











## The effectiveness of internal hydrophobization of concrete in biologically aggressive environments

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**Abstract.** The article is devoted to the effect of internal hydrophobization of concrete cement stone on the kinetics of damage by *Aspergillus niger* fungi. The studies were carried out on samples made of ordinary Portland cement with a W/C = 0,3. As a hydrophobic agent, 0,5 and 1% by weight of cement of calcium stearate were introduced into the cement mixture. The kinetics of calcium leaching from cement stone was evaluated by changes in the calcium content in the liquid when samples were exposed to water. Internal hydrophobization of cement stone with calcium stearate makes it possible to reduce the removal of calcium from the solid phase by 2,5-3 times, even with biofouling of the surface. The equilibrium state in the «cement stone – water» system occurs 70 days after the samples are immersed in a liquid medium. The profiles of calcium concentrations along the thickness of the cement stone characterize a decrease in mass transfer in samples with hydrophobic additives. The introduction of calcium stearate into the cement mixture increases the total calcium content in the structure and reduces calcium leaching as a result of liquid and fungal corrosion. Volumetric hydrophobization of cement stone leads to a decrease in the values of mass conductivity coefficients by two orders of magnitude, from  $10^{-9}$  to  $10^{-11}$  m<sup>2</sup>/s. Using a mathematical model of concrete biocorrosion, the degree of destruction under the influence of fungal microorganisms and water is predicted after 15 years. During this period, corrosion processes will occur in ordinary concrete throughout its entire thickness, in hydrophobic concrete – only in the surface layer. With calcium stearate additives to concrete, it is possible to extend the maintenance-free service life under conditions of exposure to fungi and moisture for up to 30 years.

**Keywords:** concrete fungal destruction, mass transfer in concrete, hydrophobic concrete, biostability of concrete, internal hydrophobization of concrete, hydrophobic additive in concrete, calcium leaching from concrete, concrete durability prediction, mathematical model of concrete biocorrosion

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## 1. INTRODUCTION

The process of biodegradation in cement-based composites is a result of the metabolic activity of various microorganisms, such as bacteria, fungi, lichens, and phototrophic algae. This process leads to irreversible changes in the structure of concrete, causing degradation of its mechanical and functional properties [1-5]. One of the key morphological manifestations of biodegradation is the formation of microscopic cracks, which eventually coalesce into macroscopic cracks. Additionally, the surface layers of the concrete are destroyed, material fragments separate, and a porous structure with internal voids develops. Furthermore, there is selective leaching and chemical dissolution of mineral phases present within the cement matrix.

The intricate microtopography of concrete, marked by heightened roughness and the existence of exposed pores and minute fissures, fosters an ideal environment for microbial adhesion and the formation of biofilms. Following cement hydration, the initially alkaline pH of the pore system (ranging from 12 to 13) transiently hinders microbial establishment. However, with the advancement of carbonation and a subsequent decrease in pH to between 8 and 9, microbial colonization intensifies. This process triggers metabolic activity, involving the production of acids such as formic acid, acetic acid, lactic acid, sulfuric acid, and nitric acid by microorganisms. The progressive acidification and dissolution of the concrete structure can ultimately lead to the degradation of calcium-based constituents within the material [6, 7].

The general damage to concrete cannot be fully explained by the effects of bioacids alone, rather, it is due to the influence of ongoing microbial interactions [8-12]. The activity of microorganisms leads to the constant destruction of concrete. For reinforced concrete structures, appropriate protective measures must be taken to slow down the process of concrete biodegradation and ensure the safety and durability of the structure.

Hydrophobization is one of the methods of protection against the action of liquid aggressive media and increasing the durability of concrete. This is a process in which a material acquires hydrophobic properties, that is, it is difficult to wet with water. In the case of concrete, the hydrophobization process can be carried out on the surface or in the entire volume of the material. Internal hydrophobization is carried out by adding appropriate substances (usually in the form of additives) during the production of concrete together with the mixing water or at the end of mixing the components. Unlike surface treatment, this method provides a long-term hydrophobic effect over the entire volume of the material, making it resistant to mechanical damage such as scratches. Due to the hydrophobization of the surface of the pores and capillaries inside the concrete, water resistance increases, but air permeability remains. Hydrophobic additives should effectively reduce water absorption while being resistant to ultraviolet radiation, temperature changes, alkaline environment and other external factors [13-15].

