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Mechanisms of sulfate ionic diffusion in porous cement based composites

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Abstract. The paper considers a theoretical model for the study of the process of transfer of sulfate ions in saturated porous media - mineral composites. In its turn, the model treats diffusion of sulfate ions into cement based composites, accounting for simultaneous effects such as filling of micro-capillaries with ions and chemical products and liquid push out of them. The proposed numerical algorithm enables one to account for those simultaneous effects, as well as to model the diffusive behavior of separate sections of the considered volume, such as inert fillers. The cases studied illustrate the capabilities of the proposed model and those of the algorithm developed to study diffusion, considering the specimen complex configuration. Computations show that the theoretical assumptions enable one to qualitatively estimate the experimental evidence and the capabilities of the studied composite. The results found can be used to both assess the sulfate corrosion in saturated systems and predict and estimate damage of structures built of cement-based mineral composites.

Keywords: diffusion; sulfate attack; cement paste; corrosion; mathematcal model; numerical analysis.

1. Introduction

Mineral cement-based composites such as concrete are widely applied in structure building. They are often exposed to the influence of aggressive liquid media. The sulfate corrosion of real concrete structures is a popular phenomenon. To analyze its destructive effects, one needs to study the behavior of the most important concrete component - the cement paste (cement stone), immersed in a liquid

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aggressive sulfate medium. The impact of the aggressive medium is realized by a penetration of sulfate ions into the liquid that fills the pores of the cement paste. Since ions are charged particles, an electric potential occurs when they enter the pore-filling liquid. Possibilities of modeling the transfer of ions in unsaturated systems are discussed in Marchand, *et al.* (2002), and in saturated systems - in Marchand, *et al.* (2001). The ion transfer, accounting for the action of electrostatic forces, is followed by employing the Nernst-Plank model, (Stanish, *et al.* 2004, Samson, *et al.* 1999c), while in cases of strong ionic solution and especially under the strong interaction of several ion species, an extended model that regards chemical activity is used in Samson and Marchand (1999). Considering saturated system, the mathematical model needs to be completed with Poisson's equation in order to find the electric potential, while relations for the calculation of the coefficients of ions chemical activity in electrolytic solutions are part of the extended model (Samson, *et al.* 1999a). Samson, *et al.* (1999b) proposes a homogenization technique which allows for averaging the results for the concentration of the pore-filling solution over the entire material volume.

Our studies consider the action of an aggressive sulfate medium in a saturated system, assuming that the effect of other ion species can be disregarded. The pore space of the investigated cement paste prismatic specimen has been previously filled with water, and the specimen has been immersed and kept in water for 28 days after casting. It is also assumed that ion motion can only occur in the liquid phase.

2. Mathematical model

Ion transfer in the liquid phase that fills the pores of a saturated system is generally due to two mechanisms - diffusion transfer and migration owing to electrostatic forces. On the other hand, liquid motion within the pores is due to filling them with products of the developed heterogeneous chemical reaction. That reaction takes place on the pore wall as a result of the interaction of ions with the cement stone. The pores are formally treated as capillaries (micro-capillaries), shaped as straight circular cylinders and with symmetry axes parallel to the coordinate axes. The present study accounts for the effect of the sulfate ions, only, while their interaction with other ion species is disregarded.

Consider cement stone capillaries in particular and the material balance of an elementary volume of the area under control. Then, the following equation of ion transport can be written, accounting for the heterogeneous chemical reactions that develop on the capillary walls:

$$\frac{\partial c}{\partial t} = \mathrm{div}(J_T) - kc \tag{1}$$

or in the one-dimensional case

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}(J_T) - kc \tag{2}$$

where J

$$J_T = J_{\mathrm{diff}} + J_U \tag{3}$$

As stated, since ions are electrically charged particles, an electric potential occurs when they enter the solution that fills the capillaries. Thus, the flux of ion transfer J_T has two components - the first one J_{diff} is due to the diffusion force while the second one J_U - to the driving force of the electric potential U (Stanish, *et al.* 2004).

