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STUDY OF DIFFERENT TYPES OF CORROSION PROCESSES SIMULATED IN MODEL CONDITIONS

Existing evidence has shown that in many concrete structures exposed to aggressive aqueous environments corrosion problems are present. In places like marine environments, sewers, agricultural structures, underground and hydraulic structures, chemical plants, industrial structures, liquid-containing structures these problems are especially very well visible. Degradation mechanisms such as alkali silica reaction, chloride penetration, carbonation, acid corrosion, leaching etc. have necessitated the renewal of complete structures. Leaching and acid corrosion mechanisms were chosen for detailed study and partial results are present in this paper. Concrete samples without coal fly ash addition and as well as sample with addition of 5% resp. 10% of coal fly ash were used for experiment. Paper is aimed on study and evaluation of chemical corrosion and leaching due to sulphuric acid/distilled water influence on concrete samples. After the experiment of exposure of concrete samples to these different environments the concrete surface changes and the pH values changes of leachate were measured and evaluated.

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].

Additives and admixtures are used to improve the properties of the concrete. Fly ash can be one of the admixtures and it is used to influence the

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properties of new or hardened concrete or to gain some special features [2]. Fly ash is obtained by electrostatic or mechanical separation of dust-like particles from the flue gases of furnaces fired with coal or lignite at 1100 to 1400°C. Fly ash is a fine powder, which is mainly composed of spherical glassy particles mainly consisting of SiO_2 and Al_2O_3 and at least of 25% active SiO_2, which is responsible for pozzolanic activity (latent hydraulicity). Depending upon the type of boiler and the type of coal, siliceous and calcareous fly ashes with pozzolanic and/or latent hydraulic properties are produced [3]. Thanks to this feature it is classified as so called additive type II, which alike presents hydraulic activity concrete [4].

Approach to the structural changes of concrete samples as well as biofilm analysis include many methods, including microscopy, which plays the paramount role in surface and intersurface characterizing techniques. There has been an increasing application of microscopic methods in general over the past years due to the possibility of coupling them with automated digital on-line image acquisition and image analysis methods [5].

The concrete degradation is common in structures located in aggressive environments and subject to, for instance, sulphate attack, chloride penetration or leaching.

In this paper, simulation of leaching process in concrete was made by inserting the concrete samples into the distilled water. According to Moskvin [6] classification it is corrosion so called the I type corrosion. Leaching in concrete is the process by which soluble material is extracted from the concrete by flowing water. The water may flow over the concrete surface or percolate trough cracks. Water readily extracts sodium and potassium hydroxide from the concrete pore fluid, lowering the pH; it is also progressively dissolves calcium hydroxide and decomposes calcium silicate hydrate (C-S-H), ettringite and others.

The II type corrosion – acidic corrosion, was simulated using 0,5% H_2SO_4 solution. All 3 types of prepared concrete samples were partly immersed into the sulfuric acid. Concrete in is general insufficiently resistant against liquid with pH < 7. When sulphuric acid reacts with concrete it leads to neutralization among its and other hydratation products of cement, for example calcium hydroxide as is in Eqn.:

$$H_2SO_4 + Ca\;\; OH\;_2 \rightarrow CaSO_4 + H_2O.$$

Our previous work was aimed on study of the biocorrosion degree of concrete samples exposed to the model conditions [7, 8]. In others works we were oriented on the investigation of biodeterioration of concrete in sewer pipes [9, 10]. In this paper the influence of H_2SO_4 and distilled water as a comparative study were simulated and consequently evaluated. This simulation were processes on 6 concrete samples prepared using different mixture. Some of them were prepared according to classics recipe, in some of them the cement was replaced for 5% respectively 10% coal fly ash. In this paper were pH changes in each leachate the corrosive effect were assessed. Among other thing the visual changes were observed.

