Application of Granulated Blast Furnace Slag in Cement Composites Exposed to Biogenic Acid Attack

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Abstract. The deterioration of cement-based materials used for the civil infrastructure has led to the realization that cement-based materials, such as concrete, must be improved in terms of their properties and durability. Leaching of calcium ions increases the porosity of cement-based materials, consequently resulting in a negative effect on durability since it provides an entry for aggressive harmful ions, causing corrosion of concrete. The use supplementary cementing composite materials have been reported to improve the resistance of concrete to deterioration by aggressive chemicals. The paper is focused on the investigation of the influence of biogenic acid attack on the cement composites affected by bacteria Acidithiobacillus thiooxidans. The concrete specimens with 65 wt. % addition of antimicrobial activated granulated blast furnace slag as durability increasing factor as well as without any addition were studied. The experiments proceeded during 150 days under model laboratory conditions. The pH values and chemical composition of leachates were measured after each 30-day cycle. The calcium and silicon contents in leachates were evaluated using X–ray fluorescence method (XRF). Summarizing the results, the 65% wt. addition of antimicrobial activated granulated blast furnace slag was not confirmed to be more resistant.

1. Introduction
Huge amount of concrete and cementitious materials is used in the wastewater systems. Some of the microorganisms in sewer pipes can generate aggressive aqueous solutions which may damage cementitious materials and reduce the material service time [1]. Thus, there is great interest in predicting the corrosion rate and the service life of sewer pipes.

The most prominent biodegradation is biogenic sulfuric acid corrosion on concrete sewer pipes, wastewater collection systems, and treatment plants [2]. The main source of biogenic sulfuric acid is...
hydrogen sulfide, produced by sulfate reducing bacteria (SRB, e.g. *Desulfovibrio* sp.). The latter are active under anaerobic conditions and reduce oxidised sulfur compounds to H$_2$S. The transformation of H$_2$S into sulfuric acid occurs after the sorption of H$_2$S from the sewer atmosphere into the concrete, or the biofilm on the surface of the pipelines above the water line, under aerobic conditions. Once the H$_2$S has reached the atmosphere, it may react with oxygen to elemental sulfur, which is deposited on the slime-layer, coating the walls. Sulfur is a substrate for many thiobacilli, such as *Acidithiobacillus thiooxidans*, *Acidithiobacillus neapolitanus*, *Acidithiobacillus intermedius* [3, 4], which metabolise it into sulfuric acid. The sulfuric acid produced is aggressive and may attack the inner surface of the concrete pipe and other parts of the treatment and transportation facilities. Ensuing, corrosion products like gypsum (CaSO$_4$ · 2H$_2$O) and ettringite (CaO · Al$_2$O$_3$ · 3CaSO$_4$ · 32H$_2$O) can be formed [5]. These expansive products can lead to increased internal pressure resulting in small cracks. Furthermore, the corroded materials can be removed by the flow of sewage, which also results in the acceleration of corrosion [6].

Ground granulated blast furnace slag is a by-product of the iron-making process and because of its high calcium silicate content it has excellent cementitious content and has been used in the construction industry for years as a replacement for ordinary Portland cement [7]. The replacement of Portland cement by blast furnace slag is an advantageous practice to produce construction materials of improved long-term mechanical properties and durability at relatively lower costs [8]. Use of ground granulated blast furnace slag as a cementitious material blended with Portland cement is based on its activation with alkalis (mainly Ca(OH)$_2$) released from hydration of the Portland cement [9, 10]. When cement reacts with water, it hydrates and produces calcium silicate hydrate (CSH), the main component to the cement strength, and calcium hydroxide (Ca(OH)$_2$). When ground granulated blast furnace slag is added to the mixture, it also reacts with water and produces CSH from its available supply of calcium oxide and silica. A pozzolanic reaction also takes place which uses the excess SiO$_2$ from the slag source, Ca(OH)$_2$ produced by the hydration of the Portland cement, and water to produce more of the desirable CSH making slag, a beneficial mineral admixture to the durability of concrete [11].

