Evaluation of concrete deterioration under simulated acid rain environment

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Abstract

Acid rain is identified as one of the most serious environmental problems nowadays and it is mainly a mixture of sulfuric and nitric acids. Deterioration of concrete structures exposed to aggressive acid rain attack is a key durability issue that affects the performance and maintenance costs of vital civil infrastructures. The motivation for understanding the acid rain corrosion process is high because of the early age deterioration of many concrete structures exposed to acid rain. The main objective of this study was to investigate the durability of concrete specimens with different supplementary cementitious materials, such as fly ash, zeolite and blast furnace slag against acid rain attack. Experiments of acid rain simulation influence on the composites were carried out for 7 weeks and parameters like visual changes, absorbability and leachability of calcium and silicon ions were evaluated. The increase in absorbability was detected for all samples while the sample with blast furnace slag was identified to be the most durable in this point of view. The most durable sample considering leached-out calcium and silicon ions was found to be sample with fly ash.

Key words: concrete, supplementary cementitious materials, deterioration, acid rain

1 Introduction

As one of the most used building material, concrete is inevitably exposed to different acidic substances and from this point of view the durability of concrete structures in aggressive environments has become a major concern over the past several decades [1-3]. Suitable compressive strength, large resources of concrete components and cost effectiveness are concrete characteristics that are desirable for various applications [4,5]. When concrete is exposed to acidic environments, deterioration of material occurs, because acidic molecules penetrating the concrete reacts with compounds in concrete matrix [4,6].

British chemist R.A. Smith first observed the pollution of acid rain in 1852, which attracted much attention from researchers, environmentalists and experts from many different fields all over the world [7]. Acid rain attack caused by atmospheric precipitation leads to degradation

of concrete strength and structural stability. With the development of the industry, the acid rain corrosion has become a more serious problem. Studies have showed, that the rainwater of most parts of Europe, the eastern parts of the United States, the southwest parts of China and parts of Japan has been strongly acidified [1].

Acid rain is a corrosive medium containing not only H^+ cations but also other species including NH_4^+ , Mg^{2+} , and SO_4^{2-} ions. Based on its composition, the mechanism of degradation of cement-based materials like concrete by acid rain attack is quite different from and more complicated than the mechanisms of pure acid attack [2].

Value of pH in pore water solution of concrete is typically ranging from 12 to 13.5. Acid rain induces physical and chemical reactions in the matrix, which results in a reduction in the pH. Continued reactions lead the concrete structure to gradually lose its strength and durability characteristics followed by possible structural failure [2,8,9]. Therefore, the mechanism of deterioration of concrete structures under acid rain attack should be studied further to minimize its impact [2].

Under a corrosive environment, concrete properties can be improved by using supplementary cementitious materials either from natural resources like zeolite or in a form of industrial by-products like blast furnace slag and fly ash. Benefits of using supplementary cementitious materials in concrete include increased long-term compressive strength, better workability and reduced permeability [10].

In this paper, the influence of different supplementary cementitious materials (zeolite, blast furnace slag and fly ash) on performance of concrete under acid rain attack has been studied. Parameters like leachability of calcium and silicon ions from concrete matrix, absorbability and visual changes on the surface of 28-day cured composite samples after 7 weeks of their storage in aggressive solution were investigated.

2 Materials and methods

2.1 Concrete specimens

Four concrete mixtures containing different supplementary cementitious materials were prepared for the acid rain corrosion experiment. Specimen A-0 represents the reference mixture made with Portland cement (CEM I) only, in the mixture A-1 was Portland cement partially replaced by zeolite, in the mixture A-2 with fly ash and in the mixture A-3 with blast furnace slag, respectively.

Concrete samples were prepared according to Slovak standard STN EN 206-1+A1 [11] in a form of prisms of size 100 x 100 x 400 mm. After 24 hours the samples were demoulded and cured for 28 days in tap water. Concrete prisms were cut into small prisms with dimensions of 50 x 50 x 10 mm for the accelerated corrosion experiments. Table 1 shows the mixture designs with appropriate w/c ratio for tested concrete specimens.

Table 1: Concrete mixture design of studied specimens

Component	A-0	A-1	A-2	A-3
Cement (kg/m ³)	360	331	304.75	54
Natural aggregates, fraction 0/4 mm	845	825	845	825

(kg/m ³)				
Natural aggregates, fraction 4/8 (kg/m³)	405	243	405	235
Natural aggregates, fraction 8/16 (kg/m³)	590	752	590	740
Water (L)	190	190	190	162
Fly ash (kg/m³)	-	-	41.30	-
Blast furnace slag (kg/m³)	-	-	-	306
Zeolite (kg/m³)	-	29	-	-
Plasticizer (L)	-	2.65	-	-
w/c	0.53	0.53	0.55	0.45

Before the start of the acid rain corrosion experiments the samples were brushed in order to remove polluting particles and dried at 105 ± 5 °C in the laboratory oven.

The simulated acid rain solution with pH 1.6 was prepared by mixing pure chemical reagents such as H₂SO₄ and HNO₃ in a ratio 1:1.5, respectively and deionized water.

The volume of the liquid solution was based on the volume ratio of the concrete specimens and liquid phase and was set at 1:10. The ratio was selected according to accelerated short-term corrosion experiments to achieve desired deterioration of concrete samples. The acid rain corrosion tests of concrete samples were carried out in glass beakers during 7 weeks at laboratory temperature of 23 °C.

