

Experimental Research of Building Materials Based on the Natural Cellulosic Fibers under Biogenic Acidic Exposition

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Abstract: The paper is aimed at the study of the building materials based on the natural cellulosic fibers in aggressive environment. The fiber cement boards' samples were analyzed in terms of dissolving the main cement matrix compounds representing by calcium and silicon leaching. Aggressive environment was represented by bacteria influence. The results indicate substantial differences on the leaching of calcium and silicon ions in presence of bacteria and without bacteria.

Key words: cement composite, sulphate-reducing bacteria, sulphur-oxidising bacteria, sulphuretum, leaching

1. Introduction

Fibres of various types are used frequently in the building industry to achieve desired properties or to reduce the cost of the final products. One of the main ingredients of fibre cement products is cellulose fibre from wood or non-wood sources, which are added to reinforce the cement composite. Natural cellulose fibre cement composite products can be made use of in exterior and interior of a building such as siding, roofing, external cladding, internal lining, floors, walls, building boards, bricks, bracing, fencing and decorative elements. Fibre cement is also used in construction works such as dam, bridge deck, road building, sidewalk, flagstone paving, and so on.

There is a bio-corrosion phenomena associated with the cement composites used in various environments including not only sewerages and waste water plants but siding and roofing as well [1]. This phenomenon

consists on both the influence of the microorganism directly in contact with the artificial material or indirectly in degradation of materials by its metabolic products [2]. Sulphur-oxidising and sulphur-reducing bacteria represent the most important species in cement composites biodeterioration process causing the deterioration through the biogenic sulphuric acid production [3].

Cement fibres boards exposed to simultaneous deleterious effect of sulphur-oxidising (*Acidithiobacillus thiooxidans*) and sulphur-reducing bacteria (*Desulfovibrio desulfuricans*) were studied by weight and surface changes of the specimens and pH values changes in leachates in our previous works [4, 5]. This paper presents the results of a comparative analysis of an individual bacterial attack of *Acidithiobacillus thiooxidans* and *Desulfovibrio desulfuricans* in terms of changes in dissolved calcium and silicon concentrations from the fibre-cements samples under individual microbial exposition.

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2. Material and Methods

The fibre-cement boards commonly used in the Slovak Republic were chosen for the experiments. Composition of boards consisted is shown in Table 1.

The prepared boards' specimens of size 100×150×8 mm were treated during 2 hours in distilled water and then dried in aseptic box. Chemical sterilization of samples has been carried by treating the specimens in ethanol for 12 hours and by following drying in aseptic box during 2 hours. Thermal sterilization of samples has been carried at 80°C during 3 hours.

The bio-corrosion experiment was based on the cultivation of the sulphur-oxidising (*Acidithiobacillus thiooxidans*) and sulphur-reducing bacteria (*Desulfovibrio desulfuricans*) individually as well as simultaneously at optimal growth conditions in presence of fiber-cement samples by using the cultivation media. *Acidithiobacillus thiooxidans* representing sulphur-oxidising bacteria were isolated from the mixed culture obtained from the mine water (the shaft Pech, the locality Smolník, Eastern Slovakia). Optimal growth temperature of 28-30°C and pH of 2.0-3.5 were set to cultivation of bacteria using the selective nutrient medium 9K [6]. *Desulfovibrio desulfuricans* representing sulphate-reducing bacteria were isolated from a mixed culture obtained from the potable mineral water (Gajdovka spring, the locality Kosice-north, Slovakia). The selective nutrient medium DSM-63 [7] was used for isolation and cultivation of bacteria by ensuring the optimal growth conditions of pH ranging from 6.5 to 7.3 and temperature of 30°C.

Table 1 Composition of Fibre-Cement Boards

Component	Wt. %
Portland cement	40-80
Celluloses	4-15
Limestone	10-50
Polyvinyl alcohol fibres	0-2
Colorants based on chromium oxide	0-10
Colorants based on cobalt oxide	0-5
Colorants based on iron oxide	0-5
Acrylic paint	0-3

The individual effect of bacteria on fibred boards was studied by partial immersing the samples into the liquid media of bacterial cultures mentioned above. The liquid medium was consisted of 150 ml of selective nutrient medium with 10% of bacterial inoculum. The aerobic conditions were ensured in case of *Acidithiobacillus thiooxidans* (A.t.) and the anaerobic ones in case of *Desulfovibrio desulfuricans* (D.d.). The characterization of samples and liquid media is summarized in Table 2.

The laboratory model tests were performed over a period of 90 days. Leaching of the main cement matrix elements — calcium and silicon ions was investigated by X-ray fluorescence analysis (XRF). Microscopy method SEM/EDAX and AFM were used for the surface changes analyses.

