

Article

Calcium Extraction from Blast-Furnace-Slag-Based Mortars in Sulphate Bacterial Medium

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Abstract: Wastewater structures, such as treatment plants or sewers can be easily affected by bio-corrosion influenced by microorganisms living in waste water. The activity of these microbes results in deterioration and can cause the reduction in structural performance of such structures. In order to improve the durability of mortar and concrete, different admixtures are being used and the best impact is observed in cement based materials combined with blast furnace slag. In this study, mortar samples with blast furnace slag were exposed to bacterial sulphate attack for 90 and 180 days. The leaching of calcium ions from the cement matrix and equivalent damaged depths of studied mortar samples were evaluated. The results showed more significant leaching of samples placed in bacterial environment, compared to the samples placed in non-bacterial environment. Similarly, the equivalent damaged depths of mortars were much higher for the bacteria-influenced samples. The slag-based cement mortars did not clearly show improved resistance in bacterial medium in terms of calcium leaching.

Keywords: calcium leaching; bio-deterioration; microbiological corrosion; cement mortars; blast furnace slag

1. Introduction

The facilities for sewage transportation and treatment are generally underground and because this they are subjected to many different corrosive agents like sulphates, chlorides or different types of microorganisms [1]. These aggressive agents can easily deteriorate the structures, causing the reduction in material durability and performance [2,3]. This is thus a challenging problem mainly because of significant maintenance costs [4–6].

Durability of wastewater facilities can be influenced by chemical (i.e., acid), physical (i.e., erosion) or biological agents (i.e., living microorganisms). Microbes are known to produce the enzymes and corrosive metabolites such as acids, which can react with the binding material of concrete and mortar materials surface. Microbial involvement in deterioration of concrete was first reported by Parker [7], who isolated five strains of bacteria belonging to *Thiobacillus* sp. from corroded concrete exposed to atmosphere rich of H₂S in sewer pipes [8]. It was proven that sulphate-reducing bacteria in anoxic water and sewer sediments produce hydrogen sulphide (H₂S) and carbon dioxide (CO₂). These gases volatilise and react with fresh alkaline concrete or mortar surfaces and gradually reduce the initial alkaline pH to tolerable pH for acid-producing microbes. At low pH, strong sulphur-oxidising bacteria such as *Acidithiobacillus thiooxidans* and *Acidithiobacillus intermedius*, start colonising the surface of concrete material. These bacteria are capable of further reducing the pH by oxidising thiosulphate and elemental sulphur to sulphuric acid [4]. Microbiological sulphate attack include a series of interactions occurring within the cement matrix as sulphates penetrate through it [9,10]. The reason why these

sulphur-oxidising bacteria are so damaging to cement based structures is because sulphuric acid produced by the *A. thiooxidans* reacts with calcium hydroxide present in concrete and mortar and forms gypsum and ettringite. Both of these compounds are expandable products and the result of their action increases internal pressure of concrete material and production of cracks. Cracks in the structure provide greater surface area for the aggressive sulphuric acid to react and also enable deeper penetration of acid, causing structural failure [4].

Another main concern in sulphate attack of mortar and concrete structures constantly exposed to low pH environment is the leaching of calcium ions from the cement paste matrix [11]. The concentration gradients between the pore solution and the waste water cause diffusion of calcium ions from the pore solution to the surrounding water. The reduction in concentration of calcium ions in the pore solution forces the dissolution of calcium hydroxide and calcium–silicate–hydrate gel and decrease the alkalinity of the pore solution [12,13]. Calcium leaching also causes the increased porosity, and permeability of material and the reduction of concrete strength [2,11].

Both blast furnace slag used in mixture and the reduction in water-binder ratio can improve microstructures of concrete and mortars. Because of the improved microstructure, both of these measures could also increase the calcium leaching resistance of concrete in water environment [2].

Several methods have been developed to control calcium leaching and bio-deterioration concerning concrete and mortar structures. There are mainly two kinds of measures, the modification of concrete or mortars mixtures and coating protection [3,14,15]. The objective of modification of mixtures is to improve the acid resistance, impermeability and crack resistance of the used cement based materials [3,16]. The replacement of cement with waste materials such as ground granulated blast furnace slag has previously been recognised as a substantial factor in increasing the sulphate resistance. This was observed particularly at higher levels of replacement [10,17–19].

