Physical and mathematical modelling of the mass transfer process in heterogeneous systems under corrosion destruction of reinforced concrete structures

S V Fedosov, V Eu Roumyantseva, I V Krasilnikov and V S Konovalova

Ivanovo State Polytecnical University, 8th Marta str., 20, Ivanovo, 153037, Russian Federation

fedosov-academic53@mail.ru

Abstract. The article presents the equations of "free calcium hydroxide" mass transfer describing the liquid corrosion of cement concretes. The boundary value problem of "free calcium hydroxide" mass conductivity in dimensionless variables is obtained. Also, in order to obtain a solution to the boundary value problem of mass conductivity, it is proposed to use a combined approach, which consists in the fact that at the beginning of each microprocess an analytical solution is obtained, and then the whole process is gradually calculated on a computer. It should be noted that the method gives good results if it is carried out in conjunction with the Laplace integral transformation method. In addition, the Laplace transform often makes it possible to obtain a solution in two forms: at $Fo_m > 0,1$ and $Fo_m \ll 0,1$, this is the advantage of using this transformation. The solution of the boundary value problem of mass conductivity is obtained, which allows to find not only the profiles of dimensionless and dimensional concentrations of "free calcium hydroxide" in concrete thickness, but also makes it possible to determine the value of this value gradient at the phases interface. The obtained solution allows further determining the time of reaching the critical concentration of "free calcium hydroxide" at the phases interface, corresponding to the beginning of high-basic components decomposition, and hence moving on to the further stages of study and corrosion processes modeling, which is confirmed by the graphical dependencies presented in the paper.

1. Introduction

During operation, any structure is exposed to the environment, which generates a variety of corrosion processes in the concrete. Corrosion of concrete is a complex physical and chemical process, which ultimately leads to the destruction of the structure.

According to the generally accepted international classification proposed by Professor Moskvin V.M. [1], the corrosive effect of any media on concrete is divided into three main types. Particular danger one is the exploitation of concrete and reinforced concrete structures in the conditions of their washing with water with various salts and acids dissolved in it. In this case, the crystals of calcium hydroxide contained in the cement stone are gradually dissolved, and the molecules of other compounds dissolved in water enter into chemical reactions with the molecules of "free calcium hydroxide". As a result of such processes, the chemical equilibrium between the pore liquid and cement stone components (high-basic compounds) is broken, which undergoes a stepwise

decomposition, leading to loss of strength, and as a consequence to the destruction of cement stone [2, 3].

According to Professor Moskvin V.M. [2], after removing 20 % CaO from the cement of its total content, a strength loss by 20 % occurs, and if 30 % of CaO is lost, the mechanical strength will decrease already to 33 % of the initial, which is likely to lead to complete destruction of the structure. Thus, it is clear that the existence stability of concrete high-basic compounds (alite, belite, tricalcium aluminate, four-calcium aluminate) is responsible for the "free calcium hydroxide" contained in the pores of the concrete, so it will be logical to predict the life of the product based on its amount in the body of the structure [1].

2. Relevance

Concrete is the most common building material for the manufacture of buildings and structures' elements. During operation, concrete and reinforced concrete products are exposed to various aggressive environments. The corrosion processes occurring under this influence lead to irreversible changes in the strength characteristics and to destruction of concrete or reinforced concrete products and whole structures. Thus, it is very important to understand the causes of building materials corrosion, to identify the factors that affect this complex process, to establish and generalize the patterns of mass transfer in concrete and reinforced concrete under the influence of different media.

3. Problem statement

Our school works begun with a series of publications devoted to theoretical research and mathematical modeling of concretes corrosion processes proceeding according to the mechanisms of the first and second types [4-7].

The development of mathematical models is impossible without a clear understanding of the processes mechanism, experimental data characterizing the influence of various factors on the kinetics and dynamics of processes and reliability verification of the prediction methodology under natural conditions.

The solution of these complex problems is possible from the positions of the mass transfer theory. The laws of mass transfer are common for the whole variety of natural phenomena. They enable rational design of building structures in accordance with operating modes, optimal selection of materials, and evaluation of the structures' state. Therefore, from the scientific and practical points of view, the study of mass transfer processes occurring during corrosion destruction is currently an urgent task.