In the experiments discussed in this paper, the influence of the addition of granulated blast furnace slag on the resistance of the concrete to biogenic sulfuric acid was investigated.

### 2. Materials and methods

#### 2.1. Concrete samples

The effects of sulphur-oxidizing bacteria *Acidithiobacillus thiooxidans* on concrete samples with addition of ground granulated blast furnace slag were investigated during 150 days under model conditions.

The concrete samples used in the experiment were prepared using cement CEM I 42.5 N as one of the common cements. The composition of concrete mixtures has been chosen to be similar to the concrete composition used in sewerage systems. Mixtures A and B were designed to meet the requirement of at least C25/30 concrete strength class in accordance with EN 206-1. The concrete samples have been prepared considering exposure class XA1 - slightly aggressive chemical environment. This corresponds to conditions when the concrete is subjected to an aggressive chemical action that takes place in the natural soil and in wastewater with the speed of the water, low enough to be accepted for hydrostatic factor of impact. Mix proportion of two different concrete mixtures is shown in table 1.
Table 1. Mix proportion per 1 m$^3$ of concrete mixtures.

| Component | CEM I 42.5 [kg] | Addition of slag [kg] | Water [L] | Aggregate fraction [kg] |
|-----------|----------------|------------------------|-----------|------------------------|
|           |                |                        |           | 0/4 mm | 4/8 mm | 8/16 mm |
| Mixture A | 360            | -                      | 162       | 825   | 235   | 740    |
| Mixture B | 126            | 234                    | 162       | 825   | 235   | 740    |

The standardized concrete specimens with dimensions of 100 x 100 x 400 mm were prepared in accordance with EN 206-1, cured for 28 days in water environment and afterwards cut into small prisms with dimensions of 50 x 50 x 10 mm. The test specimens were slightly brushed in order to remove polluting particles, sterilized in 70% ethanol for 24 hours and dried at 80°C to constant weight before use in the cultivation experiments.

2.2. Microorganisms
In the experiment, the bacterial culture of sulphur-oxidising bacteria – *Acidithiobacillus thiooxidans*, isolated from the acid mine drainage (the shaft Pech, the locality Smolník, Eastern Slovakia) was used. The selective nutrient medium Waksman and Joffe (pH 4.0) was used for the preparation of the active bacterial culture as well as for the isolation and cultivation of *Acidithiobacillus thiooxidans* in the presence of the concrete samples [12]. Its composition is described in table 2.

Table 2. The selective nutrient medium by Waksman and Joffe.

| Chemical compound | Amount         |
|-------------------|----------------|
| CaCl$_2$.6H$_2$O  | 0.25 g/L       |
| (NH$_4$)$_2$SO$_4$| 0.2 g/L        |
| K$_2$HPO$_4$      | 3.0 g/L        |
| MgSO$_4$.7H$_2$O  | 0.5 g/L        |
| FeSO$_4$.7H$_2$O  | Trace amount   |
| S°                | 10.0 g/L       |
| Distilled water   | Up to 1000 mL  |

The prepared concrete samples were exposed to the medium of activated bacteria. The volume ratio of solid concrete sample to the liquid phase was set to 1:10. Experiments carried out in covered glass jars in an aerobic atmosphere at laboratory temperature using liquid selective culture medium inoculated at 7 day intervals with bacteria *Acidithiobacillus thiooxidans*. The 20% vol. inoculum of bacteria *Acidithiobacillus thiooxidans* relative to the total of the liquid phase was used. pH value of liquid phase was kept at an optimal level of 4.0. After each 30 day-immersion period, the change in pH as well as the dissolved concentration of calcium ions was measured in leachates.

2.3. Analytical methods
The chemical composition of leachates was analysed during the experiments by X-ray fluorescence analysis (XRF). 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 at voltage of 25 kV and 50 kV at current of 0.5 and 1.0 mA under helium atmosphere by
using the standardized method of fundamental parameters for leachates. pH changes were measured by pH meter FG2- FiveGo (Mettler-Toledo, Switzerland).