The aim of this work was to evaluate the leaching characteristic of calcium ions of mortar composites with blast furnace slag of various proportions. The novelty of study is the examination of the durability of mortars with high replacements of cement by blast furnace slag, up to 95 wt %, under bacterial attack. Based on the leaching results, the damaged depth of the studied mortars exposed to bacteria *Acidithiobacillus thiooxidans* were evaluated.

2. Materials and Methods

2.1. Cement Mortar Mixtures

A series of cement mortar mixtures with varying percentages of blast furnace slag (0–95%) was employed for the experiment. R sample, considered as the reference sample, was based on ordinary Portland cement (OPC) only. The reference mixture has been designed according to the EN 196-1 [20] of CEN-Standard sand (1350 ± 5 g), cement (450 ± 2 g) and water (225 ± 1 g) having water-to-binder ratio (w/b) = 0.5. The CEN-Standard sand is a quartz material characterised by its specific grain size distribution ranging between 0.08 and 2.00 mm. In other mixtures, the ordinary Portland cement was partially replaced by ground granulated blast furnace slag in 65% (CM1), 75% (CM2), 85% (CM3), and 95% (CM4), by weight of cement, respectively. Measured amounts of OPC, ground granulated blast furnace slag, and sand were mixed with water in a concrete mixer, and then shaped using a jolting table for compacting cement samples. The prepared mortar samples with dimensions 160 mm × 40 mm × 40 mm were cured in water for 28 days according to the standard method [20]. After the curing duration, the mortar specimens were treated by ethanol for 24 h to remove the potential biological impurities. After that, the specimens were kept in an aseptic box over a period of 2 h at laboratory temperature. All mortar specimens were consequently dried to a constant weight at 105 °C in a laboratory oven. Subsequently, the specimens were immersed in bacterial medium (*Acidithiobacillus thiooxidans*) simulating wastewater-like environment and in control medium without bacteria.

The chemical composition and potential mineral proportions of used Portland cement as well as the chemical composition of incorporated ground granulated blast furnace slag (GBFS) are shown in Table 1. The Bogue calculation was used to calculate the approximate proportions of the four main minerals in Portland cement clinker: alite-tricalcium silicate (C_3S), belite-dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF).

Table 1. Cement and slag composition.

Components		OPC	GBFS
Chemical composition [% by mass]	Calcium oxide (CaO)	57.15	39.55
	Silica (SiO ₂)	19.01	38.95
	Alumina (Al ₂ O ₃)	4.02	8.33
	Iron oxide (Fe ₂ O ₃)	2.69	0.54
	Sulphur trioxide (SO ₃)	1.49	0.57
	Magnesium oxide (MgO)	1.37	10.11
	Potassium oxide (K ₂ O)	1.12	0.48
	Phosphorus pentoxide (P ₂ O ₅)	0.33	0.04
	Magnesium oxide (MnO)	-	0.74
	Titanium dioxide (TiO ₂)	0.18	0.37
	Chlorine (Cl)	0.06	0.02
	Other	12.58	0.30
	Mineralogical composition [% by mass]	Tricalcium silicate (C_3S)	64.10
Dicalcium silicate (C_2S)		11.34	-
Tricalcium aluminate (C_3A)		8.18	-
Tetracalcium aluminoferrite (C_4AF)		6.12	-
Gypsum (CSH ₂)		up to 5	-
Other		5.26	-

2.2. Bacterial Solution

The bacterial culture was represented by sulphur-oxidising bacteria *A. thiooxidans*, because of their ability to produce sulphuric acid. *A. thiooxidans* originated from an acid mine drainage, Pech shaft, located in Eastern Slovakia. The active bacterial culture was treated by Waksman and Joffe's nutrient medium [21] consisting of 0.25 g/L CaCl₂·6H₂O, 0.2 g/L (NH₄)₂SO₄, 3.0 g/L K₂HPO₄, 0.5 g/L MgSO₄·7H₂O, and traces of FeSO₄·7H₂O. The bacterial solution consisted of bacteria *A. thiooxidans* inoculum (20 vol %) and a Waksman and Joffe nutrient medium with a pH 4.0 (80 vol %). 10.0 g/L elementary S was added to the solution and the adjusted to 1000 mL by distilled water.

The leaching tests of cement mortars were carried out in glass containers filled with bacterial and non-bacterial solutions, respectively, under aerobic laboratory conditions (see Figure 1), over a periods of 90 and 180 days. A solution-to-mortar ratio (V_s/V_m) of 10 was used and the activity of bacterial culture was checked periodically. Optimal growth temperature of bacterial culture (28–30 °C) and pH interval (2.0–4.0) were kept constant during the experiment [22–24].



