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Diffusion of sulfate ions into cement stone regarding simultaneous chemical reactions and resulting effects

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Abstract

This study presents a model of sulfate ion diffusion into cement stone, in particular the simultaneous chemical reactions and resulting effects (filling of material voids with chemical products and hampering of ion motion within the specimen). The diffusion development is followed by the solution of the diffusion equation, introducing a specific relation for the diffusion coefficient and considering appropriate initial and boundary conditions. The change of the material structure is theoretically and experimentally assessed. A possibility for studying diffusion in multiply connected areas (i.e., in real materials that contain inclusions, inert filler, and reinforcement) is outlined. Good agreement between theory and experiment is obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Diffusion; Sulfate attack; Cement; Modeling

1. Introduction

A model of ion diffusion into a porous body that disregards the material packing due to filling the void with chemical products is given elsewhere [1,2], while cement stone is considered in particular in Ratinov and Ivanov [3]. We propose a further development of this model under several assumptions. Consider a rectangular specimen of cement stone with length much larger than its other dimensions, which has been kept for some time in pure water and at room temperature. Consider also that the specimen has been immersed and kept for different periods of time in a water solution of sodium sulfate, where diffusion of sulfate ions from the solution and into the specimen occurs. Assume that the solution has a large enough volume and its sulfate concentration remains constant in time (i.e., the solution ion loss due to evaporation or penetration into the material is disregarded). Then the concentration of sulfate ions at the solid-liquid interface is also kept constant. As a result of the occurring molecular diffusion, the sulfates migrate from the surrounding sulfate solution and penetrate into the water-saturated specimen voids. Next, the sulfates react with the cement stone, forming various chemical compounds. The chemical reactions that take place are considered to be irreversible. Hence, a part of the newly formed chemical compounds, together with molecules of chemically linked water, remain in the material voids as precipitants. This process develops in time and yields a gradual filling of the void and a change of the coefficients of diffusion and chemical reaction.

We assume that the specimen overall dimensions do not change during diffusion and chemical reaction, although we assume that the material degrades under the sulfate attack (i.e., the specimen volume remains constant in time). Consider now the simplest model of a porous body, such as with capillaries that pass through its whole volume [4]. Consider also that capillaries do not cross each other. Then, the following equation of ion transfer through the specimen cross section can be written for the ion concentration c, disregarding the capillary filling with chemical products and liquid motion through the capillaries [see Eq. (1)]:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) + kc \qquad (1)$$

where D is the generalized diffusion coefficient that accounts for ion motion in the capillary space and accounts for the number of capillaries per unit section and for the capillary shape, while k is a constant of chemical reaction rate and c is the ion concentration per unit volume.

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When treating diffusion of electrolytes, one must note that the diffusion coefficient D depends on the ion concentration in the solution [2,5] and increases with the concentration increase. Moreover, for considerably high concentrations near the solution saturation concentration, the motion of ions is strongly hampered due to their interaction with one another. We assume in the present study the following dependence of the diffusion coefficient D on the concentration current value shown in Eq. (2):

$$D = k_{\mathrm{diff}}\exp[\beta(c(x,y,t)-c_0)] \tag{2}$$

Here k_{diff} is the coefficient of sulfate ion diffusion in water (regarding cement stone porosity and grain size), as well as the capillary cross-section shape; β is a constant with dimensions opposite to these of c; while c_0 is a characteristic value of the concentration—in this particular case, the concentration of the water solution surrounding the cement stone specimen. Note that these quantities consider capillaries that cross sections do not change in time.

In fact, however, the capillary cross section changes due to the precipitation of part the chemical products on the capillary walls. Hence, the diffusion Eq. (1) needs a certain modification. Following Matros [4], we consider diffusion in a single capillary, the latter assumed to be rectilinear. Then, the following effective diffusion coefficient can be introduced as seen in Eq. (3):

$$D_{\mathrm{eff}} = D\frac{F(z)}{F_0} \tag{3}$$

where z is the coordinate along the capillary length, F_0 is the capillary average cross section at zero time, and $F(z)$ is the current cross section at a moment t and at a distance z [$F(z) < F_0$].

