

Determination of durability of mortar with slag exposed to bacterial environment

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Abstract. Leaching of cement based materials and dissolution of cement hydrates under biogenic acid attack result in an increase of the porosity and changes in the pore structure of the building materials. The impact of certain physicochemical concrete/mortar parameters such as cement chemistry, water/binder (w/b) ratio, porosity and fluid permeability of cementitious materials has been recognized from a material sciences perspective. In this work the durability of cement composite made with blast furnace slag exposed to sulphur oxidizing bacteria *A. thiooxidans* during the period of 12 months was investigated. Leaching of calcium and silicon ions, water absorbability and porosity of the slag based composite using X-ray computed tomography was evaluated.

1. Introduction

For many years, cement-based materials have been used as structural or filling materials in a great variety of applications, such as building materials. The durability of these materials is affected as they are altered in contact with water or exposed to various environmental conditions [1]. Durability of cement based materials has become a main concern mainly for safety, economic and environmental reasons. It is well known that the durability issues, such as chloride or sulphate-induced corrosion, carbonation, freeze-thaw action are closely linked with fluid and ion transport in cementitious materials [2].

Pore network in cement pastes plays a fundamental role in the transport processes of elements (major and trace elements) within the matrix and hence their potential release in the environment [1]. In the hardened cement paste, there are complex pore structures, including gel pores, capillary pores, and air voids [3]. Pore size distribution in composite matrix is ranging from few nanometers (nm) up to tens of micrometers (μm) [1,4]. Such a diverse pore system is closely associated with the mechanical performance and transport properties of the matrix. To a large extent the pore structure determines the ingress of surrounding water molecules into the cement material. Entrained aggressive substances, such as sulphate, carbonate and chloride ions, penetrate the cement matrix through pore transportation, resulting in neutralization of cover of cement-based material and possible generation of chemical stress. In addition to the external load, the porosity of cement composites downgrades their mechanical properties [3].

Concrete corrosion is a complex process which involves the physical adsorption of hydrogen sulphide, chemical and biological oxidation of sulphide to various sulphur species, including sulphuric acid, and reaction between the sulphuric acid and the cement matrix. During active sewer corrosion sulphur oxidizing bacteria (SOB) oxidize the sulphur compounds resulting in sulphuric acid production which then diffuses into the inner corrosion layer and reacts with alkaline compounds



released from the material. Ultimately, the loss of cement mass occurs and the microbial conversions of sulphur compounds are critical for the process [5].

Recently, the utilization of waste materials and supplementary cementitious materials (SCMs) with fine size has been found to compensate both physically and chemically the deficiency in manufacturing denser and more compact cement-based structures [3,6,7,8]. Granulated blast furnace slag (GBS) and silica fume (SF) are two cement replacements which have grown in popularity in recent years. Slag is a by-product from blast furnaces used to make iron. There are many advantages of GBS as: greater compressive and flexible strengths, greater workability and the ability to produce a denser matrix [9,10,11]. GBS provides greater mechanical and durability properties as it significantly decreases both the content and the size of $\text{Ca}(\text{OH})_2$ crystals in the aggregate-paste interface, which makes the microstructure of the transition zone dense and strong [9,12].

This paper presents an attempt to determine the durability of mortar sample made with blast furnace slag affected by the action of *Acidithiobacillus thiooxidans* after long-term, 12-month exposition. Evaluated characteristics were leaching of calcium and silicon ions, water absorbability and porosity of composite sample which was characterised by X-ray computed tomography.

2. Material and Methods

2.1 Mortar sample

Two mixtures were designed for the experiment, whereas S0 sample represents the reference sample made with ordinary CEM I Portland cement (OPC) and sample S1 was made with 35 wt.% of ordinary Portland cement (OPC) and with 65 wt.% of blast furnace slag, respectively. The mortar specimens with dimensions approximately 160 mm × 40 mm × 40 mm were designed in cooperation with cement factory plant which we cooperate with. Chemical composition of OPC and blast furnace slag is shown in table 1.

Table 1. Chemical composition of ordinary Portland cement and blast furnace slag.

