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The effect of liquid push out of the material capillaries under sulfate ion diffusion in cement composites

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Abstract

The paper treats complex phenomena that accompany the diffusion of sulfate ions into cement paste or systems. The ion distribution within the material was studied by designing a specific diffusion model. The model accounts for two phenomena: capillary filling with products of the chemical reactions and the subsequent liquid push out of the capillary. The approach allows to quantify the concentration of free ions having penetrated the cement stone and that of chemically reacted ions, and to assess the liquid push out. Experimental data are also presented. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Diffusion of active agents in a porous body is an object of study of a number of papers [1]. Ratinov and Ivanov [2] considered the diffusion transfer of sulfate ions from a liquid solution and into the matrix of cement paste, disregarding the occurring chemical reactions. However, the chemical reactions and filling of the material voids with chemical products significantly affect diffusion transfer [3]. In the present study, a model was developed to predict the diffusion of sulfate ions into cement stone, regarding some phenomena that accompany the process: (i) heterogeneous chemical reactions, (ii) void (capillary) filling with precipitants and (iii) *resulting liquid push out of the material capillaries*. The paper is a continuation of our previous studies on diffusion [4].

Two types of cement stone specimens were considered—a plate whose thickness is much smaller than its other dimensions and a prismatic specimen whose length is significantly larger. Hence, one-dimensional and plane diffusion was treated. The specimens were kept in water before their immersion in a sulfate solution. Thus, water filled cement stone capillaries and sulfate ions subsequently penetrated there.

2. One-dimensional diffusion accounting for the liquid push out of the material capillaries

In a previous paper [4], we proposed a model of sulfate ion diffusion into cement system, accounting for a heterogeneous chemical reaction and filling of the material capillaries with chemical products. The model assumes that diffusion takes place in the capillaries where the liquid is immovable. To assess liquid push out of the capillary as a result of capillary filling with solid chemical products, we consider one-dimensional nonsteady diffusion in a plate with thickness $2L$. We take into account the precipitation of the chemical compounds on the capillary walls and the formation of a layer with thickness $\delta(z,t)$. Thus, the capillary volume decreases and the precipitants push the liquid out of the capillary.

We assume that the capillary is a straight circular cylinder, filled with a liquid (Fig. 1). Such a set up is simplified, but it allows to consider the most important phenomena related to the liquid motion within the cavity. The results may be useful also when considering two-dimensional diffusion. As said, part of the ions, together with the newly formed chemical

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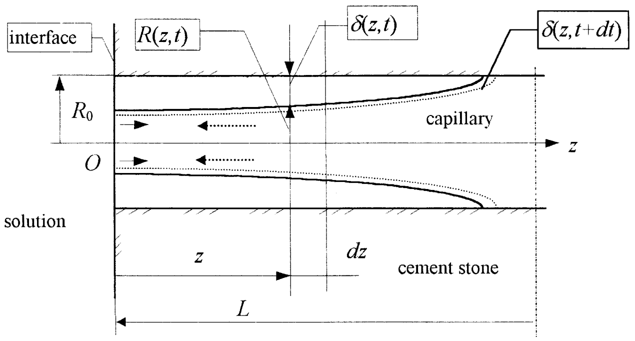

R_0 – capillary radius at moment $t = 0$, $R(z,t)$ – capillary current radius
L – capillary length, z – capillary current length
$\delta(z,t)$ – layer thickness at moment t, $\delta(z,t+dt)$ – layer thickness at moment $t+dt$

Fig. 1. Cement stone capillary filled with liquid.

compounds, precipitates on the capillary wall and decreases capillary cross-section and volume. Consider a differential element dz at a distance z from the origin of the coordinate system. Denote by R_0 the capillary radius at the moment $t = 0$. Note that the volume of the differential element remains constant, regardless of the capillary filling with precipitants. We may determine the change in time of the quantity of penetrating ions using the balance of in-flowing and out-flowing ion flux and considering the occurring heterogeneous chemical reactions:

$$\begin{aligned}\pi R_0^2 \mathrm{d}z \frac{\partial c}{\partial t} &= (J\pi(R_0-\delta)^2)|_z - (J\pi(R_0-\delta)^2)|_{z+\mathrm{d}z} \\ &\quad + (Wc)|_z - (Wc)|_{z+\mathrm{d}z} - kc\pi(R_0-\delta)^2 \mathrm{d}z. \qquad (1)\end{aligned}$$

As said, R_0 [m] in the above equation is the capillary radius; $c(z,t)$ [kg/m^3] is the ion concentration; and δ [m] is the layer thickness. The rest of the variables are specified in the analysis that follows.