Quantity $c(x, t)$ in Eqs. (1)-(2) is the current concentration value, $q(x, t)$ is the quantity of chemically reacted ions at a point with coordinates x and at a moment t, and k is the coefficient of chemical reaction rate. The first term in the right-hand side (RHS) of Eq. (3) can be expressed by Fick's first law:

$$J_{\text{diff}} = k_{\text{diff}} \frac{\partial c}{\partial x} \tag{4}$$

while the second one has the following form according to the simplified model of Nernst-Plank, (Samson, *et al.* 1999c):

$$J_U = \frac{z_V F k_{\text{diff}}}{RT} c \frac{\partial U}{\partial x} \tag{5}$$

Multiplier k_{diff} in Eq. (4) is the coefficient of diffusion of sulfate ions within the whole volume, consisting of a cement matrix and capillaries filled with liquid. It reflects the material porosity, structure and capillary shape. z_V is the valence of sulfate ion, F is Faraday's constant, U is the diffusion potential, R is the universal gas constant, T is the temperature.

The mathematical model should be completed with an equation for determining the diffusion potential U. It has the form (Samson, *et al.* 1999c):.

$$\nabla^2 U + \frac{\rho}{\varepsilon} = 0 \tag{6}$$

where ρ is density of the electric charge and ε is the medium dielectric constant.

The consideration of the ion flux due to the driving force of the diffusion potential is significant in two cases, mainly - when an external electric potential is applied or a simultaneous transfer of two and more ion species is in operation. When considering the transfer of sulfate ions, only, under isothermal conditions, the account for the effect of Nernst-Plank yields model complications. On the other hand, the model proposed by Eqs. (1)-(6) does not account for some characteristic features of the process, i.e., change of the capillary volume as a result of the precipitation of chemical reaction products on the capillary walls, as well as the resulting push out of the capillary-filling liquid. Note also that liquid motion exports part of the ions out of the capillaries and in a direction opposite to that of flux J.

In previous papers (Gospodinov, *et al.* 1999), (Mironova, *et al.* 2002) we propose a model of diffusion transfer considering heterogeneous chemical reaction and liquid push out of the capillaries resulting from the capillary filling. The model can be presented in the following form:

$$\frac{\partial c}{\partial t} = \operatorname{div}(D_{\text{eff}} \operatorname{grad} c) - \operatorname{div}(\mathbf{V} c) - k(1 - k_z q)^2 c \tag{7}$$

where the spatial operators ( ) and grad( ) are of the type

$$\operatorname{div}(\ ) \equiv \sum_{i=1}^{K} \frac{\partial}{\partial x_i}(\ )_i \qquad \operatorname{grad}(\ ) \equiv \sum_{i=1}^{K} \mathbf{j}_i \frac{\partial}{\partial x_i}(\ )_i \tag{8}$$

For one dimensional case - K=1.

The last term in the RHS of Eq. (7) is a source term which models the heterogeneous chemical reaction between the sulfate ions in the solution and the capillary walls. The term also reflects the change of the capillary reacting surface. Projections V_i, $i = 1, K$ of velocity **V** in Eq. (7) denote the liquid mean velocity within the cross section of the capillary along axes x_i, $i = 1, K$.

The effective diffusion coefficient within the whole volume has the form (Gospodinov, *et al.* 1999):

$$D_{\text{eff}} = D(1-k_z q)^2 \tag{9}$$

where

$$D = k_{\text{diff}}\exp[\beta(c(x_1,\ldots,x_R,t)) - 0.5c_0] \tag{10}$$

Constant β is a parameter and c_0 is a characteristic value of the concentration - the concentration of the solution which the specimen is immersed in, k_z denotes the coefficient of capillary filling and the quantity of chemically reacted ions q is found from

$$q(x_1,\ldots,x_R,t) = \int_0^t kc(x_1,\ldots,x_R,\tau)d\tau \tag{11}$$

For fixed values of the rest of the coordinates x_m, $m \neq i$, the velocity component V_i is calculated by means of the following integral along the capillary length, within boundaries $[0, x_i]$, (Mironova, *et al.* 2002).

$$V_i = \int_{\eta=U}^{\eta=G} -2kk_z(1-k_z q)c\,d\eta \tag{12}$$

$$U = L_i/2 - x_i, \quad G = L_i/2, \quad i = 1, R$$

Since the origin of the coordinate system is the center of the specimen symmetry, the velocity is zero for $x_i = 0$ and it is maximal for $x_i = L_i/2$. The velocity direction coincides with the positive direction of axis Ox_i. V_i is found calculating the integral - Eq. (6). The lower integration limit is $x_i = L_i/2$, while the upper one - $L_i/2$. Thus, velocity $V_i(x_1,\ldots,x_R,t)$ can be found at each point of the area considered. Velocity components $V_m(x_1,\ldots,x_R,t), m \neq i, m \in [1,\ldots,R]$ are similarly found. The model is completed by specifying a zero initial distribution of the concentration, conditions at the specimen-solution interface and symmetry conditions, Mironova, *et al.* 2002.