Figure 1. Mortar specimens in bacterial (a) and non-bacterial (b) medium.

The mortar specimens exposed to bacterial medium with *A. thiooxidans* were labelled as A samples: R/A, CM1/A, CM2/A, CM3/A, CM4/A, and the control samples placed in abiotic environment, were labelled as C samples: R/C, CM1/C, CM2/C, CM3/C, CM4/C respectively.

2.3. Measuring the Extraction of Calcium from the Mortars

Bacterial and non-bacterial solutions were investigated once a month using X-ray fluorescence (XRF) spectrometer SPECTRO iQ II (Ametek, Weiterstadt, Germany) in order to determine the leached-out quantities of calcium ions. 4 mL of the solution was filtered, stabilised by 0.1 M nitric acid and consequently analysed by XRF. The XRF measurement conditions were previously described in more detail [25] where we studied the leaching of calcium from concretes under chemical sulphate attack. The concentrations of calcium in liquid solutions were calculated using the factory-calibrated, standard compliant application package for liquids. The calibration was based on fundamental parameters approach. The concentrations/mass fractions of the elements to be determined were calculated during fitting a modelled X-ray spectrum to the measured one.

2.4. Damaged Depth Calculation

Hardened cement paste includes hydration products such as portlandite ($\text{Ca}(\text{OH})_2$ or CH), calcium silicate hydrates (CSH), and AFm and AFt phases: ettringite, monosulphate, and monocarbonate. When exposed to water solution, portlandite dissolves first and the CH concentrations decreases to zero in the damaged areas. Thus the mortars degradation is manifested by portlandite dissolving and calcium ions leaching. The calculation of the equivalent damaged depth (DD) of mortars was based on the hypothesis that no portlandite (CH) remained in surface layers of mortar samples after the 90 and 180-day leaching, respectively, and that the calcium was fully extracted in a damaged depth [26]. Considering the leached-out concentrations of calcium ions, assuming that they origin from the CH decomposition, damaged depths of particular mortar samples were calculated, according to Roziere et al. [26]. The equivalent damaged depths of studied cement mortars, after both bacterial and non-bacterial exposures, were evaluated using Equation (1), by dividing the total amount of leached calcium by the theoretical initial total calcium content of mortar. The theoretical equivalent damaged depth would actually estimate the damaged depth of cementitious material and thus it could predict the deterioration stage of material.

$$DD = \frac{c(\text{Ca})_{\text{extracted}} (\text{mg}/\text{cm}^2)}{c(\text{Ca})_{\text{initial}} (\text{mg}/\text{cm}^3)} (\text{cm}) \quad (1)$$

where $c(\text{Ca})_{\text{extracted}}$ is the amount of leached-out calcium per unit area (mg/cm^2) of mortar sample and was calculated from the experimental leaching data by converting the measured amounts in leachates

to 1 cm² of sample. $c(Ca)_{initial}$ represents an initial calcium content in mortar per 1 cm³ of sample and was calculated from CaO content of the cementitious materials by dividing the calcium concentration by mortar's volume (mg/cm³). The calcium concentrations originating from the nutrient medium were subtracted from the measured leached-out calcium concentrations in liquid solutions.

3. Results and Discussion

3.1. Leaching Trends of Calcium Ions

The leaching fluxes of calcium ions from the plain cements mortars in de-ionised water are proportional to the square root of the leaching time [11,12]. Figures 2a and 3a show the experimental cumulative quantities of leached calcium by the mortars as a function of the square root of the leaching time for bacterial solutions whereas Figures 2b and 3b for the non-bacterial ones.