The LHS of Eq. (1) gives the change of the whole quantity of ions having penetrated into the elementary volume at moment t. The first and second terms in the RHS of Eq. (1) denote the diffusion ion flux through the cross-sections for z and $z+\mathrm{d}z$, respectively. Regarding the changing cross-section of the capillary and Fick's first law, we can write those terms in the following form:

$$\begin{aligned}&(J\pi(R_0-\delta)^2)|_z - (J\pi(R_0-\delta)^2)|_{z+\mathrm{d}z} \\ &\quad = -\pi R_0^2 \left(1 - \frac{\delta(z,t)}{R_0}\right)^2 \frac{\partial J}{\partial z} \mathrm{d}z \qquad (2)\end{aligned}$$

where (Eq. (3))

$$J = -D\frac{\partial c}{\partial z}. \qquad (3)$$

Here, D is the coefficient of ion diffusion in the liquid, and J is the diffusion mass flux through unit surface.

The third and fourth terms in the RHS of Eq. (1) express the convective ion transfer owing to liquid motion within the capillary, and W [m^3/s] is the liquid volume velocity (debit) at z. Introduce for convenience a new variable average liquid velocity U at z (Eq. (4)):

$$U = \frac{W}{\pi R_0^2}. \qquad (4)$$

Using the new variable, rewrite the difference between the third and the fourth terms in the RHS of Eq. (1) as follows:

$$(Wc)|_z - (Wc)|_{z+\mathrm{d}z} = -\pi R_0^2 \frac{\partial}{\partial z}(Uc)\mathrm{d}z. \qquad (5)$$

The last term in the RHS of Eq. (1) considers the change of the ion concentration in the free part of the elementary volume, nonfilled with precipitants. Note that it gives the ions consumed by the heterogeneous chemical reaction. We can rewrite the member as:

$$-k(c\pi(R_0-\delta)^2)\mathrm{d}z = -kc\pi R_0^2\left(1 - \frac{\delta(z,t)}{R_0}\right)^2 \mathrm{d}z \qquad (6)$$

where k is the rate constant of the heterogeneous chemical reaction. Eqs. (2) and (6) contain the ratio between the layer thickness δ and the capillary initial radius R_0. We may express the ratio, assuming that it is proportional to the quantity of the chemically reacted ions q [4]:

$$\frac{\delta(z,t)}{R_0} = k_z q \qquad (7)$$

where k_z denotes the coefficient of capillary filling. The dimension of k_z is opposite to that of the quantity of chemically reacted ions q. Express q at the current moment by means of the concentration c:

$$q = \int_0^t kc(z,\tau)\mathrm{d}\tau. \qquad (8)$$

Consider relations (7) and (8). The introduction of Eqs. (2), (5) and (6) into the transfer Eq. (1), written along the capillary, yields:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial z}(Uc) - k(1-k_z q)^2 c. \qquad (9)$$

We use here, as in Ref. [4], an effective diffusion coefficient, D_{eff}, similar to the coefficient of diffusion in a capillary with varying cross-sections [3], i.e.,

$$D_{\mathrm{eff}} = D(1-k_z q)^2. \qquad (10)$$

Eq. (9) thus designed presents the diffusion transfer of ions from the solution and into the cement stone matrix. Hence, we account for how capillary filling, resulting liquid push out and the occurring heterogeneous chemical reaction affect the change of the ion concentration.

We use the following form of the diffusion coefficient D:

$$D = k_{\mathrm{diff}} \exp[\mathrm{b}(\mathrm{c}(\mathrm{x},\mathrm{y},\mathrm{t}) - 0.5\mathrm{c}_0)]. \tag{11}$$

Relation (11) presents D as dependent on the ion concentration in the solution, considering diffusion of electrolytes [6,7], and the diffusion coefficient D increases with the concentration increase. For an arbitrary high concentration close to that of the solution saturation, ion motion slows down since ions interact with each other. The denominator k_{diff} in Eq. (11) is the coefficient of diffusion of sulfate ions in the whole solid volume, consisting of cement matrix and cavities filled with liquid. It accounts for the material porosity and grain structure, as well as for the capillary shape. On the other hand (Eq. (10)), D_{eff} is effective coefficient of ion diffusion in the whole volume, accounting for the effect of pore filling.