Content of main components	OPC (wt.%)	Slag (wt.%)
CaO	57.15	39.55
SiO₂	18.11	38.95
Al₂O₃	4.02	8.33
Fe₂O₃	2.69	0.54
SO₃	1.49	0.57
MgO	1.37	10.11
K₂O	1.12	0.48
TiO₂	0.18	0.37
P₂O₅	0.33	0.04
Cl	0.06	0.02

2.2 Microbiological exposure

In the experiment, sulphur-oxidising bacteria *Acidithiobacillus thiooxidans* was used to create the aggressive acidic environment, because of their ability to produce sulphuric acid. *A. thiooxidans* were isolated from an acid mine drainage from Pech shaft (locality of Smolník, Eastern Slovakia). The nutrient medium by Waksman and Joffe [13] 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 g/L $(\text{NH}_4)_2\text{SO}_4$, 3.0 g/L K_2HPO_4 , 0.5 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, traces of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 10.0 g/L elementary S and up to 1000 mL supplemented by distilled water. Elemental sulphur was added to the nutrient medium.

The exposure of mortar samples to acidic bacterial environment has taken place in glass containers under aerobic laboratory conditions over a period of 12 months. Optimal growth temperature of bacterial culture (28 - 30°C) and pH interval 2.0-3.5 were controlled during the experiment [14,15].

2.3 X-ray fluorescence analysis

X-ray fluorescence analysis (XRF) was used to analyze the chemical composition of leachates. After placing samples into the bacterial medium, a chemical composition of mortar sample leachates was investigated every 2 months. SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with a resolution of 145 eV was used for the analysis. The samples were analysed for 300 s (solid specimens) and 180 s (liquids) using X-ray tube (25 kV and 50 kV, 0.5 mA and 1.0 mA) combined with a Highly Ordered Pyrolytic Graphite (HOPG) crystal for polarization of the primary beam. The measurement proceeded under helium atmosphere. The concentrations of the elements were calculated by using the calibration method for cements and liquids, respectively [14].

2.4 Water absorbability test

The water absorbability test was performed on mortar specimens in accordance with a corresponding national standard [16]. All samples were dried at $105 \pm 5^\circ\text{C}$ to the constant mass and consequently weighted (m_D). After that, the reference samples were immersed in water for 72 hours and weighted again (m_W). Based on these two mass values, the original absorbability of samples, before the experiment, was determined. The final absorbability of the exposed samples was calculated using wet mass of the samples (m_W) measured after 12 months when the samples were removed from the liquid medium. Water absorbability for both samples was determined using equation (1) [16]:

$$v = \frac{m_W - m_D}{m_D} \cdot 100\% \quad (1)$$

where m_W refers to the weight of wet sample and m_D is weight of dried sample.

2.5 Micro X-ray computed tomography

X-ray computed tomography (CT) is a non-destructive method for obtaining a large number of consecutive sectional images of the internal microstructure of specimens. It has been used in several studies to characterize the engineering properties of cement-based materials in terms of such parameters as pore network, air-void space, or spatial distribution of air content under axial loading [17,18,19].

To study the inner structure of mortar sample, the Nikon Metrology XT H 225 industrial micro X-ray CT system with reflex X-ray source and flat detector with resolution of 4000x4000 pixels was used. It is a fully automated apparatus with a rotating scanning system equipped with a micro focal X-ray source which generates cone-shaped beams. Studied volumes were reconstructed using CT Pro 3D and CT Pro 2D software (by Nikon Metrology NV). Visualization was provided by a VGStudio Max software (by Volume Graphics), version 2.2, with additional modules for proper image analysis [20].

3. Results

The changes in Ca and Si ion concentrations in leachates of studied mortar sample are given in figure 1. The highest concentration of Ca ions was observed for sample S1 at the end of the experiment with the value of 841.6 mg/L. Highest amount of leached Ca ions (578.1 mg/L) for reference sample was also observed at the end of the experiment. The leaching of Si ions for specimen S1 was most intensive with maximum reached after 6th month of bio-corrosion experiment (603.4 mg/L). For the reference sample S0 the highest concentration of leached out Si ions was measured after the 12 month period with the value of 663.6 mg/L. The increase in the values of leached out calcium and silicon ions are linked with gradual deterioration of sample caused by dissolving the composite's hydrates.

