Changes in water absorptivity of slag based cement mortars exposed to sulphur-oxidising *A. thiooxidans* bacteria

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Abstract. Water absorptivity is heavily influenced by the volume and connectivity of pores in the pore network of cement composites and has been used as an important parameter for quantifying their durability. To improve the durability and permeability of mortars, various mineral admixtures such as furnace slag, silica fume or fly ash are added into the mortar and concrete mixtures. These admixtures provide numerous important advantages such as corrosion control, improvement of mechanical and physical properties and better workability. This study investigated the changes in absorptivity of cement mortars with different amounts of mineral admixture, represented by granulated blast furnace slag, under aggressive bacterial influence. The water absorptivity of mortars specimens exposed to sulphur-oxidising bacteria *A. thiooxidans* for the period of 3 and 6 months has changed due to bio-corrosion-based degradation process. The differences in water absorptivity in dependence on the mortars composition have been observed.

1. Introduction

One of the most important characteristic of concrete structures is durability, which is defined as the capability of concrete to resist weathering action, chemical attack and abrasion while maintaining its desired properties [1]. For concrete buildings, one of the major forms of environmental attack is sulphate ingress, which leads to corrosion of the structure and a subsequent reduction in the strength, serviceability and aesthetics. This may result in to the early repair or replacement of the structure. Using concretes and cement based materials with lower permeability is a common method of preventing the degradation caused by ingress of sulphate ions [2]. Research by Nolan et al [3] indicated that materials with low permeability last longer without showing signs of distress and deterioration and thus the permeation properties are used for determination of the durability of concrete [4,5,6]. Porosity of building materials along with ingress of moisture and other harmful chemicals such as sulphates affect this material and seriously reduce its strength and life span of the structure. A suitable solution is the use of an additive that seals the pores and cracks and thus reduces the permeability of the structure [7].

Sulphate resistance in cement based material can be improved by adding supplementary cementing materials (SCM). Use of SCM such as granulated blast furnace slag improves the microstructure of the cement matrix, resulting in the lower permeability of concrete, because of extreme fineness and high silica content. Once lower permeability is enhanced, concrete becomes more durable against sulphate attack. For this reason, it also enhances the chemical durability [1].

Another way of increasing the permeability of cement based materials is microbial mineral precipitation, which has leads to several investigations on the use of bacteria in concrete and cement materials. Different microorganisms have been used to decrease the permeability of cement mortar and for the remediation of cracks in concrete [4,8,9]. Bacterial culture causes bacterial deposition of a calcite on the surface of the materials. This process is dependent on the type of bacteria and the crystal morphology of calcium carbonate. Microbial mineral precipitation, also called bio-deposition, involves various microorganisms and environments [7]. Muynck et al. [5] observed that durability of mortar specimens with different porosity was affected by bio-deposition. The surface deposition of calcite decreased the water absorption with 85% depending on the porosity of the studied samples [2]. This paper presents the results of water absorptivity of slag based cement mortars exposed to an aggressive bacterial activity of *Acidithiobacillus thiooxidans* for 3 and 6 months.

2. Material and Methods

2.1 Cement composites mixture proportion and dimension of specimens

In the experiment, 5 different mortar mixtures were studied. The reference sample with ordinary Portland cement (OPC) was represented by sample S0. In the samples S1, S2, S3 and S4 cement was partially replaced by 65 %, 75%, 85% and 95% granulated blast furnace slag by weight of cement. The proportions of the mixtures by mass was one part of cement, three parts of CEN standard sand, and one half part of water (w/c 0,50). Each batch shall consist of (450 ± 2) g of cement, (1 350 ± 5) g of sand and (225 ± 1) g of water. Mixtures were designed in cooperation with a cement factory plant which we collaborate with. Cement mortars samples used in the water absorption test had dimensions (approx.): 160 mm × 40 mm × 40 mm. Chemical composition of used cement and blast furnace slag is given in table 1.

Table 1. Chemical composition of OPC and slag.

Content of main components	% By mass (OPC)	% By mass (Slag)
CaO	57.15	39.55
SiO_2	18.11	38.95
Al_2O_3	4.02	8.33
Fe_2O_3	2.69	0.54
SO_3	1.49	0.57
MgO	1.37	10.11
K_2O	1.12	0.48
TiO2	0.18	0.37
P2O5	0.33	0.04
Cl	0.06	0.02

2.2 Liquid medium

Sulphur-oxidising bacteria *Acidithiobacillus thiooxidans* represented the aggressive sulphate environment used in the experiment. 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* and the composition of the nutrient medium is as follows: 0.25 g/L $CaCl_2$.6H2O, 0.2 g/L $(NH_4)_2SO_4$, 3.0 g/L K_2HPO_4, 0.5 g/L $MgSO_4.7H_2O$, traces of $FeSO_4.7H_2O$, 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 Smolnik, Eastern Slovakia).

Elemental sulphur was added to the nutrient medium. The exposure of mortars specimens to bacterial culture proceeded in glass containers under aerobic laboratory conditions over a periods of 3 and 6 months. Optimal growth temperature of bacterial culture (28 - 30°C) and pH interval 2.0-3.5 were ensured during the experiment [10,11,12].

