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MODELING OF INFLUENCE OF MICROBIOLOGICAL AGGRESSIVE MEDIA ON CORROSION OF CEMENT STONE

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Due to the complex and constantly changing global environmental situation, the study of the resistance of mineral binder-based building composites to the effect of the metabolism products of microscopic organisms seems particularly relevant. Taking into account the nature of the effect of bacteria and mycelial fungi on cement stone, a method of evaluating the resistance on the basis of modeling by replacing the real development of colonies of microorganisms with chemically aggressive aqueous solutions of their life products is proposed. It is allowed to study the current processes of phase transformations, as well as changes of operational parameters in the form of regression dependencies.

Key words: cement stone, mycelial fungi, bacteria, metabolism products, x-ray phasic analysis, regression dependence

INTRODUCTION

During operation, building materials may be adversely affected by various aggressive environments. Among them, biological media have a significant aggressive effect [1-5, 12]. The literature shows that more than 40% of the total volume of biological injuries is related to the activity of microorganisms - bacteria and fungi [6-8, 13]. To a greater extent, biodamages of building materials are caused by products of the metabolism of microorganisms [9-11, 14]. These processes are particularly intense in environments of biogenic organic and inorganic acids, which are typical for sewage treatment plants and wastewater treatment plants made of cement concrete [15, 16].

The intensity of corrosion processes when exposed to metabolic products is determined by the rate of chemical reactions at the phase contact boundary and the rate of their diffusion into the material structure. In addition, consideration should be given to the interaction of microorganisms with the components of the material.

Portland cement based materials are not a breeding medium for microorganisms and settlement on the surface occurs when there is contamination or constant moistening. Considering that the minerals of Portland cement stone are viable only in a highly alkaline environment, the most aggressive products of metabolism in the form of acids. Acids are produced in amounts not exceeding the self-ingibation limit at which the colony ceases to develop.

Mycelial fungi develop at substrate humidity of more than 75%. Thus, cement stone aggressive acids act on it as an aqueous solution. Mainly biodegraders are in the class of deuteromycetes: Scopulariopsis, Alternaria, Claudospo-

rium, Aspergillus, Fusarium, Paecilomyces, Penicillium, Trichoderma. Of the wide range of acids produced by mycelial fungi, the largest amounts are citric, acetic and oxalic (more than 15% of all extracellular excretions).

Colonies of bacteria are settled on the surface of cement composites in liquid media: seawater, waste water, wetted soils, etc. Under the influence of bacteria, the pH of the liquid medium can decrease to 0.5-1. Thion, sulfate reducing and nitrification bacteria release mainly sulfuric, nitric acids and ammonia.

Under the influence of aggressive metabolites there is a decrease in the pH of cement stone, decomposition of its minerals, formation of water-soluble or fragile calcium salts as a result of exchange reactions. The result of these processes is a reduction in performance - up to unacceptable values.

METHODOLOGY

As an object for experiments, 1×1×3 cm prism samples made of normal density cement dough were used. Cement with active mineral additive (opoca, 20%) of strength class 32.5 was used. The normal density was determined using the Vicat apparatus, and the cement dough was made in a standard mixer according to GOST 30744-2001 «Cements. Methods of testing with using polyfraction standard sand».

X-ray phasic analysis was applied to analyze chemical changes of cement stone components in interaction with products of microorganisms metabolism. A DRON-6 unit (Cu radiation, Ni filter) was used. Survey conditions: anode current of x-ray tube 10 mA, voltage 30 kV, slot width 0.5 mm, angular speed of counter 4 deg/min, recording time constant 20s, intensity range 500 pps. Specific sur-

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face area of powders from cement stone samples: 4000 - 4500 cm²/g.

Experiment planning methods were used to estimate the degree of reduction of mechanical properties. The plan of the experiment to determine the change in the breaking load during compression was implemented in the cubic planning area, depending on three influencing factors:

- for products of bacteria metabolism: concentration in aqueous modeling solutions of sulfuric and nitric acids and ammonia from 0 to 1%;
- citric, oxalic and acetic acids with concentration from 0 to 1% are selected for simulation of effect of products of metabolism of mycelial fungi.