To estimate the effect of the occurring chemical reactions on the capillary filling with chemical products and on the change of the capillary cross section, we consider that chemical products precipitate on the capillary walls and a layer with a thickness $\delta(z, t)$ is formed as a result (Fig. 1). As shown in the figure, this thickness is larger near the solution/cement stone interface where the quantity of chemically reacted ions is also larger. Thus, the diffusion process is hampered, together with the filling of the capillary initial part. Let R_0 be the capillary average radius corresponding to a cross section F_0 at zero time. Then, the following equality for the cross section $F(z)$ at a moment t can be written as Eq. (4):

$$F(z) = \pi R(z,t)^2 = \pi(R_0-\delta(z,t))^2 \tag{4}$$

While using Eq. (3), we obtain the form of the effective diffusion coefficient, shown in Eq. (5):

$$D_{\mathrm{eff}} = D\left[1-\frac{\delta(z,t)}{R_0}\right]^2 \tag{5}$$

Here, $\delta(z,t)/R_0$ (the ratio between the thickness of the layer formed on the capillary wall as a result of the chemical reaction) and the capillary initial radius is present. Assuming that this ratio is proportional to the quantity of chemically reacted ions q (kg/m ^{3}), we can write Eq. (6):

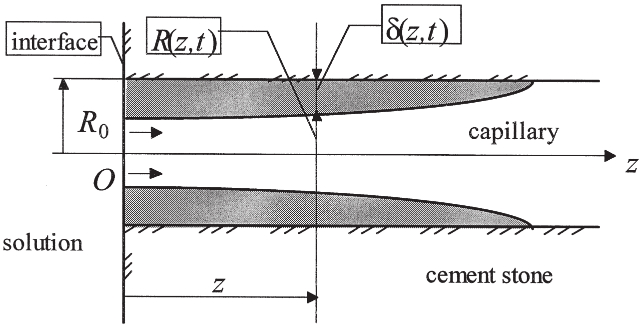

Fig. 1. Scheme of capillary filling with precipitants.

$$\frac{\delta(z,t)}{R_0} = k_z q \tag{6}$$

The proportionality coefficient k_z in Eq. (6) is in fact the coefficient of capillary filling with chemical products. It expresses the phenomenon that part of the chemical products migrate into the cement stone matrix. Its dimension is opposite that of the quantity of chemically reacted ions, k_z (m^3/kg) here. Thus, the ratio $\delta(z,t)/R_0$ in Eq. (6) can be substituted for Eq. (7):

$$D_{\mathrm{eff}} = D(1-qk_z)^2 \tag{7}$$

We can similarly consider how the capillary filling affects the source term in Eq. (1), which regards an irreversible first-order reaction. Thus, through Eq. (1) and relations (3), (6) and (7), we obtain the following differential equation for the ion concentration c [see Eq. (8)]:

$$\frac{\partial c}{\partial t} = \left[\frac{\partial}{\partial x}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial x}\right)+\frac{\partial}{\partial y}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial y}\right)\right]+k(1-k_z q)c. \tag{8}$$

The introduction of D_{eff} in the above equation enables one to account for the material structure (grain size and porosity) [6], capillary filling with chemical products, and diffusion hamper during the penetration of sulfate ions into the cement stone.

Eq. (8) can be completed by corresponding boundary and initial conditions. The value of the solution concentration is given as a "boundary condition" at the solution/cement stone interface, as seen in Eq. (9):

$$c(x,y,t)|_{\Gamma} = c_0 \tag{9}$$

where Γ is the interface contour. If the cross section is symmetric with respect to the coordinate axes Ox and Oy, the problem is solved for a 1/4th of the cross section only, and the symmetry conditions are given for $x = 0$ and $y = 0$. The initial sulfate concentration in the specimen cross section is zero, since the specimen has been kept in pure water before the diffusion start.

Experimental evidence is used to determine the constants that take part in Eqs. (1) through (8).

Table 1
Mineral composition of SRP cement type "Devnya" (% by weight)

C_3S	42.83
C_2S	27.75
C_3A	2.81
C_4AF	16.29
Na_2O	0.64
K_2O	1.46
MgO	0.80
Others	7.42