The samples exposed to bacterial medium with *A. thiooxidans* were labelled as S0/A, S1/A, S2/A, S3/A and S4/A and the control samples placed in abiotic environment, with no bacteria, were labelled as S0/C, S1/C, S2/C, S3/C and S4/C respectively.

The volumes of liquid phase for the mortar samples used in experiment is described in table 2.

Table 2. Volume of liquid phase used in the experiment.

Mortar sample	Volume of inoculum of A.thiooxidans (ml)	Volume of nutrient medium (ml)	Volume of sterilized water (ml)	Amount of elemental sulphur (g)
S0/A	512	768	1280	6.4
S0/C	-	1280		
S1/A	512	768		
S1/C	-	1280		
S2/A	512	768		
S2/C	-	1280		
S3/A	512	768		
S3/C	-	1280		
S4/A	512	768		
S4/C	-	1280		

2.3 Water absorption testing

An absorptivity test, based on the national standard [13], was carried out before and after the experiment on the 2 sets of samples. Before the experiment, the samples of cement mortars were dried at 110 ± 5 °C to the constant mass and weighted. After that, the samples were placed into tap water and kept in water until establishing a mass equilibrium up to 72 hours. Consequently, the weight of water-saturated samples was measured. After the experiment, the same procedure was applied to the exposed samples. The absorption capacity was determined using equation (1):

$$v = \frac{mv - md}{md} .100\% \tag{1}$$

where m_v represents the weight of wet sample after immersion and m_d is weight of dried sample.

3. Results

The results of water absorption capacity weights cement composites samples before the experiment and after 3 and 6 months of sulphate exposure are given in table 3.

Table 3. Water absorption capacity prior the experiment and after 3 and 6 months.

Mortar sample	Water absorbability [%]			
	Before the experiment	*After 3 months*	*After 6 months*	*Variance**
S0/A	7.98	8.34	9.04	1.06
S0/C		9.25	8.34	0.36
S1/A	8.55	8.78	8.81	0.26
S1/C		10.02	10.7	2.15
S2/A	8.75	9.44	9.86	1.11
S2/C		10.06	10.25	1.52
S3/A	9.20	9.21	9.25	0.05
S3/C		10.05	9.56	0.36
S4/A	9.20	9.51	10.68	1.48
S4/C		10.01	10.77	1.57

* Variances in water absorbability were calculated as the difference between the absorptions after the 6-month experiment and the absorptions before the experiment

Average water absorbability of cement mortars has increased after 3 months of mortars exposure to both bacterial and non-bacterial liquid media. When compared the absorbabilities measured after 3-month exposure and 6-month exposures, we can conclude that the absorbability increased for all samples excluding S0/C sample. Anyway, the obtained absorption of S0/C after the 6-month exposure was higher than the original one. The highest absorption capacity of 10.77 % was measured for sample S4/C with 95 wt.% of granulated blast furnace slag and the lowest one equal 8.34% was measured for reference sample S0/A after 3 months and S0/C after 6 months.

Based on the variances in water absorbabilities, the samples placed in non-bacterial environment have been observed to have more significant increase in absorption than the samples exposed to bacteria. This was not confirmed for the reference sample without any slag addition. The finding could be likely linked to the ability of bacteria to create a calcite layer on the surface of the cement composites, despite the fact that the bacterial culture of *A. thiooxidans* was in the experiment used for the simulation of corrosive environment. This layer creates a barrier against the penetration of water and the outcome is lower permeability, which may lead to enhanced durability of cement based material. In the paper from authors N. Chahal et al [2] the deposition of a layer of calcium carbonate on the surface and inside pores of the concrete specimens resulted in a decrease of water absorption and permeability, which was observed in the experiment. Once the pores are sealed, reduction in water ingress is observed. The presence of crystalline calcium carbonate associated with bacteria indicated that bacteria served as nucleation sites during mineralization process. As Chahal et al. mentioned, distinct calcite crystals embedded with bacteria have been observed by scanning electron microscopy [2]. Castainer et al. [14] and Riding [15] reported that bacteria and fungi can induce precipitation of calcium carbonate extracellularly through a number of processes that include photosynthesis, ammonification, denitrification, sulphate reduction and anaerobic sulphide oxidation [16].

4. Conclusion

This paper assesses the water absorbability of slag based cement composites in microbial sulphate environment after 3 and 6 months. Composites sample (S0/A, S1/A, S2/A, S3/A and S4/A) placed in sulphate environment with bacterial culture of *A. thiooxidans* had lower water uptake in comparison with the samples (S0/C, S1/C, S2/C, S3/C and S4/C) placed in non-bacterial environment, except for samples S0/A and S0/C after 6-month experiment. It seems that bacterial deposition of calcite layer on the specimens resulted in decrease of the permeation properties of cement composites. This could indicate that durability of mortar specimens with different porosity was affected by *A. thiooxidans* carbonate precipitation.

The highest increase in absorption capacity was observed for the samples with 95% of blast furnace slag. To make a definitive conclusion regarding the water absorbability of cement composites samples in sulphate environment with *A. thiooxidans*, the long-term experiments are in progress.

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