4. Results of experimental studies

According to the mass transfer theory of academician Lykov A.V. [8, 9], in general, for corrosion of the first and second types, diffusion of calcium hydroxide in the concrete porous structure is described by a nonlinear differential equation of the second order mass conductivity:

$$\frac{\partial C(x,\tau)}{\partial \tau!} = div[k(x,\tau)gradC(x,\tau)] + \frac{q_v(x,\tau)}{\rho_{con}} \qquad (1)$$

where $k(x,\tau)$ is mass conductivity (diffusion) coefficient, m^2/s; $C(x,\tau)$ is the concentration of "free calcium hydroxide" in concrete at the time τ at any point with the coordinate x, kg CaO/kg concrete; $q_v(x,\tau)$ is the bulk source power of mass due to chemical or phase transformations, kg CaO/(m^3·s); ρ_{con} - concrete density, kg/m^3.

The wall of the reservoir, or some other structure, is modeled by an unlimited plate I of thickness δ and a corresponding density ρ and porosity ε. The pores of concrete contain "free calcium hydroxide", which concentration at the initial time of the structure operation is assumed to be uniform, and then, due to the influence of the aggressive medium, it changes with time and takes an uneven appearance [10, 11].

In the liquid phase, an aggressive component is distributed, which concentration generally changes in time $C_{liq}(\tau)$ (kg of the component/kg of the liquid) (Figure 1). The transfer intensity of the aggressive component is characterized by the mass flow density of the substance $q_f(\tau)$ (kg/(m^2·s)).

When the liquid and solid phases come into contact, the reaction of the calcium hydroxide interaction with salts or acids dissolved in the liquid phase begins. The reaction is accompanied by a mutual diffusion: calcium hydroxide to the boundary with the liquid from the inner layers and an aggressive component from the liquid phase into the solid [12, 13]. The order of reaction is calculated from the data obtained experimentally.

Thus, for arbitrary time moments τ_1 and τ_2 ($\tau_2 > \tau_1$), the concentration distribution of the transferred components can be illustrated by Figure 2. Here: $C_1(x,\tau)$ is concentration of calcium hydroxide in concrete, $C_2(x,\tau)$ is concentration of aggressive component in concrete. The process rate is determined by the chemical kinetics and diffusion of the components [14].
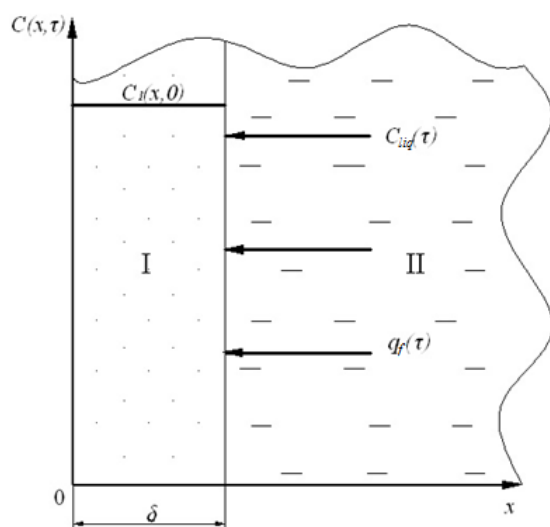

Figure 1. To the mathematical model development of mass transfer: I – concrete, II – medium.
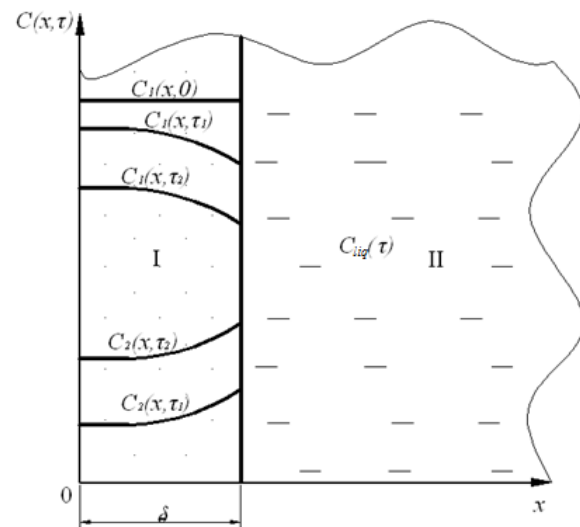
Figure 2. Profiles of components concentrations in concrete.