1. First of all, specimens (plates of cement stone with dimensions $1.5 \cdot 10^{-2} \times 1.5 \cdot 10^{-2} \times 0.2 \cdot 10^{-2}$ m) are kept for different periods of time in solutions of sodium sulfate with different concentrations (0.5, 1, 3, and 5%). The cement paste is prepared of commercial, sulfate resistant Portland cement 35, type "Devnya," following the Bulgarian standard. The cement mineral composition is given in Table 1 [6].
2. Second, as our observations show, a relatively homogeneous structure of the cement stone is obtained for specimen time of immersion of 180 days (Fig. 2a), while over this time limit cracks develop within the material. Fig. 2b shows material swell and macrocracking for a longer period of time (365 days of specimen immersion) [6]. Hence, we assume that the cement stone specimen can take maximum quantity of sulfate ions without material cracking for not more than 180 days of immersion into a 5% water solution of sodium sulfate. During this period of time the ions and the newly formed chemical compounds become evenly distributed within the specimen. Note that since we do not have more detailed experimental evidence, this time limit of 180 days is more or less conditional, but it seems plausible and suits the model.
3. Thus, considering a 5% water solution of Na_2SO_4, the constants k_{diff}, β, and k can be calculated by numerically solving Eq. (8). This is done by assuming values for k_z and by varying the rest of the unknown quantities until a constant concentration c within the specimen cross section for $t = 180$ days is obtained.
4. The values of k_{diff}, β, k, and k_z thus established are used to solve Eq. (8) for lower sulfate concentrations, where cement stone "saturation till fracture" by sulfate ions has not yet taken place.

As previously mentioned, the obtained results are more or less illustrative. They can be improved by gaining a more detailed experimental evidence on the actual chemical composition and structure of the cement stone subjected to sulfate attack. This will be an object of further study.

When solving the diffusion problem, we consider the one-dimensional case (i.e., the ion penetration is assumed as developing through the specimen thickness only, since the latter is significantly smaller than the specimen's other dimensions). Due to symmetry, the problem is solved for ion penetration starting from the solid/liquid interface and reaching the specimen middle surface (the plane of symmetry), where appropriate symmetry boundary conditions are

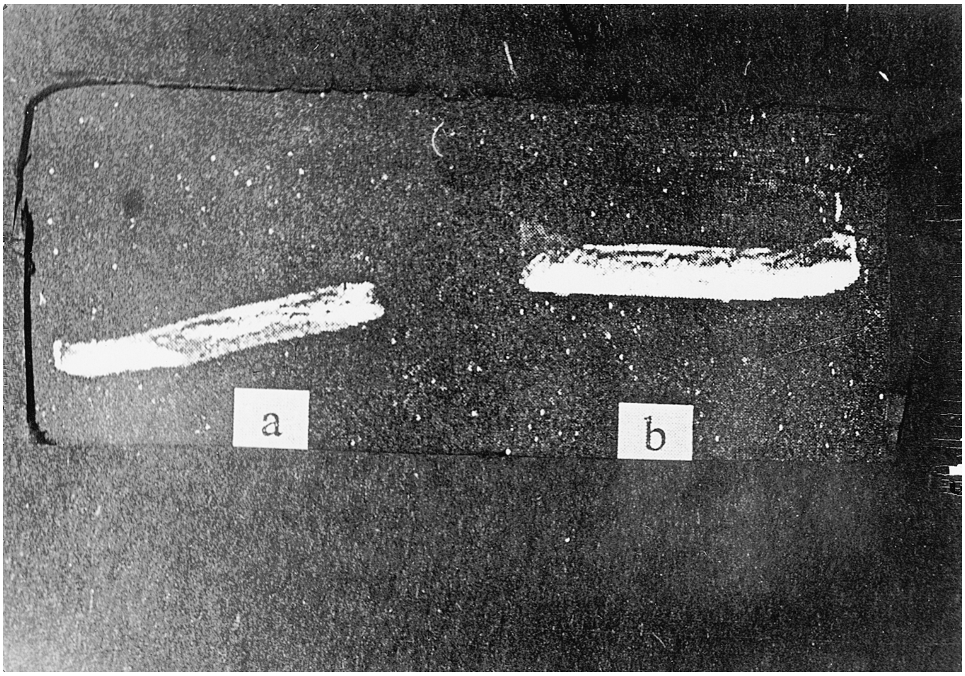

Fig. 2. (a) Cement stone specimen immersed in a 5% sulfate water solution for 180 days; (b) cement stone specimen immersed in a 5% sulfate water solution for 365 days.

given. The averaged values of the calculated quantities k_{diff}, β, and k for assumed values of $k_z = 0$ [1 and 2 (m^3/kg)] are as follows:

> coefficient of ion diffusion $k_{\mathrm{diff}} = 0.361 \cdot 10^{-13}$ m^2/s or
> a constant present in relation (2) $-$ $\beta = 0.2917$ m^3/kg
> constant of the chemical reaction rate is $k = 0.305 \cdot 10^{-7} s^{-1}$

