Mathematical Model of Mass Transfer Processes in Biological Corrosion of Cement Concretes

Sergey Fedosov¹, Varvara Rumyantseva², Viktoryia Konovalova² and Svetlana Loginova²

¹ Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, Russia
² Ivanovo State Polytechnic University, department of natural sciences and technosphere safety, Sheremetevsky av., 21, Ivanovo, 153000, Russia

E-mail: fedosov-academic53@mail.ru, varrym@gmail.com, kotprotiv@yandex.ru, sl79066171227@yandex.ru

Abstract. Timely protection of underwater concrete and reinforced concrete objects from biofouling will significantly reduce the economic damage from the effects of corrosion damage, improve the reliability of structures operated in high humidity conditions, and reduce the likelihood of accidents. Despite the abundance of ways to protect against fouling, there are still no radical methods of struggle. It is expedient to find a solution to the problem of predicting the durability of concrete and reinforced concrete structures in biologically aggressive liquid media from the point of view of the theory of mass transfer. The model of mass transfer in an unlimited two-layer plate is considered for the first time in the form of a system of partial differential equations of parabolic type with boundary conditions of the second kind at the interface between concrete and liquid and the fourth kind at the interface between concrete and biofilm, which describes diffusion processes in the system of «cement concrete – biofilm – liquid». The proposed physical and mathematical model takes into account the properties of the solid and liquid phases, as well as the kinetics of growth, reproduction and death of microorganisms. The results of calculating dimensionless concentrations of «free» calcium hydroxide over the thickness of the concrete structure and biofilm are presented. The application of the obtained solutions will allow timely monitoring of the biocorrosion destruction of underwater structures and select effective protection methods.

1. Introduction

Currently, the biodegradation of concrete and reinforced concrete structures is increasingly attracting the attention of scientists as a serious problem related to the structural integrity and service life of bridge structures and various hydraulic structures [1-4]. The danger of biocorrosion is that microorganisms multiply intensively, easily adapting to changing physical and chemical conditions of the environment.

The work of many scientists is devoted to the study of the influence of service environments on the biostability of building composites [5-11]. As a result of a number of studies [2, 4, 5], it was found that in most cases biological destruction proceeds everywhere with other types of corrosion. Biodegradation of concrete structures increases the porosity of concrete and accelerates diffusion processes in it, thereby stimulating corrosion processes.
The destruction of cement concretes in biocorrosion, as in other types of corrosion destruction, is determined by the laws of mass transfer processes and chemical kinetics in the solid phase. Successful prediction of the durability of building structures operated in an aqueous environment is possible by mathematical modeling [12, 13], which takes into account both the properties of cement concrete and the parameters of the liquid, and the nature of the impact of microflora.

Using the mathematical apparatus to study microbiological corrosion makes it possible to understand the essence of exchange processes between a cement stone and a bacterial cell, to predict this exchange and to outline possible ways to prevent corrosion destruction.

Currently known anti-corrosion measures are not enough because they provide effective protection from acids and other corrosive chemical compounds and often do not take into account the impact of microorganisms on concrete.

2. Materials and methods
Corrosion resistance was studied on cube samples with a face of 3 cm made of Portland cement of the CEM I 42,5 brand of normalized composition without mineral additives with a water-cement ratio W/C = 0,3. As test strains, Aspergillus niger van Tieghem fungi and Bacillus subtilis bacteria were used. Nutrient media with pH = 6,8-7,0 were used for the transfer of strains, the compositions of which are shown in Table 1. Infected concrete samples were kept in the aqueous environment. Distilled water (pH = 6,6) was used as the reaction medium for studying the corrosion process.

| Table 1. Compositions of nutrient media. |
|-----------------------------------------|
| Component                          | g/l   |
|-----------------------------------------|
| For fungi:                            |       |
| Malt extract                         | 30,0  |
| Peptone                               | 1,0   |
| Agar-agar                            | 20,0  |
| Distilled water                       | 949   |
| For bacteria:                         |       |
| Meat water                            | 965   |
| NaCl                                  | 5,0   |
| Peptone                               | 10,0  |
| Agar-agar                             | 20,0  |

3. Discussion and results
During the experimental study, it was found that the studied microorganisms have a high adaptability to cement concretes. On the 28th day of the experiment, the formation of a clearly visible biofilm by microorganisms was observed.