2.2 Absorbability test of concrete specimens

The absorptivity test was performed on concrete specimens according to Slovak Standard STN 73 1316 [12]. Before the corrosion tests, the concrete prisms were dried at 105 ± 5 °C and their weight was determined. The testing of concrete prisms for acid rain solution absorption was performed prior and after the 7 weeks long experiment. At the end of the corrosion tests, the weights of wet specimens were measured and specimens were again dried at 105 ± 5 °C and weights of dry specimens were determined. Absorbability before the experiments and after was calculated using equation (1) [12]:

$$v = \frac{m_W - m_D}{m_D} \cdot 100\% \quad (1)$$

Where m_W refers to the weight of wet specimen and m_D is weight of dried specimen.

2.3 Leachability of Ca²⁺ and Si⁴⁺ ions

X-ray fluorescence analysis (XRF) was used to analyze the leach-out quantities of Ca²⁺ and Si⁴⁺ ions in concrete leachates after 4th and 7th week of experiment. Spectrometer SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses was used. Detailed measurement conditions of the XRF analysis were previously described in [13].

3 Results and discussion

3.1 Visual changes

Table 2 shows concrete samples prior and after the exposition to acid rain environment.

Table 2: Visual changes of samples before and after the corrosion experiment

Concrete specimens	Surface prior the experiment	Surface after the experiment
A0		
A1		
A2		
A3		

Due to high concentration of H^+ ions, corrosion due to acid rain solution occurs rapidly on the surface of samples, leading to the failure of cementitious material. Simulated acidic solution severely damaged the samples and the deterioration was significant for all specimens. White crystals identified on the surface of the tested samples A0, A2 and A3 were related to various calcium sulfates. For the sample A1 with zeolite, white to yellow rough-surfaced compounds were detected. Simultaneously, the aggressive solution damaged the cement binder and exposed the coarse aggregates of samples.

3.2 Absorbability

Absorbability of concrete specimens before and after the simulated acid rain experiments is given in Fig. 1.

Figure 1: Absorbability of concrete specimens

The absorbability test performed on concretes with different supplementary cementitious materials proved an increase in water absorption for all tested samples after the simulated acid rain exposition. Table 3 shows the percentage increase in absorbabilities of concretes after 7 weeks long corrosion experiment.

Table 3: Change in absorbability after acid rain exposition

Concrete sample	A0	A1	A2	A3
Change in absorbability [%]	2.24	3.26	2.03	1.58

The highest absorbability was observed for sample A3 with blast furnace slag, however the change in absorbability prior and after the acid exposure was the lowest among all the specimens (1.58 %). Sample A1 made with zeolite showed highest change after the corrosion experiment (3.26 %).

3.3 Leachability of Ca^{2+} and Si^{4+} ions

Fig. 2 presents the leaching trends Ca^{2+} ions of concrete samples during the acid rain corrosion experiment.

Figure 2: Concentration of dissolved calcium ions of concrete specimens during 7 week long acid rain exposure

The highest amount of leached Ca^{2+} ions was observed after 7 weeks of exposure (5474 mg/L) for the reference sample A0 made with ordinary Portland cement. Leaching trends of samples A0 and A2 were similar throughout the corrosion experiment, where the concentration of calcium ions increased with time. However leaching of Ca^{2+} ions of samples A1 and A3 had different course, where after 7 weeks the concentration of calcium ions decreased in comparison with the concentration after 2 week long period. The decrease in leached amounts of calcium ions for samples A1 and A3 after 7th week could be likely connected with stronger formation of crystal compounds on the surface of concrete samples. Concentration of leached-out Si^{4+} ions is presented in the Fig. 3.

Figure 3: Concentration of dissolved silicon ions of concrete specimens during 7 week long acid rain exposure

Similar to leaching trends of Ca^{2+} ions, the leaching of Si^{4+} ions was the most intensive for reference sample A0 after the 7th week of acid rain corrosion (6365 mg/L). Trends of leached-out silicon ions were the same for samples A0, A1 and A3, where the highest leached-out concentrations of Si^{4+} ions were observed after the end of corrosion experiment. Sample A2 with incorporated fly ash had opposite leaching trends of silicon ions, with the maximum leached-out Si^{4+} ions at the beginning of experiments.

4 Conclusion

This paper was focused on evaluation of durability of concrete samples with incorporated supplementary cementitious materials (zeolite, fly ash and blast furnace slag) exposed to simulated acid rain environment during a period of 7 weeks. To predict the degradation effect of acid rain on concrete samples, characteristics like absorbability, leaching of basic inorganic elements (Ca^{2+} and Si^{4+} ions) and visual changes were determined. From the obtained results following conclusions can be drawn:

- The aggressive effect of simulated acid rain environment was confirmed in relation to all studied parameters.
- The concrete specimens show a steady rate of increased absorbability when exposed to the acid rain solution. The increased absorbability goes up gradually with the increase of immersion time, and the most durable sample was the sample with blast furnace slag.
- The leaching trends confirmed the degradation effect on all tested samples. The most durable sample considering leached-out calcium and silicon ions was found to be sample with fly ash.

To give a clear conclusion about the durability of the concrete samples made with different supplementary cementitious materials, more research considering higher substitution of pozzolanic materials and testing mechanical parameters like compressive and flexural strengths or porosity is needed.

Acknowledgements

This research was funded by VEGA - Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences, grant number 1/0648/17.

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