2. Numerical solution

The numerical solution of the outlined diffusion problem is obtained by employing an indirect implicit scheme. Eq. (8) and the corresponding boundary conditions are approximated on an orthogonal grid. Using an appropriate assembly on the grid knots at each time step, the difference problem is reduced to the solution of a linearized system of algebraic equations with a diagonal, weakly filled matrix. This matrix is generally nonsymmetric with respect to its main diagonal. The obtained algebraic system is exactly solved by using the decomposition method. Due to nonlinearity, an internal iteration process is applied where the coefficients of transport and the values of the quantity of chemically reacted ions are corrected by means of the newly obtained values at each grid knot. The process is repeated several times until attaining a previously given accuracy and then the next time step is performed.

When tackling diffusion, it is worth considering multiply connected areas. These are, for instance, cross sections of a cement stone/concrete element that contains apertures, reinforcement, or rubble. Diffusion through the inclusions either does not take place or its rate can be disregarded. Cross sections with a complex shape of the bounding contour are also worth considering. Hence, the algorithm used by Gospodinov et al. [6] for solving the diffusion problem is modified and developed here for multiply connected areas. Additional numerical procedures are included and regions with different diffusion permeability are given with their corresponding analytical equations, for example, second degree curves or rectangles approximated on the grid knots. The shape of the cross section bounding contour can be similarly given.