An illustration of a physical and mathematical model of the mass transfer process of the target component from a solid phase (concrete) to liquid (water) during biofouling is shown in Figure 1 [14]. This type of model formulation is explained by the fact that in real conditions, hydrodynamic loads of liquid media in the boundary layer lead to a violation of the integrity of the biofilm [15], so the most favorable conditions for biofouling are formed on the rear end parts of the supports in the area of low pressures.
From a mathematical point of view, the «cement concrete – biofilm – liquid» system can be represented by two unlimited plates in contact, each of which is characterized by its size (the concrete support with a thickness of $\delta_1$ on the right side is covered with a biofilm with a thickness of $\delta_2$ (Figure 1)) and properties. In this case, the task is reduced to determining the change in the concentration of «free» calcium hydroxide in time ($\tau$) by the thickness of the structure ($x$).

The physical and mathematical model of mass transfer in an unlimited two-layer plate is a system of partial differential equations of the parabolic type with boundary conditions of the second kind at the interface between concrete and liquid and the fourth kind at the interface between concrete and biofilm:

$$\frac{\partial C_1(x, \tau)}{\partial \tau} = k_1 \frac{\partial^2 C_1(x, \tau)}{\partial x^2}, \tau > 0, -\delta_1 \leq x \leq 0,$$

$$\frac{\partial C_2(x, \tau)}{\partial \tau} = k_2 \frac{\partial^2 C_2(x, \tau)}{\partial x^2}, \tau > 0, 0 \leq x \leq \delta_2.$$

Initial conditions:

$$C_1(x, \tau)|_{\tau=0} = C_1(x, 0) = C_{1,0}.$$

$$C_2(x, \tau)|_{\tau=0} = C_2(x, 0) = C_{2,0}.$$

Border conditions. Left:

$$\frac{\partial C_1(x, \tau)}{\partial x} \bigg|_{x=-\delta_1} = 0.$$

At the point of contact between concrete and biofilm, the equilibrium in the system obeys Henry's law:

$$C_1(x, \tau)|_{x=0} = m \cdot C_2(x, \tau)|_{x=0},$$

$$-\rho_{con} \cdot k_1 \cdot \frac{\partial C_1(x, \tau)}{\partial x} \bigg|_{x=0} = -\rho_{biom} \cdot k_2 \cdot \frac{\partial C_2(x, \tau)}{\partial x} \bigg|_{x=0}.$$

On the right:

$$-k_2 \cdot \frac{\partial C_2(x, \tau)}{\partial x} \bigg|_{x=\delta_2} = q_H(\tau).$$

Where: $C_1(x, \tau)$ is the concentration of «free» calcium hydroxide in terms of CaO in concrete at the time $\tau$ at an arbitrary point with the $x$ coordinate, (kg CaO/kg of concrete); $C_2(x, \tau)$ is the concentration of «free» calcium hydroxide in terms of CaO in the biofilm at the time $\tau$ at an arbitrary point with the $x$ coordinate, (kg CaO/kg of biomass); $k_{1,2}$ are mass conductivity coefficients, m$^2$/s; $\delta_1$ is the concrete structure thickness, m; $\delta_2$ is biofilm thickness, m; $C_{1,0}$ is initial concentration of «free» CaO, kg CaO/kg of concrete; $C_{2,0}$ is initial concentration of «free» CaO, kg CaO/kg biomass; $m$ is Henry's
equilibrium constant, kg of biofilm/kg of concrete; $\rho_{\text{con}}, \rho_{\text{biom}}$ are concrete and biomass densities, kg/m$^3$; $q_{ld}(\tau)$ is density of the mass flow leaving the biofilm into the liquid flow.

