

Evaluation of the damaged depths of slag-based mortars in aggressive sulphate conditions

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Abstract. Resistance of cement composites against various chemical processes such as sulphate attack and corrosion is nowadays one of the most desired property. Mechanism largely involved in sulphate corrosion is the ingress of aggressive ions through diffusion. The result of the ingress of aggressive ions is leaching of the elements from the mortar matrix and the deterioration of the composite. In the experiment, the slag-based cement mortars samples were exposed to an aggressive microbiological sulphate environment, represented by the bacteria *A. thiooxidans*, for the period of 6 months. The paper presents the investigation of damaged depths of cement mortars based on the leaching characteristics of the Ca ions. The damage depths (EDD) of cement composites were much higher (up to 0.2 mm) for samples placed in the biotic environment, which confirms the aggressive action of *A. thiooxidans*.

1. Introduction

In urban environmental engineering, most of the facilities for sewage transportation are made from concrete and mortar structures. They are generally placed underground and are affected by the acid, erosion, microorganisms and other corrosive agents. The growing problem of concrete deterioration and bio-deterioration results in a huge economic losses all around the world [1].

To date, sulphate attack is still a significant problem in soil or solutions containing SO_4^{2-} , because it affects the mechanical performance and durability of mortar and cement concrete infrastructures [2,3]. The mechanism of concrete degradation exposed to external sulphate attack depends on exposure conditions, such as temperature, associated cations and sulphate concentration [4,5,6,7].

Most hydraulic structures have components that are constantly or partially submerged in water. The varying water chemistry of different water bodies affects the surface of these structures in many ways. For example, water can have the ability to dissolve components of the cement, i.e., leaching. The leaching kinetics is generally slow, but the impact can be essential from a long-term standpoint.

It is well known that cementitious materials are not thermodynamically stable, when they are in contact with more or less aggressive water. Portland cement concrete and mortars are easily attacked by water and acidic solutions with low pH. Compounds with elements such as Na and K, are quickly leached out when concentration gradients are present. In this case, the pH of the concrete pore solution may considerably decrease [8,9].

Leaching is a diffusion reaction which takes place when concrete is exposed to poorly mineralized water, acid water or biogenic acids made by microorganisms. Degradation consists in dissolution of calcium and hydroxide ions out of the cement matrix, which causes an increase in porosity and



transport properties of concrete surface. Leaching is accelerated in neutral and acid solutions, and it may be coupled with the ingress of aggressive ions such as sulphate, chloride or magnesium [7,10,11, 12]. It is widely known that leaching of calcium ions can have enormous effects on the physical characteristics of the structure. Leaching of Ca leads to loss of mass and mechanical strength and alkalinity. Loss of mass in the cement matrix is linked with an overall increase in porosity [9,13,14,15]. The diffusion kinetics can be described by Fick's law, which relates the altered thickness to the square root of time [16,17]. Leaching is consequently quite rapid at the beginning. As leaching progresses, porosity of the cement paste and ionic diffusivity increases, because ions diffuse through interconnected pores. It has been reported that the leaching rate of cement mortars is lower than that of cement pastes because particles in the corroded layer increase the diffusion pathway. In general, the lower the pH of the external solution is and the higher the concentration gradient is, the faster the transfer kinetics will be [9].

Effects like leaching needs to be taken into consideration in the design of concrete structures, which are in contact with wastewater treatment plants, mortar and concrete products such as sewage pipes and also water tanks [7].

The objective of this work was to evaluate the leaching characteristic of main inorganic components of cement mortars with ground granulated blast furnace slag exposed to microorganisms *Acidithiobacillus thiooxidans* for the period of 6 months and consequently, based on the leach-out amounts, to assess the damaged depths.

2. Material and Methods

2.1. Mortar mixtures

Three mortar mixtures were designed for this experiment. Sample R represents the reference sample made with ordinary Portland cement (OPC) only. Samples M1 and M2 represents the samples where the cement was partially replaced by ground granulated blast furnace slag in 65 % and 95 % by weight of cement, respectively. The mixtures were designed according to standard STN EN 196-1 [18] and were made of three parts of normalized sand (1350 ± 5 g), one part of cement (450 ± 2 g) and half part of water (225 ± 1 g) having water to cement ratio $w/c = 0.50$. The test samples with dimensions $160 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$ have been designed in cooperation with cement factory plant which we cooperate with.