Constant β is a fitting parameter and has dimensions opposite to those of the concentration c, while c_0 is a concentration characteristic value. Here, c_0 is the concentration of the solution where the specimen is immersed and kept for a definite period of time.

We include also initial and boundary conditions in the designed mathematical model. The initial sulfate concentration within the capillary is zero. We assume that the sulfate concentration at the left boundary $z=0$ is equal to that of the solution, and symmetry conditions at the right boundary $z=L$.

3. Determination of the velocity of liquid push out

We determine the velocity of liquid push out of the capillary, regarding the set up shown in Fig. 1. The boundary $z=0$ is the solution/cement stone interface. We assume symmetry conditions for $z=L$. Obviously, the liquid velocity is zero at $z=L$ and maximal at $z=0$. Let W be the liquid volume velocity (debit) through the cross-section z. Consider a capillary section located to the right of section z. Consider also the section internal volume Q at times t and $t+\mathrm{d}t$. Then, one may express the volume Q at time t as (Eq. (12)):

$$Q = \pi \int_{\eta=z}^{\eta=L} (R_0 - \delta(\eta,t))^2 \mathrm{d}\eta = \pi R_0^2 \int_{\eta=z}^{\eta=L} (1-k_z q)^2 \mathrm{d}\eta \tag{12}$$

and the liquid volume velocity for z is

$$W = \frac{\partial Q}{\partial t} = \pi R_0^2 \frac{\partial}{\partial t} \int_{\eta=z}^{\eta=L} (1-k_z q)^2 \mathrm{d}\eta. \tag{13}$$

Using the quantity of chemically reacted ions (Eq. (8)), we may rewrite Eq. (13) as (Eq. (14)):

$$W = \pi R_0^2 \int_{\eta=z}^{\eta=L} [-2kk_z(1-k_z q)c]\mathrm{d}\eta = \pi R_0^2 U. \tag{14}$$

Introduce for convenience in the above equation the average liquid velocity U at section z:

$$U = \int_{\eta=z}^{\eta=L} -2kk_z(1-k_z q)c\mathrm{d}\eta. \tag{15}$$

Note that the designed equations are valid until the moment of capillary block up and after that the velocity of liquid push out becomes zero.

4. Model of nonsteady plane diffusion

To design the equation of nonsteady *plane* diffusion, we use the relations introduced so far. Consider sulfate ion diffusion from a sulfate solution and into a long cement stone specimen. Then, the diffusion equation has the form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial y}\right) - \frac{\partial}{\partial x}(V_x c) - \frac{\partial}{\partial y} \times (V_y c) - k(1-k_z q)^2 c. \tag{16}$$

Here, V_x and V_y denote the average velocity of the liquid flow in the capillary, along axes x and y. The geometrical center O of the cross-section is the origin of the coordinate system, while axes Ox and Oy coincide with the symmetry axes. The cross-section dimensions along x and y are L_1 and L_2, respectively (Fig. 2).

Denote the interface "water solution–cement stone" by Γ, giving there the value of the solution concentration as a boundary condition:

$$c(x,y,t)|_{\Gamma} = c_0. \tag{17}$$

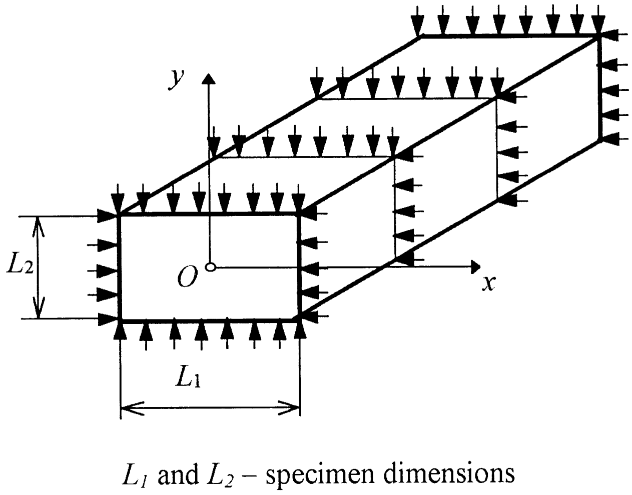

Fig. 2. Scheme of the plane diffusion.

