(SO_4)_3$  as is shown in Table I. CFA in this table stands for coal fly ash.

Table I Characterization of concrete specimens used for the experiment

Concrete specimens					
Distilled water		0.5% $H_2SO_4$		0.5% $Al_2(SO_4)_3$	
1	0% CFA	4	0% CFA	7	0% CFA
2	5% CFA	5	5% CFA	8	5% CFA
3	10% CFA	6	10% CFA	9	10% CFA

### B. Concrete specimens

As it is shown in Table I, concrete specimens without coal fly ash addition (reference specimens 1,4,7) and as well as specimens with addition of 5% (specimens 2,5,8) or 10 % of coal fly ash (specimens 3,6,9) were used for experiment. Used coal fly ash with volumetric weight of 2381 kg/m<sup>3</sup> originates from black coal's burning process in Kosice city heating plant (Teplaren Kosice a.s. TEKO, Slovakia). The coal fly ash was used for cement composite preparation without any modification. The chemical composition of used coal fly ash can be seen in Fig. 2.

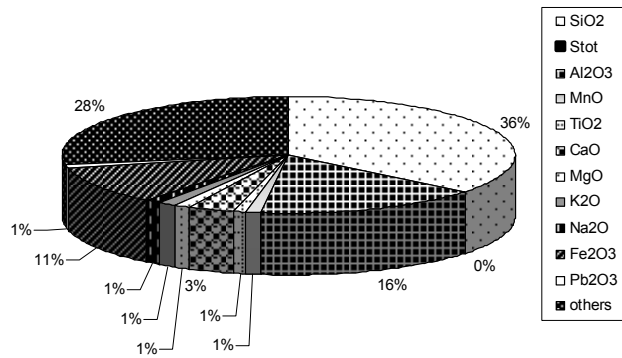


Fig. 2: Chemical composition of coal fly ash

The more detailed information about the chemical compositions of the examined samples is in [11].

### C. Methodology

The volumes of all three liquids in the start of experiment were 20 ml. Experiments ran in 5 consecutive cycles. Each of the cycle consists of 3 phases: 7 days of liquid media effect, 2 days of drying at room temperature and afterwards removing of precipitations by little brush. During the first 7 days of each cycle proceeded the daily pH values measurements of liquid phases.

The weight changes were determined by gravimetric method using analytical balance. Before the weight measurements the specimens were inserted into desiccator and consequently dried to the constant weight.

The visual changes and after experiment of each sample in each media exposed were documented using mineralogical microscope with combination of digital camera Olympus – C-770 Ultra Zoom.

pH changes in leachate were evaluated as differences between initial pH and final pH after the experiment. The values of leachate pH were measured by pH meter PHH – 3X Omega.

The chemical composition of the liquid media was investigated after removing the samples in 7 day-intervals by X-ray fluorescence spectrometry using SPECTRO iQ II (Ametek, Germany) with silicon drift detector SDD 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 liquid samples were measured during 300s at voltage 24.8 kV and current of 1.0 mA under helium atmosphere.

X-ray fluorescence spectrometry was used also for investigation of the chemical composition of the solid cement samples before and after the experiment. The concrete samples were pulverized by using planetary ball miller SFM (MTI corp.,USA) and prepared as pressed tablets of 32 mm diameter by pressing equipment using 10 tons. The tablets were measured at voltage 24.8 kV and current of 1.0 mA and at 48 kV and 0.5 mA, respectively. The standard calibration method of fundamental parameters for cements was used.

## III. RESULTS

The results of the weight changes measurements after 50 day-experiment are presented in Table II (before = before experiment, after = after experiment).

Table II Weight changes of concrete composites

N	weight of sample [g]		change of weight		
	before	after	[g]	[%]	
Distilled water	1	11.18	11.15	↓ 0.03	↓ 0.27
	2	26.05	26.06	↑ 0.01	↑ 0.04
	3	26.26	26.29	↓ 0.03	↓ 0.11
0.5% solution H <sub>2</sub> SO <sub>4</sub>	4	12.53	12.17	↓ 0.36	↓ 2.88
	5	25.49	25.22	↓ 0.27	↓ 1.06
0.5% solution Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	6	26.86	26.2	↓ 0.26	↓ 2.46
	7	11.41	11.47	↑ 0.06	↑ 0.52
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	8	26.54	26.55	↑ 0.01	↑ 0.04
	9	26.19	26.22	↑ 0.03	↑ 0.11