3. Results and discussion
Leaching of calcium and silicon ions from the concrete matrix due to the action of an aggressive environment on concrete samples causes degradation of concrete structures [13]. For this reason, leached out amounts of calcium and silicon ions during the experiment were studied.

3.1. Ca leaching due to biological corrosion
Changes in the concentration of calcium ions in leachates of samples A and B are illustrated in table 3.

| Days of exposition | Ca concentration (mg/L) |
|-------------------|-------------------------|
|                   | Sample A | Sample B |
| 30                | 684.5     | 705.6     |
| 60                | 832       | 840.5     |
| 90                | 691.8     | 755.4     |
| 120               | 719.6     | 799.8     |
| 150               | 793.3     | 838.4     |

The concrete sample A affected by bacteria *Acidithiobacillus thiooxidans* was found to have better leaching performance of calcium ions over a whole period of the experiment. After the experiment, the final concentrations of dissolved Ca ions were determined of 793.3 mg/L and 838.4 mg/L for sample A and B, respectively.

Comparison of quantities of calcium ions leached out due to biological corrosion from samples made of two different mixtures during 150-day experiments corresponding to 1 g of concrete sample is shown in figure 1.

*Figure 1.* Dissolved calcium ions corresponding to 1 g of concrete samples.
The most intensive leaching of calcium ions (3.497 mg/g) during the 150 days of exposition was observed for concrete sample A after 60 days of exposition as it can be seen in figure 1. The Ca ions leaching was observed to be the lowest (2.877 mg/g) for sample A after 30 days of exposition (figure 1). The concentration of dissolved Ca ions in leachates was observed to be higher for sample B compared to the sample A during the experiment except the measurement after the 60-day exposition.

3.2. Si leaching due to biological corrosion
Quantities of dissolved silicon ions during the experiment are illustrated in table 4.

| Days of exposition | Si concentration (mg/L) |
|--------------------|-------------------------|
| Sample A           | Sample B                |
| 30                 | 876.9                   | 784                     |
| 60                 | 1386                    | 1184                    |
| 90                 | 484.9                   | 488.2                   |
| 120                | 669.3                   | 819.3                   |
| 150                | 1042                    | 1361                    |

Table 4 illustrates the changes in the concentrations of Si ions in the leachates of samples A and B during the experiment. The concentration of silicon ions in liquid phase for sample A was lower till 60 days of the experiment and subsequently the concentration increased when compared to sample B.

Leaching performance of silicon in sulfate environment for concrete samples A and B corresponding to 1 g of concrete samples is illustrated in figure 2.

Based on the leached-out masses of silicon after the experiment, sample B was found to be less durable when compared to sample A. Achieved concentrations of dissolved silicon ions were in the range of 2.038 - 5.826 mg/g and 2.021 – 5.634 mg/g for sample A and B, respectively. The concrete sample B with slag addition was found to have better leaching performance of silicon ions than sample
A during 90 days of experiment. The lower durability of sample B with slag addition was detected after 90 days of experiment. As reported in our previous study [14], granulated blast furnace slag based cement composites in terms of silicon ion leaching are more durable in short term experiment. The final concentration of Si ions in leachate of sample A affected by bacteria *Acidithiobacillus thiooxidans* (5.634 mg/g) was observed to be 1.29 times lower than for sample B.

However, to definitely confirm better performance of the analysed samples in the sulphate environment in terms of the dissolved calcium and silicon ions, the calculation of the percentage of leached out ions related to the total ion content and calculations of the leaching rates is needed and is in progress.

4. Conclusion

This paper presents the partial results of the study of the deterioration of concrete samples caused by microbiological attack. Attention was paid to the leachability of the most important components of cement matrix – silicon and calcium compounds.

Many factors, such as elemental chemical composition, replacement rate of cement with slag and slag particle size induce a great variability of the efficiency of the admixture. The 65% wt. addition of antimicrobial activated granulated blast furnace slag was not confirmed to be more resistant, so further research is, indeed, necessary.

5. References

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