ZESZYTY NAUKOWE POLITECHNIKI RZESZOWSKIEJ Nr 283
Budownictwo i Inżynieria Środowiska z. 59 (2/12/I) 2012

Vlasta ONDREJKA HARBULÁKOVÁ
Adriana EŠTOKOVÁ
Nadežda ŠTEVULOVÁ
Technical University of Kosice, Civil Engineering Faculty, Institute Environmental Engineering, Vysokoskolska 4, Kosice, SLOVAKIA

Katarina FORAIOVÁ
Slovak Water Management Enterprise, s.c. headquarter Kosice, Komenskeho 50, Kosice, SLOVAKIA

STUDY OF CONCRETE CHANGES CHARACTERISTICS AFTER BIOCORROSION PROCCESSES AFFECTED BY WASTEWATER

Numerous studies have addressed the problem of chloride ingress in concrete structures. However, in addition to sulphate penetration, biological processes can accelerate the deterioration process by modifying severely the structural durability and reliability. In this study, the degree of concrete biocorrosion caused by wastewater from combined sewage (domestic and storm water) was investigated by testing of compressive strength and weight changes. X-ray fluorescence spectrometry was used for determination of chemical composition of the concrete samples before and after the experiment.

1. Introduction

Cementing materials were used widely in the ancient world. The Egyptian used calcined gypsum as cement. The Romans found that cement could be made with set under water and this was used for the construction of harbours. The cement was made by adding crushed volcanic ash to lime, and was later called a "pozzolanic" cement [1].

Deterioration of materials is a common process in structures located in aggressive environments and it is subject to, for instance, sulphate attack, chloride penetration and microorganisms' activity. Numerous studies have addressed the problem of chloride ingress in concrete structures. However, in addition to sulphate penetration, biological processes can accelerate the deterioration process by modifying severely the structural durability and reliability. This aspect is particularly important in marine structures (e.g., ports and offshore platforms), wastewater treatment plants and sewage systems [1, 2].

The normal pH of wastewater in sewage is slightly acidic (pH 5-6). At these pHs, hydrogen sulphide H_2S is dominated sulphide species (pKa=7.05).

Sulphuric acid has been identified as a corrosive agent not only in corroding sewers but also in wastewater treatment plants [3,4]. An attack by sulphuric acid however is a combined acid sulphate reaction with the hydrogen ion causing a dissolution effect, coupled with corrosive role played by the sulphate ion [5,6]. When sulphuric acid reacts with a cement matrix, the first step involves a reaction between the acid and the calcium hydroxide ($Ca(OH)_2$) forming calcium sulphate according to the following equation:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \tag{1}$$

This is subsequently hydrated to form gypsum ($CaSO_4 \cdot 2H_2O$), the appearance of which on the surface of concrete pipes takes the form of a white, mushy substance which has no cohesive properties and has, "the consistency of cottage cheese" [7]. In the continuing attack, the gypsum would react with the calcium aluminates hydrate (C_3A) to form ettringite, an expansive product.

Hydrogen sulphide formation is a microbial process taking place under anaerobic conditions. When dissolved oxygen and nitrate in wastewater of sewer systems are depleted, sulphate-reducing bacteria use sulphate as an acceptor in their use of wastewater organic matter (organic carbon) as substrate. This process results in the formation of hydrogen sulphide.

H_2S is poorly soluble in water and will diffuse into the headspace of the sewer based on Henry´s law. The H_2S is converted to HS^- or S^{2-} at these pHs, which pulls more H_2S into the condensate layer. In the presence of oxygen the sulphide species will react to form partially oxidized sulphur species such as thiosulphate, elementary sulphur and polysulphate species. These reactions will provide additional driving forces to pull more H_2S into the condensate layer.

Our previous work was aimed at study of the biocorrosion degree of concrete samples exposed to the model conditions [8, 9].

In this paper, the weight changes and compressive strength of concrete material exposed to the real wastewater from gravitational combined sewage system were studied. Changes in chemical composition after the exposition of concrete samples to aggressive environment were also investigated.

2. Material and methods

The concrete samples used for the experiments were prepared in accordance with 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 were used.