Note however that the model outlined above describes the distribution of sulfate ions within the liquid phase that fills the capillary space of the cement paste.

3. Numerical solution

The equations of transfer Eqs. (7) - (8), together with the initial and boundary conditions pose a non-steady boundary value problem. It is completed by the integral relations Eq. (12), giving the quantity of chemically reacted ions, as well as by the integral relations Eq. (13), necessary for the calculation of the velocity field of the liquid pushed out of the cement stone capillaries.

The problem is solved using an implicit difference scheme and it is reduced to solving a sparse system of linear algebraic equations with a non-symmetric band matrix. The algorithm used is described in detail in Gospodinov (2005).

The discretization scheme is shown in Fig. 1(a). Numbers of N, M and L cross sections with planes perpendicular to the coordinate axes x, y and z, respectively, are introduced along each axis, starting from the coordinate system origin. Let i_x, i_y and i_z are numbers of the discretization sections

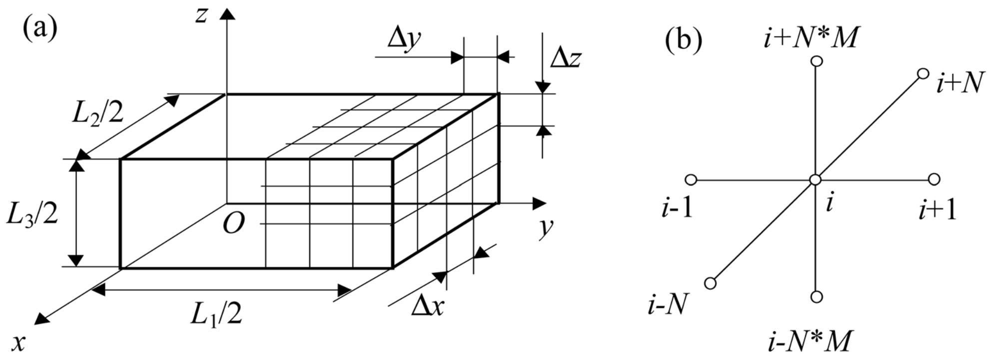


Fig. 1 Coordinate system and discretization scheme

(Fig. 1) perpendicular to axes x, y and z. Obviously, $1 \le x_i \le N$, $1 \le i_y \le M$, $1 \le i_z \le L$. The number of a grid knot for fixed values of i_x, i_y and i_z is determined by the following relation:

$$i = i_x + (i_y - 1)*N + (i_z - 1)*N*M \tag{13}$$

Thus, the unknown values of the quantities sought at each knot of the discretized area can be numbered using one index, only. Besides, the solution of the initial boundary value problem outlined above is reduced to the solution of a difference value problem for a linearized system of ($N*M*L$) algebraic equations with a diagonal and weakly filled matrix. The algorithm thus developed is completed by a numerical procedure for calculating the integrals of type Eq. (13) along the three coordinate axes. The specific features of cases of sub-areas with conductivity, distinctly different from that of the matrix (e.g. inert filler), are discussed in Gospodinov (2005). The model thus designed can be effectively applied to disclose the character of a number of complex phenomena observed during the sulfate aggression of cement paste.

4. Results and discussion

Having set forth the mathematical model of diffusion transfer of sulfate ions in cement stone, we proceed with the discussion of some experimental evidence and calculation results. We have considered in our previous study (Mironova, *et al.* 2002), sulfate ions diffusion in prismatic specimens, thus modeling the development of the sulfate attack on real structural elements, which is

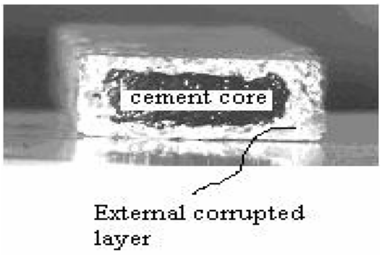
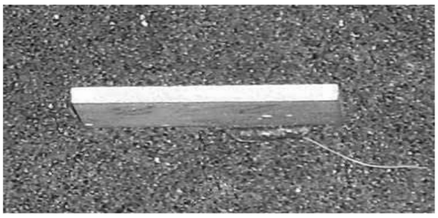


Fig. 2 Prismatic cement paste specimen, layered after a sulfate attack from 5% sulfate solution; time of immersion - 9 months. The specimens tested are long prisms with cross section $0.8 \times 10^{-2} \times 1.5 \times 10^{-2}$ m.



