Computers and Concrete, Vol. 4, No. 2 (2007) 157-166
DOI: http://dx.doi.org/10.12989/cac.2007.4.2.157

Modeling of sulfate ionic diffusion in porous cement based composites: effect of capillary size change

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(Received October 26, 2006, Accepted February 5, 2007)

Abstract. The paper considers a theoretical model to study sulfate ion diffusion in saturated porous media - cement based mineral composites, accounting for simultaneous effects, such as filling micro-capillaries (pores) with ions and chemical products and liquid push out of them. Pore volume change and its effect on the distribution of ion concentration within the specimen are investigated. Relations for the distribution of the capillary relative radius and volume within the composite under consideration are found. The numerical algorithm used is further completed to consider capillary size change and the effects accompanying sulfate ion diffusion. Ion distribution within the cross section and volume of specimens fabricated from mineral composites is numerically studied, accounting for the change of material capillary size and volume. Characteristic cases of 2D and 3D diffusion are analyzed. The results found can be used to both assess the sulfate corrosion in saturated systems and predict changes occurring in the pore structure of the composite as a result of sulfate ion diffusion.

Keywords: diffusion; sulfate corrosion; cement paste; porous composite; mathematical model; numerical analysis.

1. Introduction

The investigation of ion transport in cement-based mineral composites is an essential part of the overall study of sulfate corrosion of concrete structures undergoing an attack of liquid aggressive media. Mathematical models based on Nernst-Planck equations of ion transport in saturated cement-based materials are given in Samson, *et al.* (1999a), Marchand, *et al.* (2001). A comprehensive overview of the various types of chemical reactions that can occur in reactive porous solids is presented (Samson, *et al.* 2000). In Samson, *et al.* (1999b), the transport and mass conservation equations are first written at the microscopic scale to describe the movement of particles in the fluid phase of the material. These equations are then averaged over the entire volume of the material. The main features of the numerical model developed to predict the microstructural alterations of concrete subjected to external sulfate attack are presented in Marchand, *et al.* (1999). The model accounts for transport by diffusion and advection of five different ionic species. A digital-image-based model of the microstructure of the cement paste, coupled with exact transport algorithms, are used to study the diffusivity of portland cement paste. The principal variables considered are water/cement ratio, degree of cement hydration, and capillary porosity (Garboczi and Bentz 1992). Considering processes based on diffusion transport, the chemical reactions and filling of the voids

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of a porous catalyst with chemical products significantly affects that transport (Matros 1988).

A model of sulfate ion transport in a porous composite - cement paste (cement stone), is designed in previous papers (Gospodinov, *et al.* 1999, Mironova, *et al.* 2002, Gospodinov 2005). The process of ion transport is treated as diffusion accompanied by pore filling and liquid motion within pores. The model assumes that ion transport within the liquid that fills the microcapillaries (capillaries) of the composite takes place in a saturated system. Ion penetration from the surrounding liquid into the cement paste specimen immersed in it, takes place under a constant concentration of the surrounding sulfate solution. Due to the concentration driving force, ions penetrate the liquid that fills the cement paste pores. Pores are treated as capillaries shaped as straight circular cylinders with symmetry axes parallel to the coordinate axes. Capillaries of the composite material are filled with drinking water prior to the specimen immersion into the solution.

As a result of the heterogeneous chemical reaction occuring in the solution, its products precipitate on the capillary walls and partially fill the capillaries. This phenomenon initiates decrease of the capillary cross section and liquid push out of the capillary, in a direction opposite to that of the ion diffusion flux.

2. Mathematical model

The following mathematical model of ion transport is derived on the basis of the balance of inflowing and outflowing mass fluxes, considering an elementary volume with dimensions *dx, dy, dz* (Gospodinov, *et al.* 1999, Mironova, *et al.* 2002, Gospodinov 2005).

