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Development of Compressive Strength of Slag Based Cement Mortars Exposed to an Aggressive Sulphate Environment

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Abstract. Sulfuric acid corrosion can cause severe damage to concrete and cement composites. There are a variety of approaches to enhancing the sustainability of concrete and mortar one of which is to enhance the durability of concrete using different cement replacement. Granulated blast furnace slag is used in mortar and concrete, as a partial replacement of Portland cement, and this use has resulted in significant savings in the cost of production of concrete. Moreover the use of conventional concrete is notoriously subject to durability and corrosion issues. Laboratory experiments were conducted to investigate the compressive strength of cement mortars samples with cement partially replaced by blast furnace slag. The samples with different share of slag (65, 75, 85 and 95 wt.%) were exposed to a bacterial sulphate environment for 90 days. A decrease in compressive strengths of reference samples by 8% as well as an increase in compressive strengths of all slag-based sampless up to 95 % have been observed. Surface structure and chemical compositions of cement mortars´ leachates confirmed a deterioration process under the microbial exposure of Acidithiobacillus thiooxidans.

Keywords: compressive strength, biogenic sulphuric acid, bio-corrosion .

Conference topic: Environmental protection.

Introduction

Durability of concrete and cement composites is the ability of the materials to prevent weathering, chemical, physical and biological attack and abrasion while preserving its engineering properties such as compressive strength, modulus of elasticity, shrinkage, etc. Depending on the environment and desired properties, cement composites requires different degrees of durability (Siddique *et al.* 2016). Among different types of aggressive environment condition sulphate attack are the most widely exposing, therefore the reduction in compressive strength of cement materials is a direct effect of the sulphate exposure (Diab *et al.* 2014).

Biogenic sulphuric attack is the processes taking place in sewerage systems, where microorganisms' *A. thiooxidans* form sulphuric acid and attack the cement paste matrix. Hydrogen sulphide in the atmosphere of sewer can be oxidized by *Acidithiobacillus thiooxidans* producing sulfuric acid and this can lead to lower the pH value on the surface to 1.0 or even lower and cause a very severe acid attack. The result of such an attack is besides lowering of pH the reduction in the compressive and tensile strength of cement composites. Approximately 40% of the damage in concrete sewers can be attributed to biogenic sulphuric acid attack and the damaged sewer systems are one of the main sources of underground contamination with sulphate, chloride and nitrogen compounds. The resistance of conventional concrete and mortar is not sufficient to prevent biological corrosion and so components as ground blast furnace slag are used to enhance the resistance against corrosion (Kaempfer, Berndt 1999).

Furnace slag is the non-metallic by-product of the transformation of iron ore formed in a molten state simultaneously with iron in a blast furnace. The slag is derived from silicate and oxide components of the raw materials used in the smelting process. Little or no crystallisation occurs if the molten slag is cooled and solidified to a glassy state and this granular material is milled to a powder, the ground granulated blast furnace slag, which exhibits latent hydraulic properties. The main chemical composition includes CaO, SiO_2, and Al_2O_3 and high proportions of CaO, Al_2O_3, and MgO are advantageous to the activity of slag. The use of this material has expanded because it has various advantages over other cementitious materials, such as a relatively constant chemical composition compared to silica fume, fly ash etc., high sulphate and acid resistance, better workability, low heat of hydration and ultimate strength (Fu *et al.* 2000; Öner *et al.* 2003; Gruskovnjak *et al.* 2008).

This paper investigates the changes of compressive strength, changes of surface and chemical composition of cement mortars of different blast furance slag portions placed in sulphate environment with bacteria *A. thiooxidans* after 90 days.

Material and Methods

Five cement mortars´ samples of different share of granulated blast furnace slag with dimensions of 40×40×16 mm were analysed in the experiment. The S1, S2, S3 and S4 samples were prepared based on the blast furnace slag and Portland cement and the S0 sample with Portland cement only and no slag addition was considered as reference sample (Table 1).

Table 1. Share of granulated blast furnace slag in the samples

Samples	Granulated blast furnace slag [wt.%]	Portland Cement CEM I 52.5 R [wt.%]
S0	0	100
S1	65	35
S2	75	25
S3	85	15
S4	95	5

Content of main components in used Portland cement CEM I 52.5 R (Povazska cementaren, Slovakia) was as follows: 57.15 wt.% of CaO, 18.11 wt.% of SiO_2, 4.02 wt.% of Al_2O_3, 2.69 wt.% of Fe_2O_3, 1.49 wt.% of SO_3, 1.37 wt.% of MgO, 1.12 wt.% of K_2O, 0.33 wt.% of P_2O_5, 0.18 wt.% of TiO_2, 0.06 wt.% of Cl. Chemical composition regarding of incorporated blast granulated furnace slag was: 39.55 wt.% of CaO, 38.95 wt.% of SiO_2, 10.11 wt.% of MgO, 8.33 wt.% of Al_2O_3, 0,74 wt.% of MnO, 0.57 wt.% of SO_3, 0.54 wt.% of Fe_2O_3, 0.48 wt.% of K_2O, 0.37 wt.% TiO_2, 0.04 wt.% of P_2O_5, 0.02 wt.% of Cl.

