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MATHEMATICAL MODELING OF DIFFUSION PROCESSES OF MASS TRANSFER OF "FREE CALCIUM HYDROXIDE" DURING CORROSION OF CEMENT CONCRETES

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Abstract: The paper presents a mathematical model of mass transfer in the processes of corrosion of the first type of cement concrete at the level of phenomenological equations for a closed reservoir-liquid system. A step-by-step transition to the recording of the boundary value mass conduction problem in dimensionless coordinates is shown. The solutions of the boundary value mass conduction problem for the region of large and small values of Fourier numbers are obtained.

Keywords: cement concrete, corrosion, mathematical model, mass transfer, concentration of "free calcium hydroxide"

МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ ДИФФУЗИОННЫХ ПРОЦЕССОВ МАССОПЕРЕНОСА «СВОБОДНОГО ГИДРОКСИДА КАЛЬЦИЯ» ПРИ КОРРОЗИИ ЦЕМЕНТНЫХ БЕТОНОВ

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Аннотация: В статье представлена математическая модель массопереноса в процессах коррозии первого вида цементных бетонов на уровне феноменологических уравнений для замкнутой системы «резервуар-жидкость». Показан пошаговый переход к записи краевой задачи массопроводности в безразмерных координатах. Получены решения краевой задачи массопроводности для области больших и малых значений чисел Фурье.

Ключевые слова: цементный бетон, коррозия, математическая модель, массоперенос, концентрация «свободного гидроксида кальция»

1. INTRODUCTION

Durability of buildings and structures can be provided by the use of corrosion-resistant materials. Forecasting the service life of concrete and reinforced concrete structures is a complex analytical process [1]. In most cases, the main causes of damage are corrosion processes caused by adverse environmental effects.

Reliable prediction of durability of building structures is impossible without experimental analysis and theoretical developments [2] aimed at creating mathematical models of processes occurring at all stages of production and operation [1, 2].

One of the directions of the scientific school, which works fruitfully at Ivanovo state Polytechnic University, is the theoretical study and mathematical modeling of corrosion processes of concretes proceeding along the mechanisms of the first and second types [3-9]. To date, the authors of the article have developed a complex of mathematical models of corrosion processes in different environments, and proposed ways to combat corrosion destruction [6-9].

First of all, calcium oxide is responsible for the strength of concrete, which is part of the main minerals of Portland cement [1, 10]. The decrease in the content of "free calcium hydroxide", which is the main component that determines mass transfer, causes a change in the phase and thermodynamic equilibrium in the system, leads to the decomposition of the main components of the cement stone, and as a result, to the loss of the strength properties of concrete.

2. MATHEMATICAL MODEL OF MASS TRANSFER IN CORROSION PROCESSES OF THE FIRST TYPE AT THE LEVEL OF PHENOMENOLOGICAL EQUATIONS FOR A CLOSED "RESERVOIR-LIQUID" SYSTEM

Mass transfer in the "reservoir-liquid" system according to the first type of corrosion is determined by the boundary value problem of mass conductivity of the type [3, 4]:

$$\frac{\partial C(x,\tau)}{\partial \tau} = k\frac{\partial^2 C(x,\tau)}{\partial x^2}, \tau > 0, 0 \leq x \leq \delta. \quad (1)$$

Initial condition:

$$C(x,\tau)|_{\tau=0} = C(x,0) = C_0. \quad (2)$$

Border conditions:

$$\frac{\partial C(0,\tau)}{\partial x} = 0, \quad (3)$$

$$k\frac{\partial C(\delta,\tau)}{\partial x} = \beta[C_e(\tau) - C(\delta,\tau)]. \quad (4)$$

where: $C(x,\tau)$ is concentration of "free calcium hydroxide" in concrete at a time τ at an arbitrary point with x coordinate, in terms of CaO, kg CaO / kg of concrete; $C_0(x)$ is concentration of "free calcium hydroxide" in concrete at the initial moment of time at any point with x coordinate, in terms of CaO, kg CaO / kg of concrete; k is mass conductivity coefficient in solid phase, m^2/s; δ is wall thickness of the structure, m.

The value of the equilibrium concentration on the surface of the solid C_e is not constant, but depends on the concentration of the component in the liquid phase:

$$C_e(\tau) = f[C_{liq}(\tau)].. \quad (5)$$

The simplest form of this dependence is Henry's law [9]:

$$C_e(\tau) = mC_{liq}(\tau), \quad (6)$$

where: m is Henry's constant, kg of liquid / kg of concrete.