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

Spatial operators **div( )** and **grad( )** in the above equation have the form

$$\mathrm{div}(\ ) \equiv \sum_{i=1}^{S} \frac{\partial}{\partial x_i}(\ )_i, \quad \mathrm{grad}(\ ) \equiv \sum_{i=1}^{S} \mathbf{j}_i \frac{\partial}{\partial x_i}(\ )_i \tag{2}$$

The number of dimensions of the area in Eq. (2) is S. Obviously, $S \in [1,2,3]$, and $x_1 = x$; $x_2 = y$; $x_3 = z$ denote the spatial coordinates. Quantity $c(x_1, \cdots, x_S, t)$ in Eqs. (1)-(2) is the concentration current value and $q(x_1, \cdots, x_S, t)$ is the quantity of chemically reacted ion at point $(x_1, \cdots, x_S)$ and at a moment t. k is coefficient of chemical reaction rate and k_z is the coefficient of capillary filling. The last term at the RHS of Eq. (1) is a source term which models the heterogeneous chemical reaction between the sulfate ions within the solution and the material. It also accounts for the change of the capillary reacting surface.

Deriving the model set forth by Eqs. (1)-(2), it is assumed that the thickness of the layer $\delta(x, t)$ deposited on the capillary walls - Fig. 1, is proportional to the capillary initial mean radius R_0 and to the quantity of chemically reacted ions according to the relation:

$$\delta(x,t) = k_z q(x,t) R_0 \tag{3}$$

The effective coefficient of ion diffusion includes the effect of capillary filling as a result of the occurrence of a heterogeneous chemical reaction. Consider diffusion in a single capillary (Fig. 1). Then:

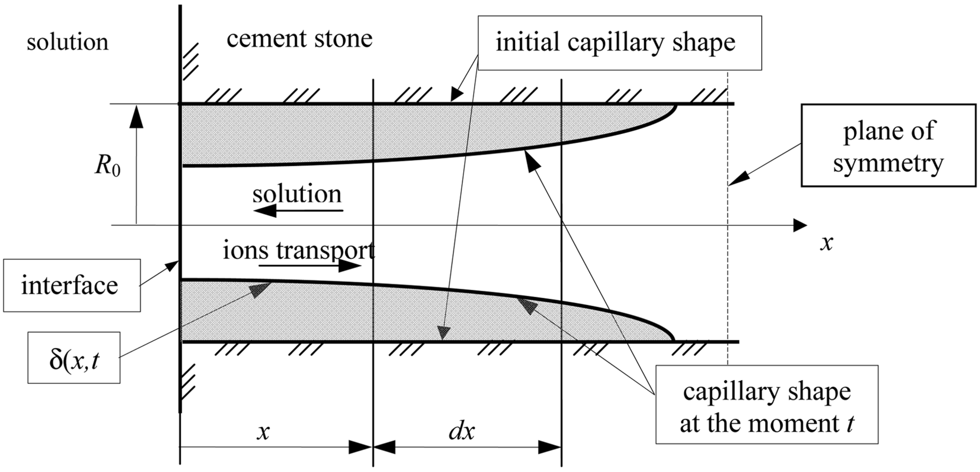


Fig. 1 A scheme of the process of capillary filling

$$D_{\mathrm{eff}} = D\frac{F(x,t)}{F_0} \tag{4}$$

where x is the coordinate along the capiilary length, F_0 is the capillary cross section at zero time and $F(x, t)$ is the current cross section at a moment t and at a distance x. Obviously $F(x, t)=\pi(R_0-\delta(x, t))^2$. The insertion of Eq. (3) in Eq. (4) yields the following expression

$$D_{\mathrm{eff}} = D(1-k_z q)^2 \tag{5}$$

where

$$D = k_{\mathrm{diff}}\exp[\beta(c(x_1,\ldots,x_S,t)-0.5c_0)] \tag{6}$$

The capillary filling effect over the source term at the RHS of Eq. (1) is similarly considered.

k_{diff} in Eq. (6) is the coefficient of diffusion sulfate ions for the volume consisting of a cement matrix and voids filled with liquid. It reflects material porosity, structure and capillary shape. Constant β is a parameter and c_0 is a concentration characteristic value, i.e., the concentration of the solution which the specimen is immersed in. Note that experimental evidence is used to find the form of Eq. (6), as described in Gospodinov, *et al.* (1999), Mironova, *et al.* (2002).

