Leaching of Ca, Si, Fe and Al from concretes, based on sulphate resistant cement, due to bacterial attack - a correlation study

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Abstract. Investigation of biological corrosion of concrete requires that composition of material, surface and aggressive environment have to be taken into account. Sulphate resisting cement, as one of the resistivity improving factors, was used for preparation of concrete samples studied in this experiment. Dependences of leached-out quantities of selected ions regarding bacterial versus non-bacterial environments were investigated and evaluated using correlation analysis. Leaching trends of calcium, silicon and aluminium strongly depends on the aggressiveness of medium which are the samples exposed to. A weak correlation was found for the leaching trends of aluminium and iron in both bacterial and non-bacterial media.

1. Introduction

Presence of microorganisms in sewer systems is associated with several problems, including microbial corrosion of concrete, release of obnoxious odours to the urban atmosphere and emissions of sulphide gas to sewer workers [1,2,3]. Formation of biological induced corrosion of concretes is linked with bacteria Acidithiobacillus thiooxidans, identified in the sewers, which are responsible for sulphate attack and consequently, for the deterioration of concrete matrix [4]. The sulphate resistant cement is applied in concrete structures in order to increase the resistivity against the sulphate attack and durability of concretes.

Deterioration of concretes due to bacterial sulphate attack is often manifested by leaching of the main concrete components representing by calcium, silicon, iron, and aluminum compounds. Because sulphate attack on concrete is not characterized by a single chemical process, when considering the best preventive measures one has to take into consideration the processes involved in concrete production and the environmental conditions to which the concrete will be exposed throughout its service life. However, some basic rules apply in most cases. The most important among them are using of proper structural design, drainage, protective barriers/coatings, using of low w/c mixture proportions, adequate cement content, proper consolidation or using of low-calcium cements, including sulphate-resisting cements and cements containing pozzolans or slag [5]. The application of a multi proxy approach, including chemical, mineralogical, biological and isotopic analyses as a very powerful tool to investigate complex reactions induced by biogenic sulphuric acid attack was presented in paper by Grengg et al. [4,6]. According to Grengg et al. [7] A. thiooxidans are likely to dominate the oxygen rich zones close to the surface, while A. ferrooxidans are proposed to adopt the pore spaces within deeper, anaerobic, corrosion layers.
The results of calcium, silicon, iron and aluminium leaching under the influence of *Acidithiobacillus thiooxidans* bacteria from concrete composites during 90 days are presented in the paper. Dependences of leached-out quantities of selected ions regarding bacterial versus non-bacterial environments were investigated and evaluated using correlation analysis.

2. Materials and methods

2.1. Preparation of samples
Concrete samples were made of sulphate resisting cement CEM I 42.5 N-SR 0 produced with clinker with a very low tricalcium aluminate (C₃A) content. Concrete mixture contested of sulphate resisting cement (360kg), water (170L), three fractions of aggregates: 0/4 mm (825kg), 4/8 mm (235kg), and 8/16 mm (740kg) and plasticizer (3.1L) per 1 m³ of fresh concrete. The proposed composition of mixtures resulted in water to cement ratio w/c = 0.47. Standardized concrete prisms with dimensions of 100 × 100 × 400 mm³ were cured for 28 days in an aqueous environment prior to testing the required mechanical parameters. Consequently, the concrete samples were cut to prepare the test specimens of smaller dimensions. After removal of fine surface impurities by brush, the small specimens of dimensions approx. 50 × 50 × 20 mm³ were immersed into distilled water for 2 hours, then dried on the air and subsequently immersed in ethanol for 24 hours to ensure sterile conditions. The samples were then placed on a sterile filter paper in an aseptic box. After drying for 2 hours at room temperature, the specimens were dried to a constant weight at 105 °C using laboratory oven. Subsequently, samples of cement composites were immersed in the bacterial and reference media over a period of 90 days.

2.2. Experimental testing
Experimental simulation was focused on leaching the main components under biocorrosion caused by sulphur oxidizing bacteria *Acidithiobacillus thiooxidans* (samples marked as BM). Bacterial medium consisted of *A. thiooxidans* inoculum and cultivation medium in 1:4 ratio. Sulphur oxidizing bacteria *A. thiooxidans* were isolated from the mixed culture obtained from the mine water (the shaft Pech, the locality Smolník, Eastern Slovakia). The selective nutrient medium according to Waksman was used for the isolation and cultivation of bacteria at the temperature of 28 - 30°C and pH of 2.0 – 3.5 and as reference medium without bacteria as well (samples marked as CM).

Leaching trends of calcium, silicon, iron and aluminium ions measured in each liquid phase were studied by X-ray fluorescence analysis (XRF) using SPECTRO iQ II equipment (Ametek, Kleve, Germany) with a silicon drift detector (SDD) with a resolution of 145 eV at 10,000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite—HOPG target. The sample measurement was performed at 180 s at a voltage of 25 kV with an applied current of 0.5 mA and 50 kV at 1.0 mA. The sample was flushed with helium. The intensities for all elements were corrected automatically for line interference and absorption effects due to all the other elements using the fundamental parameter method.