Immersion duration – 8640 hours (12 months); lateral specimen view
a) concentration of Na_2SO_4 in the solution – 1%

Immersion duration – 8640 hours (12 months); lateral specimen view
b) concentration of Na_2SO_4 in the solution – 5%

Immersion duration – 8640 hours (12 months); lateral specimen view
c) concentration of Na_2SO_4 in the solution – 10%

Fig. 3 Cement paste degradation in time, regarding different solution sulfate concentrations

a problem of essential practical importance. The specimens tested are long prisms with cross section $0.8\times10^{-2}\times1.5\times10^{-2}$ m. As found, they are divided into two parts - a thin external corrupted layer and an intact cement core, Fig. 2.

However, the study of the mechanism of formation of the external corrupted layer as a result of the sulfate attack is a difficult task. To model that process, we have studied the development of sulfate ions diffusion in thin cement paste specimens, immersed in aqueous solutions of Na_2SO_4. The specimens have been fabricated form SRP cement, type 35, in compliance with the Bulgarian standard. The material chemical composition is specified in Mironova, *et al.* (2002). Specimens have been solidifying for 28 days in pure water after preparation and prior to immersion. Then, they have been immersed and kept in water solutions of Na_2SO_4 of different concentration and for different periods of time. Fig. 3 shows the sequence of cement stone degradation in time, depending on the solution sulfate concentration. It summarizes the experimental findings of our previous studies (Mironova, *et al.* 2002, Kazandijev, *et al.* 2005).

As seen in Fig. 3 and specifically for the higher concentrations of the sulfate solution, partial destruction of the specimen takes place after a period of 12 months of immersion, and diffusion and its accompanying effects (filling of the cement stone pores with ions and chemical products,