Diffusion processes in concretes proceed with low intensity, their duration is determined by years, and sometimes even by decades. Therefore, for the considered system "calcium hydroxide – aggressive component" the mass transfer equations for calcium hydroxide can be written as the following boundary value problem [12, 15]:

$$\frac{\partial C(x,\tau)}{\partial \tau} = k \cdot \frac{\partial^2 C(x,\tau)}{\partial \tau^2} + \frac{q_v(x)}{\rho_{con}} \quad \tau \geq 0, \; 0 \leq x \leq \delta, \tag{2}$$

$$C(x,\tau)\big|_{\tau=0} = C_0(x), \tag{3}$$

$$\frac{\partial C(x,\tau)}{\partial x}\bigg|_{x=0} = 0, \tag{4}$$

$$-k \cdot \rho_{con} \frac{\partial C(x,\tau)}{\partial \tau}\bigg|_{x=\delta} = q_f(\tau) \tag{5}$$

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

Equation (2) is a partial differential equation of parabolic type. In general, the bulk source power of mass is a quantity distributed along a coordinate according to an arbitrary law.

The initial condition (3) shows that the reference point taken at the time, the concentration of the transferred component (calcium hydroxide) has a distribution over the thickness of the concrete structure.

The boundary condition (4) is a non-penetration condition on the outer boundary of the structure. The boundary condition (5), which is a condition of the second type, shows that at the boundary of the structure with the liquid medium. There is a mass transfer between the solid and liquid phases.

For the convenience of mathematical operations and analysis of the process dynamics, we translate the system of equations (2)-(5) into a dimensionless form, introducing a dimensionless concentration of the form [16]:

$$\theta\left(\overline{x}, Fo_m\right) = \frac{C\left(x, \tau\right) - C_0}{C_0}, \tag{6}$$

as well as similarity criteria: $Fo_m = k \cdot \tau/\delta^2$ is Fourier mass transfer criterion; $Po_m(\overline{x}) = q_v(x) \cdot \delta^2/(k \cdot C_0 \cdot \rho_{con})$ is modified mass transfer criterion of Pomerantsev; $Ki_m = q_f \cdot \delta/(k \cdot C_0 \cdot \rho_{con})$ is modified criterion of Kirpichev.

Finally, the boundary value problem of "free calcium hydroxide" mass conductivity in dimensionless variables has the form:

$$\frac{\partial\theta\left(\overline{x}, Fo_m\right)}{\partial Fo_m} = \frac{\partial^2\theta\left(\overline{x}, Fo_m\right)}{\partial\overline{x}^2} + Po_m\left(\overline{x}\right); \quad Fo_m > 0;\; 0 \le \overline{x} \le 1, \tag{7}$$

$$\theta\left(\overline{x}, Fo_m\right)\big|_{Fo_m=0} = \theta_0\left(\overline{x}\right), \tag{8}$$

$$\frac{\partial\theta\left(\overline{x}, Fo_m\right)}{\partial\overline{x}}\bigg|_{\overline{x}=0} = 0, \tag{9}$$

$$-\frac{\partial\theta\left(\overline{x}, Fo_m\right)}{\partial\overline{x}}\bigg|_{\overline{x}=1} = Ki_m. \tag{10}$$

Due to the rapid development of computer technology, numerical methods based on the solution of partial differential equations using computers are increasingly used. The use of computer technology often allows to reduce the nonlinear problem to a linear one. If we divide the whole process into n elementary microprocesses, within all parameters can be considered constant, then the nonlinear problem can be reduced to a set of n linear problems [17]. In this case, a combined approach can be used, which consists in the fact that an analytical solution is obtained at the beginning of each micro-process, and then the whole process is gradually calculated on a computer. It should be noted that the method gives good results if it is carried out in conjunction with the Laplace integral transformation method [18, 19]. This is due to the fact that the results are quite accurate, using only the first few terms of the series in the large Fourier numbers region. With a decrease in the Fourier number, the number of terms in the series that must be taken into account to ensure a given accuracy of calculations increases sharply, but modern computers are able to cope quickly with this problem. In addition, the Laplace transform often makes it possible to obtain a solution in two forms: at $Fo_m > 0.1$ and $Fo_m << 0,1$, this is the advantage of using this transformation [8].