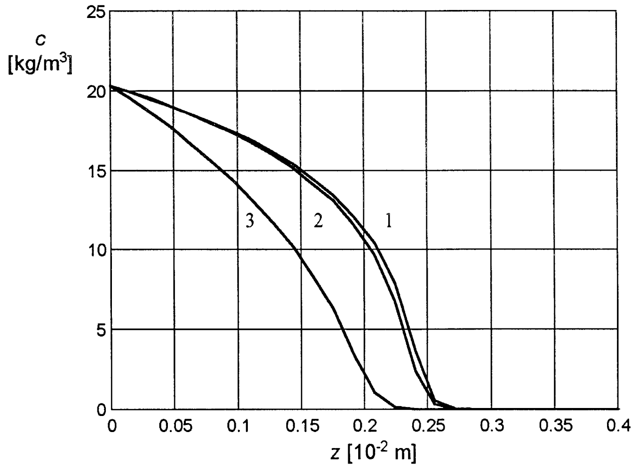

Fig. 3. Comparison of the distribution of the sulfate ion concentration, $t = 9$ months. (1) Ion distribution, disregarding capillary filling and liquid push out. (2) Ion distribution, regarding capillary filling but disregarding liquid push out. (3) Ion distribution, regarding both capillary filling and liquid push out.

Due to symmetry, we solve the problem in 1/4 of the area and give symmetry conditions along axes $x = 0$ and $y = 0$:

$$\frac{\partial c}{\partial x} = 0,\ 0 \leq y \leq L_2/2; x = 0,$$
$$\frac{\partial c}{\partial y} = 0,\ 0 \leq x \leq L_1/2;\ y = 0. \tag{18}$$

The initial ion concentration within the specimen cross-section is taken to be zero, since we previously keep the specimen in drinking water whose sulfate ion concentration is negligible, i.e.,

$$c|_{t=0} = c(x, y, 0) = 0. \tag{19}$$

We find the coordinate components of the liquid velocity, participating in Eq. (16), by using the procedure described in paragraph 2. We solve an integral that has the form (Eq. (15)) for each fixed value of y, in order to determine the velocity field V_x. However, since we introduce a coordinate system whose origin is the symmetry center of the cross-section, the velocity is zero for $x = 0$ and maximal for $x = L_1/2$. The velocity direction coincides here with the positive direction of axis Ox. For a given value of y within the interval $[0, L_2/2]$, we determine the velocity component V_x by calculating the integral (Eq. (15)). Note that the lower integration limit here is $L_1/2 - x$, and the upper integration limit is $L_1/2$. Thus, we get the velocity $V_x(x,y,t)$ at each point of the area under consideration. We obtain in the same manner the velocity field $V_y(x,y,t)$ where the lower integration limit is $L_2/2 - y$ and the upper one is $L_2/2$.

5. Numerical solution

We use an implicit difference scheme to solve the formulated diffusion problem [4]. The initial boundary value problem comprises Eq. (16) and the boundary and initial conditions Eqs. (17), (18) and (19). We approximate those equations on an orthogonal grid, performing an appropriate assembly of the grid knots at each time step. Thus, we reduce the difference value problem to the solution of a linearized system of algebraic equations that has a diagonal and weakly filled matrix. The system matrix is nonsymmetric with respect to the main diagonal. Before performing the calculations at the next time step, we determine the liquid velocity in the capillary. To calculate the velocity fields, considering each coordinate axis, we complete the algorithm with a numerical integration procedure. Due to the nonlinearity of the problem, we use an internal iteration process. After attaining a previously prescribed accuracy, we find the distribution of the chemically reacted ions for the current time and then turn to the next time step.

We present a numerical solution of the one-dimensional diffusion problem as a variant of the numerical algorithm. We use this numerical variant together with the experimental evidence given in Refs. [4,5] in order to make precise the dimension and dimensionless constants that participate in Eqs. (9), (11), (15) and (16). Thus, we get the following constant values:

- coefficient of ion diffusion in the water solution
  $k_{\text{diff}} = 0.361 \times 10^{-9}\ \text{m}^2/\text{s}$
- fitting parameter participating in Eq. (11)
  $\beta = 0.2917\ \text{m}^3/\text{kg}$