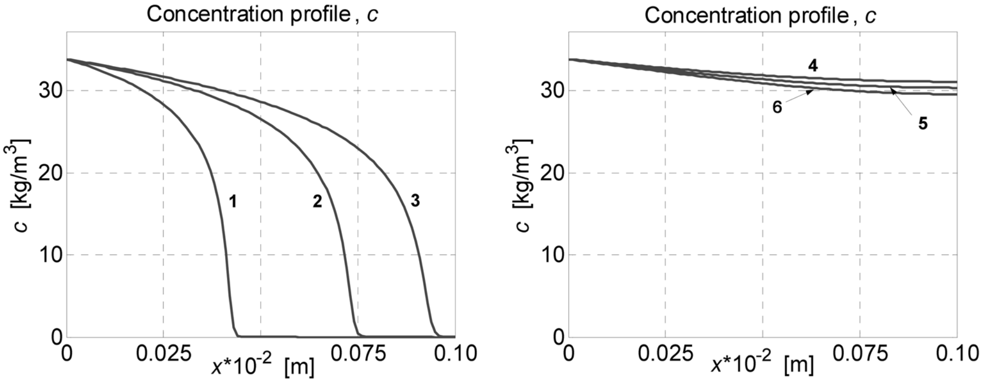


Fig. 4 Distribution of the ions concentration - 1D case

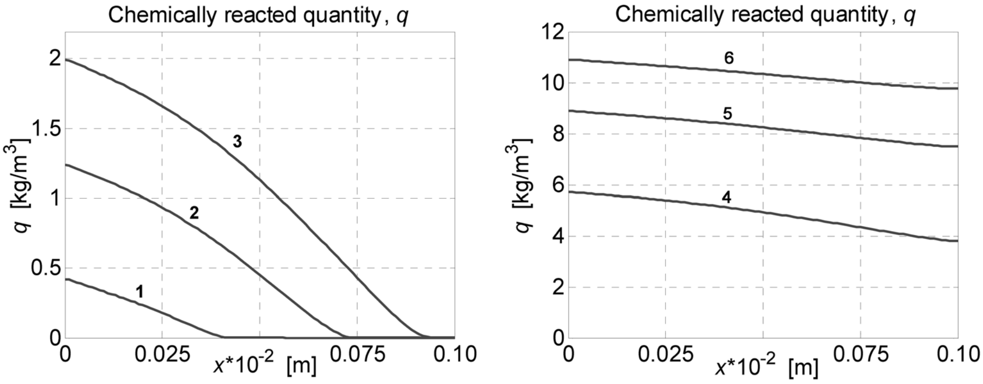


Fig. 5 Distribution of the chemically reacted quantity of ions - 1D case

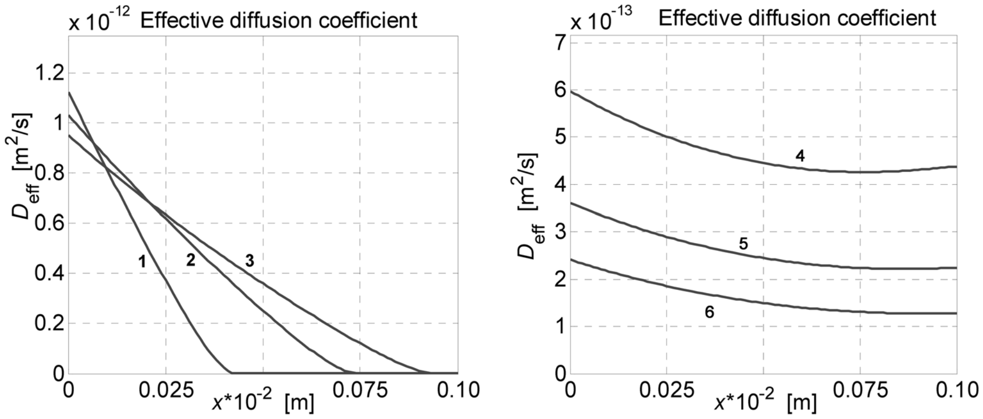


Fig. 6 Distribution of the effective diffusion coefficient - 1D case

microcrack formation etc.) change the material structure. Hence, a period shorter than 12 months of immersion can be taken as a reasonable time limit for the cement stone saturation with sulfate ions from the higher sulfate solutions, where the material diffusive behavior can be taken as similar to that of the external corrupted layer of the bulk specimen shown in Fig. 2. Thus, the analysis of ions diffusion in thin specimens, based on the model proposed proves useful for analyzing the ion transfer in bulk specimens and in real structural elements. In what follows, we give some calculation results found using the diffusion model designed.

We consider sulfate ions diffusion into thin cement paste specimens with dimensions $1.5\times10^{-2}\times1.5\times10^{-2}\times0.2\ast10^{-2}$ m, being immersed in 5% aqueous solution of Na_2SO_4. The calculation are performed using the following values of the parameters, participating in the model (1)-(11) and found analyzing the experimental evidence of Gospodinov, *et al.* (1999):

- coefficient of ion diffusion in the water solution $k_{\mathrm{diff}} = 0.341\times10^{-13}$ m^2/s
- fitting parameter participating in Eq. (11): $\beta = 0.2917$ m^3/kg;
- constant of the chemical reaction rate: $k = 0.305\times10^{-7}$ s^{-1}
- coefficient of pore filling: k_z=0.05 m^3/kg
- content of the sulfate ions in the 5% sulfate solution - 33.803 kg/m^3

Figs. 4, 5 and 6 present the numerical results of the study of 1D diffusion of sulfate ions within the specimen. Due to symmetry, ions penetration from x=0 to the symmetry line x=0.1×10^{-2} m is followed.

Notations of the curves in Figs. 4, 5 and 6 correspond to the following periods of immersion: 1 - 120 hours, 2 - 360 hours, 3 - 600 hours , 4 - 2160 hours (3 month), 5 - 4320 hours (6 months), 6 - 6480 hours (9 months).

The calculation results show that ions penetration is comparatively intensive at the start of process, while the current concentration attains a maximal value on the symmetry line for a 3-months of immersion and then it starts decreasing but with weaker intensity - Fig. 4. This is due to the proceeding chemical reaction, where part of the penetrating ions precipitate on the capillary walls as participating in chemical compounds, and to the inverse convective transfer owing to the occurring liquid push as a result of the capillary partial filling. Besides, the process of ion connection due to the chemical reactions is more intensive than the transfer of ions incoming from the surrounding solution. This is confirmed by the increase in time of the quantity of chemically reacted ions - Fig. 5. The character of the process is additionally elucidated by the results found for the change of the effective diffusion coefficient - Fig. 6. At the process start and near the interface,