The decreases of weight were determined in all specimens immersed into the 0.5% solution H<sub>2</sub>SO<sub>4</sub> and they ranged from 1.06 to 2.88 %. The most visible decrease of 2.88% was observed for the specimen without coal fly ash replacement immersed to the 0.5% solution H<sub>2</sub>SO<sub>4</sub>. Small increase was measured for sample exposed to 0.5% solution Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> prepared without coal fly ash replacement and it equals to 0.52%. For sample with 5% and 10% replacement immersed into the aluminium sulphate weight increase was from 0.04% to 0.11%, so the changes were not considerably visible. In case of the specimens exposed to distilled water measured weight changes were not significant too.

Together with concrete weight determination the visual changes were observed. Especially in sample 5 (5% coal fly ash replacement immersed in H<sub>2</sub>SO<sub>4</sub>) considerably changes on the concrete surface and color changes were observed. The sample 5 is shown Fig. 3.



Fig. 3: Concrete samples before and after corrosion experiment (immersed into the  $H_2SO_4$ )

The surface before experiment is depicted in the first line of the Fig. 3 and the changes after corrosion process simulation using  $H_2SO_4$  solution are visible in the second line of Fig.3. The white coating and the formation of the orange precipitates is visible.

The similar changes were also found out for sample 4 (0% coal fly ash replacement immersed in  $H_2SO_4$ ) shown in Fig. 4.



Fig. 4: Concrete samples before and after corrosion experiment (immersed into the  $H_2SO_4$ )

In the case in Fig. 4 (sample 4), the creation of white film and the visible iron ions of the top of the composites were confirmed.

The concrete surface of sample with 10% coal fly ash replacement (sample 6) before and after the exposure to the sulphuric acid is shown in Fig. 5.



Fig. 5: Concrete samples before and after corrosion experiment (immersed into the  $H_2SO_4$ )

In Fig. 5, the white coating on the composites surface and

the start of the orange iron precipitates formation is clearly visible.

The pictures of all samples immersed into the sulphuric acid and aluminium sulphate took after the experiment showed the formation of precipitates. White precipitates and miniscule amount of orange precipitates were observed on the non-immersed parts of the samples (the top of the samples and non immersed sides). These parts were immersed into the  $H_2SO_4$  solution, but the media rised by capillary action thought the sample up to the top. The part of samples were „wet“ so the effect of the acid was confirmed. Significant amounts of orange precipitates were discovered on the immersed part of the samples. The most visible creation of the crystals was detected in cases of samples without fly ash addition. For better understanding the determination of chemical composition of concrete sample leachates as well as chemical composition of elements of solid phase is necessary.

Better comparisons with situation when the samples are immersed in the distilled water are shown in Fig. 6.

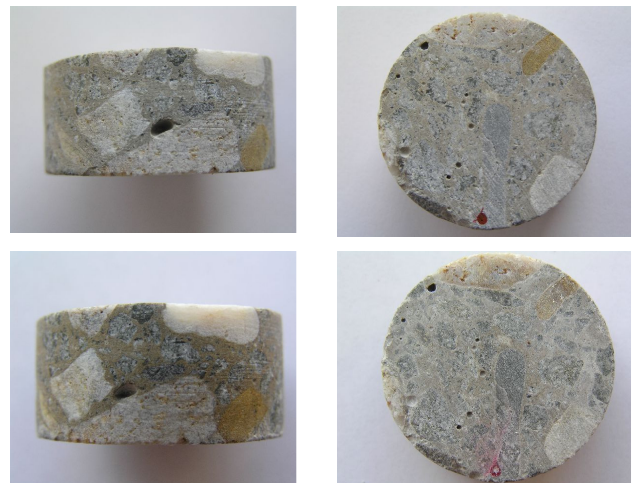


Fig. 6: Concrete samples before and after corrosion experiment (immersed into the distilled water)

It is clearly visible, that after composites were immersed into distilled water no significant changes were observed (first line composites before experiment, second line is after corrosion experiment).

During the all five cycles pH values were measured after first 30 minutes in each leachate for each sample. In Fig. 7 pH values changes during the first cycle are shown.

