Modeling the process of biodeterioration of cement compositions

Farid Shakirzyanov,[0000-0002-6514-8335], Rashit Shakirzyanov,[0000-0002-1446-2703], Rashit Kayumov,[0000-0003-0711-9429], Viktor Stroganov,[0000-0001-9680-6698] and Evgeny Sagadeev,[0000-0003-2258-8119]

1 Kazan State University of Architecture and Engineering, Kazan, 420043, Russia
E-mail: faritbox@mail.ru

Abstract. The paper studies the problem of developing the theoretical foundations of the processes of diffusion biodegradation of mineral building materials (cement composites) under the action of aggressive microorganism vital products. The impact of the aggressive environment of microorganisms on the material is taken into account on the basis of Fick’s 2nd law. The resulting equation is solved by the finite difference method. Some experimental and theoretical studies of influence of the aggressive environment of microorganisms on the strength characteristics of the samples of cement composites have been carried out. The mathematical regularities of influence of the exposure time to the aggressive environment of microorganisms and the diffusion coefficient on the strength characteristics of composites have been established.

Key words: cement composite, biodeterioration, cement-sand mortar, test-sample, aggressive environment, mathematical modeling, Fick’s law, diffusion coefficient.

1 Introduction

It is known that building materials during operation are exposed to corrosion damages caused by the vital activity of biodestructors [1]. Among the most important biodestructors are microorganisms (bacteria, molds) [2-5], as well as mosses, lichens, algae, mussels [6], birds [7] etc. The most aggressive biodestructors of building materials are microorganisms and, first of all, mold fungi [8]. They account for more than 40% of all biodegradation in the construction industry. In the case of mineral building materials (cement concretes), biodegradation begins with adhesion violation of the constituent components of the materials due to chemical reactions between the cement stone and microorganism vital products [9, 10]. The result of the biodegradation process is a change in the physicochemical properties of concrete, destruction of their structure and a decrease in performance, leading to loss of strength and destruction of building materials, products and structures [11]. In addition, the process of biological destruction of building materials endangers the health of people, causing diseases of the upper respiratory tract and causing allergic reactions [12, 13]. The total global damage to construction sites as a result of biodegradation is tens of billions of dollars every year [1]. The problem of biodegradation is also very relevant in Russia, as evidenced by the data on economic damage from corrosion, which annually amounts to about 3% of GDP [2]. Thus, all of the above indicates the importance and relevance of the problem of biological destruction, which, of course, causes scientific and practical interest.

Based on the analysis of the literature reports on this problem, we can conclude that among various types of microorganisms the greatest damaging effect on mineral building materials is exerted by mold (mycelial) fungi [2, 8]. The high destructive activity of mold fungi of the genera Aspergillus, Penicillium, Trichoderma, Alternaria, etc. is due to the ability to adapt to building materials of various
chemical nature as a substrate, which is associated primarily with the presence of a well-developed enzymic complex. The destructive effect of molds on cement concrete is due to the aggressive effect of mushroom metabolites (organic acids, various reductive-oxidative and hydrolytic enzymes) on individual components of the materials [2]. The products of microorganisms’ metabolism (vital products), that settle on the surface of cement concrete (having an alkaline reaction), are a spectrum of one-, two- and tribasic low molecular weight carboxylic acids (lactic, oxalic, malic, citric, etc.) which are secreted by microorganisms in the fairly large quantities and form an aggressive acidic “film” with a fairly low pH value (concentration) on the external surface of the material. It should be noted that the pH of each acid is determined by its structure and basicity. During interaction of the carboxylic acids with cement concrete, the calcium (magnesium) ions are released and the complex formation reactions take place on its surface (with formation of the water-soluble chelate complexes), what leads to an increase in porosity of the building material and a loss in bonding ability (cohesive strength) of the cement. Further, from the surface of the material the solution of organic acids in the pores starts diffusing into the concrete and the process of back diffusion - elution of alkali from the samples in the opposite direction (leaching) - begins. All these processes determine appearance of the microcracks on the surface of the concrete structures, which gradually expand and deepen. When rainwater penetrates into the microcracks, it freezes in a winter period, the cracks increase in size, and as a result the corrosion progresses. Apparently, it is the biodeterioration process that initiates destruction of the concrete surface and, accordingly, corrosion of the concrete and stone structures [2, 3]. The determining factor in the biodegradation process of mineral building materials is a diffusion of metabolic products of microorganisms into the structure of the material [14]. In addition, it should be noted that the biodegradation process of mineral building materials from the point of view of chemical kinetics consists of at least three main stages: transfer of reactants to the phase interface - reaction zone, occurrence of a heterogeneous reaction at the phase boundary and removal of reaction products from the reaction zone. Each of these stages, in turn, can consist of a series of elementary reactions proceeding sequentially or in parallel. Obviously, the resulting rate of biodegradation of mineral building materials is determined by the speed of the individual stages. With a large difference in reaction rates, the slowest stage of the concrete biodegradation process is crucial. Based on the foregoing we can conclude that the process of biodegradation of mineral building materials is multi-stage and has a diffusion nature. It should be noted that in the literature, in addition to the experimental studies [3, 11] and others, attempts were made to mathematically describe concrete biodeterioration [14, 15]. However, apparently, due to the use of an insufficient number of the reliable parameters for modeling, the satisfactory results in these studies were achieved not in all the cases.