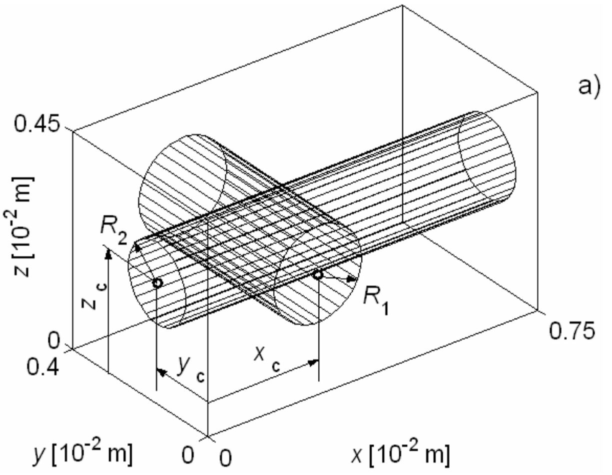


Fig. 7 Schematic representation of the inert filler sub-area in 1/8th of the specimen volume: $R_1 = 0.1\times10^{-2}$ m; $R_2 = 0.085\times10^{-2}$ m; $x_c = 0.25\times10^{-2}$ m; $y_c = 0.15\times10^{-2}$ m; $z_c = 0.25\times10^{-2}$ m