There is no substance flow at the left border of the concrete structure (equation (5)). At the point of contact of the plates, the mass flow densities are equal (equations (6) and (7)). To solve the system (1)-(8), the Laplace integral transformation method was used. The general solution of the mass conductivity problem describing the dynamics of concentration fields has the form:

$$Z_1(\bar{x}, F_{0m}) = \frac{1}{1 + N K_k K_\delta} \left\{ 1 - N K_\delta + N K_{i_H} \left[ F_{0m} + \frac{(1 - \bar{x})^2}{2} + \phi(K_k, N, K_\delta) \right] \right\} +$$

$$+ 2 \sum_{n=1}^{\infty} \frac{1}{\mu_n^2 \psi_1^2(\mu_n)} \left[ \mu_n \sin \mu_n \left[ \cos(\mu_n \bar{x}) \cos(\mu_n \sqrt{K_k K_\delta}) - \sqrt{K_k K_\delta} \sin(\mu_n \bar{x}) \sin(\mu_n \sqrt{K_k K_\delta}) \right] - \frac{N}{\sqrt{K_k}} \cos(\mu_n (1 + \bar{x})) \exp(-\mu_n^2 F_{0m}) \right].$$

$$Z_2(\bar{x}, F_{0m}) = \frac{1}{1 + N K_k K_\delta} \left\{ 1 - N K_\delta + K_{i_H} [\bar{x} - F_{0m} K_k K_\delta] + N K_{i_H} \phi(K_k, N, K_\delta) \right\} -$$

$$- \frac{1}{2} \sum_{m=1}^{\infty} \frac{f}{\mu_m^2 \psi_1^2(\mu_m)} \left[ \mu_m \sin \mu_m \cos(\mu_m \sqrt{K_k (K_\delta - \bar{x})} \right]$$

$$- \frac{\mu_m}{\sqrt{K_k}} \sin(\mu_m \sqrt{K_k K_\delta}) \left[ N \cos \mu_m \cos(\mu_m \sqrt{K_k \bar{x}}) \right]$$

$$+ \frac{f}{\sqrt{K_k}} \sin(\mu_m \sqrt{K_k K_\delta})$$

$$+ K_{i_H} \left[ N \cos \mu_m (\mu_m \sqrt{K_k \bar{x}}) \right]$$

$$+ \frac{1}{\sqrt{K_k}} \sin \mu_m \left[ \mu_m \sqrt{K_k \bar{x}} \right] \exp(-\mu_m^2 K_k F_{0m}) \right].$$

$$\phi(K_k, N, K_\delta) = \frac{1 + K_k K_\delta (3 K_\delta + 3N + NK_k K_\delta^2)}{6(1 + NK_k K_\delta)}.$$  

$$J = \int_0^1 Z_{1,0}(\xi) \cos[\mu_m (1 - \xi)] d\xi.$$  

$$tg \mu_m = N \sqrt{K_k} t g(\mu_m \sqrt{K_k K_\delta}).$$

Where: $Z_1(\bar{x}, F_{0m})$ is dimensionless concentration of the transferred component over the concrete thickness; $Z_2(\bar{x}, F_{0m})$ is dimensionless concentration of the transferred component by the thickness of the biofilm; $\bar{x} = x/\delta_1$ is dimensionless coordinate; coefficient $K_k = k_k/k_1$; coefficient $K_\delta = \delta_2/\delta_1$; $q_{ld}$ is mass flow density leaving the biofilm in the fluid flow; $m$ is Henry's equilibrium constant, kg of biofilm/kg of concrete; $N = (\rho_{\text{bio}}/k_2)/(\rho_{\text{con}} k_1 m)$ is coefficient that takes into account the characteristics of the phases; $F_{0m} = (k_1 \tau)/\delta_1^2$ is the Fourier criterion; $\mu_\alpha$ are roots of the characteristic equation (13); $K_{i_H} = (q_H \cdot \rho_{\text{con}} \cdot m \cdot K_\delta)/\left(\delta_2 \cdot \rho_{\text{bio}} \cdot k_2 \cdot C_0\right)$ is Kirpichev's mass transfer criterion.