The total volume of the modeling aggressive solution was 1 liter. In aggressive environments, the samples were held for 5 months. The solution was not replaced during exposure, simulating self-inhibition of microbial colonies. Then the compressive strength was determined by determining the breaking load over an area of 1 cm² of the cross-section of the sample on a hydraulic press.

In the planning area, 13 observation points are selected, taking into account the symmetry of the plan. The experiment planning matrices are given in Table 1.

As an indicator characterizing the change of operational characteristics, the breaking load during compression is selected.

The mathematical model for changing the destructive load is adopted in the form of a second degree regression polynomial containing 10 members, which provides good correlation of the model with experimental data.

RESULTS

After exposure and testing of the samples, the following data on the destructive load were obtained (Table 2).

After processing the results of the experiment, the following regression relationships were obtained:

for samples held in aggressive environments simulating the effects of bacterial metabolism products:

$$\begin{aligned} &P_{\text{bact}} = 3,6 + 1,462 \bullet X_{1} - 1,737 \bullet X_{2} - 1,575 \bullet X_{3} - 0,55 \bullet X_{12} + \\ &+ 0,7 \bullet X_{22} + 1,275 \bullet X_{32} - 0,3 \bullet X_{1} X_{2} + 0,775 \bullet X_{1} X_{3} - \\ &0,725 \bullet X_{2} X_{3} \end{aligned}$$

 for samples held in aggressive media simulating the effect of products of the metabolism of mycelial funqi:

$$\begin{array}{l} P_{\text{fungi}} = 3,6 - 0,438 \bullet X_{1} + 0,575 \bullet X_{2} - 0,488 \bullet X_{3} + 0,125 \bullet X_{12} + \\ + 1,25 \bullet X_{22} + 1,275 \bullet X_{32} - 0,825 \bullet X_{1} X_{2} + 0,15 \bullet X_{1} X_{3} + \\ + 0,075 \bullet X_{2} X_{3} \end{array}$$

Table 1: Planning Matrix

_										
Nº p/o	X ₁	X ₂	X ₃		in aqueous so ing of bacteria		Content in aqueous solution,% (modeling of exposure to mycelial fungi)			
				ammonia	sulfuric acid	nitric acid	citric acid	oxalic acid	acetic acid	
1	0	-1	-1	0,5	0	0	0,5	0	0	
2	0	+1	-1	0,5	1	0	0,5	1	0	
3	0	-1	+1	0,5	0	1	0,5	0	1	
4	0	+1	+1	0,5	1	1	0,5	1	1	
5	-1	0	-1	0	0,5	0	0	0,5	0	
6	+1	0	-1	1	0,5	0	1	0,5	0	
7	-1	0	+1	0	0,5	1	0	0,5	1	
8	+1	0	+1	1	0,5	1	1	0,5	1	
9	-1	-1	0	0	0	0,5	0	0	0,5	
10	+1	-1	0	1	0	0,5	1	0	0,5	
11	-1	+1	0	0	1	0,5	0	1	0,5	
12	+1	+1	0	1	1	0,5	1	1	0,5	
13	0	0	0	0,5	0,5	0,5	0,5	0,5	0,5	

Table 2: Results of the experiment on simulating the effects on cement stone of products of the metabolism of microorganisms

Nº p/o	1	2	3	4	5	6	7	8	9	10	11	12	13
P _{bact} , kN	8,4	6,5	6,1	1,3	4,9	6,3	0,8	5,3	3,8	7,3	0,8	3,1	3,6
P _{fungi} , kN	5,8	7,0	5,1	6,6	6,5	4,9	4,8	3,8	3,9	5,1	6,5	4,4	3,6



Sections of the planning area with the most noticeable changes in destructive load are shown on Figure 1 and Figure 2.

In order to study chemical-phase transformations under aggressive action, x-ray phasic analysis of samples from cement dough of normal density was carried out, held for 1 month in an aggressive modeling aqueous solution containing 2.5% oxalic and 2.5% citric acid (Figure 3). For comparison, PFA was performed for control samples held in water (Figure 4).

CONCLUSIONS

The analysis of the obtained data makes it possible to draw the following conclusions:

 the presence of ammonia in the aggressive environment, due to its alkaline nature, even contributes to a 40% increase in the breaking load as compared

- to samples exposed to the same period of time in water:
- aggressive media containing nitric and sulfuric acids lead to a sharp decrease in the value of the breaking load, there is a significant decrease in the bearing core of the sample as a result of the formation of low-strength corrosion products;
- in aggressive media modeling the action of mycelial fungi resulting from interaction with calcium oxalate cement stone minerals, a protective film is formed, partially neutralizing the action of significantly more aggressive citric and acetic acids.