The chemical composition of main components of used Portland cement CEM I 52.5 R was as follows: 57.15 wt.% of CaO, 18.11 wt.% of SiO₂, 4.02 wt.% of Al₂O₃, 2.69 wt.% of Fe₂O₃, 1.49 wt.% of SO₃, 1.37 wt.% of MgO, 1.12 wt.% of K₂O, 0.33 wt.% of P₂O₅, 0.18 wt.% of TiO₂, 0.06 wt.% of Cl. The content of main components of incorporated ground granulated blast furnace slag (GBFS) was as follows: 39.55 wt.% of CaO, 38.95 wt.% of SiO₂, 10.11 wt.% of MgO, 8.33 wt.% of Al₂O₃, 0.74 wt.% of MgO, 0.57 wt.% of SO₃, 0.54 wt.% of Fe₂O₃, 0.48 wt.% of K₂O, 0.37 wt.% of TiO₂, 0.04 wt.% of P₂O₅, 0.02 wt.% of Cl.

2.2. Bacterial exposure

The wastewater-like environment was simulated by sulphur-oxidising bacteria *Acidithiobacillus thiooxidans*, because of their ability to produce sulphuric acid. The nutrient medium by Waksman and Joffe (Waksman, S.A; Joffe, J. S. 1922) was used for the preparation of the active bacterial culture of *A. thiooxidans* in the experiment. The composition of the nutrient medium was as follows: 0.25 g/L CaCl₂·6H₂O, 0.2 g/L (NH₄)₂SO₄, 3.0 g/L K₂HPO₄, 0.5 g/L MgSO₄·7H₂O, traces of FeSO₄·7H₂O, 10.0 g/L elementary S and up to 1000 mL supplemented by distilled water. Bacteria *Acidithiobacillus thiooxidans* were isolated from an acid mine drainage from Pech shaft (locality of Smolník, Eastern Slovakia). Elemental sulphur was added to the nutrient medium.

The exposure of cement mortars to bacterial culture has taken place in glass containers under aerobic laboratory conditions over a period of 6 months. Optimal growth temperature of bacterial culture (28 - 30°C) and pH interval 2.0-3.5 were ensured during the experiment [19,20,21].

The mortar specimens exposed to bacterial medium with *A. thiooxidans* were labelled as R/A, M1/A, M2/A, and the control samples placed in abiotic environment, with no bacteria, were labelled as R/C, M1/C, M2/C, respectively. The volumes of liquid phase for the mortar samples used in experiment are described in table 1.

Table 1. Volume of liquid phases used in the experiment.

Mortar specimen	Volume of inoculum of <i>A. thiooxidans</i> (ml)	Volume of nutrient medium (ml)	Volume of sterilized water (ml)	Amount of elemental sulphur (g)
R/A	512	768		
R/C	-	1280		
M1/A	512	768		
M1/C	-	1280	1280	6.4
M2/A	512	768		
M2/C	-	1280		

Chemical composition of concrete samples' leachates was investigated once a month using X-ray fluorescence analysis. The 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 basic measurements conditions were as follows: time of measurement - 180 s; voltage - 25 kV and 50 kV; current - 0.5 and 1.0 mA; atmosphere - helium. The concentrations of measured elements were calculated using the calibration method of fundamental parameters for liquids.

2.3 Equivalent Damaged Depth

The damaged depths of studied cement mortars after the bacterial exposition were evaluated using equation (1) Equivalent Damaged Depth (EDD) (mm) according to [7]:

$$EDD = \frac{c(Ca)_L}{c(Ca)_{composite}} \quad (1)$$

Where $c(Ca)_L$ is total amount of leached calcium (mg/cm^2) and $c(Ca)_{composite}$ is theoretical initial total calcium content in volume unit of composite (mg/cm^3). Equivalent damaged depth (EDD) was selected based on the hypothesis that the calcium was totally leached in damaged depth. Assuming that Ca ions only came from composite and that no portlandite remained in corroded layers, equivalent damaged depths may be used to evaluate the level of deterioration regarding the depth [7].