After the samples were brushed, sterilized with 70% ethanol and dried to a constant weight, they were placed in the medium with sulphur-oxidising bacteria *A. thiooxidans*, which represented the aggressive sulphate environment. Nutrient medium by Waksman and Joffe (Waksman, Joffe 1922) was used for the isolation, cultivation and preparation of the active bacterial culture of *Acidithiobacillus thiooxidans*. Bacterial culture of *A. thiooxidans* was isolated from an acid mine drainage from Pech shaft (locality of Smolnik, Eastern Slovakia). To ensure the growth of bacteria elemental sulphur was added to the nutrient medium. The exposure of cement mortars specimens to bacterial infulence proceeded in glass containers under aerobic laboratory conditions over a aperiod of 90 days. Optimal growth temperature of bacterial culture (28–30°C) and pH interval 2.0–3.5 were ensured during whole experiment.

X-ray fluorescence analysis (XRF) was used to analyse the chemical composition of samples and samples leachates as well. SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses was used for the analysis. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite – HOPG target. The samples were measured during 300 and 180 s, respectively at voltage of 25 kV and 50 kV at current of 0.5 and 1.0 mA while have been flushed by helium. The standardized methods of fundamental parameters for cements and liquids were aplied to convert the measured intensities to concentrations of elements (Kovalčíková *et al.* 2015).

The compressive strength tests were carried out according to the methodology described in the standard STN EN 196-1 (“Methods of testing cement – Part 1: Determination of strength”). Cement mortars samples used in the compressive strength test had dimensions (approx.): 160 mm × 40 mm × 40 mm. Compressive strength of specimens was determined after 28 and 90 days by using the instrument ADR 2000 (ELE International, England).

Discussion

Surface changes

Changes of samples´ surface after the 90-day exposure to the sulfate environment were observed on all composite specimens (Fig. 1). The most significant changes can be observed on surface of the sample S4, which was made of 95 wt.% of blast furnace slag. More visible corrosive surface defects on the samples due to sulphate environment would be observed after longer period of bacterial exposure (Eštoková *et al.* 2016).

Leaching of basic elements

After 90 days of exposure to biogenic sulphuric acid produced by bacteria *A. thiooxodans,* chemical composition of leachates showed that corrosive process was taking place due to leaching of basic elements (Ca, Si, Al and Fe) from cement matrix of samples (Fig. 2). The most significant leaching was observed for calcium for all samples whereas the highest leached amount was calculated 3.59 % of total calcium content in the sample before the experiment for S4 sample. The dissolving of the main componets e.g. calcium compounds starts immediately when the samples are placed in aggressive environment or even water solution and finally, after certain time, depending on the aggressivity of medium, it can cause a loss of properties of composites. Eštoková *et al.* (2016) reported that bacterial exposure can be definitely considered as much aggressive in terms of elements leaching than chemical sulphate corrosion or leaching due to water solutions.

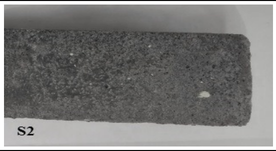
Sample	Surface of samples prior the experiment	Surface of samples after the 90 days of exposure to bi-ogenic sulphuric acid
S0		
S1		
S2		
S3		
S4		