According to the law of mass conservation, the mass flow of substance emerging from the concrete surface should be equal to the amount of substance arriving in the liquid phase.

$$-S\rho_{con}k\frac{\partial C(\delta,\tau)}{\partial x} = V_{liq}\rho_{liq}\frac{\partial C_{liq}(\tau)}{\partial \tau}, \quad (7)$$

where: S is internal surface of the tank, m^2; V_{liq} is tank volume m^3; ρ_{con}, ρ_{liq} are densities of concrete and liquid, respectively, kg/m^3.

To obtain generalized solutions suitable for qualitative analysis of corrosion processes, we introduce dimensionless variables of the form:

$$Z(\bar{x}, Fo_m) = \frac{C_0 - C(x,\tau)}{C_0}, \bar{x} = \frac{x}{\delta}, \quad Fo_m = \frac{k\tau}{\delta^2}. \quad (8)$$

We transform the equation (1) with regard to (8):

$$\frac{\partial C[C_0 - C(x,\tau)]}{\partial\tau\cdot C_0} = = k\frac{\partial^2 C[C_0 - C(x,\tau)]}{\partial x^2\cdot C_0}. \tag{9}$$

This implies:

$$\frac{\partial Z(\bar{x}, Fo_m)}{\partial\tau} = k\frac{\partial^2 Z(\bar{x}, Fo_m)}{\partial x^2}. \tag{10}$$

Multiply by δ^2 and divide by k both parts of the equation:

$$\frac{\partial Z(\bar{x}, Fo_m)\delta^2}{\partial\tau\cdot k} = \frac{\partial^2 Z(\bar{x}, Fo_m)\delta^2}{\partial x^2}. \tag{11}$$

In dimensionless coordinates, the boundary value problem (1)-(4) is transformed to the form [5]:

$$\frac{\partial Z(\bar{x}, Fo_m)}{\partial Fo_m} = \frac{\partial^2 Z(\bar{x}, Fo_m)}{\partial\bar{x}^2}, \quad Fo_m > 0,\ 0 \le \bar{x} \le 1. \tag{12}$$

Initial condition:

$$Z(\bar{x}, 0) = 0. \tag{13}$$

Border conditions:

$$\frac{\partial Z(0, Fo_m)}{\partial\bar{x}} = 0. \tag{14}$$

$$\frac{1}{Bi_m}\cdot\frac{\partial Z(1, Fo_m)}{\partial\bar{x}} = = [Z_e(Fo_m) - Z(1, Fo_m)]. \tag{15}$$

where:

$$Bi_m = \beta\cdot\frac{\delta}{k}$$

is Bio mass transfer criterion;

$$Fo_m = k\cdot\frac{\tau}{\delta^2}$$

is Fourier mass transfer criterion.

We transform the equation (7) by multiplying the summands on the left by

$$\frac{\delta}{\delta},$$

and on the right by

$$\frac{\delta^2}{\delta^2}:$$

$$-S\rho_{con}k\frac{\partial[C_0 - C(\delta,\tau)]\delta}{C_0\partial x\cdot\delta} = = V_{liq}\rho_{liq}\frac{\partial C_{liq}(\tau)\delta^2}{\partial\tau\cdot C_0\delta^2}. \tag{16}$$

Assuming that the equilibrium in the system obeys Henry's law (6), we write:

$$\frac{S}{V}\cdot\frac{\rho_{con}}{\rho_{liq}}\cdot\frac{k}{\delta}\cdot\frac{\partial Z(0, Fo_m)}{\partial\bar{x}} = -\frac{\partial Z\left[C_0 - mC_{liq}(\tau)\right]}{m\partial\left(\frac{\tau}{\delta^2}\right)C_0\delta^2} = = -\frac{\partial Z_{liq}(Fo_m)}{m\partial\left(\frac{\tau}{\delta^2}\right)\delta^2}. \tag{17}$$

Divide by k:

$$\frac{S}{V}\cdot\frac{\rho_{con}}{\rho_{liq}}\cdot\frac{1}{\delta}\cdot\frac{\partial Z(1, Fo_m)}{\partial\bar{x}} = = -\frac{\partial Z_{liq}(Fo_m)}{m\partial\left(\frac{k\tau}{\delta^2}\right)\delta^2}. \tag{18}$$

