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Study of the deterioration of concrete influenced by biogenic sulphate attack

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Abstract

Corrosion is present in many concrete structures associated with water and wastewater treatment, i.e. in sewer systems. The bacterial activity in the sewers creates a sulphur cycle, which can lead to the bacterial formation of sulphuric acid. The sulphate-reducing bacteria, e.g. *Desulfovibrio* spp. and sulphur-oxidising bacteria, *Acidithiobacilli* spp. play very important role in biogenic sulphate attack to the concrete samples. The concrete samples with 10 % of fly ash addition were used for the experiment in both in situ and laboratory model conditions. Experiments proceeded during 90 days and the corrosion process was demonstrated by the changes of the concrete samples surface detected by SEM/EDX. The chemical composition before and after the experiments was investigated by XRF, FTIR and DTA/TG analyses. The significant changes of surface roughness have been observed for all samples after 90-day exposition to the aggressive environment.

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1. Introduction

In 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.

Microorganisms that produce sulphuric acid accelerate the deterioration of concrete sewer pipes in a process termed “Microbially Induced Concrete Corrosion” (MICC) [4]. The theory describing MICC has been under development since 1900, when Olmstead and Hamlin first mentioned it in the literature [5]. Sulphuric acid has been identified as a corrosive agent not only in wastewater treatment plant but also in corroding sewers [6,7].

Concrete sewer corrosion is initiated through a series of steps [8]. First the pH of the alkaline and moist concrete surface is chemically lowered towards a more neutral pH by dissociation of hydrogen sulphide and by carbonation. Hereafter, different neutrophilic sulphide oxidizing bacteria and fungi colonize the concrete surface and contribute to a successive oxidation of reduced sulphur compounds to dissociated sulphuric acid. The last step is characterized by the pH of the concrete surface falling below 2 as acidophilic organisms take over and *A. thiooxidans* becomes the dominating microorganism [9,10]. The sulphuric acid produced by *A. thiooxidans* reacts with the surface of the concrete converting the cementitious material into ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Ettringite is a friable material that forms from the incomplete reaction of sulphuric acid and cement [11]. The cement paste is weakened because calcium to make ettringite is provided by CH and decalcified C-S-H. The sulphate is provided by the source of sulphate that is causing the sulphate attack, e.g. ingressing groundwater containing dissolved sulphate. Therefore two processes occurring at the same time. Cracking is generally due to the expansive pressure caused by growth of ettringite within the cement paste. Weakening of paste by decalcification of the calcium silicate hydrate (C-S-H) that gives concrete its strength causes further damages. Eventually, the concrete disintegrates. Usually, sulphate attack involves a deterioration of the cement paste in the concrete with the aggregate taking no part in the reaction. However, occasionally the aggregate can be the cause of the problem if it contains soluble forms of sulphate. Also the thaumasite is formed of sulphate attack. It requires sources of sulphate and carbonate. Thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$) occurs as a natural mineral as an alteration product of limestone, although it is rare. Thaumasite can form in both concrete and mortar. The normal cement hydration products, mainly calcium silicate hydrate and calcium hydroxide, are decomposed as a result of both sulphate attack and carbonation. Thaumasite itself is a weak and friable material, so when it replaces the calcium silicate hydrate, the concrete is severely weakened [12].

The objective of the experiment was to compare MICC processes proceeded in laboratory conditions to the real conditions of a sewer pipes system with the wastewater representing an aggressive medium. The paper is aimed at the investigation of the concrete deterioration using various analytical methods.

2. Material and Methods

Concrete samples were investigated in terms of the concrete deterioration influenced by both biogenic sulphate attack (in situ experiments) and 0.5 % sulphuric acid exposition (laboratory experiments). The chemical composition and surface changes were studied before and after the experiments using standard analytical methods.

2.1. Concrete samples

The concrete samples used for the experiments were prepared in accordance with the Slovak standard STN EN 206-1 – C35/45 using cement CEM I 42.5 R. The concrete samples were prepared considering the exposure classes (XC2 and XF3) in accordance with standard mentioned above. For concrete preparation plasticizer Murasan BWA 14 was used.

In the coal fly ash based samples, 10 % of cement was replaced by coal fly ash. The used coal fly ash with volumetric weight of 2381 kg.m⁻³ originated from black coal's burning process in Kosice city heating plant (Teplaren Kosice a.s. TEKÖ, Slovakia). The coal fly ash was used for cement composite preparation without any modification. The chemical composition of main component of used coal fly ash was: 36.57 % of SiO₂, 16.06 % of Al₂O₃, 10.82 % of Fe₂O₃, 3.3 % CaO, 1.41 % of K₂O and 1.22 % of MgO.