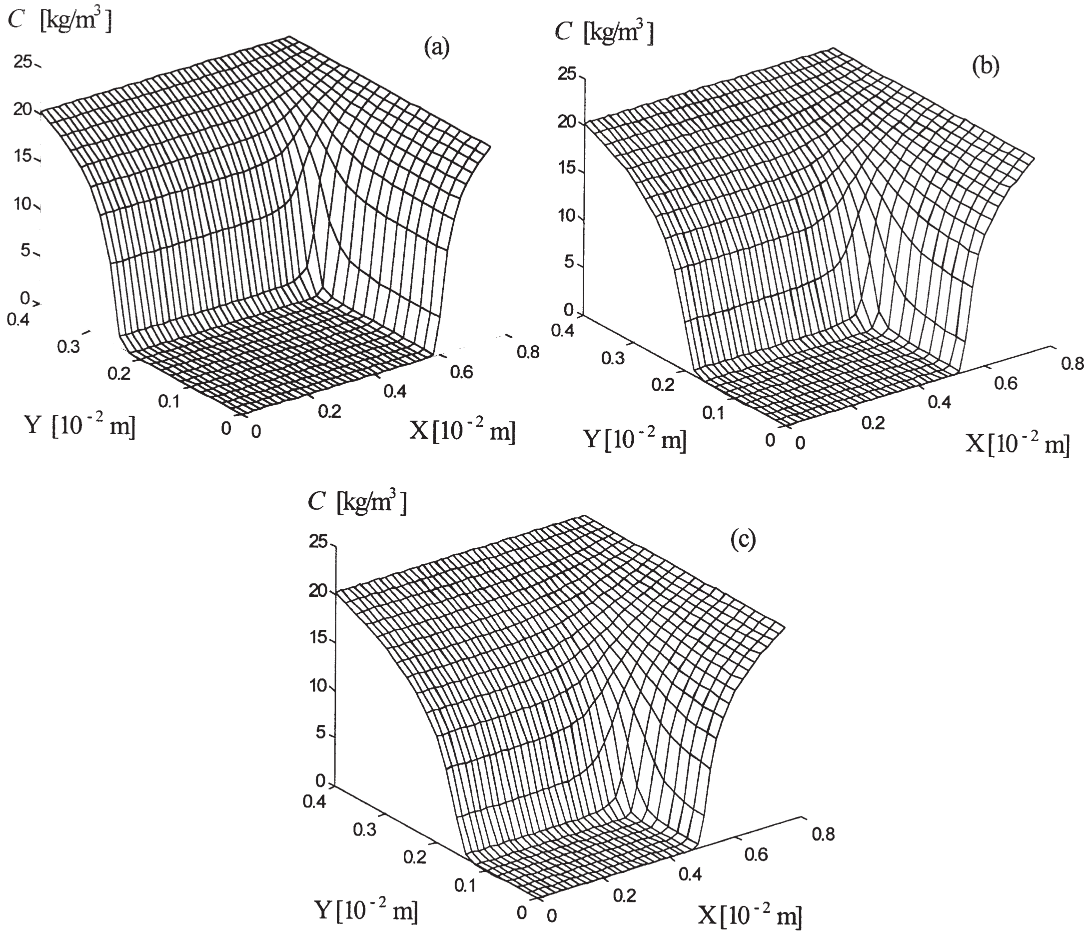

Fig. 3. Concentration distribution in the cross section of a prismatic specimen ($0.8 \cdot 10^{-2} \times 1.5 \cdot 10^{-2}$ m) immersed in a 3% water solution of Na_2SO_4, $k_z = 0$. Time of immersion: (a) 3 months; (b) 6 months; (c) 9 months.

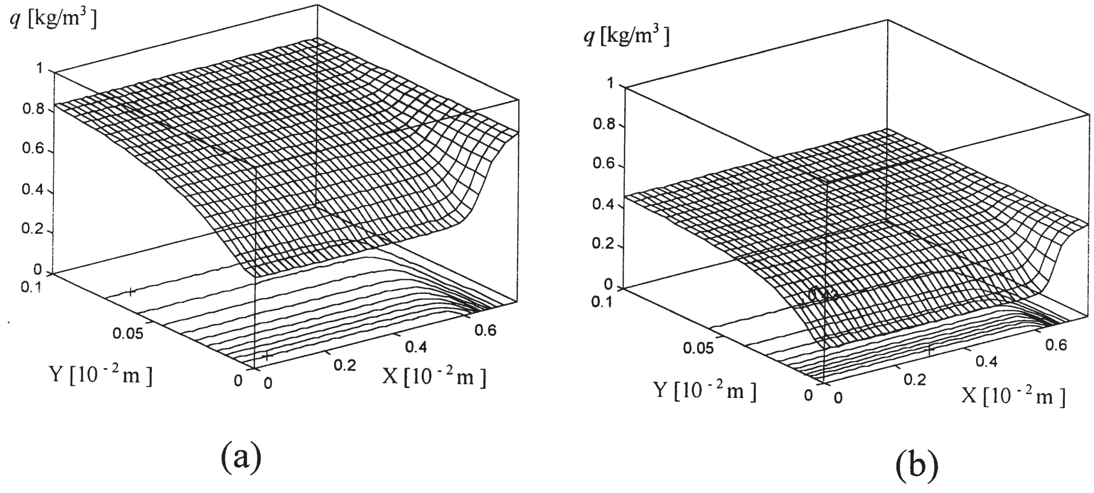

Fig. 4. Quantity of chemically reacted ions after 3 months of immersion into 3% water solution of Na_2SO_4. Cross section dimensions are $0.2 \cdot 10^{-2} \times 1.0 \cdot 10^{-2} \times 1.5 \cdot 10^{-2}$ m. (a) $k_z = 1$ m³/kg ; (b) $k_z = 2$ m³/kg.

3. Numerical results

The numerical results are grouped as follows:

1. A group of numerical results illustrate the character of the transfer process, employing the discussed mathematical model and including the void filling (Figs. 3, 4, 5a).
2. The second group demonstrates, on one hand, the possibilities of considering cross sections with a complex shape (multiply connected areas). On the other hand, it enables one to consider how different inclusions (inert filers or steel reinforcement, for instance) affect the diffusion process (Fig. 5b and Fig. 6).

The character of ion penetration is given in Fig. 3, without accounting for capillary filling. The distribution of ion concentration after keeping the specimen in a 3% sodium sulfate solution for 3, 6, and 9 months shows that the concentration front in the cross section is moving as a running wave (Figs. 3a, b, and c).

As shown above, the filling of the cement stone capillaries affects the intensity of the diffusion process and, most of all, the quantity of chemically reacted sulfate ions. This is illustrated in Fig. 4a and Fig. 4b, where the quantity of chemically reacted ions in a cement stone specimen subjected to sulfate attack from a 3% water solution of $Na\ _2SO_4$ is shown for two different values of the coefficient of capillary filling k_z ($k_z = 1$ and $k_z = 2$). The record of the process of capillary filling significantly affects the precipitation of chemical products within the cross section, but additional physical experiments are needed to more completely clarify the nature of this process.