2. Material and methods

2.1. Concrete samples and liquids

Concrete samples without coal fly ash addition (reference samples 1,4) and as well as sample with addition of 5% (samples 2,5) or 10% of coal fly ash (samples 3,6) were used for experiment. Used coal fly ash with volumetric weight of 2381 kg/m^3 originates from black coal's burning process in Kosice city heating plant (Teplaren Kosice a.s. TEKO).

Distilled water used in experiment was prepared using ELGA – PURELA OPTION apparatus in the Laboratory of Institute of Geotechnics, Slovak Academy of Science in Kosice as well as The solution of 0,5 M H_2SO_4 were prepared by dissolving of 98% H_2SO_4 of analytical grade in distilled water. Simulation of leaching process in concrete was made by inserting the concrete sample into the distilled water and acidic corrosion were simulated using 0,5% H_2SO_4 solution as is shown in Tab. 1.

Table 1. Characterization of concrete samples used for experiment

Concrete samples			
Distilled water		**0,5% H_2SO_4**	
1	0% coal fly ash	4	0% coal fly ash
2	5% coal fly ash	5	5% coal fly ash
3	10% coal fly ash	6	10% coal fly ash

Concrete cylinder samples of a 32 mm diameter and 15 mm height formed as a drilled core from concrete cube (150 x 150 x 150 mm) using drilling mechanism STAM were used for experiment. The cylinder specimens were rid of impurity and polished.

2.2. Methodology

Experimental part was aimed on study and evaluation of chemical corrosion and leaching due to sulphuric acid/distilled water influence on concrete samples (with/without coal fly ash replacement). This observation was under way in model conditions and selected liquid media presents 2 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.

The volumes of both liquids in the start of experiment were 20 ml. Experiments runs 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 runs the daily pH values measurements of liquid phases.

Measurements of pH of liquid phases were realized using the pH-meter PHM210 MetLab. The pH values were monitored every 24 hours during five 7-days cycles. The changes of concrete surface were observed before and after experiments by mineralogical stereomicroscope STM 723 ZOOM with the combination of digital camera Olympus – C-770 Ultra Zoom.

3. Results and discussion

Concrete samples surfaces exposed to effect of distilled water were not noticed considerably surface changes. The surfaces changes of selected concrete samples immersed into sulphuric acid are depicted in Tab. 2. As is seen from the pictures after experiments the formation of precipitations on the concrete samples surface is visible. Except this white crystals and slight amount of orange precipitations were observe on non-immersed part of the samples (top part). These parts were not immersed, but liquid phase rise up by capillary action from the bottom to the top of the samples. So this top part was „wet“ too and the solution of H_2SO_4 should continue to effect. Considerably amounts of orange and white crystals were observed on the immersed part of the samples. The largest amount of precipitations were confirm in case of sample 1 (without coal fly ash replacement).

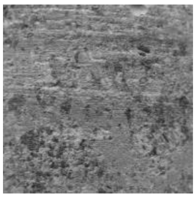
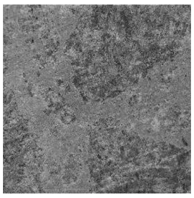
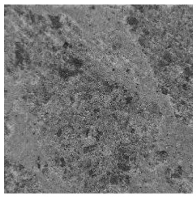
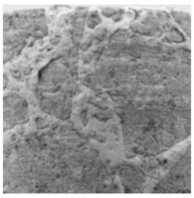
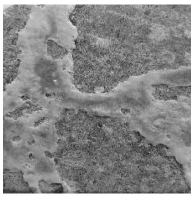
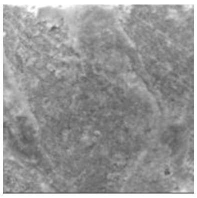
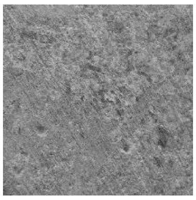
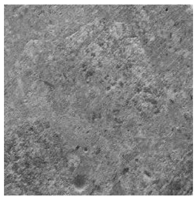
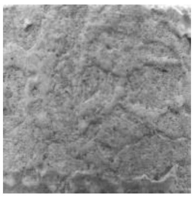
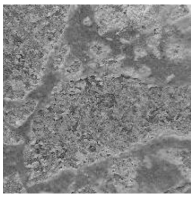
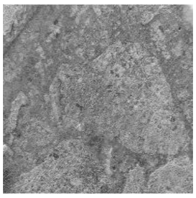
The pH values changes of each selected liquid phases in the beginning of chemical corrosion experiment and after 30 minutes from the start of samples immersing are shown in the Fig. 1.