Concrete cylinder samples of a 32 mm diameter and 15 mm height were formed as a drilled core from concrete cube (150x150x150 mm) using drilling mechanism STAM. All samples have been prepared having the same shape and size. The cylinder specimens were rid of impurity.

2.2. Laboratory experiments

The concrete samples were exposed to the liquid media (distilled water and 0.5 % solution of H₂SO₄) during 90 days at laboratory temperature of 23 °C. The volumes of each liquids in the start of experiment was 20 ml.

2.3. In situ experiments

In situ experiments proceeded in real sewage system by immersing the concrete samples into the waste water during 90 days. The wastewater parameters tested are presented in Table 1. pH value of wastewater was 7.42. The presence of sulphate-reducing and sulphur-oxidising bacteria *Desulfovibrio* spp. and *Acidithiobacilli* spp., respectively were confirmed in the wastewater as reported in our previously work [13]. The bacteria mentioned are responsible for the start and the course of biogenic sulphate attack (MICC) on the concrete samples.

Table 1. Chemical analysis of the waste water

Parameter	(mg/l)
Soluble substances	418.00
Insoluble substances	23.00
Total amount of phosphorus	1.01
Total amount of nitrogen	8.96
Ammonia nitrogen	8.55
Biological Oxygen Demand BOD ₅	17.68
Chemical Oxygen Demand COD (using Cr ₂ O ₇ ²⁻)	45.93

2.4. X – ray fluorescence analysis XRF

Chemical composition of tested concrete samples was investigated 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 concrete samples were pulverized by using planetary ball miller SFM (MTI corp., USA) and prepared as pressed tablets of diameter 32 mm by mixing 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m². The samples were measured during 300 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 cement pellets.

2.5. Infrared analysis FTIR

Infrared spectroscopy with Fourier transformation (FTIR) was used for the concrete samples characterization in terms of functional groups qualitative analysis. FTIR measurements were performed using a Spectrometer Alpha-T (Bruker, Germany) with ATR technique allowing the direct measurements of powder samples without KBr tablets preparation. Measurements proceeded in transmittance mode, in the range 400 – 4000 cm⁻¹ with resolution of 4 cm⁻¹.

2.6. Scanning electron microscopy SEM/EDX

Structural concrete surface changes were observed by electron scanning microscopy (SEM) with equipment Jeol JSM-35CF (Japan). The elemental EDX analysis were carried out on the micro-analytical system LINK AN 10 000 operating in secondary mode at a potential 25 kV and at extension 90-5500.

2.7. Thermal analysis DTA/TG

Thermal properties of prepared concrete composite were studied by using STA 449F3 thermo analyser (Netzsch, Germany) in the temperature range from 25 to 1000 °C with the heating rate of 10 K/min under nitrogen atmosphere using DTA/TG mode. The concrete samples of weight about 13.0 mg were heated in Al₂O₃ crucibles.

3. Results

3.1. XRF analysis

The percentage concentrations of tested concrete samples (CS) by using XRF analysis are summarised in Table 2 in form of oxides. Obviously, the concentrations of studied elements were measured to be lower after the experiments comparing to the reference concrete sample measured before the experiments (except for sulphur, manganese, calcium and iron). The lowest concentrations were detected in case of concrete samples after 90 day waste water exposition. The concentrations of sulphur increased significantly by 3.66 and 1.97 times in samples immersed into waste water and sulphuric acid, respectively (Table 2). The massive increase of sulphur content confirms the presence of biogenic sulphates forming in the waste water environment; the increase of iron concentrations by 1.48 times in concrete samples after waste water exposition is likely caused by other bacteria's activities e.g. *Ferrooxidans*' species occurring in wastewater [14].

Table 2. Chemical analysis of tested concrete samples

(%)	In situ experiment		Laboratory experiment	
	CS before the experiment	CS after waste water exposition	CS after distilled water exposition	CS after H ₂ SO ₄ exposition
Na ₂ O	0.57	less than 0.11	0.51	0.44
MgO	3.59	3.19	3.37	3.27
Al ₂ O ₃	12.56	11.1	12.48	12.24
SiO ₂	45.83	42.37	44.14	44.28
P ₂ O ₅	0.23	0.16	0.17	0.17
SO ₃	0.77	2.84	0.55	1.52
Cl	0.07	0.02	0.07	0.07
K ₂ O	1.38	1.2	1.29	1.27
CaO	19.25	18.0	19.69	17.2
TiO ₂	0.64	0.54	0.62	0.59
MnO	0.15	0.35	0.19	0.17
Fe ₂ O ₃	5.68	8.42	5.77	5.78

Considering the most significant changes in chemical composition detected for the concrete sample exposed to waste water environment, the attention was paid to the investigation of the concrete sample immersed into the waste water and reference sample without corrosion attack.