Projections V_i, i=1, ⋯, S, of velocity **V** in Eq. (1) are the mean velocities of liquid motion within the capillary along axes x_i, i=1, ⋯, S.

The quantity of chemically reacted ions q, at a moment t and at a point with fixed coordinates (x_1, ⋯, x_S), can be found by integrating the concentration value at that point as a function of time t:

$$q(x_1,\ldots,x_S,t) = \int_o^t kc(x_1,\ldots,x_S,\tau)d\tau \tag{7}$$

The studied prismatic specimens are symmetric with respect to the coordinate axes Ox, Oy and Oz. The specimen geometrical center O is the origin of the coordinate system, while axes Ox, Oy and Oz coincide with the symmetry axes. Specimen dimensions along x, y and z are denoted by L_1, L_2, L_3 , respectively.

To find the velocity component V_i for a fixed coordinate value x_m, $m\neq i$ along a capillary which symmetry axis coincides with x_i, the following integral should be calculated:

$$V_i = \int_{\eta=U}^{\eta=G} -2kk_1(1-k_z q)c\,d\eta$$

$$U = L_i/2 - x_i, G = L_i/2, i = 1,\ldots,S \tag{8}$$

Since the origin of the coordinate system coincides with the specimen symmetry center, velocity V_i is zero for $x_i=0$ and maximal for $x_i=L_i/2$. The lower integration limit in Eq. (8) is $L_i/2-x_i$, while the upper one is $L_i/2$. Thus, velocity $V_i(x_1, \cdots, x_S, t)$ can be found at each point of the area under consideration. Velocity components $V_m(x_1, \cdots, x_S, t)$, $m \neq i, m \in [1,\ldots,S]$ are similarly found. A detailed calculation of the velocity field of the solution within the capillaries, including diffusion into more complex samples (e.g. a sample with inert filler), is given in Gospodinov (2005).

The above presented model is a continuation of a model designed in our previous papers, where its reliability is verified.

3. Effect of capillary size change

The model thus designed treats transport processes within the solution filling the pores of the composite material, and the results found consider the change of the concentration within that solution. An important part of the process is the change of the microcapillary volume as a result of microcapillary filling with products of the heterogeneous chemical reaction. This results in change of material porosity and additional change of the ion concentration with respect to the capillary initial volume.

Consider the case of 1D diffusion, as shown in Fig. 1. A cylindrical microcapillary with radius R_0 occupies the elementary volume between planes x and $x+dx$ at a moment $t=0$.

For time interval $[0, t]$ the radius of a microcapillary in a cross section x changes from R_0 to $R_0-\delta(x, t)$, and the elementary volume considered changes, too. Thus, the following ratio between the elementary volumes can be written at moments $t=0$ and t

$$\overline{V} = \frac{\pi(R-\delta(x,t))^2 dx}{\pi R_0^2 dx} = (1-k_2 q(x,t))^2 \tag{9}$$

The ratio in Eq. (9) presents the relative capillary volume in cross section x and at moment t.

The ion concentration $c(x, t)$ within the capillary-filling liquid is found via the solution of the model proposed. Pore volume decrease yields decrease of the liquid volume within the pores and hence, decrease of the total quantity of ions within the initial volume $\pi R_0^2 dx$. Ion concentration with respect to the capillary initial volume can be recalculated as follows:

$$c_N(x,t) = \frac{c(x,t)\pi(R_0-\delta(x,t))^2 dx}{\pi R_0^2 dx} = c(x,t)(1-k_2 q(x,t))^2 \tag{10}$$

Change of the microcapillary volume does not affect the quantity of chemically reacted ions that precipitate on the capillary walls.