Thus, a scientific task to develop mathematical models of processes of diffusion biodegradation of mineral building materials allows (compared with existing models) describing more accurately the concrete biodegradation processes in various environments and temperatures.

2 Materials and methods

2.1 Objects and research methods

The test-samples of cement compositions being under study are cement-sand mortar (CSM) (modeling fine-grained concrete) of 160×40×40 mm in size (small beams) based on Portland cements М400 CEM II/A-P 32.5 N and M500 CEM I 42.5 N manufactured by LLC «Ulyanovskcement», quartz sand of fraction 0.5-0.25 mm, water-bidistillate. Cement and sand were mixed at the ratio of 1:3. Water-cement ratio (W/C) of the CSM samples is 0.35.

To assess biostability of the samples an indirect method of keeping samples of materials in the weakly concentrated solutions of carboxylic acids, modeling the products of mold metabolism, is used. For this purpose, a laboratory kinetic setup is used [16], which allows testing any building materials for biostability in a wide range of temperatures and pH of the environment (negative logarithm of hydrogen ions concentration). The setup includes a test container in which the CSM test-samples are installed, immersed in a model environment, as well as make-up, drain tanks, a measuring tank for...
determining pH of the model environment and calibration of pH-electrode, as well as an electronic control unit that performs the functions of measuring pH, the temperature of the model environment and maintaining them at a given level. The model environments are both aqueous solutions of mono-, dibasic and tribasic carboxylic acids (lactic, oxalic, malic, succinic, citric, etc.) of various concentrations, and mixtures of these acids. The scheme of the laboratory kinetic setup is shown in Figure 1.

**Figure 1.** Scheme of the laboratory kinetic setup: 1 – test container; 2 – perforated double bottom of a test container; 3 – experimental CSM test-samples; 4 – angled plates at the bottom of a test container forming a thin-layer sump; 5 – model environment flow distributor in a test container; 6 – nozzle for supplying the model environment to a test container; 7 – nozzle for suction of the model environment from a thin-walled sump into the pump; 8 – centrifugal pump for suction of the model environment; 9 – peristaltic pump for adding the model environment from a feed container with a solution; 10 – feed container with a solution; 11 – electric heater of the model environment; 12 – temperature sensor of the model environment; 13 – measuring container for determining pH of the model environment and calibration of pH-electrode; 14 – temperature sensor of the model environment in a measuring container; 15 – pH-electrode of the model environment in a measuring container; 16 – peristaltic pump for pumping the model environment from a test container to a measuring one; 17 – peristaltic pump for pumping the model environment from a measuring container to a drain one; 18 – drain container; 19 – peristaltic pump for pumping a fixanal solution with pH = 1.65 from a container 20 to a measuring one; 20 – container with a fixanal solution with pH = 1.65; 21 – peristaltic pump for pumping a fixanal solution with pH = 9.18 from a container 22 to a measuring one; 22 – container with a fixanal solution with pH = 9.18; 23 – electronic control unit.