3.2. FTIR analysis

Qualitative estimation of various functional groups in concrete samples proceeded with infrared analysis FTIR. The transmittances measured relating to the reference concrete sample (before the experiment) and the concrete sample exposed to the waste water are illustrated in Figures 1 and 2.

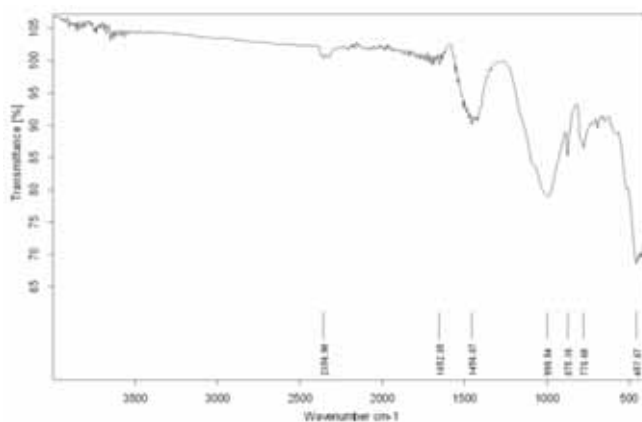


Fig. 1. FTIR spectrum of reference concrete sample

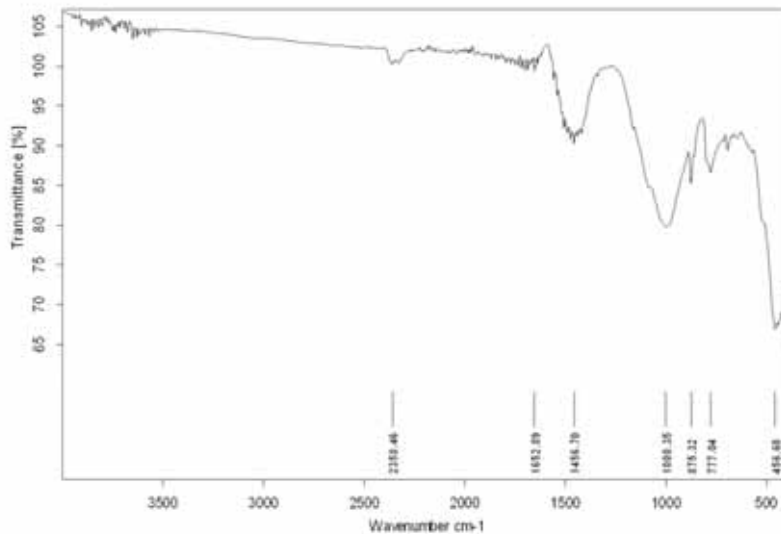


Fig. 2. FTIR spectrum of concrete sample after wastewater exposition

Transmittances associated with the principal concrete functional groups were measured in accordance to the literature [15] e.g. Si-O vibrations at 456 and 777 cm^{-1} ; CO_3 vibrations at 875 cm^{-1} , ettringite at 1456 cm^{-1} etc. When compared the FTIR spectra of measured concrete samples (Figures 1 and 2) no significant changes have been detected after the biocorrosion process.

3.3. SEM/EDX analysis

The morphology of corroded concrete samples surface was observed by scanning electron microscopy (SEM). Plenty of disruption and missing aggregates of concrete were observed. The presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) as surface precipitate product was observed on the concrete sample surface by electron microscopy and detected by EDX analysis as it is illustrated in Figures 3 and 4.