The distribution of the relative mean pore radius R_R within the specimen cross section is also of interest. It can be found as

$$R_R = \frac{R(x,t)}{R_0} = \frac{R_0-\delta(x,t)}{R_0} = 1-k_z q(x,t) \tag{11}$$

Note that Eqs. (9)-(11) keep their form for 2D and 3D diffusion transport of sulfate ions.

4. Numerical solution

The model presented by Eqs. (1)-(8) is numerically solved. It has been completed by a symmetry boundary condition on the coordinate planes $x_i=0$, $i=1, \cdots, S$. A condition for equality between the concentration of ions having penetrated into the specimen and the concentration of the surrounding solution is given on specimen planes $x_i=L_i/2$, $i=1, \cdots, S$ which are solution/composite interfaces. It is assumed that the initial ion concentration within the liquid in capillaries of the specimen is zero, since the specimen has been previously kept in drinking water.

The equation of transport (1)-(2), together with the initial and boundary conditions, set forth the non-steady boundary value problem. It is completed by the integral relations (7) for the calculation of the quantity of chemically reacted ions and by the integral relations (8) needed to calculate the velocity field of the liquid pushed out of the capillaries. An implicit difference scheme is used to solve the problem which is reduced to solving a linearized system of algebraic equations with a semi-diagonal and weakly filled matrix. The algorithm allows modeling numerically sub-areas with different conductivity - inert fillers, inclusions, reinforcement etc. Details on the discretization scheme and numbering of the knots of the orthogonal grid introduced, as well as details regarding the calculation of the velocity field of the solution within the capillaries, including cases of more complex bodies, are given in Gospodinov (2005).

The following values of the dimension and dimensionless constants are used in the calculations: coefficient of ion diffusion in the water solution $k_{\text{diff}}=0.361 \cdot 10^{-13}$ m^2/s; fitting parameter participating in Eq. (4) $\beta=0.2917$ 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. Those values are specified in Gospodinov, *et al.* (1999) , where data on sulfate resistant Portland cement, used for the preparation of the cement mineral composition are also submitted.