12 concrete samples of sizes 150x150x150 mm prepared for the experiment were divided into 4 sets; each containing of 3 concrete samples

(Fig. 1). Set 1 was intended as reference set without exposure to wastewater. Concrete samples of sets 2 – 4 were placed into the sewer wastewater for 6, 12 and 18 month, respectively (Table 1). The strength parameters and weight changes were evaluated as an average value from 3 concrete samples.

Table 1. Characterisation of studied samples

Set of samples No.	Time of exposition [months]
S1	0
S2	6
S3	12
S4	18

Fig. 1. Concrete samples prepared for the sewer system experiment

Table 2. Chemical analysis of wastewater from combined sewage system

Parameter	
pH	7.42
Soluble substances	418.00 mg/l
Insoluble substances	23.00 mg/l
Total amount of Phosphorus	1.01 mg/l
Total amount of Nitrogen	8.96 mg/l
Ammonia Nitrogen	8.55 mg/l
Biological Oxygen Demand BOD_5	17.68 mg/l
Chemical Oxygen Demand COD (using $Cr_2O_7^{2-}$)	45.93 mg/l

The parameters of wastewater (Table 2) from gravitational combined sewage (domestic and storm water) were tested in Laboratories of Wastewater in Koksov Baksa, Slovak Water Management Enterprise, s.c. headquarter Kosice.

The weight changes were determined by gravimetric method using laboratory balance. Samples were weighed before the experiment started. After the end of the period of placement, specimens were cleaned of wastewater sediment and consequently dried to the constant weight. After these procedures, the weights of concrete samples were again measured.

Compressive strength value of reference samples were measured at the concrete cubes (150 mm x 150 mm x 150 mm) after 28 days of hardening; other samples were tested after taken out the sewerage (using an ELE ADR 2000 equipment). All samples were evaluated according to the STN EN 206.

Fig. 2. Concrete samples after compressive strength testing

X-ray fluorescence method was used for investigation of the chemical composition of the concrete 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 mixing of 5 g of concrete powder and 1 g of special material and follows by pressing at pressure of 0.1MPa.m^{-2}. The tablets were measured 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 samples were measured during 300 s at voltage of 25 kV and 50 kV respectively, at current of 0.5 and 1.0 mA under helium atmosphere by using the standardized method of fundamental parameters for cement pellets.

3. Results and discussion

The results of the weight changes measurements after 6, 12 and 18 months of sewage wastewater exposition are presented in Table 3.

Table 3. Weight changes of concrete samples

Set of samples No.	Weight before the experiment [kg]	Weight after the experiment [kg]	Weight changes	
			[kg]	[%]
S1	7.80	7.80	0.00	0.00
S2	7.75	7.89	↑ 0.14	↑ 1.81
S3	7.70	7.65	↓ 0.05	↓ 0.65
S4	7.65	7.52	↓ 0.13	↓ 1.70

Considering the first set of samples S1 was not be exposed to wastewater no weight changes were observed. The increase of weight by 1.81 % was determined in case of S2 samples immersed into the wastewater for 6 months. That may be caused by precipitation of new crystal products on the samples surface and start of forming the new products in the concrete matrix. In the samples exposed to the aggressive environment for longer time, the process of compounds leaching from cement matrix likely override up the process of surface precipitation and thus the weight loss starts. The average weight of sample set S3, exposed for 12 month, decreased slightly by 0.65 % (Table 3). In case of sample set S4 (exposed for 18 month), much higher decrease of concrete samples weight was observed when comparing to the S3 (1.7 %).

The results of the concrete cubes compressive strength measurements are illustrated in Figure 3.