The general solution of problem (7)-(10) for the initial stages of corrosion, when $Fo_m << 0,1$ has the form:

$$\theta\left(\overline{x}, Fo_m\right) = Ki_m\left(1 \mp \overline{x}\right)erfc\left[\frac{\left(1 \mp \overline{x}\right)}{2\sqrt{Fo_m}}\right] - 2Ki_m\sqrt{\frac{Fo_m}{\pi}}\exp\left[-\frac{\left(1 \mp \overline{x}\right)^2}{4Fo_m}\right] +$$

$$+\frac{1}{2\sqrt{\frac{Fo_m}{\pi}}}\left\{\int_0^1 \theta_0(\xi)\exp\left[-\frac{(\bar{x}\mp\xi)}{4Fo_m}\right]d\xi+\int_0^1 \theta_0(\xi)\exp\left[-\frac{(2\mp\bar{x}-\xi)^2}{4Fo_m}\right]d\xi\right\}+ \qquad (11)$$

$$+\sqrt{\frac{Fo_m}{\pi}}\int_0^1 Po_m(\xi)\exp\left[-\frac{(\bar{x}\mp\xi)^2}{4Fo_m}\right]+\sqrt{\frac{Fo_m}{\pi}}\int_0^1 Po_m(\xi)\exp\left[-\frac{(2\mp\bar{x}-\xi)^2}{4Fo_m}\right]d\xi-$$

$$-\frac{1}{2}\int_0^1 Po_m(\xi)(\xi\mp\bar{x})erfc\left[\frac{(\xi\mp\bar{x})}{2\sqrt{Fo_m}}\right]d\xi-\frac{1}{2}\int_0^1 Po_m(\xi)(2\mp\bar{x}-\xi)erfc\left[\frac{(2\mp\bar{x}-\xi)}{2\sqrt{Fo_m}}\right]d\xi.$$

The obtained solution allows finding not the profiles of dimensionless and dimensional concentrations of "free calcium hydroxide" in the concrete thickness, as well as makes it possible to determine the value of the quantity gradient at the interface of phases. When corrosion of reinforced concrete products in an acidic environment, the reaction rate of the target component "free calcium hydroxide" and acid is necessary [20].

The obtained solution allows further to determine the time of reaching the critical concentration of "free calcium hydroxide" at the phases interface, corresponding to the beginning of high-basic components decomposition, and hence to move on to further study stages and corrosion processes modeling. Some results of calculations based on the obtained expression are shown in Figures 3-9.

The curves in figure 3 illustrate the "classical" behavior of the change lines in dimensionless concentrations over the concrete structure thickness depending on the mass transfer number of Fourier.

Figure 4 shows the influence of external mass transfer on the dynamics of mass transfer in the solid phase. It is clearly seen that there is a more intense transition of "free calcium hydroxide" from the solid phase layers close to the interface "solid – liquid" with the increase in the intensity of external mass transfer. It is interesting to note that the zone of intensive mass transfer in the solid phase is 0.6-1.0 in the conditions of the analyzed example.
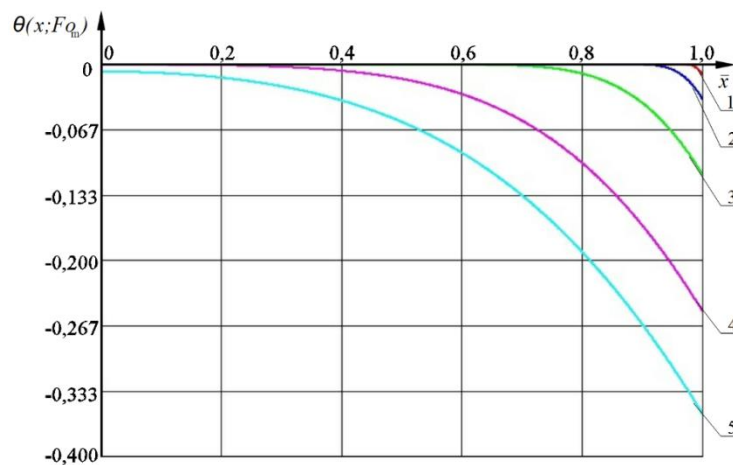