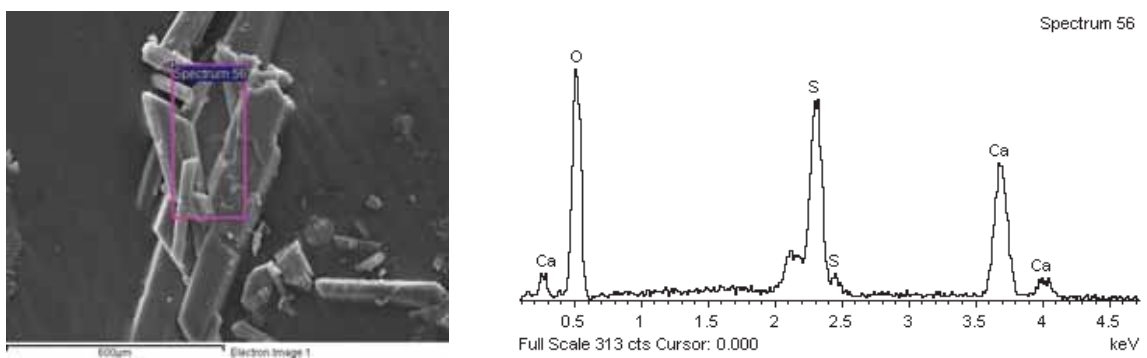


Fig. 3. SEM micrograph and EDX spectrum of gypsum precipitates

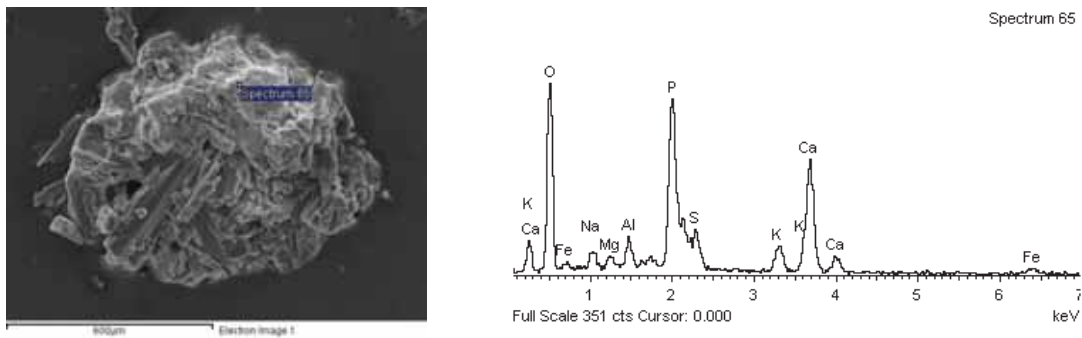


Fig. 4. SEM micrograph and EDX spectrum of ettringite precipitates

3.4. Thermal analysis

Several endothermic processes were detected in the measured concrete samples spectra (Figure 5a). Residual mass after the heating process ranged in close interval from 90.40 to 91.02 % (Figure 5b). No significant differences in peak temperatures were detected for the investigated samples evaluating the endothermic processes (Table 3). The mass changes related to the peaks were also measured to be similar.

Table 3. The peak temperatures of the principal endothermal processes measured

(°C)	Process 1	Process 2	Process 3	Process 4	Process 5
CS before the experiment	119.3	452.2	563.7	753.1	877.5
CS after waste water exposition	105.7	450.7	565.1	752.1	870.0

The comparison of DTA and TG curves related to the reference concrete sample (before the experiment) and concrete sample exposed to the wastewater is illustrated in Figures 5a and 5b, respectively. The green coloured curves belong to the concrete sample after wastewater exposition.

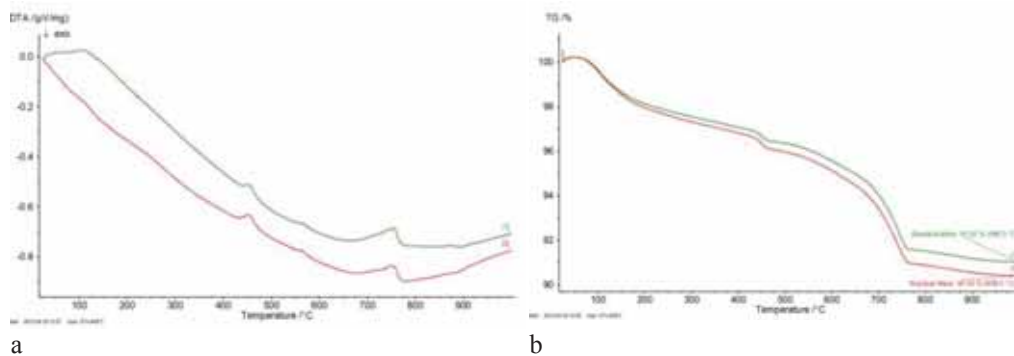


Fig. 5. Comparison of the DTA (a) and TG (b) curves of reference concrete sample before the experiments and concrete sample after wastewater exposition

4. Conclusion

The deterioration effect of biogenic sulphates originating from sewer wastewater as well as sulphate attack in laboratory conditions to the concrete composites was investigated in the study. Based on our previous research which confirmed higher durability of fly ash based composites, the concrete samples with 10 % fly ash addition were investigated by using several analytical methods. The differences in chemical composition of tested concrete composites were measured by XFR. The biggest concentrations changes of basic elements were detected when evaluating the sample exposed to the wastewater. Presence of both ettringite and gypsum precipitates on the concrete surfaces was confirmed by SEM/EDX. No significant differences in tested samples values were measured by both FTIR and DTA/TG methods.

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