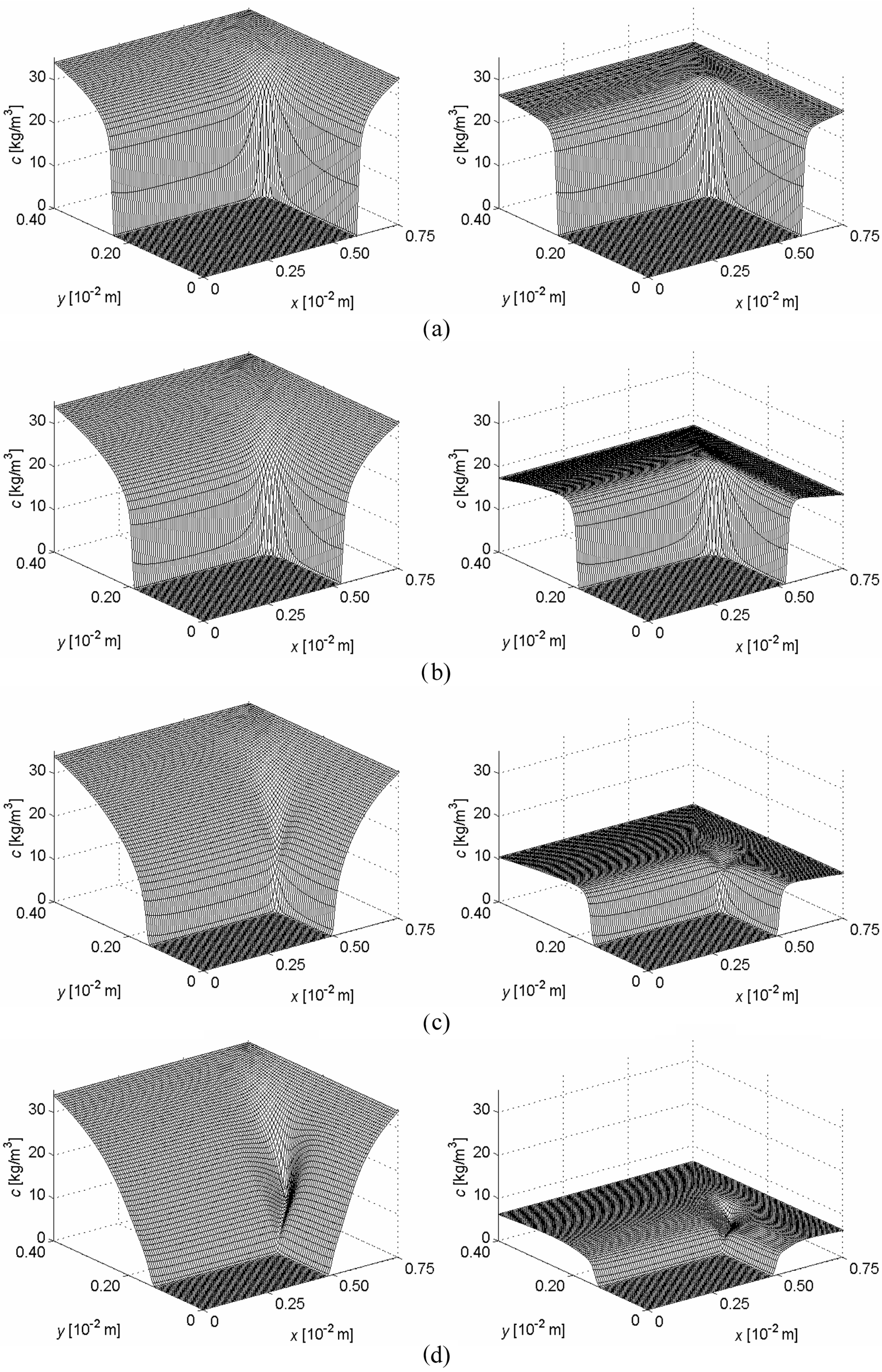
5. Results and discussion

This paragraph presents results of the study of sulfate ion diffusion in cement stone specimens having been immersed in 5% solution of sodium sulfate which concentration of sulfate ions is $c_0=33.803$ kg/m^3.

Fig. 2 shows results for the distribution of the concentration of sulfate ions within the cross section of a prismatic specimen. The cross section dimensions are $0.8\times10^{-2}\times1.5\times10^{-2}$ m, and the specimen length is significantly larger than the cross section dimensions. Thus, plane diffusion is assumed. The cross section is symmetric with respect to axes *Ox* and *Oy*.

Results of the left column of plots in Fig. 2 show the distribution of the ion concentration within the liquid phase while those of the right column - the ion concentration regarding the effect of capillary size change. A central area of zero concentration, as well as and a layer of significant concentration nearby the composite/surrounding liquid interface are present. Due to the change of capillary volume, the recalculated values of the concentration within that layer are smaller than the values of the concentration of the solution that fills the pores.