Organosilicon compounds such as silicone resins, siloxanes or silanes can be used to hydrophobize concrete [16, 17]. Metal stearates are often used as an alternative for internal hydrophobization [18-20]. The special molecular structure of calcium stearate powder allows it to perform phenomenal functions to ensure the safety of concrete, creating water-repellent barriers that significantly increase the durability and efficiency of construction work in difficult conditions. Calcium stearate has remarkable amphiphilic properties, which allows it to form a protective film and impart waterproofing properties to concrete and other building materials using both chemical and physical methods. When used in concrete, it acts as an excellent water repellent, creating an invisible hydrophobic layer around concrete particles and pore walls [21-23]. This important function significantly reduces water absorption due to the capillary effect, which is the main mechanism of moisture penetration into concrete. In addition, it acts as an effective lubricant during mixing and laying, improving workability

without adversely affecting the final strength [21, 24]. Its hydrophobic properties also provide good protection of steel reinforcement from corrosion, creating a barrier to the penetration of chloride ions and carbonization processes [25-27]. In addition, calcium stearate powder significantly improves the condition of the concrete matrix, helping to maintain its effectiveness throughout the life of the structure. These diverse beneficial properties make it an indispensable additive for creating high-strength concrete that can withstand difficult environmental conditions.

Considering the established efficacy of calcium stearate as an inhibitor of chloride corrosion in cement composites, the present study seeks to explore the impact of hydrophobic volumetric treatment on concrete's resistance to microbiological deterioration in aquatic settings [23].

A comprehensive assessment of biostability was undertaken through an analysis of the kinetics of calcium ion migration from the cement matrix upon prolonged exposure to corrosive aquatic conditions. Additionally, the distribution profile of calcium concentrations throughout the depth of degradation was meticulously examined.

To quantify the operational longevity of concrete structures subjected to simultaneous exposure to aqueous media and microbial agents, critical parameters related to mass transfer, such as diffusion flux densities for calcium hydroxide, were meticulously determined. Furthermore, effective diffusion coefficients were meticulously calculated. The data obtained through experimentation were integrated into a mathematical framework that models bio-corrosive processes. This enabled us to simulate the spatial and temporal evolution of calcium-containing phases in concrete throughout its projected service life. By employing numerical simulations of mass transport dynamics within the cement matrix, we were able to estimate the maximum viable service life of concrete structures under specific operational conditions.

## 2. METHODS AND MATERIALS

In order to study the phenomenon of mass transfer during microbiological degradation of cement, we prepared specimens measuring 30 x 30 x 3 millimeters in size. The material used to manufacture these specimens was CEM I 42.5N Portland cement, with a water-cement ratio of 0.3 in accordance with standard procedures, ensuring optimal physical and chemical properties for conducting corrosion tests. In order to establish controlled experimental conditions, five faces of each specimen were sealed with bitumen mastic to ensure airtight sealing (Fig. 1). One surface of each specimen was left exposed to direct contact with an aggressive aqueous medium in order to facilitate microbial colonization.



**Fig. 1.** Photo of a cement stone sample for corrosion testing.

To prevent biological fouling and the development of fungal destruction in wet conditions, calcium stearate in the amount of 0,5% and 1% by weight of cement was added to the cement mixture. The amount of calcium stearate was determined based on previous studies aimed at preventing chloride corrosion of concrete using this additive [23]. In addition, it was found that the hydrophobic additive effectively suppresses the colonization of *Aspergillus niger* fungi on the concrete surface, thereby increasing its operational characteristics [28]. A uniform distribution of calcium stearate in the cement mixture was achieved by mechanical stirring for 5 minutes.

The compositions of the samples per 1 kg of cement paste are shown in Table 1.

**Table 1.** The content of components for the production of cement stone samples, g.

Sample type	Cement	Water	Calcium stearate
Without additives	769,23	230,77	-
0,5 wt. % additive	766,28	229,89	3,83
1 wt. % additive	763,36	229	7,64

After a period of 28 days of hydration curing under standard conditions, cement specimens were subjected to artificial inoculation with a spore-bearing culture of the fungus *Aspergillus niger*. This procedure was carried out in accordance with the requirements set out in GOST 9.048-89, the Unified System of Corrosion and Ageing Protection for Technical Products, on Methods for Laboratory Testing Resistance to Fungi.

Following the development of microbiological colonies on the surface of the specimens, they were then immersed in distilled water to investigate the kinetics of leaching of calcium-bearing phases from the cement matrix.

The determination of calcium ion concentration in an aqueous solution was achieved through a process of complexometric titration using a standardized solution of ethylenediaminetetraacetic acid (EDTA) at a concentration of 0.05 mol/L as the titrant. This method ensures high selectivity and precision in measuring calcium concentrations in the presence of other cationic species, as it causes a color change from wine red to blue.

For the spatial analysis of calcium distribution throughout the depth of the cement matrix, a thermogravimetric analysis was performed using a Q-1500D derivative instrument under an inert gaseous atmosphere. The samples were initially separated into three distinct sections, each with a thickness of  $10 \pm 0.5$  mm, starting from the surface exposed to microorganisms. Analytical samples weighing between 0,5 and 1 g were carefully extracted from the geometric center of each layered section.