The last expression denotes:

$$Z_{liq}(Fo_m) = \frac{C_0 - mC_{liq}(\tau)}{C_0}. \tag{19}$$

We denote that:

$$K_m = \frac{mS\delta}{V_{liq}} \cdot \frac{\rho_{con}}{\rho_{liq}} = \frac{mG_{con}}{G_{liq}}, \qquad (20)$$

where: Km is coefficient considering phase characteristics; G_{con} is the mass of the concrete tank, kg; G_{liq} is the mass of liquid in the tank, kg.
In the accepted variables equation (7) will take the form:

$$-\frac{\partial Z_{liq}(Fo_m)}{\partial Fo_m} = K_m \frac{\partial Z(1, Fo_m)}{\partial \bar{x}}. \qquad (21)$$

We transform the equation (6):

$$\frac{C_0 - C_e(\tau)}{C_0} = \frac{C_0 - mC_{liq}(\tau)}{C_0}. \qquad (22)$$

In this case, the boundary value problem of mass conductivity will take the form:

$$\frac{\partial Z(\bar{x}, Fo_m)}{\partial Fo_m} = \frac{\delta^2 Z(\bar{x}, Fo_m)}{\partial \bar{x}^2}. \qquad (23)$$

The initial and boundary conditions of expression (23) are expressions (13)-(15). In equation (15), $Z_e(Fo_m)$ is the same as $Z_{liq}(Fo_m)$.
The solution of the equation (23) obtained by the Laplace integral transformation takes the form [5, 6]:

$$Z(\bar{x}, s) = \mathrm{A}ch(\sqrt{s}\bar{x}) + \mathrm{B}sh(\sqrt{s}\bar{x}), \qquad (24)$$

$$\frac{dZ(\bar{x}, s)}{\partial \bar{x}} = A\sqrt{s}sh(\sqrt{s}\bar{x}) + +B\sqrt{s}ch(\sqrt{s}\bar{x}), \qquad (25)$$

$$\frac{1}{Bi_m}\left[A\sqrt{s}sh\sqrt{s}\right] + \frac{K_m}{s}\left[A\sqrt{s}sh\sqrt{s}\right] = = \frac{Z_{liq}(0)}{s} - Ach\sqrt{s}, \qquad (26)$$

$$A = = \frac{Bi_m\sqrt{s}Z_{liq}(0)}{s\left[ssh\sqrt{s} + K_m sh\sqrt{s} + Bi_m\sqrt{s}ch\sqrt{s}\right]} \qquad (27)$$

$$Z(\bar{x}, s) = = \frac{Bi_m Z_{liq}(0)ch(\sqrt{s}\bar{x})}{s\left[ssh\sqrt{s} + Bi_m K_m sh\sqrt{s} + Bi_m\sqrt{s}ch\sqrt{s}\right]}. \qquad (28)$$

The final solution of the boundary value problem (23) for the region of large values of Fourier numbers (for $Fo_m > 0{,}1$) has the form [5]:

$$Z(\bar{x}, Fo_m) = \frac{Z(0)}{1 + K_m} - -2Bi_m Z_{liq}(0)\sum_{n=1}^{\infty}\frac{\cos(\mu_m\bar{x})}{\psi'(\mu_m)}\exp(-\mu_m^2 Fo_m), \qquad (29)$$

$$\psi`(\mu_m) = \sin\mu_m\left[3\mu_m^2 + \mathrm{Bi}_m\left(\mu_m^2\text{-}\mathrm{K_G b}\right)\right] + \mu_m\cos\mu_m\left[\mu_m^2\text{-}(\mathrm{Bi}_m \mathrm{K_G b} + 2)\right]. \qquad (30)$$

The characteristic equation for finding the roots of μ_m is:

$$tg\mu_m = \frac{Bi_m\mu_m}{\mu_m^2 - K_m Bi_m}, \qquad (31)$$

For the average concentration, we write:

$$Z_{mid}(Fo_m) = \frac{Z_{liq}(0)}{1 + K_m} - -2Bi_m Z_{liq}(0)\sum_{n=1}^{\infty}\frac{sin\mu_m}{\mu_m\psi'(\mu_m)}\exp(-\mu_m^2 Fo_m), \qquad (32)$$

$$Z_{liq}(Fo_m) = = Z_{liq}(0)\left\{1 + 2Bi_m K_m \sum_{n=1}^{\infty} \frac{sin\mu_m}{\mu_m \psi'(\mu_m)}[\exp(-\mu_m^2 Fo_m - 1]\right\}. \quad (33)$$

In cases where the condition $Fo_m \le 0,1$ is satisfied, it is advisable to obtain solutions using hyperbolic functions for large values of arguments (small Fourier numbers).