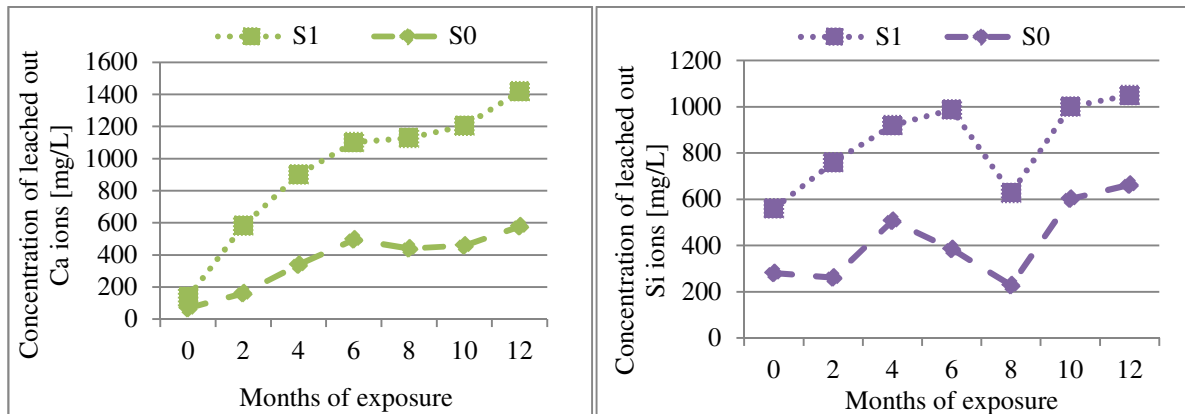


Figure 1. Concentration of leached out Ca and Si ions from mortar sample during bacterial exposition.

Water absorbability of mortar composites before and after the bio-corrosion experiment is reported in table 2.

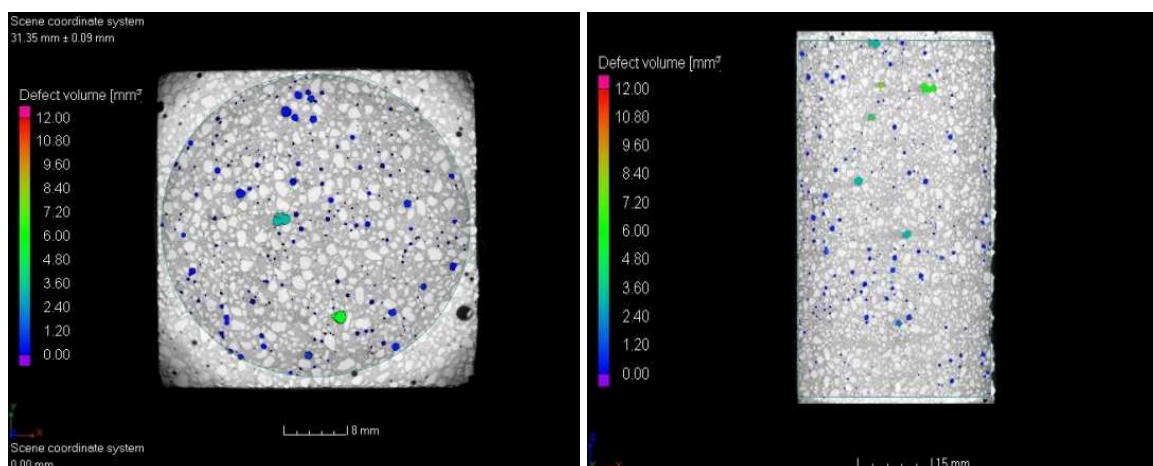
Table 2. Water absorbability of mortar composite.