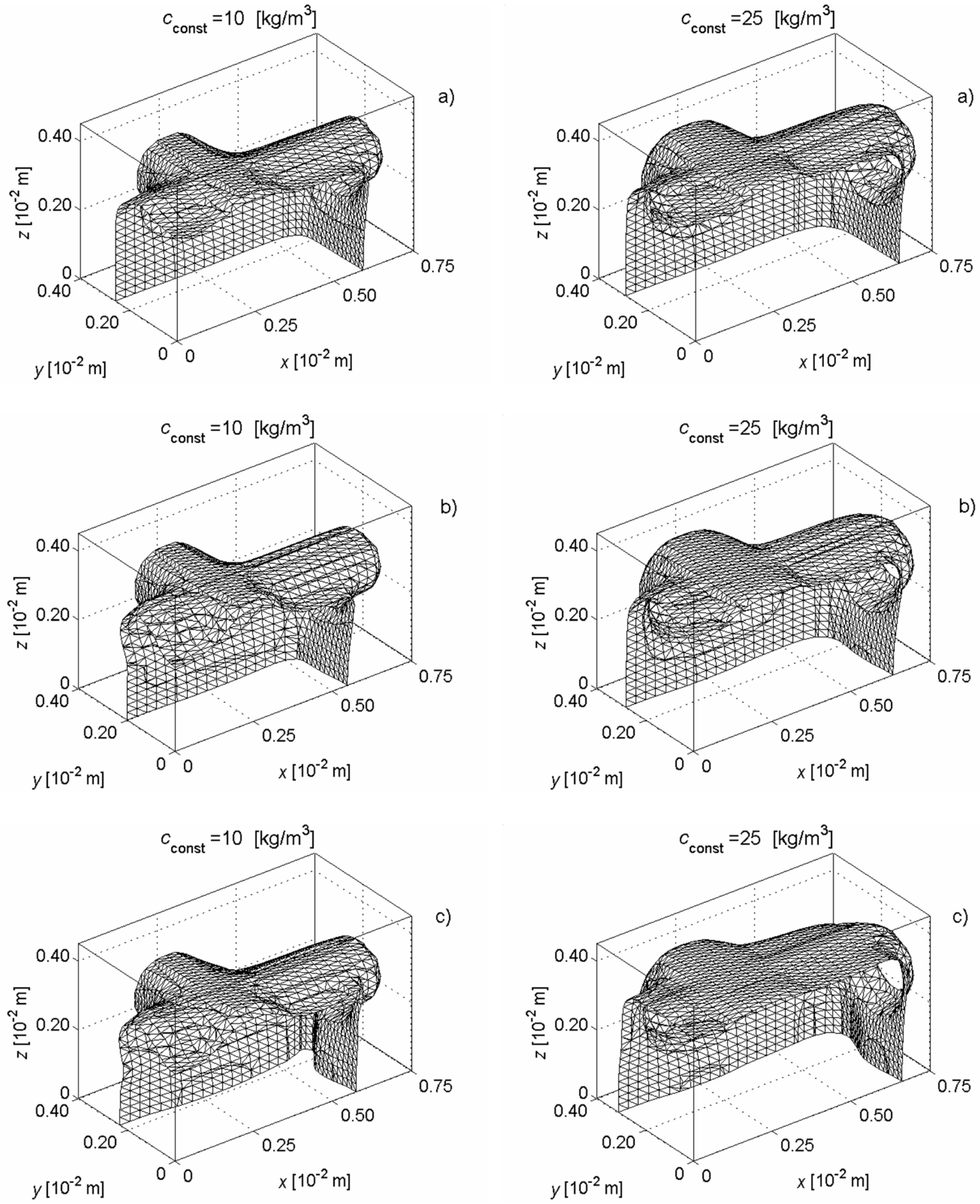


Fig. 8 Isosurfaces of the ions concentration.
Time of immersion a) 1 month b) 4 months c) 10 months

the coefficient values are the highest ones, and the coefficient varies with the largest gradient. Then, due to the pore filling and decrease of the concentration impetus, the distribution curve tends to a straight line and the mean value of the effective coefficient of diffusion tends to decrease along the coordinate axis *x*.

The model proposed, together with the numerical algorithm designed, allows considering more complex 3D cases of ions diffusion, as is that shown in Fig. 7. The specimen under consideration is a prism with dimensions $L_1 = 1.5 \times 10^{-2}$ m, $L_2 = 0.8 \times 10^{-2}$ m, $L_3 = 0.9 \times 10^{-2}$ m. It is assumed that two cylindrical bodies of inert filler are located in 1/8th of the specimen volume. Since the specimen is symmetric with respect to the coordinate axes $x = 0$ $y = 0$, $z = 0$, the spatial distribution of the ions concentration, the quantity of chemically reacted ions and the distribution of the effective diffusion coefficient are plotted for 1/8-th of the specimen volume in the figures below. This configuration of the specimen is chosen to illustrate the capabilities of the numerical solution.

The features of the concentration front distribution, outlined in the analysis of the case of 1D diffusion, are also characteristic for the 3D case. Besides, for values of the concentration closer to the concentration of the surrounding liquid this specificity is more distinct as compared to the case of higher concentrations. Fig. 8(a, b, c) shows comparison of the change in time of two isosurfaces $c_{\text{const}} = 10$ [kg/m^3] and $c_{\text{const}} = 25$ [kg/m^3]

The isosurface of the lower concentration value (10 kg/m^3) penetrates within the specimen, and the change of its location between the 4-th and the 10-th month of immersion is relatively weak. The isosurface of the higher concentration value (25 kg/m^3) penetrates within the specimen for about 4 months of immersion, and then draws back. Besides, it is observed that the isosurface location is closer to the specimen external surface for 10 months of immersion as compared to its location for 1 month of immersion. These results confirm the conclusion drawn for the 1D case and