The complex mechanism of growth, reproduction and death of microorganisms can be taken into account by introducing the $N$ coefficient, which takes into account changes in the density of biomass [16].
To assess the adequacy of the proposed mathematical model, which takes into account the degree of influence of the biological factor on the patterns of mass transfer of «free» calcium hydroxide during the corrosion destruction of concrete in a liquid medium, numerical experiments were performed, the results of which illustrate the influence of similarity criteria (Fourier, Kirpichev) on the dynamics of the process biodegradation [17].

When the mass transfer criterion of Kirpichev changes, large concentration gradients appear (Figure 2). The curves in Figure 3 illustrate the dynamics of dimensionless concentrations of the transferred component at different values of the Fourier mass transfer criterion.

**Figure 2.** Profiles of dimensionless concentrations by the thickness of concrete and biofilm at $K_k = 1; K_\delta = 0,1; N = 1; Fo_m = 1$ with different values $K(1)$: 1) -0,5; 2) -1; 3) -1,5; 4) -2; 5) -2,5; 6) -3.

**Figure 3.** Profiles of dimensionless concentrations by the thickness of concrete and biofilm at $K_k = 1; K_\delta = 0,1; N = 1; K_H^* = 0,5$ with different values $Fo_m$: 1) 0,5; 2) 1; 3) 1,5; 4) 2; 5) 2,5; 6) 3.
The obtained dependencies make it possible to solve the inverse problem and based on the available experimental data this model can be used to predict the numerical value of «free» calcium hydroxide by the thickness of the structure and the biofilm.

The evaluation of the results of numerical experiments confirms the previously accepted model ideas about the nature of mass transfer in the «cement concrete – biofilm – liquid» system under conditions of biogenic active media. This, in turn, made it possible to calculate the mass transfer characteristics of «free» calcium hydroxide in the biocorrosion of cement concretes using the developed mathematical model. For the system under consideration, the values of the mass conductivity coefficient are in the range of $2.59 \times 10^{-9} \ldots 5.01 \times 10^{-11}$ m$^2$/s for bacterial corrosion, and for fungal corrosion – $4.01 \times 10^{-9} \ldots 6.38 \times 10^{-11}$ m$^2$/s. For the «cement concrete – water» system, without taking into account the impact of microorganisms, the values of the mass conductivity coefficient are in the range of $1.47 \times 10^{-9} \ldots 2.77 \times 10^{-10}$ m$^2$/s [18].

Lower values of the mass conductivity coefficient indicate that the biofilm growing on the concrete surface inhibits diffusion processes, which means that the main factor contributing to the development of biological corrosion of concrete and deterioration of its performance characteristics are the products of microorganisms.

4. Conclusions

The obtained solutions (9)-(13) allow to determine the concentrations of the transferred component in thickness both the concrete structure and the biofilm at any time, and also allow to calculate the concentration of free calcium hydroxide in the liquid phase, to calculate the kinetics of the process in solid, liquid phase and in the biofilm that ultimately allows with minimal uncertainty to predict the durability and reliability of structures in terms of biological corrosion [19, 20].

The numerical experiment of the influence of similarity criteria (Fourier, Kirpichev) on the intensity of the corrosion mass transfer process showed that changes in the mass transfer criteria of Kirpichev and Fourier lead to large concentration gradients.

A comprehensive study of cause-and-effect factors and mechanisms of biological damage processes is important for effective prevention and control of wear of concrete structures operated in liquid media.

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