3. Results

Changes of Ca and Si ions concentrations in liquid phases of fibre boards exposed to *Acidithiobacillus thiooxidans* and *Desulfovibrio desulfuricans* bacteria, respectively as well as to the reference media without bacteria are shown in Table 3. The initial concentrations C_i of calcium ions in leachates were equal to 45.9 mg/L for A series of samples (A1, A2, AK1, and AK2) and to 27.3 mg/L for D series of samples (D1, D2, DK1, and DK2). The initial concentration C_i of silicon ions in all leachates was equal to zero.

Table 2 Characterization of Samples in Relation to the Used Liquid Media

Sample	Medium	Colorants
A1	selective nutrient medium 9K with A.t.	based on iron oxide
AK1	abiotic control to sample A1 without bacteria	
A2	selective nutrient medium 9K with A.t.	based on cobalt oxide
AK2	abiotic control to sample A2 without bacteria	
D1	selective nutrient medium DSM-63 with D.d.	based on iron oxide
DK1	abiotic control to sample D1 without bacteria	
D2	selective nutrient medium DSM-63 with D.d.	based on cobalt oxide
DK2	abiotic control to sample D2 without bacteria	

Table 3 Concentration Changes of Ca and Si Ions in Liquid Phases

	Ca [mg/L]	Si [mg/L]
Sample	$C_f - C_i$	$C_f - C_i$
A1	24.58	7.7
AK1	- 44.11	3.51
A2	13.58	3.51
AK2	- 43.81	2.97
D1	120.68	33.51
DK1	252.04	29.87
D2	110.18	23.72
DK2	163.24	19.96

C_f – final concentration (measured before the experiments)

C_i – initial concentration (measured after the experiments)

Except the control samples without bacteria (AK1 and AK2), the concentration of calcium increased in all measured leachates. The decrease in concentrations of calcium ions in the leachates of AK1 and AK2 samples after the experiment can likely be caused by massive precipitation of the calcium compounds such as gypsum and ettringite on the surface of the samples. The formation of gypsum and ettringite was confirmed by SEM microscopy.

The concentration of silicon ions increased in all measured leachates after the experiments. Calcium compounds' leaching has been observed to be more intensive when compared to the silicon compounds' leaching (Table 3).

The results of the calcium ions leaching, measured by using X-ray fluorescence analysis (XRF), due to various bacterial and abiotic exposition are compared in Fig. 1.

As it is clear from Fig. 1, the calcium compounds dissolving has been found out to be more intensive in presence of sulphate-reducing bacteria *Desulfovibrio desulfuricans* compared to sulphur-oxidising bacteria *Acidithiobacillus thiooxidans*. The measured Ca concentrations dissolved due to *Desulfovibrio desulfuricans* bacterial exposition were 4.9 times (D1/A1) and 8.1 times (D2/A2) higher than due to *Acidithiobacillus thiooxidans* bacterial exposition.

Leaching trend of measured silicon ions in the liquid phases in various environments during the experiment is illustrated in Fig. 2.

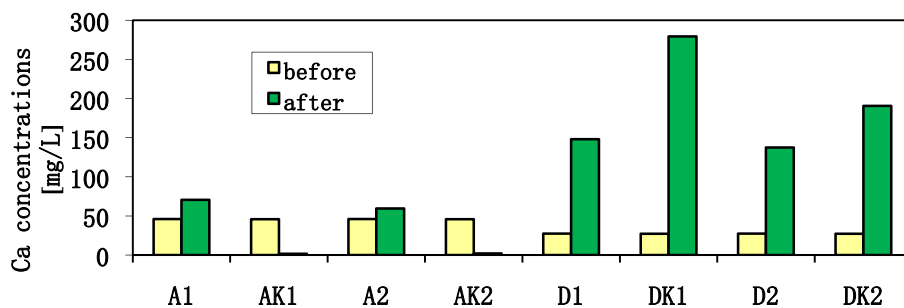


Fig. 1 Calcium Ions Concentrations during the Experiment

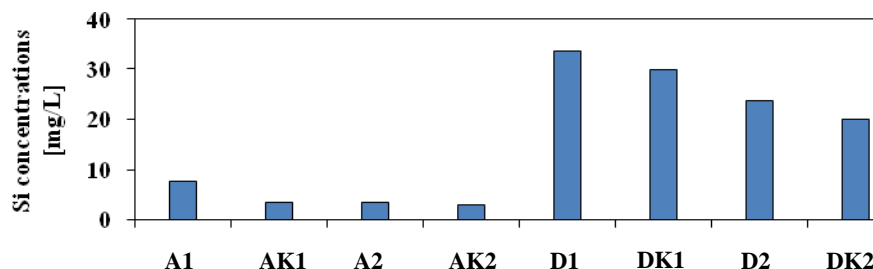


Fig. 2 Silicon Ions Concentrations after the Experiment

Comparing the influence of bacteria, a similar trend was observed for the silicon compounds leaching as for calcium leaching. Samples affected with bacteria *Acidithiobacillus thiooxidans* were found to have lower leaching performance of silicon ions from matrix of fiber-cement boards compared to samples affected with bacteria *Desulfovibrio desulfuricans*, as it is seen in Fig. 2. The dissolved silicon concentrations in presence of sulphate-reducing bacteria *Desulfovibrio desulfuricans* have been measured to be 4.4 (D1/A1) and 6.8 times (D2/A2) higher, respectively than in presence of *Acidithiobacillus thiooxidans*. The most intensive leaching of silicon ions (33.51 mg/L) was observed for sample D1 exposed to bacteria *Desulfovibrio desulfuricans* after 90 days of exposition (Fig. 2).