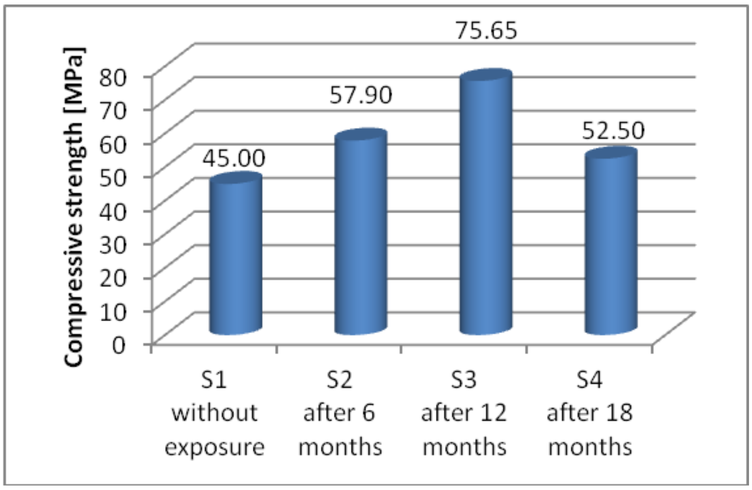

Fig. 3. Compressive strength of concrete samples

Obviously, the compressive strength increase of concrete samples was observed for all samples exposed to the wastewater comparing to the initial compressive strength value of reference set S1. This is probably caused by continual hydratation processes which took place in the concrete matrix. Significant increase of compressive strength was measured for sample set S3; it is equal to more than 68 % (Table 4).

Table 4. Changes in compressive strength compared to the initial value of reference samples

Set of samples No.	Compressive strength changes [%]
S1	0.00
S2	↑ 28.67
S3	↑ 68.11
S4	↑ 16.66

Concrete samples were prepared from high – performance concrete that is likely why the compressive strength showed the enormous increase (75.65 MPa). After the value of the compressive strength reached the critical point the concrete led to disintegration. 18 month exposition in wastewater seems to be enough for the concrete deterioration process starting resulted in compressive strength decrease by 30.60 % when compared to the 12 months exposition.

The content of the basic components of selected concrete samples was determined by using X-ray fluorescence analysis (XRF). The comparison of the chemical composition of samples before the experiment (reference sample No. 1) and after the experiment (sample No. 2 – after 6 months, sample No. 3 - after 12 months and sample No. 4 – after 18 months) is illustrated (because of scale in two separated figures) in Figures 4 and 5.

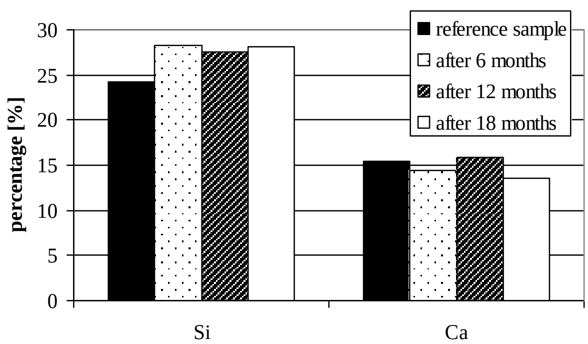

Fig. 4. Content of silicon and calcium in concrete samples before (reference sample – black) and after the experiment of biocorrosion (after 6, 12 and 18 months)

As it shown in Figure 4, the percentage content of Ca decreased for both samples exposed for 6 and 18 months; while increased for the sample exposed for 12 months in comparison to the reference sample. The course of Si showed the increase of compound in the concrete matrix for all samples after 6, 12 and 18 months exposition to aggressive environment.

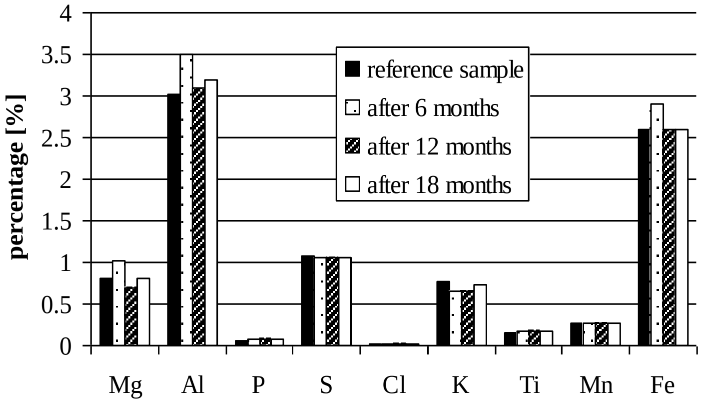

Fig. 5. Elementary composition of concrete sample before (reference sample – black) and after the experiment of biocorrosion (after 6, 12 and 18 months)

The percentage content (after 6 months) of Fe, Al and Mg has been a little increased compared to the reference sample and the similar trend was visible (after 18 months) only for Al. After 12 months exposition, the concentration of magnesium has been decreased; in case of aluminium the increase was observed and in case of iron the concentration was measured the same. In case of the other chemical components, the values remained almost the same or only very small changes were determined.