Fig. 1. Surface changes of mortar samples before and after the experiment

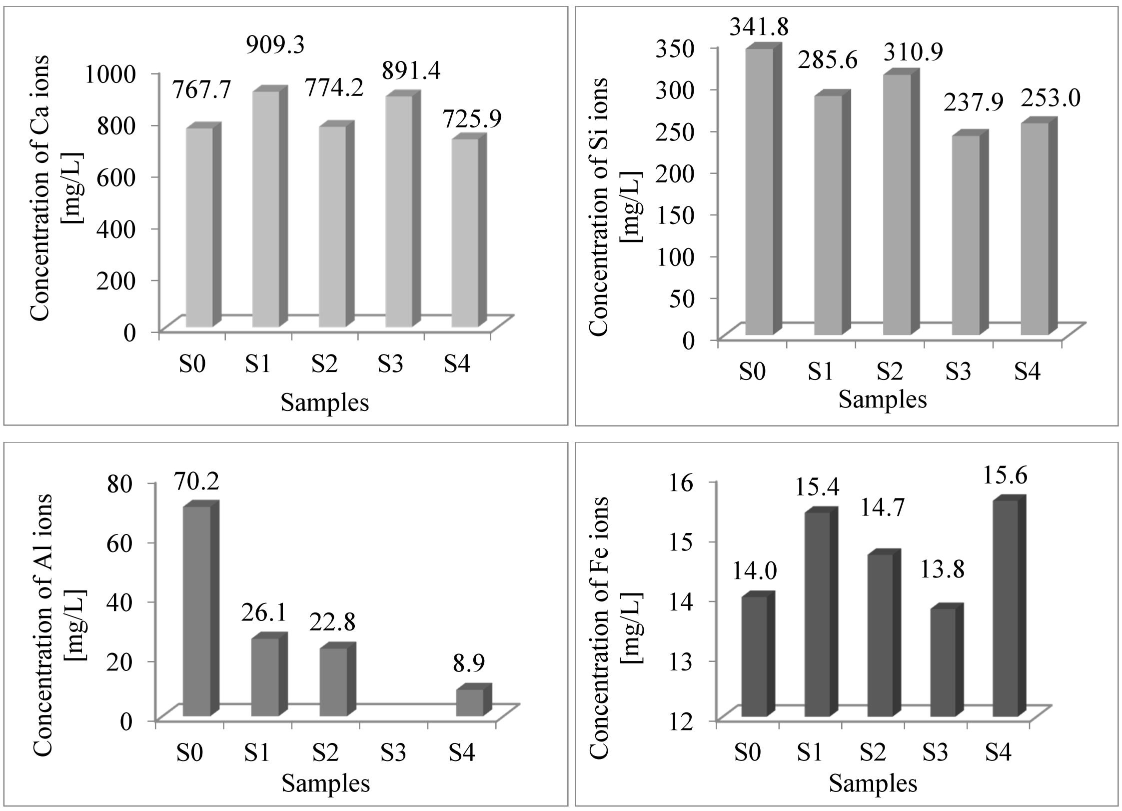


Fig. 2. Measured concentrations of dissolved main elements in leachates

Based on the measured concentrations of elements in leachates, it is difficult to evalaute the leachability of the samples. To compare the durability of the individual cement mortars in terms of main elements leaching, the percentage of leached-out masses of particular elements is in progress.

Compressive strength

Compressive strengths of investigated cement mortars after 28 and 90 days are shown in Fig. 3. A higher compressive strength after 28 days of curing compared to the compressive strength after 90 days of bacterial exposure was found only for the reference sample S0 (without any addition of slag). The initial (28-day) value has been decreased by 8 % from 57.0 to 52.8 MPa. The decrease in compressive strength of reference sample could manifest a deterioration process due to bacterial exposure.

All slag-based samples proved an increase in the compressive strength after the experiment (by 16.7, 25.7, 32.3, and even 95.6 % for S1, S2, S3 and S4 samples, respectively). Increase in compressive strengths of all samples with slag addition, after 90 days of exposure to the aggressive sulphate environment, can likely resulted in an additional hydration process which was probably more intensive compared to the corrosive process. Both of these effects take place at the same time, but although the leaching of elements from cement matrix is obvious, the hydration process in slag-based samples prevails over the corrosive process. Another explanation can be linked with metabolic production of bacteria *A. thiooxidans*. The metabolic products can also partially seal the pores of composites, which can lead to decrease in leaching process and can support the domination of inner hydration effect. Anyway, this finding confirmed the different behaviour of samples with and without slag under sulphate bacterial influence.

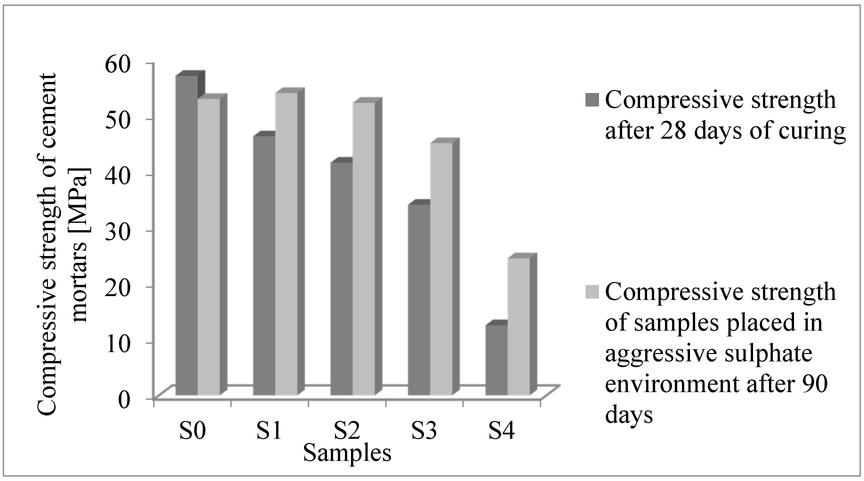


Fig. 3. Compressive strength of samples

Conclusion

This paper investigated the impact of sulphate aggressive environment on slag based cement mortars after 90 days of bacterial exposure. Based on the results of the experiment, the general conclusions are:

1. Surface changes were visible on all samples, due to the presence of corrosive biogenic sulphuric acid produced by *A. thiooxidans*.

2. Chemical composition of leachates showed the corrosive process was taking place, because of the leaching of Ca, Si, Al and Fe compounds.

3. Investigation of compressive strength of slag based samples showed an increasing trend, due to hydration which was a dominant process compared to deterioration.

4. The differencies in deterioration process of samples with and without slag due to sulphur-oxidising bacteria were confirmed.

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Contribution

A. Eštoková was responsible for conception and design of the work, for coordination of experiments and interpertation data. M. Smoláková was involved in the bacterial experiments, samples testing and drafting the article. A. Luptakova coordinated bacterial experiments.

Disclosure statement

Authors declare no competing financial, professional, or personal interests from other parties.

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