The results of changes in weight of investigated concrete samples after the experiments are given in Table 4.

The decrease in weight was noticed for fibre-cement boards with colorant based on iron oxide exposed to both biotic and abiotic conditions. Opposite result was observed for samples with colorant based on cobalt oxide. This fact corresponds to a formation of the solid phase on the surface of samples and point to the importance of chemical composition of the samples and thus the difference in leaching behaviour and consequent precipitate formation. The weight changes of tested samples after the 90-day experiment are illustrated in Fig. 3.

Table 4 Changes in Weight after the 90-Day Experiment

Sample	Weight [g]	
	Before the experiment	After 90 days
A1	18.9851	18.8091
AK1	18.1759	18.1752
A2	19.9490	20.5673
AK2	20.1917	20.5673
D1	18.3379	18.2759
DK1	18.9617	18.8152
D2	21.0289	21.3042
DK2	19.9881	20.3128

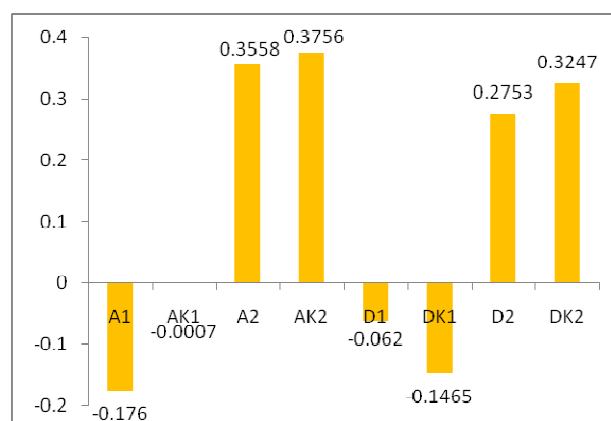


Fig. 3 Weight Change [g] of Tested Samples after the 90-Day Experiment

The most significant weight decrease was found for the A1 sample exposed to bacteria *Acidithiobacillus thiooxidans* (-0.176 g) and the lowest one for the abiotic control of that sample AK1 (-0.0007 g). The highest weight increase was observed for the sample AK2 (0.3756 g) while the lowest one for the sample D2 (0.2753 g). The percentage of weight increases and decreases of the samples varied from minus 0.93% (A1 sample) to plus 1.86% (AK2 sample).

The dissolving of the cement matrix component was manifested not only with weight changes but also with the surface roughness changes. The AFM micrographs for the samples D1 and D2 with the most intensive calcium and silicon leaching are presented in Fig. 4.

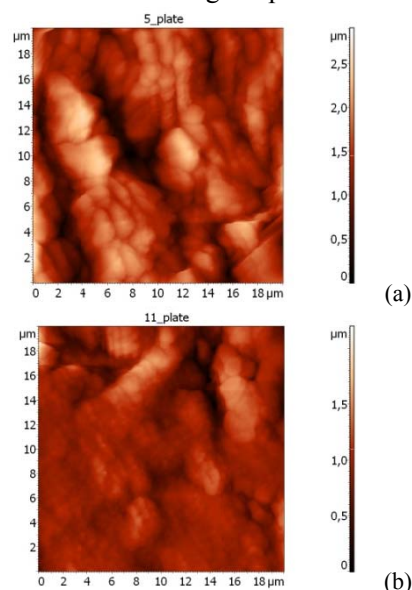


Fig. 4 (a) AFM Micrographs of D1 and (b) D2 Samples

The parameter of an average roughness, S_a , measured as an indicator of the surface deterioration, ranged 158.1 to 350.3 nm; peak-to-peak parameter, S_y , ranged 2198 to 2902 nm. The average roughness of all samples increased after the 90-day experiments. The difference in average roughness of samples with the iron oxides colorants and cobalt oxides colorants was determined. The S_a parameter of the samples A1 and D1 was measured to be two times higher than of samples A2 and D2. This corresponds to the results regarding weight changes presented above where the weight of A1 and D1 samples decreased while the weight of A2 and D2 was, on the contrary, increased.

The samples affected by bacteria reached higher values of roughness parameters than the samples under abiotic exposition.

4. Conclusion

This study shows that there are substantial differences on the leaching of calcium and silicon ions in presence of bacteria and without bacteria. *Desulfovibrio desulfuricans* bacteria seem to cause more intensive leaching when comparing to the *Acidithiobacillus thiooxidans*.

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