Mortar sample	Water absorption capacity [%]		Change [%]
	Before the experiment (72 hours)	After 12 months	
S0	7.98	10.99	3.01
S1	8.55	8.76	0.21

It can be seen that water absorbability of both samples increased due to the sulphuric acid exposure. Considerably higher change in water absorption capacity was observed for reference sample S0, which increased by 3.01%, while the change in water absorption capacity for the sample S1 made with blast furnace slag was only 0.21%. The lower water absorbability of sample S1 is likely linked to the presence of blast furnace slag in the mortar, which resulted in denser matrix of the sample with reduced porosity.

Nevertheless the sample S1 made with blast furnace slag had higher leached out amount of Ca and Si ions, what is in contrary to the water absorbability results. This contradiction can be linked to the different chemical compositions of the cement mortars.

The pore size and porosity of the sample S1 with slag, measured using X-ray computed tomography, is illustrated in figure 2. Different colours on the images indicate the different size of the pores in the sample.



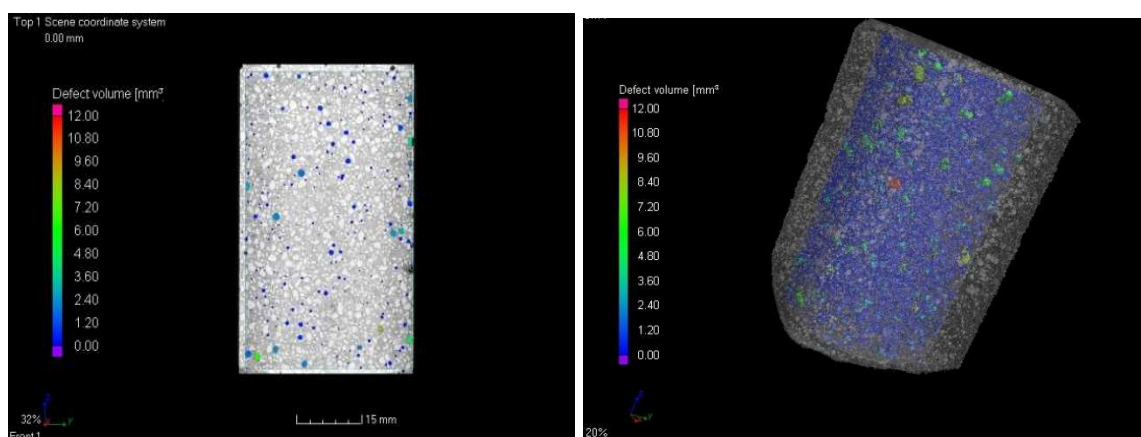


Figure 2. Micro X-ray CT images of mortar sample made with blast furnace slag.

The size of pores in sample varied from 0.01 mm to 11.54 mm, the smallest pores such as gel or capillary pores were not measured by micro computed tomography which is accordance with the study by Bossa N. et al [1]. The dimensions of tested cylinder were, the diameter 38.7 mm with height 63.6 mm. The total number of pores in the tested area of specimen were 16 690. Micro computed tomography measurements lead to a calculated porosity of 0.8% in the composite sample, in agreement with studies by Chengcheng D. et al. [19], where the cement composite samples had porosity ranging from 0.044% to 1.486%. Some authors state, that porosity of cement composites is ranging from 1.8% [1]. This result confirms that micro X-ray CT is not sensitive enough to detect all the smallest pores that represent up to 70–90% of the whole pore volume of the cement matrix [1,4].

4. Conclusion

In order to predict the biodeterioration of the material it is necessary to evaluate various physico-chemical parameters. The objective of this paper was to determine the durability of cement composite made with the addition of blast furnace slag under the 12 months long exposition of aggressive sulphate environment represented by bacteria *A. thiooxidans*. Evaluated characteristics were leaching of basic inorganic elements (calcium and silicon ions), water absorbability, porosity and pore size of the sample, which was measured by micro computed tomography. Obtained results of leaching of basic inorganic elements and increase in water absorbability of sample confirmed the degradation effect of sulphur-oxidizing bacteria, however the pore network and the overall porosity could not be properly measured due to low sensitivity of the micro X-ray computed tomography.

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