Figure 3. Effect of Fo_m on the profiles of dimensionless concentrations,
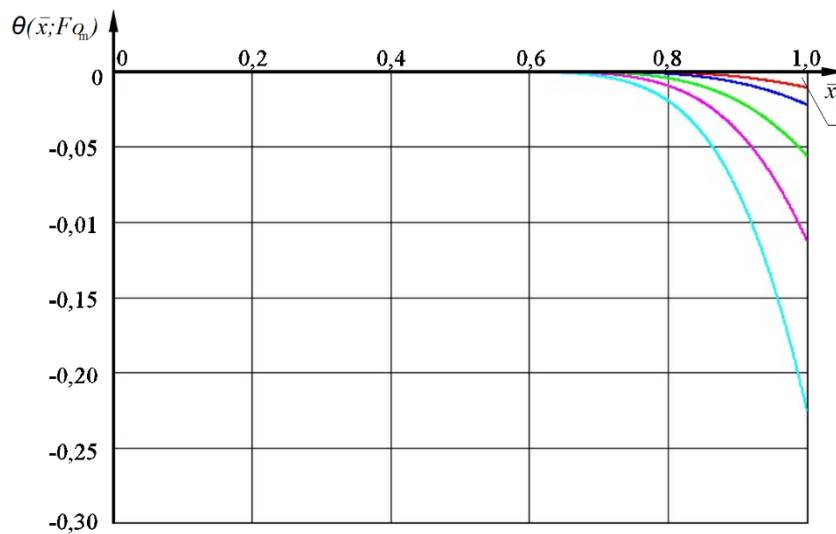at $Ki_m{}^* = 1$, $Fo_m = 0.0001; 0.001; 0.01; 0.05; 0.1$.

Figure 4. Effect of Ki_m^* on the profiles of dimensionless concentrations,
at $Fo_m = 1$, $Po_m^* = 0$, $Ki_m^* = 0,1$; 0.2;0.5; 1; 2.

The curves in Figure 5 show the influence of the mass source due to the chemical reaction on the profiles of dimensionless concentrations. It is obvious that in the case of a positive source, the concentration of the target component increases as it approaches the phase boundary, with a negative source (mass loss due to chemical reaction). There is a more intensive mass transfer of the substance to the acidic medium as a reaction product.
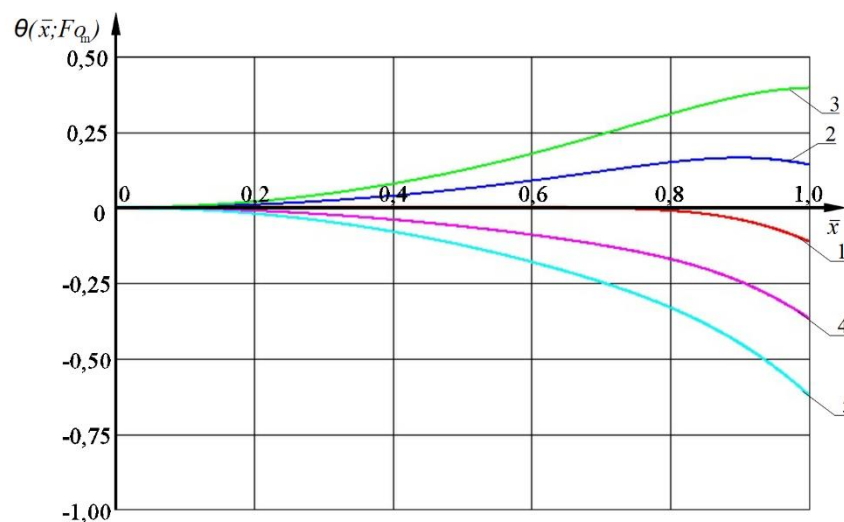

Figure 5. Influence of the internal mass source (Po_m^*) on the profiles of
dimensionless concentrations $Fo_m = 0.01$; $Ki_m^* = 1$; at $Po_m^* = 1 - 0$;   2 –
0.5; 3 – 1; 4 – -0.5; 5 – -1.