3. Results

The leaching trends of calcium during the bacterial and non-bacterial exposure are presented in figures 1 and 2. As it can be seen, the leaching trends for calcium ions was proven to be more significant for mortars exposed to *A. thiooxidans* (R/A, M1/A, and M2/A) compared to samples exposed to medium without bacteria (R/C, M1/C, and M2/C). The highest amount of leached Ca ions (923 mg/L) were noticed for reference specimen R/A. The sample with 95 wt. % of blast furnace slag was found to be the most durable after the 6-month experiment, evaluating the Ca^{2+} leaching only.

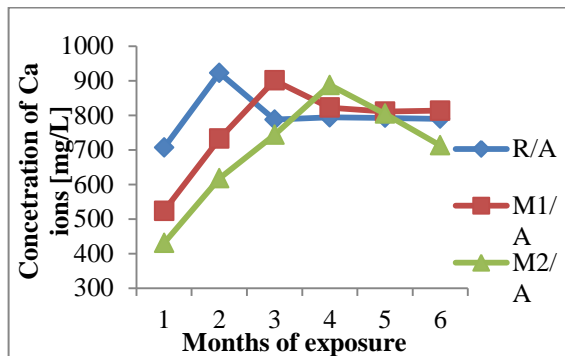


Figure 1. The concentration of Ca^{2+} ions under bacterial exposure.

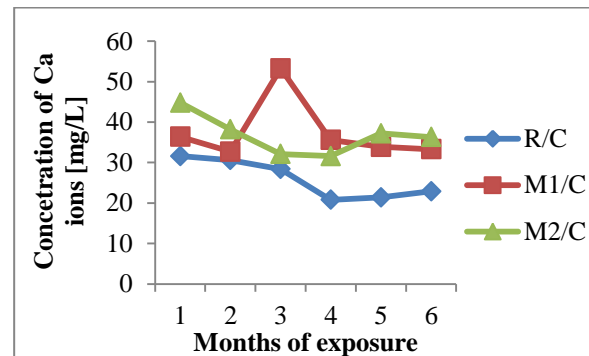


Figure 2. The concentration of Ca^{2+} ions under non-bacterial exposure.

The bacterial exposure was confirmed to be more aggressive also in terms of damaged depths of mortar samples. The calculated equivalent damaged depths (EDD) are given in table 2.

Table 2. Equivalent damaged depth (EDD).

Mortar sample	Total leached calcium (mg/cm ²)	Initial calcium content in binder (mg/cm ³)	Equivalent damaged depth EDD (mm)
R/A	8.012	350.359	0.228
R/C	0.274	357.722	0.007
M1/A	7.822	354.292	0.221
M1/C	0.462	354.609	0.013
M2/A	7.705	341.496	0.225
M2/C	0.388	348.951	0.011

As mentioned above, the most intensive Ca^{2+} leaching was observed for samples R/A, M1/A and M2/A exposed to bacteria and the calculated EDD of these samples reached much more higher values than EDD calculated for the mortars with no bacterial exposure. The calculated indicators of equivalent damaged depths of mortars due to bacterial influence were in a very close interval 0.221 to 0.228 mm.

Therefore, a longer experimental period is necessary to make any clear conclusions regarding the durability of mortars of various compositions. Similarly, the EDD of mortars samples without any bacteria ranged in a very close interval from 0.007 to 0.011 mm. Oddly enough, the reference sample without any blast furnace slag (R/C) had the lowest EDD compared to the other two samples (M1/C and M2/C, respectively).

4. Conclusion

The presented work shows the results of leaching performance of Ca ions from cement mortars with different share of blast furnace slag after 6 months in bacterial and non-bacterial environment and evaluates the equivalent damaged depths of mortars. Samples exposed to the medium with sulphur-oxidizing bacteria *A. thiooxidans* had higher leaching rates and damaged depths were therefore significantly higher.

The mortars with GBFS as admixture can lead to good resistance to leaching and binder incorporating such latent hydraulic material as slag actually produces less portlandite, with compact matrix. Different chemical composition of binder of samples M1 and M2 can lead to noticeable changes in the damaged depths of mortars.

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