To determine a diffusion coefficient in the work, to the first approximation, a simplified technique [17] of the experiment was used. The CSM test-sample (small beam) was vertically placed in a desiccator (without cover), at the bottom of which some distilled water was poured to a height of 5 mm (Figure 2). The timing of the experiment began from the moment when the distilled water in the pores began to rise vertically along the CSM test-sample, which was recorded visually. Within two days, every two hours, a moisture meter was used to determine humidity of the test-sample and height of the vertical water rise.
In order to conduct numerical experiments regarding modeling the biodeterioration process of mineral building materials, a calculation method was developed and a computer program based on the finite difference method was created.

2.2 Main provisions about modeling the process of diffusion biodegradation of mineral building materials

In continuation of the previously initiated studies [8, 18], in the laboratory kinetic setup the biodegradation process of the CSM test-samples was simulated in a slightly aggressive citric acid environment with pH = 3 (the value recommended in the literature for carboxylic acids [1]) for eight days at a temperature 40°C. The obtained experimental results were analyzed by the numerical method. The Figures 3 and 4 show the results of the experimental studies of effect on the design strength characteristics of the CSM test-samples (based on Portland cements M400 CEM II/A-P 32,5 N and M500 CEM I 42,5 N) by the exposure time of a weakly concentrated solution of the citric acid.

Figure 3. Dependence of the calculated compressive strength ($R_b$, MPa) of the CSM samples on the exposure time in a model environment of the citric acid at a temperature of 40°C: 1 – CSM based on Portland cement M500 CEM I 42.5 N; 2 – CSM based on Portland cement M400 CEM II/A-P 32.5 N.
Based on the analysis of the kinetic dependences in Figures 3, 4, decrease in the strength characteristics of the CSM test-samples from a hydrogen value pH of the aggressive environment is taken into account as the following function Eq. (1):

\[ R_b = R_{b0} + R_{b1}t + R_{b2}t^2, \]

where \( R_{b0}, R_{b1}, R_{b2} \) are mechanical (strength) characteristics, \( R_b \) is an ultimate compressive strength on the CSM test-sample.

Similarly, we take the ultimate tensile strength \( R_{bt} \) (for bending) in the following form:

\[ R_{bt} = R_{bt0} + R_{bt1}t + R_{bt2}t^2. \]

For the further calculations, we assume that on the surface of the CSM test-sample an ultimate strength \( R_b \) (for compressive) and \( R_{bt} \) (for bending) are constant:

Diffusion of the aggressive environments into the CSM test-sample is modeled based on Fick’s 2nd law (3):

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial C}{\partial y} \right), \]

where \( C \) is a hydrogen value (concentration) pH of the aggressive environment in the CSM test-sample; \( \lambda \) is a diffusion coefficient; \( x, y \) are coordinates; \( t \) is time.

A solution of the equation (3) is carried out in the finite differences both in time and coordinate, and what is more, an explicit scheme is used regarding the time [19]:

\[ \frac{C_i^{k+1} - C_i^k}{\Delta t} = \frac{\left( \lambda_{x+1}^k - \lambda_x^k \right) \left( C_{i+1}^{k+1} - C_i^{k+1} \right)}{4 \Delta x^2} + \frac{\left( \lambda_{y+1}^k - \lambda_y^k \right) \left( C_{i+1}^{k+1} - C_i^{k+1} \right)}{4 \Delta y^2}, \]

After transformations of the equation (4) we obtain the relation (5):

\[ C_i^{k+1} = C_i^k + \frac{\left( \lambda_{x+1}^k - \lambda_x^k \right) \left( C_{i+1}^{k+1} - C_i^{k+1} \right)}{4 \Delta x^2} \Delta t + \frac{\left( \lambda_{y+1}^k - \lambda_y^k \right) \left( C_{i+1}^{k+1} - C_i^{k+1} \right)}{4 \Delta y^2} \Delta t. \]
To ensure convergence of the solution of the equation (5), a restriction (Courant condition) is imposed on the time step [19]:

$$\lambda \Delta t \left( \frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} \right) \leq \frac{1}{2}.$$  \hspace{1cm} (6)