These results are for simulation of both leaching (samples 1-3) as well as acid corrosion (4-6) after first 7-day cycle. The highest changes under these conditions were in case of distilled water, especially sample 1 without coal fly ash additions (ΔpH = 4,16). The pH changes were less visible: 2,79 (sample 2); 2,97 (sample 3) in case of liquid phases of samples with coal fly ash additions.

Very small changes of pH values were noticed in each samples immersed into solution of 0,5% H_2SO_4, which were around 0,13.

The pH values changes of each selected liquid phases in the concluding i.e. fifth 7-day cycles in the beginning of chemical corrosion experiment and after 30 minutes from the start of samples immersing are shown in the Fig. 2.

Table 2. The surface changes of concrete samples without and with coal fly ash immersed into 0,5% H_2SO_4 solution after the experiment termination

Sample		**0,5% H_2SO_4 solution**		
		side	**bottom**	**top**
No 1 0% coal fly ash	B			
	A			
No 6 10% coal fly ash	B			
	A			

B – before experiment, A – after experiment

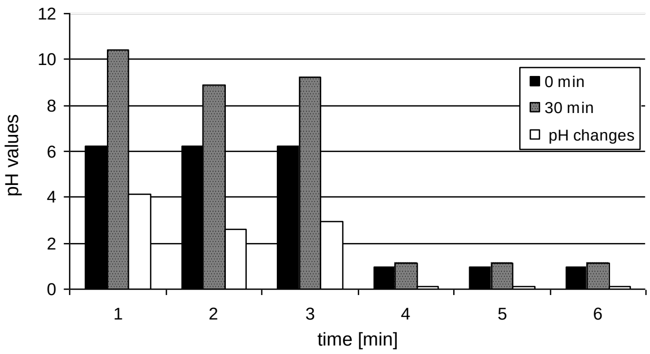


Fig. 1. pH values changes after first 7-day cycle (conditions before experiment: distilled water pH = 6,25; 0,5% H_2SO_4 pH = 1,0)

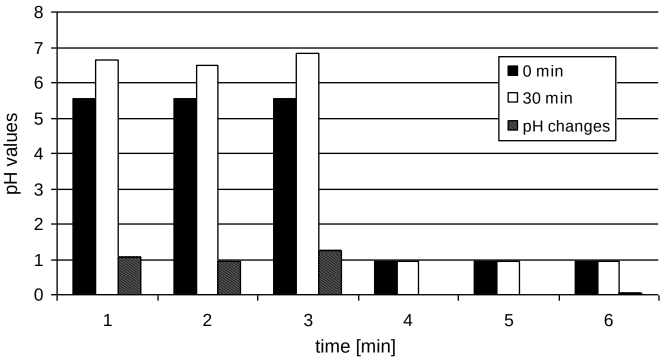


Fig. 2. pH values changes after fifth7-day cycle (conditions before experiment: 0,5% H_2SO_4 pH = 0,93; distilled water pH = 5,56)

In case of distilled water the increase of measured pH were only in their first 30 minutes of each cycle. Afterwards the increase stopped and until end of cycle (during next 7 days) and no change of pH values had been observed (data not shown here). Fig.1 and Fig. 2 comparison shows that the pH changes values gradually decreased. After the experiment the measured values for sample 1; 2; 3 were 1,07; 1,32 and 1,26.