The thermal decomposition process was carried out within a temperature range of 30°C to 1,000°C at a rate of 1°C per minute. The mass of CaO generated during the decomposition of calcium hydroxide ( $\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$  at temperatures between 450°C and 550°C) and calcium carbonate ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  at temperatures between 600°C and 800°C) was determined from the thermogravimetric curves. These results were then normalized to the initial sample weight for comparison purposes.

The parameters for mass transfer – the density of the calcium hydroxide diffusion flux ( $q$ ) and the coefficient of mass conductivity within the capillary porous structure of the concrete ( $k$ ) – were calculated using the following mathematical equations:

$$q = \frac{\Delta C_{liq}}{S \cdot \tau}, \quad (1)$$

$$k = \frac{q}{\left| \frac{dc}{dx} \right|}, \quad (2)$$

there:  $\Delta C_{liq}$  – the mass of the substance transferred to the liquid medium from the cement stone, kg;

$S$  – surface area exposed to aggressive action,  $\text{m}^2$ ;

$\tau$  – time of exposure, s;

$q$  – the flux density of calcium hydroxide is caused by a concentration gradient,  $\text{kg}/(\text{m}^2 \cdot \text{s})$ ;

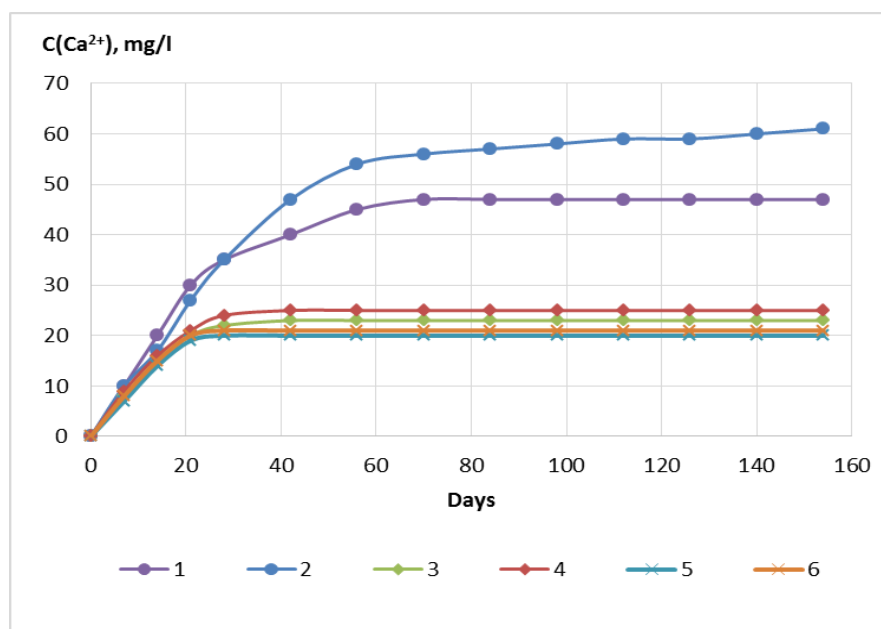
$\frac{dc}{dx}$  – the gradient of the calcium hydroxide concentration across the thickness of the sample,  $\text{kg}/\text{m}^4$ ;

$k$  – the coefficient of mass conductivity within the capillary porous structure of the concrete,  $\text{m}^2/\text{s}$ .

### 3. RESULTS AND DISCUSSION

In accordance with the established methodology for examining the corrosion resistance of cement composites, an experimental component involved a comparative evaluation of test specimens that were subjected to prolonged exposure in a corrosive aqueous environment containing simulated microbial colonies. Additionally, control samples were maintained under standard storage conditions. A distinct group consisted of specimens that were exposed to distilled water until a quasi-equilibrium state of the system was achieved, corresponding to the establishment of chemical-diffusion equilibrium between the cement matrix and its surroundings. It's been found that the biological growth on cement surfaces, no matter what their chemical or mineral composition is, causes a slowdown in how fast calcium hydroxide diffuses into water (Fig. 2). This is because of the biofilm that forms, which acts like a barrier for calcium ions to pass through. With calcium stearate added, the bad effects of microbes on corrosion processes are lessened, probably because there's a synergy between the hydrophobic qualities and the biological protection mechanisms.

A quantitative analysis of the kinetic curves shows that hydrophobic cement stones have a significantly lower rate of calcium ion buildup in water, about 2.5 to 3 times lower than non-modified samples. This means there's less calcium leaching. The reason for this is likely due to the protective measures we applied, like hydrophobic coating and creating conditions that limit microbial activity.