Using the laboratory setup to determine a diffusion coefficient, height of the distilled water rise in the CSM test-sample for two days was determined. Comparison of the obtained experimental values with the theoretical calculations according to [20] made it possible to calculate a diffusion coefficient $\lambda$ for the CSM test-sample. According to the literature reports [21], a diffusion coefficient depends on the time and pH of the aggressive environment due to the nonlinear law (7):

$$\lambda = \lambda_0 + \frac{\lambda_{\text{max}} - \lambda_0}{C_{\text{max}}} C^2(x,y,t).$$  \hspace{1cm} (7)

According to the results of the data in the work [20] all the necessary coefficients that satisfy the relation (3) were calculated. Thereafter, they were used to solve the numerical problems posed in the work.

As the aggressive environment penetrates into the cement composite, on the basis of the theory of a limiting equilibrium, [22] an ultimate load on the CSM test-sample was determined according to the equation (8):

$$P^*(t) = \int R_h(C,t) dA.$$  \hspace{1cm} (8)

where $R_h$ is a compressive strength of the CSM test-sample.

3 Results and discussion

3.1 Discussion of the results of numerical modeling of the biodeterioration process

To model a diffusion process of the aggressive environment into the CSM test-sample, according to the equation (3) it is accepted in the work that a rectangular surface of the test-sample of the cement composite (small beam) is mentally divided into many elementary points. Each elementary point, in fact, represents beginning of a microcrack on the surface of the sample, going into thickness of the material to a certain depth. Thus, diffusion of the aggressive environment into the CSM test-sample begins with its point impact on each elementary point. Fig. 5 presents a proposed scheme of the point impact of the aggressive environment on an elementary point on the side surface of the CSM test-sample face.

![Figure 5](image)

**Figure 5.** Scheme of a point impact of the aggressive environment on an elementary point on the side surface of the CSM test-sample face.

Figure 6 shows a diffusion process of the aggressive environment (biodeterioration) through an elementary point from the surface of the CSM test-sample into the depth of the material, accompanied by leaching and lowering of the pH of the environment inside the material of the composite.
As known, when modeling the biodeterioration processes of mineral building materials, a diffusion coefficient of the aggressive environment is of great importance, the value of which can either be constant in time or change as the aggressive environment penetrates into the CSM test-sample. So, Figure 7 shows the dependences of the calculated compressive strength of the CSM test-sample on penetration time of the aggressive environment into thickness of the material at the constant and variable diffusion coefficients obtained in this work.

When analyzing the dependencies in Figure 7, it can be seen that at the initial moment of the diffusion process of the aggressive environment into the CSM test-sample, the curves of the constant and variable diffusion coefficient are quite close to each other. As the time of the diffusion process of

**Figure 6.** Diffusion process of the aggressive environment (biodeterioration) through an elementary point from the surface of the CSM test-sample into the depth of the material.

**Figure 7.** Dependence of the pH on penetration time of the aggressive environment into the material at the constant and variable diffusion coefficients (B – width of the test sample): — constant diffusion coefficient; ---- variable diffusion coefficient.
the aggressive environment into the CSM test-sample increases, the curves of the constant and variable diffusion coefficient diverge from each other (Figure 7). Thus, based on the analysis of the dependencies in Figure 7, it can be concluded that the value of the diffusion coefficient will change as the aggressive environment penetrates into the thickness of the CSM test-sample, which, apparently, will be accompanied by a decrease in the pH medium both on the surface and in the depth of the composite material. In the future, in order to model more correctly the biodeterioration processes of mineral building materials and determine their tensile strengths, it is necessary to take into account the variability of the diffusion coefficient of the aggressive environment at all elementary points of the CSM test-sample.

4 Conclusion
Thus, the experimental and theoretical studies regarding influence of the aggressive environment of some microorganisms on the strength characteristics of the CSM test-samples were performed. The mathematical laws of influence of the exposure time and diffusion coefficient of the aggressive environment of the microorganisms on the strength characteristics of CSM were established.

Acknowledgments. This study was supported by the Russian Foundation for Basic Research (19-08-00349).

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