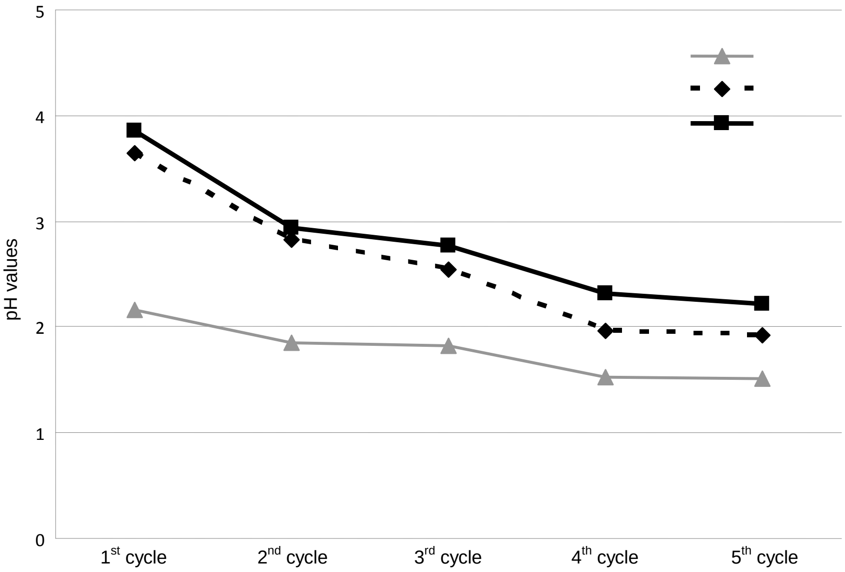


Fig. 3. The values of leachate of pH of liquid phase after ending the 1-5 cycle with using 0,5% H_2SO_4 solution

Considering H_2SO_4 the situation was reverse. pH changes in the first 30 minutes in each cycle were very low, which is showed in Fig.1 and Fig. 2 comparison (samples 4-6). Consequently from the 1 to 7 day of each cycle the pH value changes increase. For discussion the sample 4 were chosen. Measured values of pH of sample 4 leachate before experiment are: 1^{st} cycle pH = 1,0; 2^{nd} cycle pH = 0,96; 3^{rd} cycle pH = 0,98; 4^{th} cycle pH = 1,0; 5^{th} cycle pH = 0,93 and after experiment are: 1^{st} cycle pH = 2,16; 2^{nd} cycle pH = 1,85; 3^{rd} cycle pH = = 1,82; 4^{th} cycle pH = 1,52; 5^{th} cycle pH = 1,51.

The final pH values of liquid phases after ending of each cycles for samples 4-6 (using H_2SO_4 solution) are shown in Fig. 3.

The endings pH values from 1 to 5 cycles of acid corrosion simulation (using H_2SO_4) evinced decrease trend as it seen from the Figure 3. The lowest pH value after experiment were measured for the sample without coal fly ash addition (sample 4; pH = 1,51) and the highest pH value were measured for sample with 10% coal fly ash addition (sample 6; pH = 2,22).

4. Conclusion

The effect of 0,5% H_2SO_4 solution on concrete samples leads to significant surface changes. It is proven by creation of white and orange precipitations. The largest amount of them was observed in case of sample 4 (without coal fly ash addition).

The study of pH values changes of liquid phases follows that after the immersing the concrete samples into the distilled water the concentration of OH^- ions in the media increased, so pH values rise into alkali region to values 10,41 (sample 4); 8,86 (sample 5); 9,22 (sample 6).

The contact between sulphuric acid and concrete leads to neutralization. H^+ ions are consumed and it goes to alkalization of the solution. The layer of precipitations was created step by step on the concrete samples surface and it prevented the access of the corrosive solution into the concrete. It probably caused that the pH values during the each cycles increase, but the final values of the cycles had decreasing character.

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