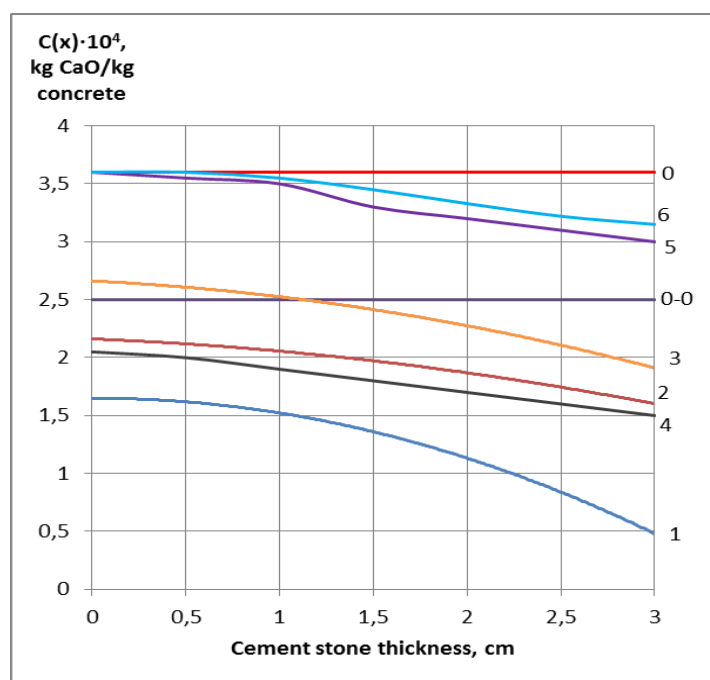


**Fig. 2.** The influence of fungal activity and intrinsic hydrophobicity on the rate of water-mediated calcium hydroxide dissolution in cement paste: 1 – without additives, infected with fungi; 2 – without additives; 3 - with 0,5% additive; 4 – with 0,5% additive, infected with fungi; 5 – with 1% additive; 6 – with 1% additive, infected with fungi.

In the system under study, the achievement of an equilibrium state is considered to be the absence of an increase in the concentration of the studied component (calcium cations) on the kinetic curve [29]. It should be noted that there is a significant difference in the timing of achieving an equal weight state of the system in the absence of calcium stearate supplementation: in samples infected with fungi, equilibrium is reached by day 84, and in samples without biofouling by day 126. The presence of the addition of calcium stearate in the cement stone significantly accelerates the achievement of an equilibrium state – up to 42 days of testing. Thus, the research results show the positive effect of calcium stearate on the kinetics of cement stone biodegradation – a decrease in the rate of corrosion by about 2,5 times. After 70 days, this equilibrium was deemed to have been reached.

Differential scanning calorimetry (DSC) analysis was used to determine the phase composition of cement stone both before and after a 70-day testing period. The analysis was carried out using a Q-1500D instrument and thermograms were collected over a temperature range of 30–1000°C at a heating rate of 10°C/min. The samples were initially divided into five successive layers, each 2 mm thick, through a meticulous layer-by-layer process of abrasion starting from the surface exposed to harsh conditions. Within each layer, the concentration of calcium hydroxide was determined based on the magnitude of an endothermic peak in the thermal profile corresponding to the dehydration of  $\text{Ca}(\text{OH})_2$  occurring between 450 and 550°C.

Utilizing the acquired data, profiles representing the distribution of concentrations of calcium hydroxide across the depth of intrusion of destructive processes were constructed (Fig. 3). These empirically derived curves can be effectively described by employing second-order polynomial equations, with a determination coefficient ( $R^2$ ) exceeding 0,95.



**Fig. 3.** Profiles of calcium hydroxide concentrations in cement stone thickness after 70 days of water action: 1 – sample without additives, infected with fungi; 2 – sample with 0,5% calcium stearate, infected with fungi; 3 – sample with 1% calcium stearate, infected with fungi; 4 – sample without additives; 5 – sample with 0,5% stearate 6 is a sample with 1% calcium stearate; 0-0 is a sample without additives before exposure; 0 is a sample with hydrophobic additives before exposure.

A comparative analysis of calcium hydroxide distribution profiles, as depicted in Fig. 3, across pairs 1–4, 2–5, and 3–6, reveals a profound influence of microbiological on the dynamics of cement stone degradation. The biogenic organic acids, including formic, oxalic, and citric acids, synthesized by metabolically active strains of *Aspergillus niger*, in conjunction with the aqueous phase, permeate the porous structure of cement stone. These acids initiate chemical reactions with free calcium hydroxide present in the pore fluid, resulting in the decalcification of hydrosilicate cement stone phases.

This process manifests itself through the formation of a distinctive diffusion front characterized by a sharp concentration gradient, approximately 2–3 mm away from the contact surface.