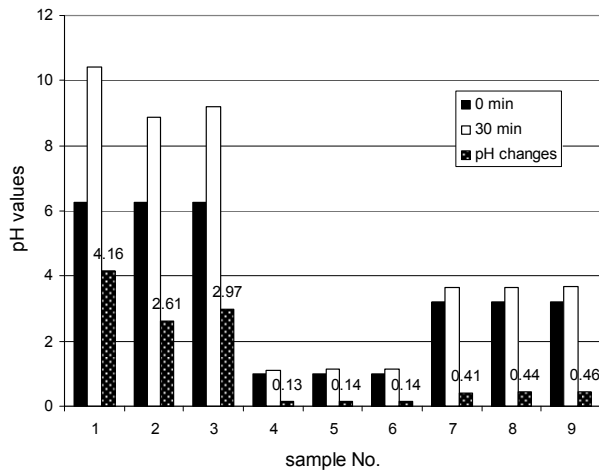


Fig. 7: pH values of the liquid phase after ending the 1-5 cycle with using distilled water

Beginning values of pH was 6.25 for distilled water, 0.99 for sulphuric acid and 3.22 for aluminium sulphate.

In case of first 30 minutes of next cycles (2<sup>nd</sup> – 5<sup>th</sup>) of chemical corrosion simulation the pH values changes has shown similar trend but pH changes were from cycle to cycle smaller and smaller.

During 2<sup>nd</sup> cycle of 0.5% H<sub>2</sub>SO<sub>4</sub> (samples 4, 5, 6) effect pH changes were almost insignificant. The same results were determined for 0.5% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (samples 7, 8, 9).

Final pH values of liquid phases after ending of each cycle for specimens 1,2,3 (immersed in distilled water); 4,5,6 (immersed into H<sub>2</sub>SO<sub>4</sub> solution) and 7,8,9 (immersed in Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution) are shown in Fig. 8, Fig. 9 and Fig. 10.

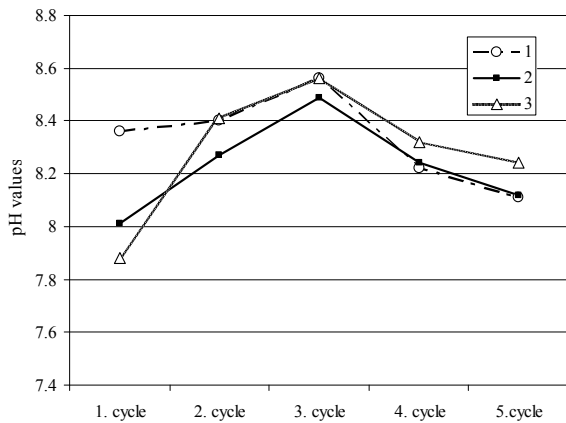


Fig. 8: pH values of the liquid phase after ending the 1-5 cycle with using distilled water

In case of distilled water during the first 3 cycles pH values were increasing. After the last fifth cycle ending leachates of specimens with as well as without reached almost the same pH values: 8.11 (sample 1); 8.12 (sample 2) and 8.24 (sample 3).

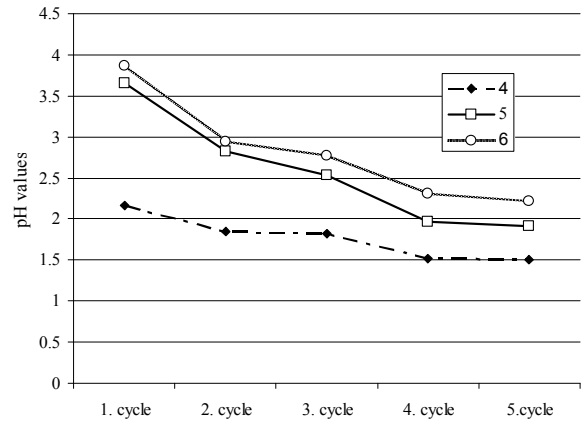


Fig. 9: pH values of the liquid phase after ending the 1-5 cycle with using 0.5% solution H<sub>2</sub>SO<sub>4</sub>

Ending pH values of case of using 0.5% solution H<sub>2</sub>SO<sub>4</sub> as a liquid phase evinced decreasing trend. After the fifth cycle ending the pH value of the leachate of the specimen without coal fly ash replacement has lowest pH (pH = 1.51). The highest pH value was determined for leachate of specimen with 10 % coal fly ash replacement (sample 3; pH = 2.22).

From the Fig. 10 follows that the course of pH values of the sample 7 and 9 is almost the same. pH values in the acid area decrease from 4.5 to 3.8 in this case.