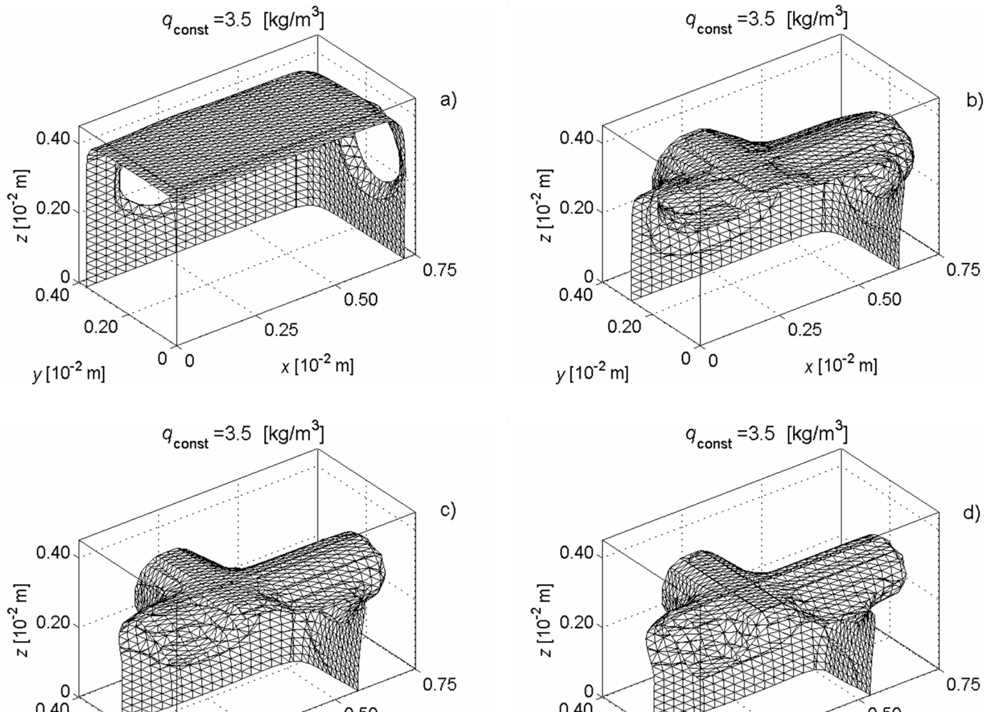


Fig. 9 Isosurfaces of the chemically reacted quantity of ions.
Time of immersion a) 1 month, b) 2 months, c) 4 months, d) 10 months

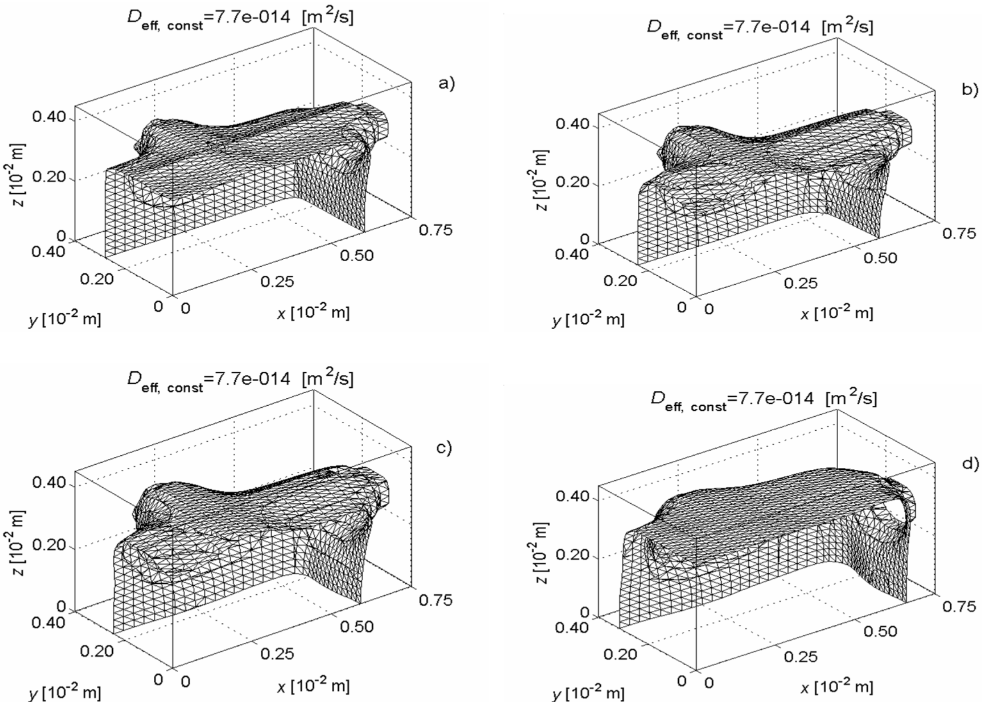


Fig. 10 Isosurfaces of the effective diffusion coefficient.
Time of immersion a) 1 month b) 2 months c) 4 months, d) 10 months

further clarify the role of the effects, accompanying the sulfate ions diffusion, i.e., capillary filling and liquid push out of them. As a further illustration, Fig. 9 shows the subsequent change in time of the quantity of chemically reacted ions.

Fig. 10 illustrate the change of the diffusion coefficient. The shift in time of the isosurface of D_{eff} to the external interface "cement stone/solution" is due partilly to the capillary filling with products of the chemical reaction and partially to the decrease of the sulfate ions concentration within the volume. The results shown in Fig. 8 - Fig. 10 also illustrate the effect of inert fillers on the ions transfer, and the capabilities of the numerical algorithm when treating a specimen with a complex shape.

5. Conclusions

The relation for the effective diffusion coefficient used allows also to follow how the current sulfate concentration within the volume affects the rate of ions transfer. The comparison of the theoretical results with the experimental data shows qualitative agreement. It may be concluded that modeling the ions transfer as a diffusion process gives plausible quantitative and qualitative description of the phenomena. The results found can be used to both assess the sulfate corrosion in saturated systems and predict and estimate damage of structures built of cement-based mineral composites.

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