The incorporation of 0,5% calcium stearate by weight into the binder material had a substantial impact on the spatial arrangement of free calcium hydroxide. In the samples that underwent hydrophobization and were not exposed to microbial action, the destructive processes were confined to a surface layer measuring approximately 0,5–1,0 mm in thickness (profiles 5 and 6), in accordance with the observed leaching kinetics (Fig. 2).

This stabilization of the chemical composition within deeper layers can be attributed to the development of a hydrophobic barrier that effectively impedes the infiltration of moisture and dissolved ions, thereby preventing their penetration.

The profiles 2 and 3 demonstrate that the incorporation of calcium stearate into cement stone enables the attainment of a quasi-equilibrium state within the system, resulting in a reduction in biogenic deterioration by 40–60% compared to undoped samples.

It has been empirically demonstrated that the proposed additive exhibits a remarkable capacity to hinder the microbial colonization of concrete surfaces, effectively reducing the diffusion coefficient of corrosive substances.

The concentration profiles constitute the quantitative foundation for mathematical modeling of mass transfer phenomena, enabling the calculation of concentration gradients ( $\partial C/\partial x$ ), which are crucial for determining the service life of structures utilizing diffusion models based on Fick's law. These models provide a comprehensive analysis of the penetration of biologically active acids into concrete, considering their production rate by microorganisms and their interaction with cement stone mineral phases.

An analysis of the kinetics of mass transfer, as depicted in Figure 4a, reveals an exponential increase in the coefficient of mass transfer at the initial phase (0–30 days) in samples inoculated with *Aspergillus niger*, this suggests an autocatalytic nature to the process of bio-corrosion.

In contrast, hydrophobic systems exhibit a linear relationship between the change in the coefficient of mass transfer and time, with a relatively low slope ranging from  $0,15$  to  $0,25 \times 10^{-12} \text{ m}^2/\text{s}$ . The disparity in the scales used to present the data in Figures 4a and 4b can be attributed to the fact that treated samples exhibit orders of magnitude lower rates of mass transfer. This observation further confirms the efficacy of the comprehensive protective measures employed to safeguard cement-based materials from biological degradation.

The experimental data obtained regarding the effect of calcium stearate on the resistance of cement composites to microbiological degradation provide a fundamental basis for the development of mathematical models of mass transport corrosion. Parameters derived from diffusion kinetics allow for quantification of the dynamics of calcium-bearing phases, specifically calcium hydroxide, within the structure of hydrophobic concrete. A critical aspect of mathematical modelling is accounting for significant differences in diffusion coefficients. In unmodified samples, the diffusion coefficient is approximately  $10^{-8} \text{ m}^2/\text{s}$ . However, when 0,5% calcium stearates are added, it decreases to  $10^{-11} \text{ m}^2/\text{s}$ , indicating a two-fold reduction in the rate of diffusion within the hydrophobic matrix.

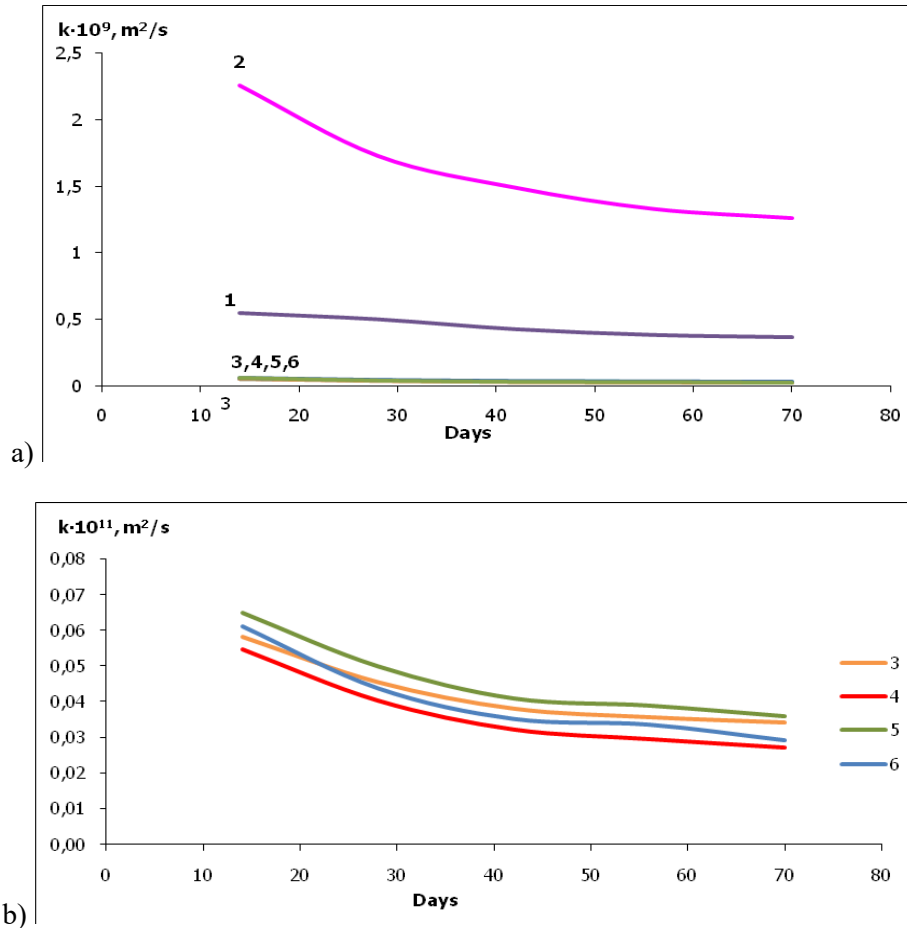
The microbial activity of *Aspergillus niger* colonies has a dual effect on the kinetics of cement stone degradation. Specifically, organic acids (formic, oxalic, and citric) produced metabolically enhance mass exchange processes by increasing the rate of mass transfer. Their chemical reaction with  $\text{Ca}(\text{OH})_2$  triggers active and passive corrosion mechanisms.