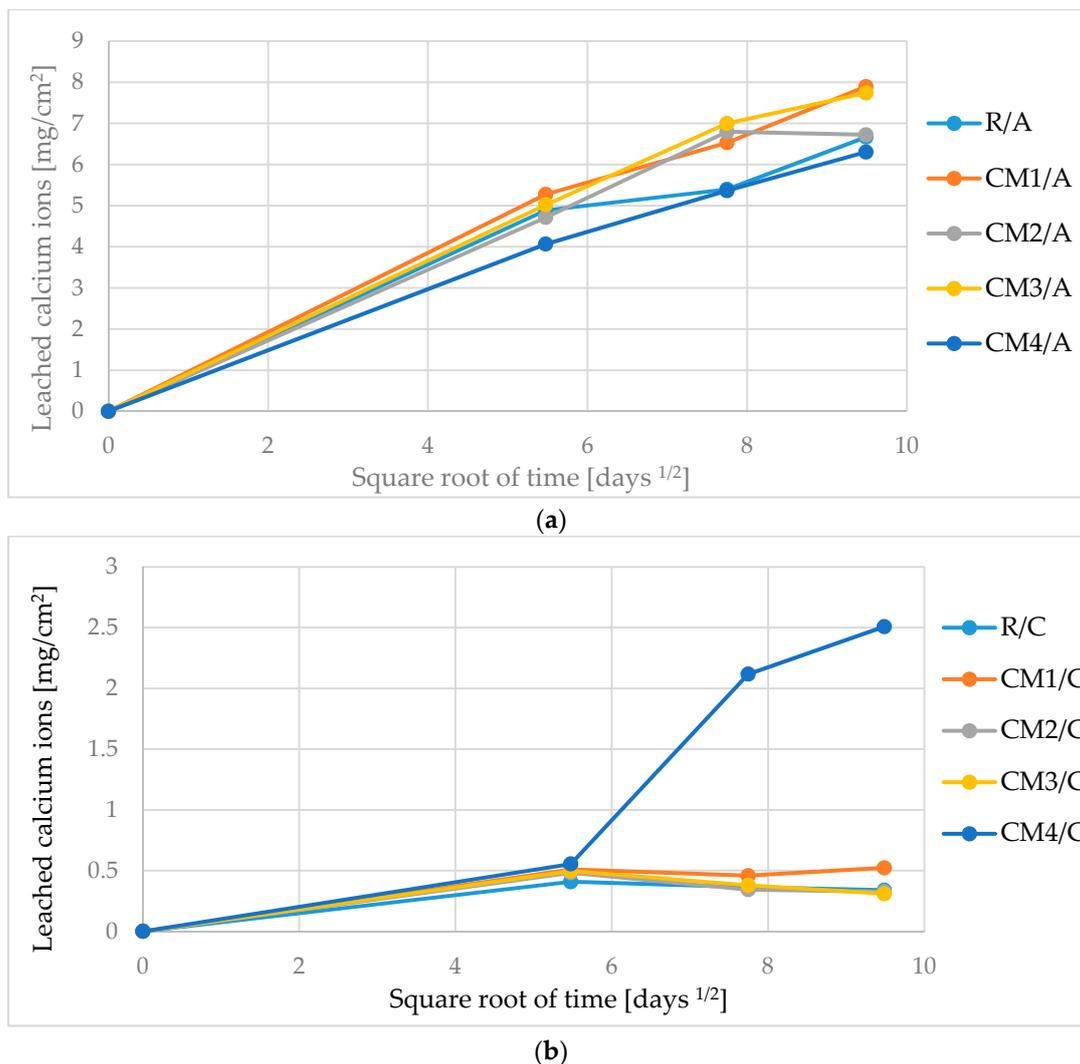


Figure 2. Leached calcium ions in (a) in bacterial and (b) non-bacterial medium during the 90-day experiment.