Comparison of the locations of the two isolines in Fig. 2(b) is shown in Fig. 3. The consideration



(a)

(b)

(c)

(d)

Fig. 2 Comparison of the distribution of sulfate ions within the cross section of the specimen: left column of plots - distrbution within the solution that fills capillaries; right column of plots - considering the effect of capillary size change. Time of immersing the specimens in the solution: (a) 1 month, (b) 3 months, c) 6 months, (d) 10 months

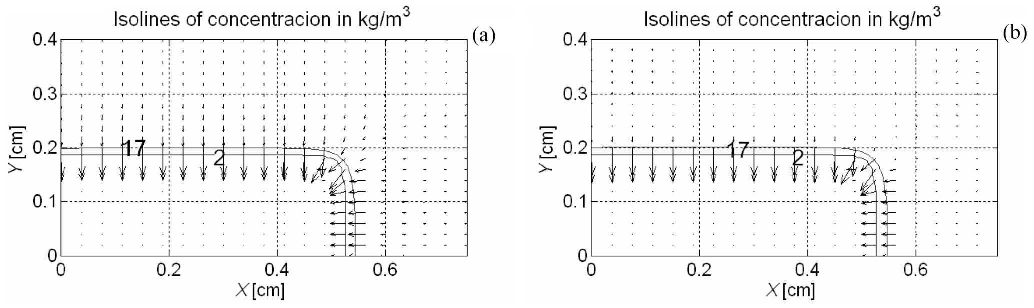


Fig. 3 Comparison between two characteristic isolines within the cross section of a specimen after 3 months of immersion 5% solution of Na_2SO_4: (a) within the solution that fills capillaries; (b) when accounting for the effect of capillary size change

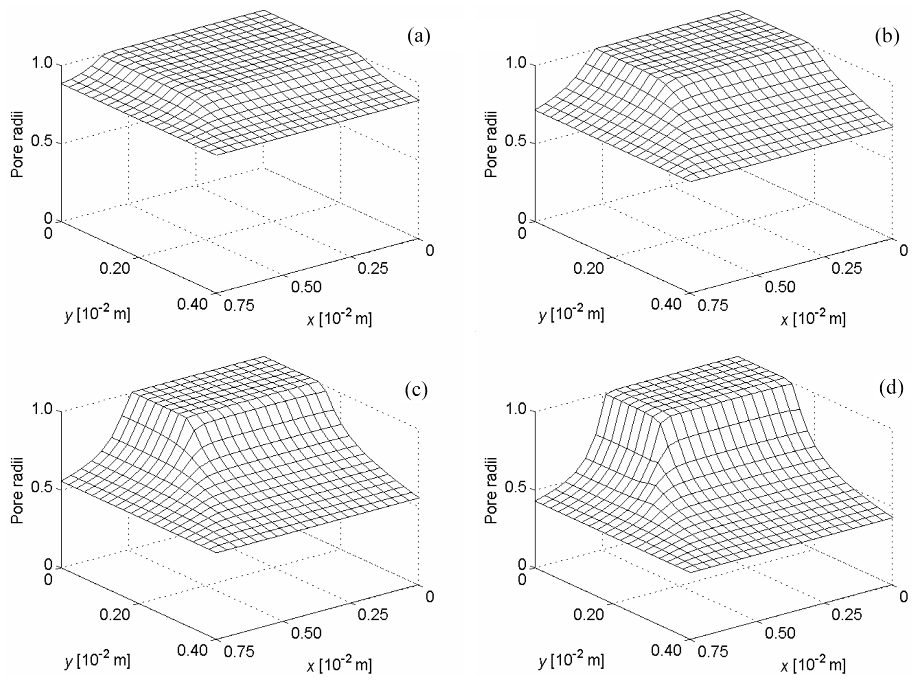


Fig. 4 Change of the relative radius of the capillaries within the specimen cross section. Time of immersion (a) 1 month, (b) 3 months, (c) 6 months, (d) 10 months

of the effect of capillary size change (Fig. 3b) does not yield change of line location as compared to lines in Fig. 3(a). This is so, since the isolines are located in an area where capillary filling and volume change has not taken place yet. Moreover, as shown in Mironova, *et al.* (2002), a two layered structure of the cross section is formed under the sulfate attack. The structure consists of a central intact core and an external corrupted layer where partial capillary filling has taken place. The results in Fig. 4 and Fig. 5 also confirm this conclusion where following Eqs. (8)-(10), the change of the capillary relative radius and volume within the specimen cross section are shown for different periods of time.