Based on experimental data, the liquid biological corrosion process is a non-steady mass transfer phenomenon in a medium with spatial and temporal gradients in potential and transfer coefficients. System dynamics are determined by changes in effective diffusion coefficient, liquid-phase mass-transfer coefficient at interface, and bio-produced acid concentration over time.

In accordance with the theory of unsteady mass transfer phenomena, mathematical modeling of corrosion degradation under the combined influence of liquids and microorganisms requires the division of the computational domain into two distinct functional areas:

- boundary Layer (Zone I): This area is characterized by intense chemisorption of free calcium hydroxide due to chemical reactions with organic acids. At the same time,  $\text{Ca}(\text{OH})_2$  diffuses from the bulk to the interface with the corrosive medium.

- deep Layers (Zone II): Processes in this area are primarily governed by the transport of calcium hydroxide through diffusion towards the boundary with Zone I. Chemical transformations occur to a lesser extent in this area.



**Fig. 4.** Changes in the values of mass conductivity coefficients in cement stone when exposed to water: 1 – sample without additives; 2 – sample without additives, infected with fungi; 3 – sample with 1% calcium stearate, infected with fungi; 4 – sample with 1% calcium stearate; 5 – sample with 0,5% calcium stearate, infected with fungi; 6 – sample with 0,5 % calcium nitrate.

In order to predict the operational lifespan of reinforced concrete structures exposed to prolonged corrosive biological conditions, a mathematical model of biocorrosion was developed (Equation 3) [29]. This model takes into account the spatial and temporal dynamics of mass transfer, as well as the incorporation of microbial influence. The model incorporates a volumetric source/sink of mass ( $q_v$ ), representing the intensity of calcium hydroxide chemisorption/liberation within the cement matrix, and transforms this phenomenon into dimensionless variables using the modified Pomerantsev criterion ( $Po_m^*$ ), which includes additional terms accounting for biological activity within the system.

$$\begin{aligned}
 Z(\bar{x}, Fo_m) &= \frac{C(x, \tau) - C_p}{C_0} = 2 \frac{Bi_m + 1}{Bi_m + 2} \int_0^1 Z_0(\xi) d\xi + \frac{Bi_m + 1}{Bi_m} \int_0^1 Po_m^*(\xi) d\xi + \\
 &+ 2 \sum_{m=1}^{\infty} \frac{Bi_m^2 + \mu_m^2}{Bi_m^2 + Bi_m + \mu_m^2} \cos(\mu_m \bar{x}) \cdot \exp(-\mu_m^2 Fo_m) \cdot \int_0^1 Z_0(\xi) \cos(\mu_m \xi) d\xi - \\
 &- 2 \sum_{m=1}^{\infty} \frac{Bi_m^2 + \mu_m^2}{\mu_m^2 [Bi_m^2 + Bi_m + \mu_m^2]} \cos(\mu_m \bar{x}) \cdot \exp(-\mu_m^2 Fo_m) \cdot \int_0^1 Po_m^*(\xi) \cos(\mu_m \xi) d\xi, \quad (3)
 \end{aligned}$$