Summarising the results of the XRF chemical analyses, the deterioration process of concrete samples was not confirmed by the significant decreases of basic cement components (except for calcium). On the contrary, our previous works at laboratory conditions showed significantly the basic cement components leaching the into the water environment. The further investigation will be aimed at the detailed study of chemical composition of concrete surface.

4. Conclusion

Compressive strength increase of concrete samples was observed for all samples exposed to the wastewater from combined sewage system comparing to the initial compressive strength value of reference set S1.

Results of the XRF analyses shown that deterioration process of wastewater was not by decreases of basic cement components (except for calcium) confirmed. On the other hand our previous works [8, 9] at laboratory conditions showed significantly the basic cement components leaching the into the water environment. The further investigation will be aimed at the detailed study of chemical composition of concrete surface.

Acknowledgement

The research has been carried out within the Grant No. 2/0166/11 of the Slovak Grant Agency for Science and the Centre was supported by the Slovak Research and Development Agency under the contract No. SUSPP-0007-09.

References

[1] Morton R.L., Yanko W.A, Grahom D.W., Arnold R.G.: Relationship between metal concentrations and crown corrosion in Los Angeles County sewers, Res. J Water Pollution Contr. Federation, vol. 63, no. 5, pp. 789-798, 1991.

[2] Cho K., Mori T.: A newly isolated fungus participates in the corrosion of concrete sewer pipes, Water Sci Technol., vol.35, pp. 263–271, 1995.

[3] Idriss A.F., Negi S.C., Jofriet J.C., Hayward G.L.: Corrosion of steel reinforcement in mortar specimens exposed to hydrogen sulfide, Part 1: Impressed voltage and electrochemical potential tests. J Agr Eng Res., vol. 79(3): pp. 223-230, 2001.

[4] Vincke E., Verstichel S, Monteny J, Verstraete W.: A new test procedure for biogenic sulfuric acid corrosion of concrete. Biodegradation; vol. 10(6): pp.421-428, 1999.

[5] Attiogbe E.K., Rizkalla S.H.: Response of concrete to sulphuric acid attack. ACI Mater J., vol., 84(6), pp. 481–488, 1988.

[6] Skalny J, Marchand J, Odler I.: Sulfate attack on concrete. London, Spon Press, 2002.

[7] Davis J.L., Nica D., Shields K., Roberts D.J.: Analysis of concrete from corroded sewer pipe. Int. Biodeter. Biodegr.; vol. 42(1), pp.75-84, 1998.

[8] Ondrejka Harbulakova V., Luptakova A., Stevulova N., Repka M.: Comparative study of acid corrosion and leaching proceeded in model conditions., In: Current Issues of Civil and Environmental Engineering in Košice, Lviv and Rzeszów : 13th International Scientific Conference, Herľany-Košice: TU, pp. 1-7, 2011.

[9] Estokova A., Ondrejka Harbuľáková V., Luptakova A., Prascakova M., Stevulová N.: The study of Resistance of Cement Composites against Microbial Attack In: Journal of Civil Engineering and Architecture. vol. 5, no. 6, pp. 555-561, 2011.

STUDY OF CONCRETE CHANGES CHARACTERISTICS AFTER BIOCORROSION PROCCESSES AFFECTED BY WASTEWATER

S u m m a r y

Numerous studies have addressed the problem of chloride ingress in concrete structures. However, in addition to sulphate penetration, biological processes can accelerate the deterioration process by modifying severely the structural durability and reliability. The strength parameters and weight changes were evaluated as an average value from 3 concrete samples. Compressive

strength value of reference samples were measured at the concrete cubes (150 mm x 150 mm x 150 mm) after 28 days of hardening; other samples were tested after taken out the sewerage (same cubes 150 mm x 150 mm x 150 mm) and were evaluated according to the STN EN 206. X-ray fluorescence method was used for investigation of the chemical composition of the concrete samples before and after the experiment. Compressive strength increase of concrete samples was observed for all samples exposed to the wastewater from combined gravitational sewage system comparing to the initial compressive strength value of reference set. The percentage content (after 6 months) of Fe, Al and Mg has been a little increased compared to the reference sample and the similar trend was visible (after 18 months) only for Aluminium. In case of the other chemical components, the values remained almost the same or only very small changes were determined.