The nature of the curves in Figure 6 is interesting. The action of a low-intensity ($Po_m^* = 0.1$) source leads to an increase in the component content in the 0.6-1.0 zone. However, an increase in the

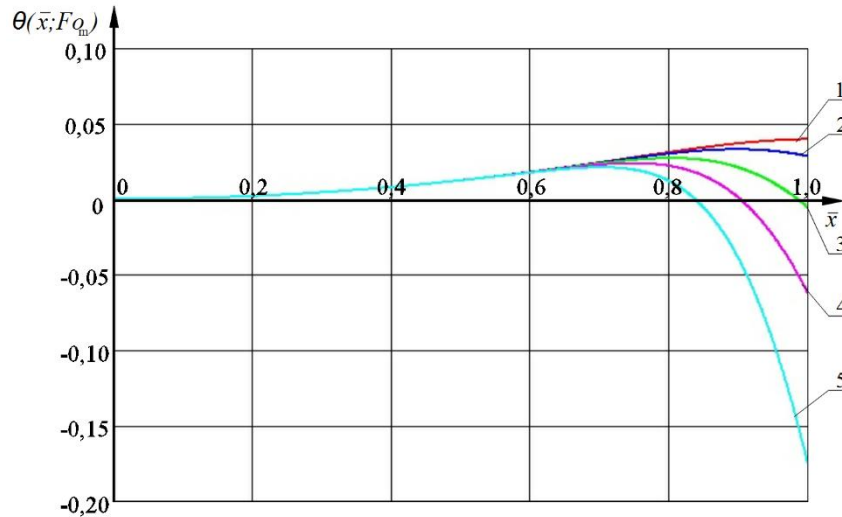intensity of external mass transfer sharply intensifies the overall convergence of the mass transfer process.

Figure 6. Effect of Ki_m^* on the profiles of dimensionless concentrations, at $Fo_m = 0.01$, $Po_m^* = 0.1$, $Ki_m^* = 0,1$; 0.2; 0.5; 1; 2.

The curves in Figures 7 and 8 illustrate the influence of the mass source nature as the dynamics of internal mass transfer. The first of them shows the results for a constant mass source ($Po_m^* = -0.1$). On the second, the mass source is distributed along the thickness of the structure according to a linear law ($Po_m^* = -0.1\xi$). It is clearly seen that the change in the source function significantly affects the concentration profiles near the concrete surface.
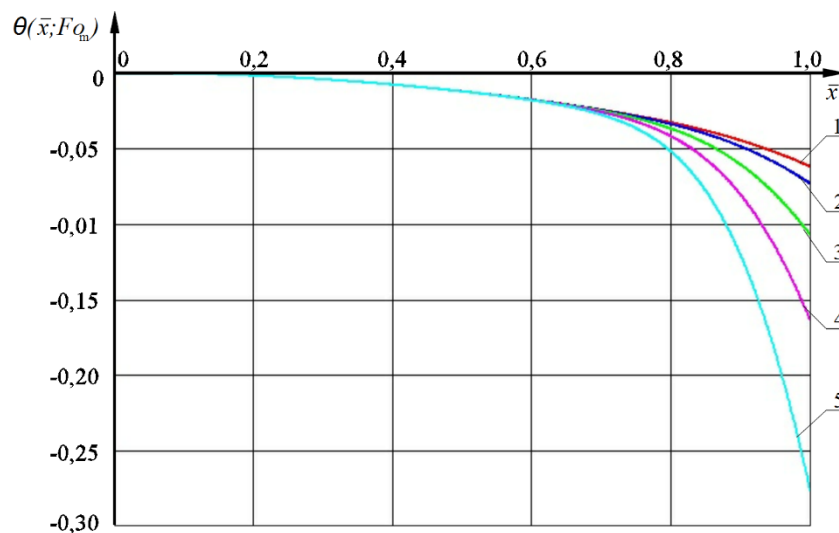