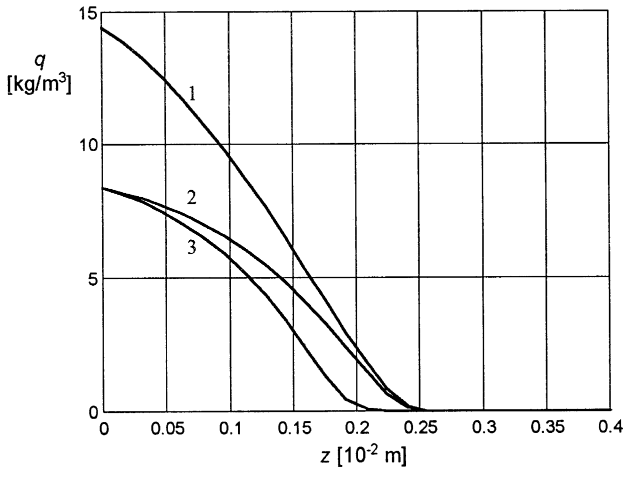

Fig. 4. Distribution of the quantity of chemically reacted ions, $t = 9$ months. (1) Ion quantity, disregarding capillary filling. (2) Ion quantity, regarding capillary filling but disregarding liquid push out. (3) Ion quantity, regarding both capillary filling and liquid push out.

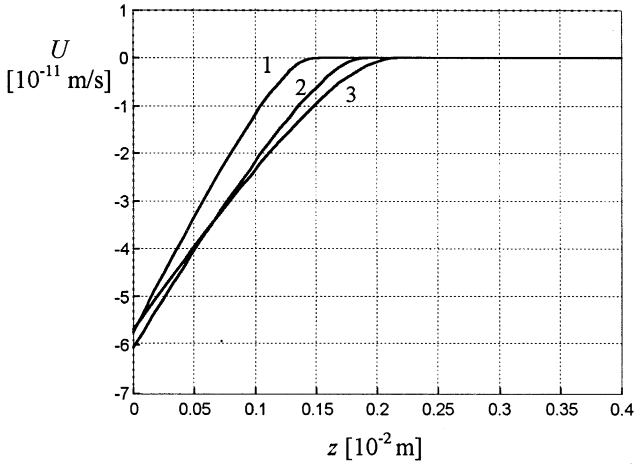

Fig. 5. Velocity profile of the liquid within the capillary k_z=.05 m^3/kg. Immersion time: (1) t = 3 months; (2) t = 6 months; (3) t = 9 months.

- constant of the chemical reaction rate

$$k = 0.305 \times 10^{-7}\ s^{-1}.$$

6. Results and discussion

We give numerical results for specimens kept in 3% water solution of sodium sulfate. The cement paste is prepared of commercial sulfate-resistant Portland cement 35, type "Devnya" according to the Bulgarian standard. Ref. [4] gives the cement mineral composition. The content of the sulfate ions in the solution is 20.282 kg/m^2. Since the solution volume is much larger than that of the cement stone specimen, we assume that the solution sulfate concentration remains constant in time.

We consider three characteristic cases, based on one-dimensional diffusion in a cement stone specimen with thickness 0.8×10^{-2} m (Figs. 3 and 4). The first curve in Fig. 3 presents ion concentration distribution, neglecting capillary filling ($k_z = 0$) and liquid motion. The second curve corresponds to ion distribution, regarding capillary filling with precipitants (k_z=.05 m^3/kg), but disregarding liquid push out. The third curve in Fig. 3 presents ion distribution, regarding both capillary filling (k_z=.05 m^3/kg) and liquid push out. Although that the value of k_z is relatively low, one may easily find that the ion penetration within the specimen slows down significantly in the three-dimensional case. As seen, the ion concentration for one and the same immersion time decreases with the separate account for capillary filling and with the account for joint capillary filling and liquid push out (Curves 2 and 3 in Fig. 3). Note also that the difference between Curves 2 and 3 is significantly larger that that between Curves 1 and 2. Hence, capillary filling joined with liquid push out slows down more significantly the ion diffusion, as compared to diffusion slow down caused by capillary filling only.

Fig. 4 gives comparison between the three cases discussed in Fig. 3, regarding the quantity of chemically reacted ions q (t = 9 months). Curve 1, as in Fig. 3, shows the change of the quantity of chemically reacted ions q in