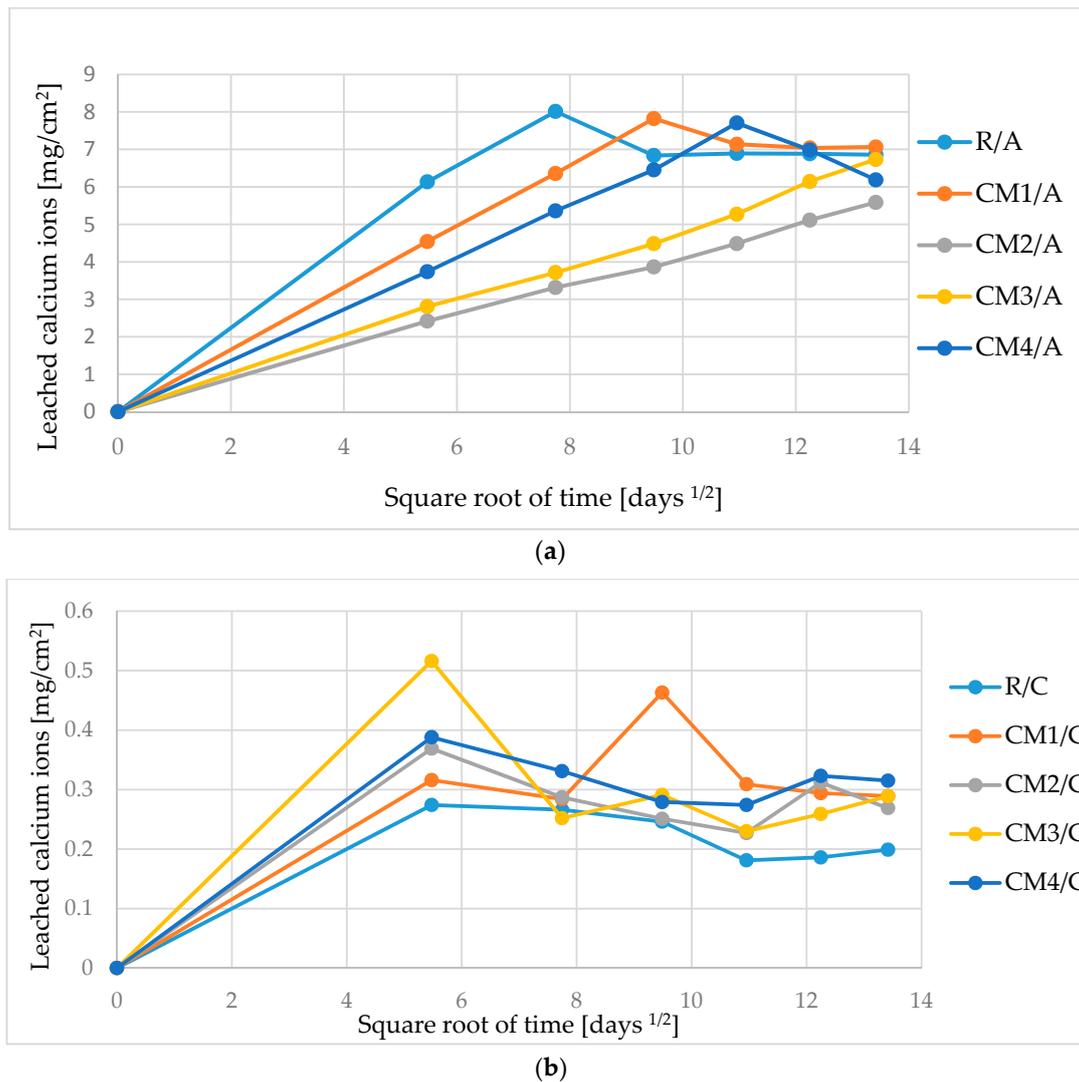


Figure 3. Leaching of calcium ions in (a) bacterial and (b) non-bacterial medium during the 180-day experiment.

As it can be seen, a linear correlation between leached calcium ion concentration and square root of the leaching time was observed in bacterial solution for all mortars after the 90-day experiment (Figure 2a,b). This could indicate a similarity between leaching kinetics of calcium ions due to biogenic sulphuric acid and de-ionised water.

Figure 3 illustrates the quantities of leached calcium ions during 180-day experiment plotted against square root of the leaching time. The proportionality of the leached calcium ions quantities to square root of leaching time was observed up to the extraction time of 90 days. After that, the leached amounts decreased for all samples except from the mortars with the highest content of slag (85 and 95 wt %). This could be linked with a finding that after a certain period the concentration of calcium ions showed a tendency to converge into a constant value, which indicates the equilibrium state of the aqueous and solid phases [11]. The kinetics of degradation are proportional to the square root of the time, as long as there is an unaltered zone and an aggressive solution with a constant composition. The decrease in the calcium concentrations in the leachates could be explained by the precipitation of newly formed sulphate compounds containing calcium on the concrete surfaces as reported previously [25,27].

Kuri reported [28], studying the plain mortars, that a water-to-binder (w/b) ratio of mortars also plays an important role in the extraction time. The calcium leaching rates for the samples with

a higher water-to-binder ratio ($w/b > 0.6$) converged into constant values during 56 days. However, leaching of the samples with low ratio ($w/b = 0.4\text{--}0.6$) continued in a longer period [28]. In our study, the equilibrium of the aqueous and solid phases has been established at about 90 days in bacterial solutions (Figure 3a). This was observed for reference sample without any slag as well as for the samples with 65 and 75 wt % of slag additions. On the other hand, no proportionality of the leached calcium ions quantities to square root of the leaching time was found in abiotic environment (Figure 3b).

3.2. Durability of Mortars in Terms of the Leached Quantities of Calcium Ions

The leaching of calcium ions was proven to be more significant for mortars exposed to *A. thiooxidans* (R/A, CM1/A, CM2/A, CM3/A, and CM4/A) compared to samples exposed to the medium without bacteria (R/C, CM1/C, CM2/C, CM3/C, and CM4/C) during both 90 and 180-day experiments.