As mentioned, real concrete structures include inert fillers, steel reinforcement, and/or apertures. These inclusions occupy additional areas and have a characteristic diffusion permeability significantly different from that of the cement stone. They cause a specific change of the character of the diffusion process. A comparison between lines of constant concentration in cross sections with and without such areas

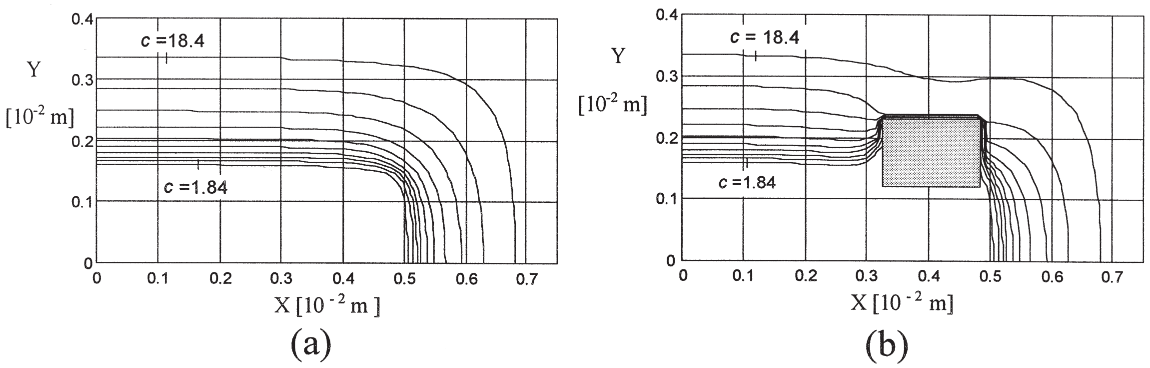

Fig. 5. Lines of constant concentration within the specimen cross section ($0.8 \cdot 10^{-2} \times 1.5 \cdot 10^{-2}$ m) for a 3% water solution of Na_2SO_4. Time of immersion, 9 months.

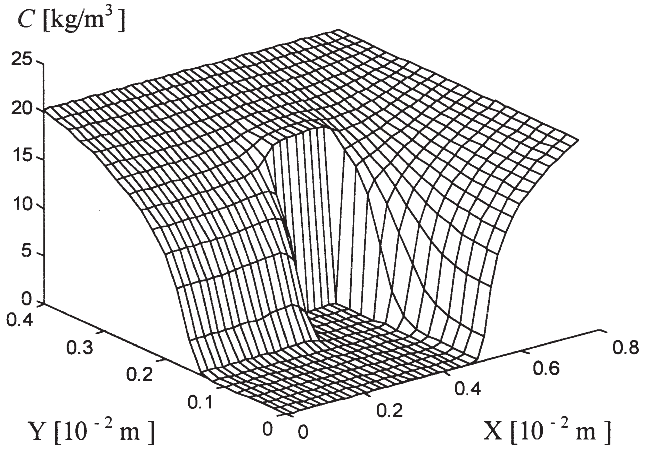

Fig. 6. Concentration distribution in the cross section of a prismatic specimen ($0.8 \cdot 10^{-2} \times 1.5 \cdot 10^{-2}$ m) for a 3% water solution of Na_2SO_4. Time of immersion, 9 months.

for a fixed time period is given in Fig. 5a and Fig. 5b as an illustration. The presence of a rectangular area occupied by an inclusion in which ion diffusion practically does not take place causes compaction of the lines of constant concentration around the area contour. The isolines, shown in Fig. 5a, correspond to the concentration distribution within the specimen cross section, given in Fig. 3c. The isolines of Fig. 5b correspond to the concentration distribution shown in Fig. 6.

Note that the area occupied by the inclusion in Fig. 5 is bounded by $x_1 \leqslant x \leqslant x_2$ and by $y_1 \leqslant y \leqslant y_2$ where $x_1 = 0.25 \cdot 10^{-2}$ m, $x_2 = 0.45 \cdot 10^{-2}$ m, $y_1 = 0.15 \cdot 10^{-2}$ m, $y_2 = 0.25 \cdot 10^{-2}$ m.

4. Conclusions

The proposed mathematical model outlines how capillary filling with chemical products affects the process of ion penetration from the surrounding sodium sulfate solution and into the cement stone. The obtained solution of the problem allows for the consideration of multiply connected areas consisting of cement stone matrix and inclusions (inert fillers, apertures, or steel reinforcement) and the results illustrate the process character. The proposed model can be used for the study of sulfate corrosion of cement/concrete structures, for the estimation of their durability, and for structural design.

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