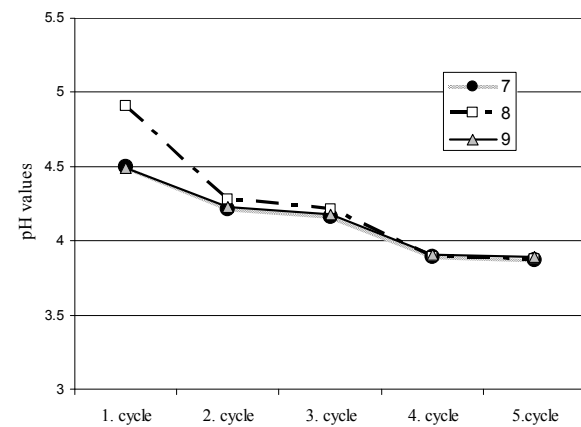


Fig. 10: pH values of the liquid phase after ending the 1-5 cycle with using 0.5% solution Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

From the sample 8 (5% coal fly ash replacement) the start of the pH value were on 4.9 but in the end of the fifth cycle it stopped in the same value as in the case of sample 7 (pH = 3.8).

The concentrations of monitored ions in investigated leachates are presented in the following tables. The concentrations of calcium in leachate after the 5 cycles described above are in Table III. Letter S in the Table III

stands for number of sample, DL – detection limit and No. 1,2,3,4,5 – results after 1, 2,3,4,5 cycle are related to the number of cycle.

Table III Calcium concentrations in leachates [mg/l]

	S	1	2	3	4	5
Distilled water	1	52.1	134.0	104.5	262.1	466.8
	2	127.4	158.3	110.1	277.2	111.4
	3	74.6	137.1	124.5	270.4	475
0.5% H <sub>2</sub> SO <sub>4</sub>	4	710.7	935.4	863.1	1264	620.5
	5	3630	5211	5141	2354	775.8
	6	5545	4516	5526	3579	644.6
0.5% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	7	129.6	733.6	419.9	602.6	411
	8	6792	3204	423.7	491.9	198.4
	9	182.8	861.6	569.6	689.8	516.4

As expected the concentrations of calcium reached the higher values after the concrete samples exposition to the sulphuric acid (from 620.5 to 5545 mg/l) in comparison to the distilled water (from 52.1 to 475 mg/l). The calcium concentrations in aluminium sulphate media were on average measured lower than in sulphate acid but higher than in water. When comparing the samples with and without coal fly ash addition, the samples with the coal fly ash released more calcium into the acidic solution. Very high calcium concentrations were measured for the sample 8 with 5% coal fly ash replacement after the first and second cycle when comparing to the other cycles. The concentrations of the calcium in distilled water are quite similar for all studied samples and the highest values were measured after the fifth cycle.

The silicon concentrations in leachate are summarised in Table IV and aluminum concentration in Table V.

Table IV Silicon concentrations in leachates [mg/l]

	S	1	2	3	4	5
Distilled water	1	164.2	398.8	291.0	575.8	466.8
	2	178.8	475.5	339.4	602.5	460.8
	3	153.8	424.2	307.2	584.2	475
0.5% H <sub>2</sub> SO <sub>4</sub>	4	264.4	528.1	484.9	874.4	644.4
	5	391.2	1171	2078	1793	729.4
	6	788.9	1574	2444	1346	516.4
0.5% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	7	129.6	773.6	419.9	602.6	411
	8	481.5	1005	542.1	613.1	379.9
	9	182.8	861.6	569.6	689.8	516.4

Table V Aluminium concentrations in leachates [mg/l]

	S	1	2	3	4	5
Distilled water	1	41.0	166.4	124.3	241.6	368.6
	2	39.8	192.0	118.1	215.9	205
	3	56.8	193.9	156.7	225.6	241.9
0.5% H <sub>2</sub> SO <sub>4</sub>	4	295.2	462.0	406.0	544.0	492
	5	168	503	565	640	728
	6	208	631	644	621	539
0.5% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	7	135	4027	2500	952	704
	8	4509	5187	3008	1357	769
	9	461	4185	4095	1665	727

The similar trend as in case of calcium was observed for aluminum and silicon. The concentrations determined in acidic solutions were much higher than in distilled water. In case of aluminium and silicon the concentration of ions in both distilled water and sulphuric acid were rising with the portion of coal fly ash addition. The similar extraordinary results as in case of calcium have been observed for sample 8. The concentrations of both aluminium and silicon ions were much higher for sample 8 when comparing the samples with coal fly ash addition in aluminium sulphate environment after the first and second cycle.