The cross section together with the surface of spatial distribution shown in Fig. 4 and Fig. 5 are

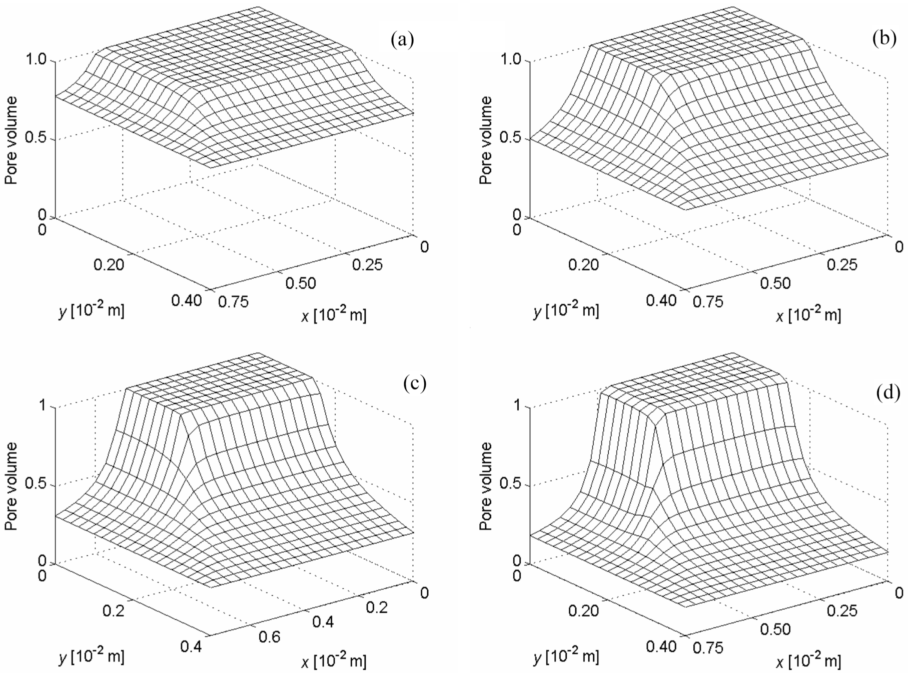


Fig. 5 Change of the relative volume of the capillaries within the specimen cross section. Time of immersion (a) 1 month, (b) 3 months, (c) 6 months, (d) 10 months

plotted after rotation around the vertical coordinate axis Oz at and angle 180^0. This is done for better visualization of the results. Results for the distribution of the relative radius of the pores within the cross section of the prismatic specimen shown in Fig. 4 are for different immersion times and in accordance with the results in Fig. 2. As outlined, an expressed two-layered structure of the cross section is formed. Capillaries in the corrupted layer are partially filled, and this hampers ion access to the central core. Similar is the conclusion drawn from the results shown in Fig. 5 where the change of the relative volume of the pores within the cross section is shown. It can be assumed that a certain packing of the structure has taken place in the corrupted layer as a result of capillary filling with products of the chemical reaction, yielding significant decrease of the capillary volume. These structure modifications result in hamper of the ion transport from the external solution to the specimen central area (core). Thus, more and more expressed two-layered structure is formed under the sulfate corrosion development.

Using the algorithm designed, isosurfaces of the mean capillary radius for a specimen with inert and impermeable inclusion with a more complex shape, immersed for 3 months in 5% solution of sodium sulfate, are calculated. The specimen has the following dimensions: $L_1=1.5\times10^{-2}$ m, $L_2=0.8\times10^{-2}$ m, $L_3=0.9\times10^{-2}$ m. The ion transport is 3D for these dimensions. Fig. 6 shows results for 1/8th of the specimen volume, containing two cylindrical inert bodies. Coordinate planes $x_i=0$, replace with, $i\in[1,\ldots,S]$ are also planes of symmetry. Body radii are $R_1=0.1\times10^{-2}$ m, $R_2=0.085\times10^{-2}$ m, and body symmetry axes are parallel to the coordinate axes x and y, respectively, lying in the plane $z_c=0.25\times10^{-2}$ m. Several isosurfaces of the distribution of the capillary mean radius are plotted. Results show the existence of a corrupted layer nearby the solution/composite interface. Isosurfaces of lower value of the mean radius are located closer to the specimen external