there:  $Z(\bar{x}, Fo_m)$  is the dimensionless concentration of calcium hydroxide in the pore structure of concrete;  $\bar{x} = \frac{x}{\delta}$  is the dimensionless coordinate;  $x$  is coordinate, m;  $\delta$  is concrete thickness, m;  $Fo_m = \frac{k\tau}{\delta^2}$  is the Fourier mass transfer criterion;  $k$  is the mass conductivity coefficient of calcium hydroxide in concrete,  $m^2/s$ ;  $\tau$  is time, s;  $C(x, \tau)$  is distribution of calcium hydroxide concentrations over the thickness of the structure, kg Ca(OH)<sub>2</sub>/kg concrete;  $C_p(\tau)$  is the equilibrium value of the concentration of calcium hydroxide on the surface of the structure, kg Ca(OH)<sub>2</sub>/kg concrete;  $Bi_m = \frac{\beta\delta}{k}$  is the Bio mass transfer criterion;  $\beta$  is the mass transfer coefficient of calcium hydroxide in a liquid medium, m/sec;  $Z_0$  is the dimensionless concentration of calcium hydroxide over the thickness of a micro-section of cement stone;  $\zeta$  is the coordinate of integration in the range  $0 \leq \xi \leq \bar{x}$ ;  $\mu_m$  is the root of the characteristic equation  $\operatorname{tg}\mu_m = \frac{Bi_m}{\mu_m}$ ;  $PO_m^* = \frac{q_v\delta^2}{C_0 k \rho_{con}}$  is the modified Pomerantsev mass transfer criterion;  $q_v$  is the power of volumetric release (absorption) of calcium hydroxide due to phase and chemical transformations, kg Ca(OH)<sub>2</sub>/(m<sup>3</sup>·s);  $C_0$  is the initial uniformly distributed value of the mass content of free calcium hydroxide in the pore structure of concrete by thickness, kg Ca(OH)<sub>2</sub>/kg concrete;  $\rho_{con}$  is concrete density, kg/m<sup>3</sup>.

Equation (3) makes it possible to calculate the dynamics of mass transfer of the target component, with convective mass transfer complicated by internal sources of absorption of calcium hydroxide, due to chemical reactions, in particular free calcium hydroxide, from the inner layers of concrete to the interface «liquid aggressive medium – concrete», as well as the kinetics of the transition of this component through the interface between the phases and the liquid entering the volume.

From the analysis of formula (3), it can be seen that it represents a convergent series, that is, an algebraic sum of cosines with gradually decaying amplitudes. The cyclic frequency of such cosines increases with increasing  $m$ .

Based on equation (3), which was formulated within the theoretical framework and assumptions of the methodmicroprocess method, a numerical simulation of the spatial and temporal dynamics of calcium hydroxide diffusion within the structure of hydrophobic concrete subjected to the combined effects of microbiological agents (specifically, *Aspergillus niger*) and an aggressive aqueous environment was carried out. Simulations were performed under operational conditions typical for reinforced concrete walls with a thickness of 300 mm, which is common for hydraulic structures (Fig. 5). A solution to the partial differential equation was found in the complex domain using the technique of conformal mapping. The results were converted into physical units for practical application.

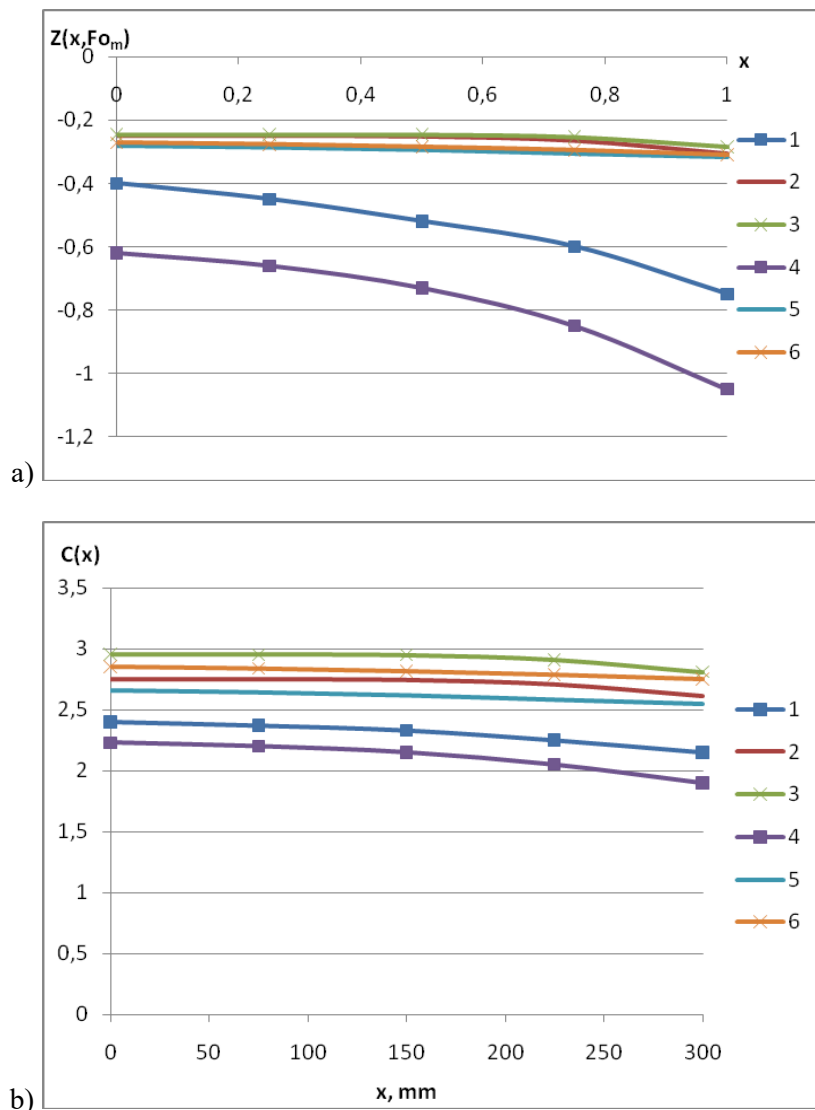
The validation of the mathematical model is supported by a strong correlation ( $R^2 > 0.93$ ) between the results of numerical simulations and experimental data obtained from physico-chemical experiments (Fig. 2 and 3). This high correlation serves as evidence for the reliability of the adopted boundary conditions and kinetic parameters. Analysis of the durability of a structure under prolonged exposure to highly corrosive biological conditions reveals that, in undifferentiated concrete, destructive processes occur in two stages. Initially, during the first five years, surface degradation of hydro-silicate phases occurs due to the action of biogenic acids, such as formic and oxalic acids. This is followed by internal propagation of destruction, resulting in a network of micro-cracks.