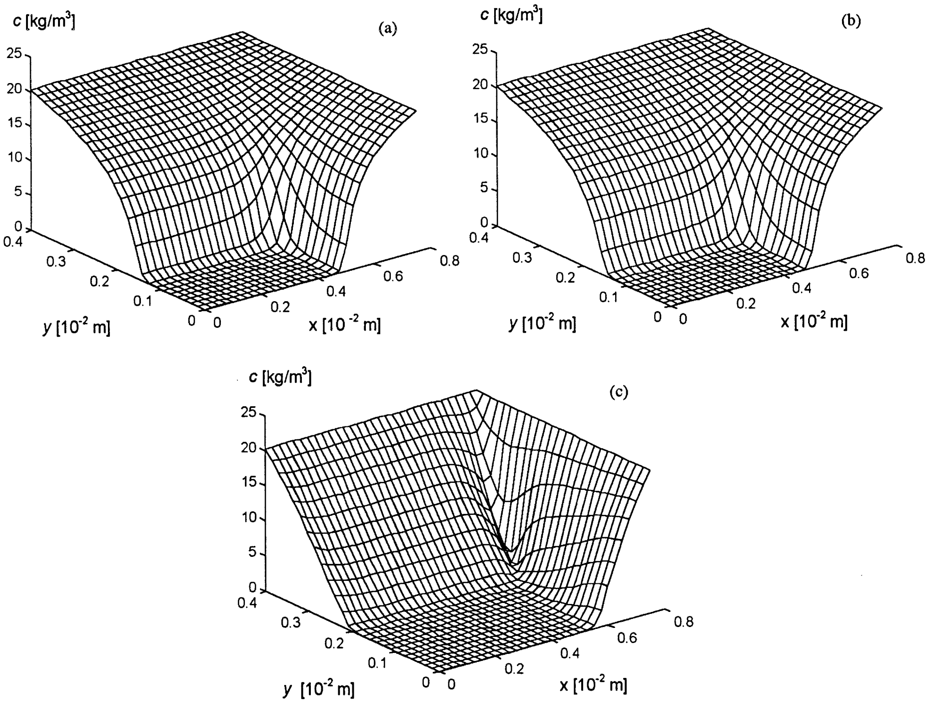

Fig. 6. Concentration distribution in the cross-section of a prismatic specimen, time of immersion 9 months, k_z=.05 m^3/kg, 3% Na_2SO_4.

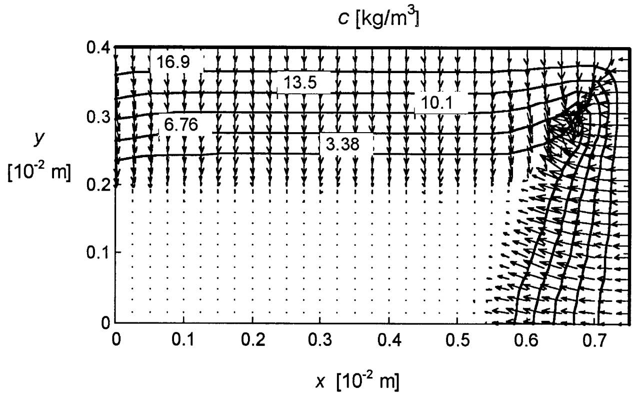

Fig. 7. Concentration isolines in the specimen cross-section (plane diffusion), $k_z = .05$ m^3/kg, immersion time 9 months.

the specimen, disregarding capillary filling and liquid push out. Curve 2 gives the quantity of chemically reacted ions q, regarding capillary filling but disregarding the liquid push out. Curve 3 gives the change of q in the specimen, regarding both capillary filling and liquid push out. As in Fig. 3, the quantity of chemically reacted ions q decreases when we account separately for capillary filling and for joint capillary filling and liquid push out. Note also the cross-points of Curves 1, 2 and 3 with the z-axis in Fig. 4. Compare the subsequent cross-point coordinates. As is seen, Curve 3 crosses the axis at a point whose coordinate z is the smallest one. This proves that the liquid push out decreases the depth of "penetration" of chemically reacted ions into the cement stone bulk.

Fig. 5 presents numerical results for the velocity of the liquid push out, the latter owing to capillary filling (k_z=.05 m^3/kg), for different times of specimen immersion. Note that the liquid velocity values are negative, since the velocity direction is opposite to that of the diffusion flux. Thus, the liquid carries out part of the ions that have already penetrated into the cement stone. The maximal absolute value of the exit liquid velocity (for $z = 0$) decreases in time. This is so, since ions react with the cement stone forming chemical compounds, and further ion penetration slows down, yielding decrease of the velocity of liquid push out.