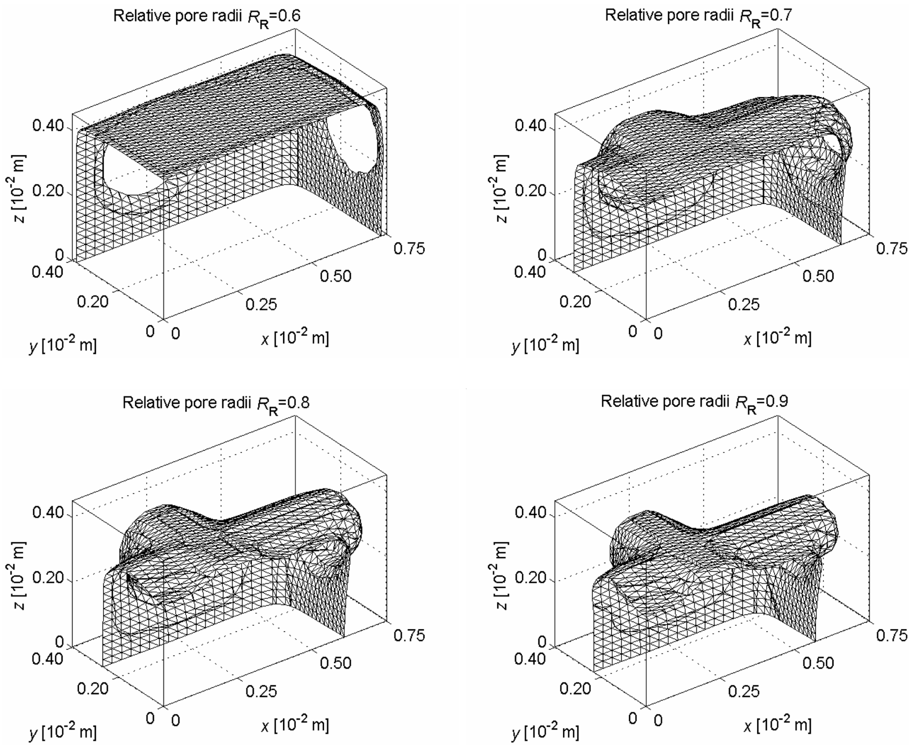


Fig. 6 Isosurface of the mean relative radius of the microcapiullaries after 3 months immersion of the specimen in 5% solution of Na_2SO_4.

boundary, and they shift inwards towards the intact core with the mean radius increase.

6. Conclusions

The mathematical model of diffusion of sulfate ions transport incorporates the effect of capillary size change. This expands the capabilities of the theoretical study of sulfate corrosion of cement based mineral composites. The numerical solution and the procedure for recalculation of the capillary relative radius and volume under diffusion accompanied by a chemical reaction allows to:

- assess the change of dimensions and volume of the pores in the area under consideration and thus, to assess porosity change of the composite material as a result of the sulfate corrosion;
- calculate the concentration within the capillary-filling liquid phase;
- calculate the change of the concentration, accounting for capillary size change;
- assess pore (microcapillary) volume change and change of the cement paste relative density.

The numerical results are found within the frames of the model proposed, considering sulfate ion transport as diffusion accompanied by a heterogeneous chemical reaction and not accounting for structure modifications due to the occurrence of phase transformations within the composite.

Acknowledgements

The research was supported by the Bulgarian Ministry of Education and Sciences, grant MM 1404/2004.

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