A significant reduction in mechanical properties exceeding 40% of initial values and loss of structural integrity due to dissolution of interfacial bonding are anticipated after  $15 \pm 2$  years from microbial colonization onset. In concrete modified with 0,5% calcium stearate by weight of cement, a protective mechanism activates, localizing destructive processes in a surface layer approximately 8-12 mm thick, preventing the penetration of aggressive substances by a hydrophobic barrier. It is expected that complete loss of hydrophobicity and progressive degradation through the entire structural thickness will occur after at least  $32 \pm 3$  years, confirming the effectiveness of this modification in improving biostability for concrete structures exposed to aggressive environments.

#### 4. CONCLUSIONS

Internal hydrophobization of cement stone with calcium stearate in an amount of 0,5–1% by weight of cement significantly increases the corrosion resistance of concrete under the simultaneous influence of water and fungal microorganisms *Aspergillus niger*. The addition of a hydrophobizer reduces the intensity of calcium leaching from the cement stone structure by 2,5–3 times compared with conventional concrete, which is confirmed both by the kinetics of changes in calcium concentration in a liquid medium and by the distribution profiles of calcium hydroxide over the thickness of the samples.

Calcium stearate provides a double protective effect: firstly, it creates hydrophobic barriers on the surface of pores and capillaries, preventing the penetration of moisture and biogenic acids; secondly, it promotes partial overlap of the pore space with hydrophobic crystals. This leads to a radical decrease in the mass conductivity coefficients by two orders of magnitude (from  $10^{-7}$  to  $10^{-11}$   $\text{m}^2/\text{s}$ ), which significantly slows down the diffusion processes of the transfer of aggressive components.



**Fig. 5.** Modeled dynamics of free calcium hydroxide concentration fields in dimensionless (a) and dimensional (b) values for the thickness of a concrete wall after 15 years of operation in an aqueous medium: 1 – sample without additives; 2 – sample with 0,5% calcium stearate; 3 – sample with 1% calcium stearate; 4 – sample without 5 – a sample with 0,5% calcium stearate infected with fungi; 6 – a sample with 1% calcium stearate infected with fungi.

Based on a sophisticated mathematical model of biocorrosion, which takes into account the complex dynamics of unsteady mass transfer characterized by fluctuating potentials and transfer coefficients, a comprehensive analysis was conducted to predict the long-term durability of concrete structures. The findings of this analysis suggest that, in typical concrete, destructive processes leading to hazardous conditions may begin after a period of 15 years in a biologically aggressive environment. However, for hydrophobic concrete containing calcium stearate, this critical time frame extends to 25 to 30 years, significantly extending the service life of the structure.

The results obtained demonstrate the high efficiency of volumetric hydrophobization with calcium stearate as a comprehensive method of protecting concrete structures in conditions unfavorable for biological fouling of surfaces (sewage treatment plants, underground structures, hydraulic engineering structures). The internal hydrophobization technology provides long-term protection over the entire volume of the material and is not susceptible to mechanical damage, unlike surface protection methods.

For the first time, the effect of fungal biocorrosion on the kinetics of mass transfer in hydrophobic concrete was quantified, criteria for protection effectiveness were established, and a mathematical model was developed that takes into account the interaction of chemical and biological factors of destruction. The experimental data and theoretical dependences obtained are consistent with each other and confirm the physicochemical validity of the proposed protection method.

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