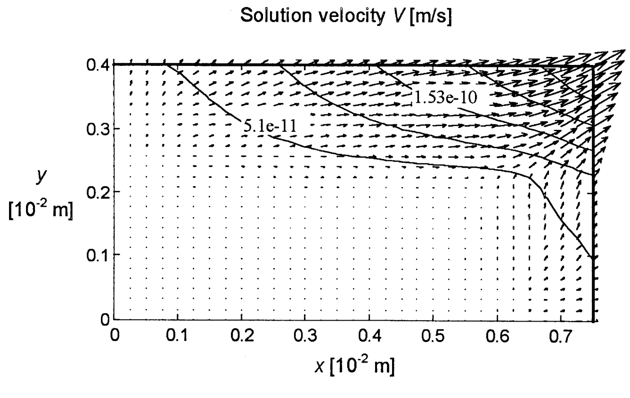

Fig. 8. Velocity field of the solution within the specimen cross-section.

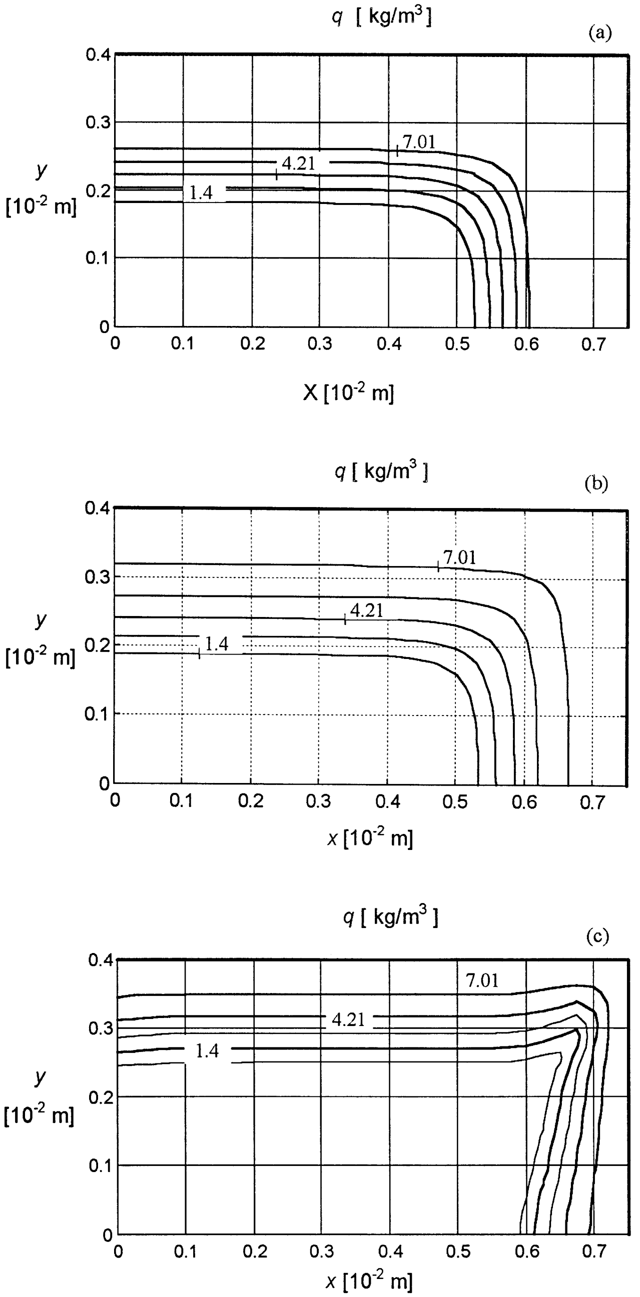

Fig. 9. (a) Isolines of chemically reacted ions, disregarding capillary filling and liquid push out, $k_z = 0$. (b) Isolines of chemically reacted ions, regarding capillary filling and disregarding liquid push out, $k_z = .05$ m^3/kg. (c) Isolines of chemically reacted ions, regarding both capillary filling and liquid push out, $k_z = .05$ m^3/kg.