2.3. Correlation analysis
The leached-out amounts of Ca, Si, Fe and Al in milligrams per litre represented deterioration parameters have been used in the correlation analysis of the concrete’s deterioration. Statistical method was used for evaluation of the trend of chemical element leaching, as well as for the description of a relation among the selected parameters. Information about the two-dimensional statistical data set gives a correlation coefficient $R_{xy}$ [8], as shown in equation (1).

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The calculated $R_{xy}$ values are in the interval $<-1,1>$. If $R_{xy} = 1$, the correlation is full linear; if $R_{xy} = -1$, then the correlation is inversely linear; and if $R_{xy} = 0$, the pairs of values are fully independent. Then, degree of the correlative closeness is defined as: medium, if $0.3 \leq |R_{xy}| < 0.5$; significant, if $0.5 \leq |R_{xy}| < 0.7$; high, if $0.7 \leq |R_{xy}| < 0.9$; and very high, if $0.9 \leq |R_{xy}|$. A high correlation means that two or more variables have a strong relationship with each other, while a low correlation means that the variables are hardly related. For the purposes of our assessment, the correlation coefficient was obtained using the function “Pearson” in Microsoft Excel.

3. Results and discussion
The concentrations of the main concrete components, measured by XRF analysis is given in table 1.

| % | CaO | SiO₂ | Fe₂O₃ | Al₂O₃ | MgO | P₂O₅ | SO₃ | Cl | K₂O | TiO₂ | MnO | other |
|---|-----|------|-------|-------|-----|------|-----|----|-----|------|-----|-------|
|   | 14.49 | 62.81 | 5.51  | 6.94  | 1.61 | 0.06 | 0.16 | 0.01 | 1.1 | 0.33 | 0.08 | 6.90  |

The chemical composition of the concrete based on the sulphate resistant cement differed slightly from the concrete based on the ordinary Portland cement only [9]. The higher percentage of iron and silicon oxides has been probably connected to the differences in silicon and iron content in ordinary Portland cement (OPC) and sulphate resistant cement, respectively. In spite of the significant difference in aluminium content in mentioned binders, the almost same concentration at about 7 wt. % was observed in studied concrete samples regarding aluminium oxide than in OPC-based concretes.

The comparisons of the leached-out quantities of Ca, Si, Al, and Fe in bacterial and reference media each other are presented in the figures 1-4.
Figure 1-2. Functionality CaBM = \( f(\text{CaCM}) \) and Functionality FeBM = \( f(\text{FeCM}) \) (from up to down).

The X-axis presents the leached-out amounts of ions due to bacterial influence, in medium of \( A. \) thiooxidans, while the Y-axis gives the values of the leached-out quantities of ions in reference non-bacterial medium.

As it is seen in figures 1-4, no dependence regarding bacterial versus non-bacterial environments was found for the leaching trends of silicon and aluminium while significant and very high correlation was found for calcium and iron. The correlation coefficient regarding the relations mentioned, are given in table 2. The results of the correlation analysis point to the fact that the more calcium was dissolved due to bacterial attack the less calcium was dissolved in the reference medium. Our previous results confirmed that the bacterial exposure causes much more extensive leaching of the main concrete components. Based on the correlation analysis, according to our previous experimental findings [10,11] and other authors results [12], it can be concluded, that the leaching trends of calcium, silicon and aluminium strongly depends on the aggressiveness of medium which are the samples exposed to and the leaching mechanisms and behaviour of the ions in solutions differ when compared the bacterial and non-bacterial environments.

Table 2. Calculated correlation coefficients for the individual ions leaching.

| Ions | \( R_{xy} \) | CaBM/CaCM | SiBM/SiCM | FeBM/FeCM | AlBM/AlCM |
|------|-------------|-----------|-----------|-----------|-----------|
|       | -0.95       | 0.02      | 0.62      | 0.16      |

The leaching trend of iron seems to be independent on the medium, the leached-out quantities have been measured very low and oscillated in a very close concentration region 6 – 10 mg/L during whole experimental period.

The calculated Pearson correlation coefficients for the leaching trends Si/Ca and Al/Fe are reported in table 3.

Table 3. Correlation coefficients for the mutual relations of ions.

| Ions | correlation coefficient \( R_{xy} \) |
|------|-----------------------------------|
|      | BM      | CM      |
| Si/Ca| 0.17    | 0.05    |
| Al/Fe| 0.75    | 0.77    |
A weak correlation was found for the leaching trends of aluminium and iron in both bacterial and non-bacterial media. On the other hand, no linear correlation was found for the leaching behaviour of calcium and silicon, as assumed.

4. Conclusion
The paper aimed at the investigation of the concrete composites, based on the sulphate resistant cement, in terms of leaching the calcium, silicon, iron and aluminium compounds due to Acidithiobacillus thiooxidans exposure. The correlation analysis was used to evaluate the leaching trends of selected ions during the experimental period. The differences in leaching rates of calcium have been found when compared the bacterial and non-bacterial exposures. The same findings have been observed for silicon and aluminium.

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