The results of the x-ray phasic analysis show that the main changes in the phase and chemical composition of the cement stone occur within the range of the diffraction angle $2\Theta = 30 \div 50^{\circ}$. Diffraction reflexes of calcium citrates and oxalates formed as a result of reactions of

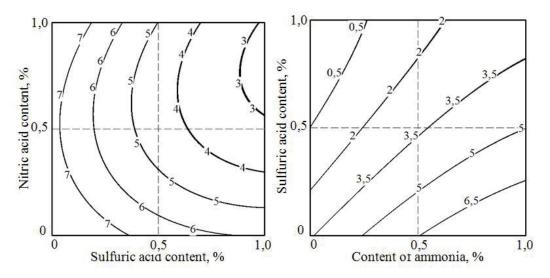


Figure 1: Exposure of samples in aggressive environments simulating the effects of bacteria. Cross sections by planes $X_1 = 1$ (a) and $X_3 = 1$ (b)

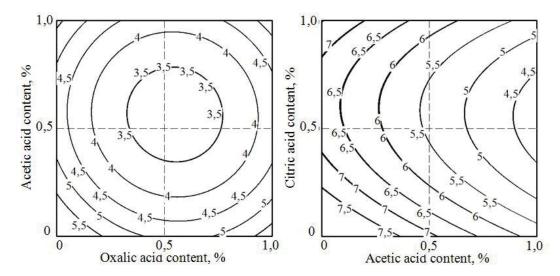


Figure 2: Exposure of samples in aggressive environments simulating the effects of bacteria. Cross sections by planes $X_1 = +1$ (a) and $X_2 = +1$ (b)



cement stone minerals with citric and oxalic acid modeling solutions were found. Calcium oxalate is insoluble in water, has a dense structure and good adhesion to ce-

ment stone. Also compounds showing decomposition of hydrated phases of calcium oxide - monobasic silicates, aluminates and ferrites are present.

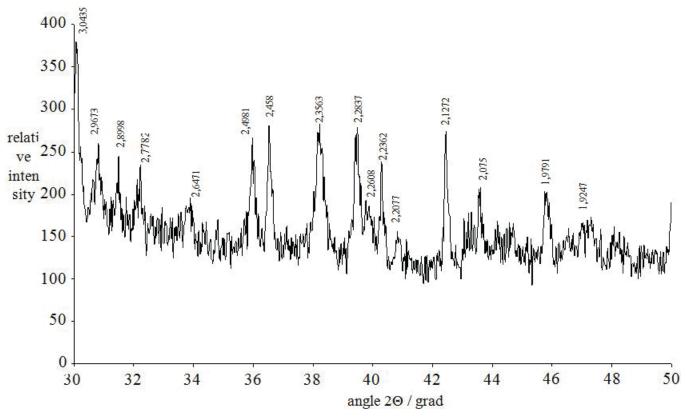


Figure 3: Diffractogram of cement stone aged in aqueous solution of oxalic and citric acids

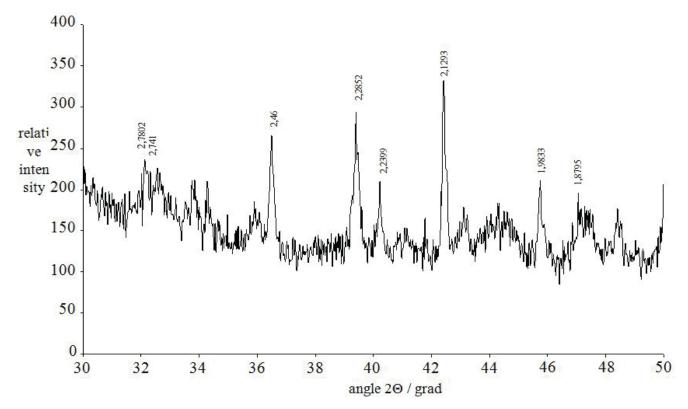


Figure 4: Diffractogram of cement stone aged in water



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