We give also some results on *plane diffusion* within a cement stone specimen (see Fig. 2). Fig. 6 gives, for comparison, results on the ion concentration distribution within the cross-section of a rectangular specimen with dimensions $0.8 \times 10^{-2} \times 1.5 \times 10^{-2}$ m. The specimen has been kept in a 3% water solution of sodium sulfate. We consider sulfate ion diffusion without capillary filling (Fig. 6a), ion diffusion with capillary filling but disregarding liquid push out (Fig. 6b) and ion diffusion regarding

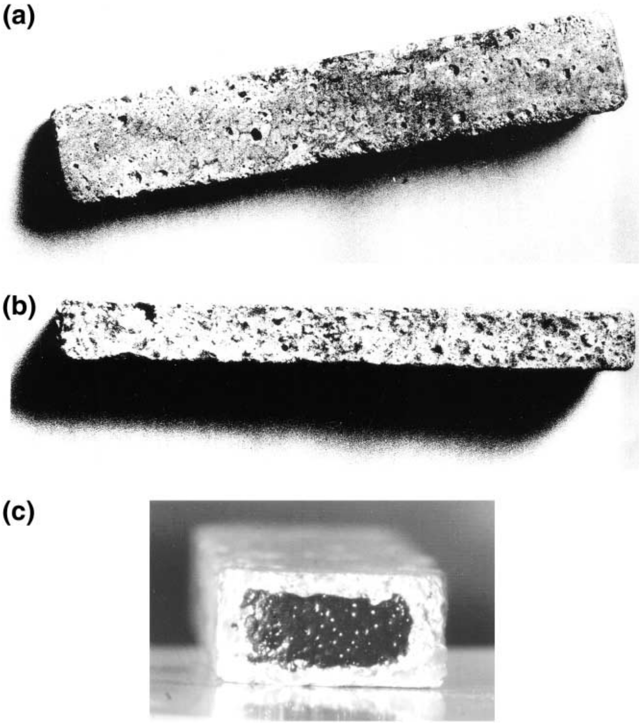

Fig. 10. Cement stone specimen corrupted by the sulfate attack.

both capillary filling and liquid push out (Fig. 6c). The time of specimen immersion is 9 months. As seen in the figures and already discussed in the case of one-dimensional diffusion, capillary filling and liquid push out slow down the ion diffusion.

Fig. 7 shows the concentration isolines for the case in Fig. 6c. Arrows map the field of the diffusion flux. The arrow length is proportional to the absolute value of the concentration gradient. Here, k_z=.05 and t=9 months.

Fig. 8 presents the velocity field of the liquid that fills the capillary. The arrow length is proportional to the velocity at the corresponding point of the cross-section. The time of specimen immersion is t=9 months. The velocity distribution clearly shows that the ion diffusion slows down when accounting for liquid push out, since the liquid carries ions out of the material. The largest value of the velocity of liquid push out corresponds to the largest portion of ions, carried out of the cement stone. This convection flux is directed opposite to the flux resulting from the difference between the ion concentration of the surrounding solution and that within the specimen. Hence, the concentration isolines within the specimen cross-section deform (see Fig. 7).

The isolines, giving the distribution of the chemically reacted ions within the specimen cross-section, clarify the sulfate corrosion. The isolines of q corresponding to the cases in Fig. 6a, b and c are shown in Fig. 9a, b and c. Compare Fig. 9a, where we disregard capillary filling, to Fig. 9b, where we account for that effect. As seen, the penetration of chemical compounds within the specimen slows down even for an arbitrary low value of the filling coefficient (k_z=.05). The combination of capillary filling and liquid push out yields an even stronger slow down of the penetration of chemically reacted ions (Fig. 9c). One may relate the change of the quantity of chemically reacted ions to the resulting structure modification of the cement stone and to the change of its mechanical properties.

Our experimental evidence shows that for a relatively longer period of specimen immersion (6–9 months and more) in 3% water solution of sodium sulfate, material mechanical properties change in a comparatively thin specimen layer. We show this effect in Fig. 10. The layer thickness is about 5–10% of the dimensions of the specimen cross-section. The rest part of the cross-section is a cement core whose structure has not been practically modified (Fig. 10c). The picture is the same for a longer period of specimen immersion in the sulfate solution. A new ion penetration within the specimen bulk takes place after the fracture of the damaged layer due to the volume change of the newly formed structures and to the significantly decreased material strength.

7. Conclusions

We propose a diffusion model of sulfate ions into cement stone regarding two important effects. On one hand, we account for capillary filling with precipitants. The precipitation of ions and chemical compounds on the capillary wall slows down ion diffusion. On the other hand, we consider liquid push out of the capillary. The liquid carries out of the capillary part of the ions that have penetrated there. The numerical results prove that the considered effects strongly influence sulfate ion diffusion. The comparison with results obtained on the basis of simplified models proves the approach applicability. One may employ the model to theoretically assess sulfate corrosion and to clarify the effect of some additional factors on the sulfate corrosion, when performing experimental and theoretical studies.

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