The concentrations of iron in liquid media after the cycles of cement samples exposition are illustrated in Table VI.

Table VI Iron concentrations in leachates [mg/l]

	S	1	2	3	4	5
Distilled water	1	under DL	under DL	under DL	under DL	7.3
	2	under DL	under DL	under DL	under DL	6.5
	3	under DL	under DL	under DL	under DL	4.6
0.5% H <sub>2</sub> SO <sub>4</sub>	4	394.4	420.6	450.4	500	473.4
	5	168	503	565	640	510.2
	6	191.5	392.8	466.2	483.1	481.3
0.5% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	7	under DL	7.5	5.2	7.7	6.3
	8	6.1	14.6	7.0	11.8	5.1
	9	under DL	7.7	7.4	6.8	7.1

As seen in Table VI, the concentrations of iron in distilled water were low and under detection limit (DL) after all cycles

except the last. This finding was for all samples without and with coal fly. In acidic solution the concentration of iron ranged from 168 mg/l to 640 mg/l. There were not found any significant differences in iron concentrations in particular cycles apart from the first cycle. In the solution of  $\text{Al}_2(\text{SO}_4)_3$  the concentration of iron increase from values under detection limit up to 14.6 for the sample with 5% of coal fly ash replacement. The distinct behaviour of sample 8 was observed also in case of iron concentrations. The measured concentrations were quite higher than those measured for the other samples.

The comparison of the content of monitored components of the original and deteriorated samples with 10% coal fly ash replacement determined by using X - ray fluorescence analysis XRF is illustrated in the Figure 11. The concentrations of iron oxide, silicon oxide, aluminum oxide, calcium and sulphur oxides before and after the experiment are presented.

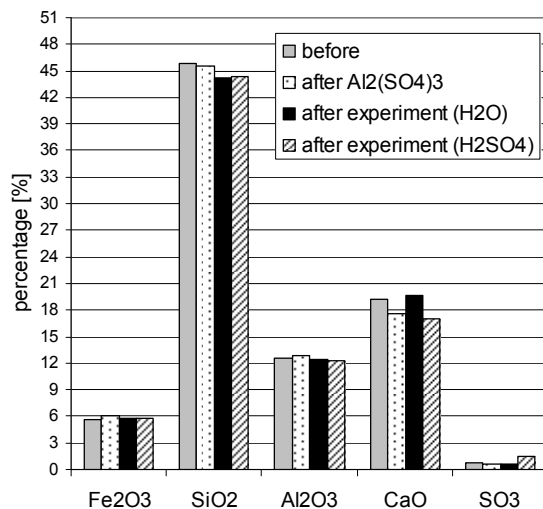


Fig. 11: Chemical composition of concrete sample (samples 3, 6, 9) before and after experiment of sulphate corrosion

Both, the increase and decrease of the ions content in solid concrete samples were observed after leaching and sulphate corrosion. Silicon oxide concentrations have been decreased in all measured samples after the experiment. The concentrations of iron and aluminum oxides increased in case of samples immersed into the aluminum sulphate and decreased in samples immersed into the sulphuric acid and water environment. Lower calcium oxide concentrations have been measured for the samples immersed into the both sulphate solutions, on the other hand raised for the sample investigated in water environment.

#### IV. CONCLUSION

The results presented are the part of the research being carried out within the materialists' research team at Institute of Environmental Engineering of Faculty of Civil Engineering. The influence of the aggressive environment represented by the sulphuric acid on the cement specimens with as well as

without coal fly ash was studied. The higher resistance of concrete samples with the addition of 5% and 10% of coal fly ash to the aggressive environment wasn't confirmed. The weight changes of samples, the pH values changes of the leachates and massive releasing of the major components from the cement matrix was observed after the experiment. For the visual changes observation the precipitation of white coating and orange crystals in case of all samples immersed into the sulphuric acid and aluminium sulphate is detected. These colour elements were observed on the non-immersed parts of the samples (the top of the samples and non immersed sides). It was caused by media risen by capillary action thought the sample up to the top. The part of samples were „wet“ so the effect of the acid was confirmed. The most significant creation of precipitates were discovered on the immersed part of the samples into the sulphuric acid and the most visible creation of the crystals were detected in cases of samples without fly ash addition (sample 4). After the study of visual changes of samples immersed into distilled water no significant changes were observed.

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