The final solution of the equation (23) for the region of small values of Fourier numbers has the form:

$$\frac{Z(\bar{x}, Fo_m)}{Z_{liq}(0)} = = -\frac{Bi_m}{\sqrt{Bi_m^2 - 4K_m}} \sum_{i=1}^{2} (-1)^i exp[-a_i(1 - \bar{x}) + a_i^2 Fo_m]\, erfc\left(\frac{1-\bar{x}}{2\sqrt{Fo_m}} - a_i\sqrt{Fo_m}\right), \quad (34)$$

$$a_i = \frac{-a \pm \sqrt{D}}{2}, \quad (35)$$

$$\mathrm{Z_{mid}(Fo_m)} = \int_0^1 \mathrm{Z(\bar{x}, Fo_m)d\bar{x}}, \quad (36)$$

$$\frac{Z_{liq}(Fo_m)}{Z_{liq}(0)} = 1 - -\frac{K_m Bi_m}{\sqrt{Bi_m^2 - 4K_m Bi_m}} \sum_{i=1}^{2} (-1)^{i+1} \left\{2\sqrt{\frac{Fo_m}{\pi}} + a_i \int_0^{Fo_m} exp(a_i^2 Fo_m) erfc(-a_i\sqrt{Fo_m}) dFo_m\right\}. \quad (37)$$

The obtained expressions allow to calculate the concentration fields of the transferred component along the thickness of the structure, to find the average concentration at any time, and to determine the value of the concentration of the "target" component in the liquid phase. Some results of calculations [5-7] are shown in Figures 1 and 2.

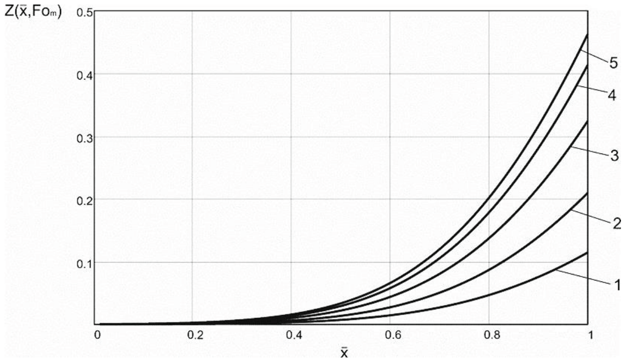

Figure 1. Profiles of the dimensionless concentrations on the thickness of the concrete at Fo_m = 0.05 at various values of Bi_m: 1 – 0.5; 2 - 1; 3 – 1.75; 4 – 2.5; 5 – 3.

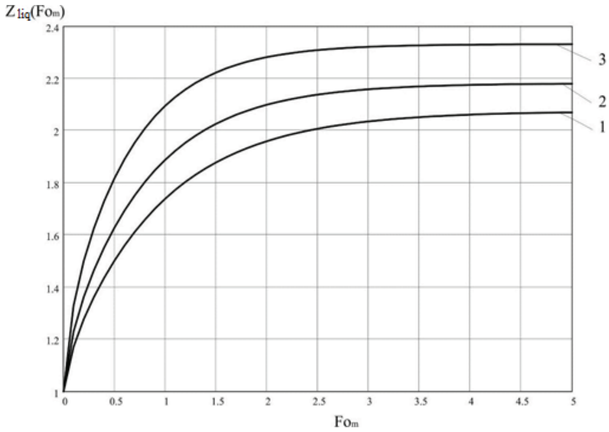

Figure 2. Concentration of the transferred component in the liquid phase at Fo_m = 0÷5; Km = 0.1; Bi_m: 1 – 0.5; 2 – 1; 3 – 1.5.

A necessary condition for the implementation of calculations is the availability of data on static and kinetic characteristics of the process, which can be obtained only on the basis of experimental studies.

3. CONCLUSION

Development of mathematical models is impossible without a clear understanding of the mechanism of the processes, experimental data characterizing the influence of various factors

on the kinetics and dynamics of processes and verification of the correctness of the forecast methodology in full-scale conditions [6, 8].
The joint analysis of the results of numerical and experimental studies confirms the adequacy of the developed mathematical models of mass transfer in the systems under study and makes it possible to use the developed mathematical models and the proposed methods for calculating the mass transfer process at the corrosion of the first and second types on real objects.

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