The most intensive leaching in the medium with *A. thiooxidans*, was observed with sample CM1/A with 65 wt % of blast furnace slag followed by the reference sample (Figure 3a). Completely largest amount of leached calcium ions (8.012 mg/cm^2) was noticed for the reference specimen R/A during the 180-day extraction (Figure 3a).

On the contrary, the least leached quantities have been found for the sample with 95 wt % of blast furnace slag (CM4/A) in the 90-day experiment and for the sample CM2/A (75 wt % of blast furnace slag) in the 180-day experiment. Considering the leached calcium amounts as deterioration parameter, the most durable were proven to be the CM2/A and CM4/A samples. These samples with 75 and 95 wt % of blast furnace slag, respectively, had proved a higher resistance against bacterial sulphate attack compared to the reference samples, evaluating the calcium leaching only.

3.3. Damaged Depths of Mortars

The calculated indicators of damaged depths of mortars due to bacterial influence during 90 and 180-day extractions ranged from 0.19 to 0.40 mm. Similarly, the DDs of mortar samples without any bacteria were ranging from 0.007 to 0.126 mm (Tables 2 and 3). Rozière et al. [26] reported that the evolution of the equivalent damaged depth of concretes was in the range of 0.25 to 0.63 mm after exposure to sodium sulphate solutions.

Table 2. Damaged depths of mortars over the 90-day extraction.

Mortar Sample	Leached Calcium (mg/cm^2)	Initial Calcium Content (mg/cm^3)	DD (mm)
R/A	6.66	348.22	0.19
R/C	0.34	353.86	0.01
CM1/A	7.89	254.57	0.31
CM1/C	0.52	253.05	0.02
CM2/A	6.72	306.24	0.22
CM2/C	0.33	307.45	0.01
CM3/A	7.74	314.66	0.25
CM3/C	0.31	313.15	0.01
CM4/A	6.30	193.49	0.33
CM4/C	2.51	197.63	0.13

Table 3. Damaged depths of mortars over the 180-day extraction.

Mortar Sample	Leached Calcium (mg/cm ²)	Initial Calcium Content (mg/cm ³)	DD (mm)
R/A	8.01	350.36	0.23
R/C	0.27	357.72	0.01
CM1/A	7.06	254.80	0.28
CM1/C	0.29	255.03	0.01
CM2/A	5.59	304.99	0.18
CM2/C	0.27	309.74	0.01
CM3/A	6.73	314.56	0.21
CM3/C	0.37	315.68	0.01
CM4/A	7.71	193.61	0.40
CM4/C	0.39	197.84	0.02

As mentioned above, the most intensive calcium leaching was observed for samples exposed to bacteria and therefore, the calculated theoretical damage depths (DD) of these samples reached much higher values than DDs calculated for the mortars with no bacterial exposure. When evaluating the DDs of the blast furnace slag-based samples, the lowest value was observed for CM2/A sample with blast furnace slag of 75 wt % during both 90 and 180-day extractions in bacterial medium. Since the least calcium leached samples do not necessarily show the lowest DDs, the long-term leaching experiment (365 days) is in progress.

4. Conclusions

This study has dealt with calcium ions leaching from cement mortars with different proportions of blast furnace slag in bacterial and non-bacterial environments. To predict the deterioration of the concrete materials the theoretical damaged depths were calculated.

- Samples exposed to the medium with sulphur-oxidising bacteria *A. thiooxidans* had proven higher calcium leaching rates and significantly deeper degradation than the samples exposed to the nutrient medium without bacteria.
- The blast furnace slag modified paste did not show definitely lower values in calculated damaged depths, comparing to the reference one.
- When evaluating the calculated damaged depths of blast furnace slag-based mortars, the sample with 75 wt % of blast furnace slag was found out to be the most resistant in *A. thiooxidans* bacterial environment. The assumption of the best performance of the sample with the highest proportion of blast furnace slag was not confirmed.

Calculation of the theoretical damaged depths of cement materials can be helpful in prediction of the deterioration stage of concrete composites, e.g., in sewage systems. However, to give a clear conclusion about the durability of the blast furnace slag-based composites, more research considering other deterioration parameters (changes in mass of composites, compressive strengths, water absorbability, surface changes, etc.) is needed. The future research is aimed at designing the optimal composition of the composites modified by blast furnace slag, regarding the improvement in durability of concretes.

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Conflicts of Interest: The authors declare no conflict of interest.

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