Figure 7. Effect of Ki_m^* on the profiles of dimensionless concentrations, at $Fo_m = 0.01$, $Po_m^* = -0.1$, $Ki_m^* = 0.1$; 0.2; 0.5; 1; 2.
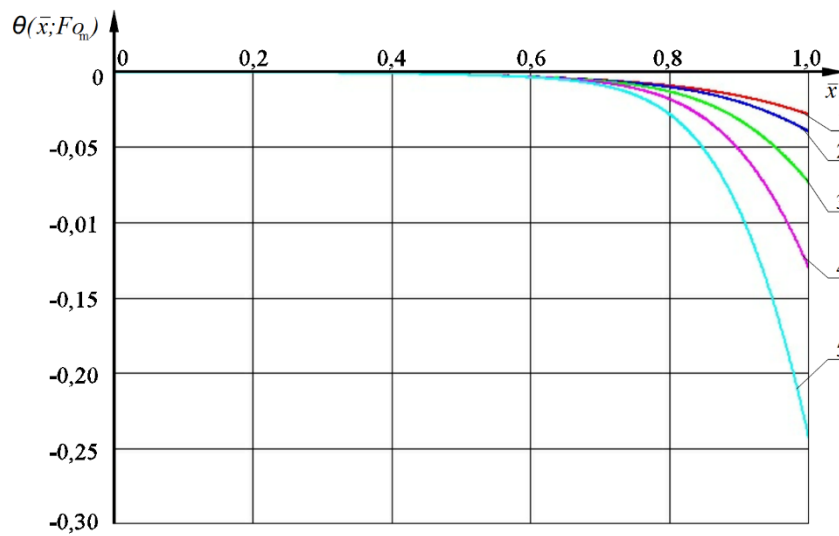
Figure 8. Effect of Ki_m^* on the profiles of dimensionless concentrations, at $Fo_m = 0.01$, $Po_m^* = -0.1\xi$, $Ki_m^* = 0.1; 0.2; 0.5; 1; 2$.

The numerical analysis is completed in Figure 9, which shows the influence of the source character on the concentration profiles of the obtained component in concrete. The curves of the Figure 9 once again confirm the obtained solutions reliability of the boundary value mass conduction problems and the prospect of their further application in the theoretical and experimental studies implementation of the corrosion processes of concrete and reinforced concrete in the liquid phase.
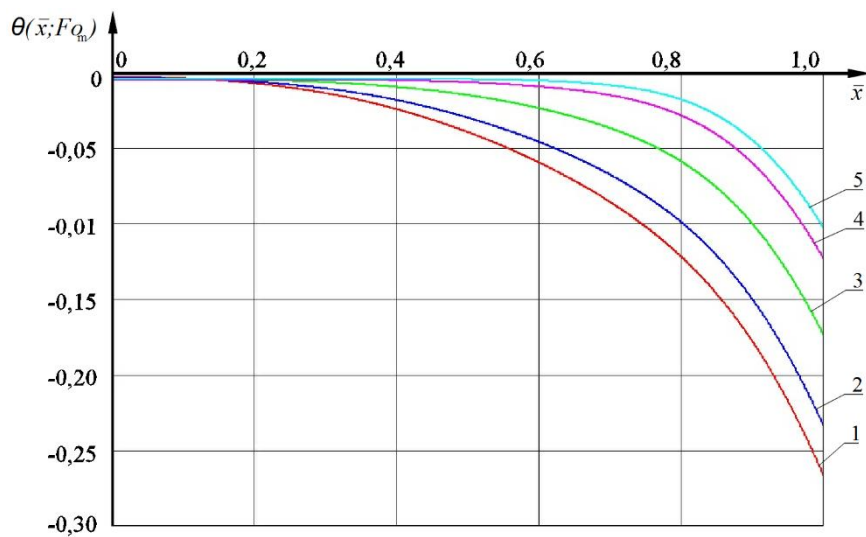

Figure 9. Influence of the internal mass source (Po_m^*) on the profiles of dimensionless concentrations $Fo_m = 0.01$; $Ki_m^* = 1$; at Po_m^*: $Po_1(\xi) = -\xi^{1/3}$, $Po_2(\xi) = -\xi^{1/2}$, $Po_3(\xi) = -1\xi^1$, $Po_4(\xi) = -1\xi^2$, $Po_5(\xi) = -1\xi^3$.

5. Conclusion

The presented physical and mathematical model of mass transfer in the concrete liquid corrosion processes, taking into account the chemical effect of a liquid aggressive medium at the level of

phenomenological equations for small values of the Fourier number allow us to calculate the concentration of the transferred component ("free calcium hydroxide") in the structure thickness, its content in the liquid phase and the average one at the thickness and volume of the structure, and also allows to determine the time of reaching on the concrete structure surface critical concentration "of free calcium hydroxide" leading to the beginning of high-basic cement concrete compounds decomposition.

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