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Numerical simulation of 3D sulfate ion diffusion and liquid push out of the material capillaries in cement composites

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Abstract

This study treats 3D diffusion of sulfate ions into cement composite and simultaneous effects, such as microcapillary filling and subsequent liquid push out of them. A numerical algorithm provides account for various conditions specified at the interface, as well as possibility to model separate volume sections as inert fillers. Cases discussed illustrate the capabilities of the proposed model and those of the algorithm designed to study diffusion and liquid push out for specimen complex configuration. Results found allow for the assessment of the effects of convective and diffusion ion transfer. Comparison with experimental observations of corrosion processes that have more or less one-dimensional character prove the necessity to use a 3D mathematical model for a fuller clarification of sulfate corrosion.

Keywords: Diffusion; Numerical modeling; Sulfate attack; Cement; Corrosion

1. Introduction

Modeling of corrosion due to ion aggression on cement composite is studied in Refs. [1,2]. Theoretical models are based on the diffusion equation, disregarding the heterogeneous chemical reaction occurring between ions and the composite matrix. Diffusion of electrolytes in a porous medium is considered in Refs. [3,4]. The 1D steady case of pore filling, in the presence of a catalyst, and its effect on the reaction rate is considered in Ref. [5].

Special attention must be paid to a number of studies referred to in what follows. They treat diffusion of ions in saturated and nonsaturated concrete systems and study the effects occurring in concrete under external attack from chemically aggressive environments. Models presented in those papers take into account the electrical coupling between various ionic species in solution. They assume that movement of the ions can only occur in liquid phase.

Ref. [6] proposes a new mathematical model for calculating the chemical activity coefficients of ions in electrolytic solutions. The model is essentially a modified version of the Davies equation. The whole system of nonlinear equations is solved in Ref. [7] using the finite-element method. 1D and 2D simulation are presented for predicting drift of ions. The model called STADIUM has been developed to predict transport of ions in unsaturated porous media [8,9]. In Ref. [10], the equations of Nernst–Planck model are then averaged over the entire volume of the material, while Ref. [11] treats microstructural alterations of concrete subjected to external sulfate attack. The numerical model also considers chemical interaction of various ions with the cement paste hydrated phases and the effects of chemically induced microstructural alterations on the transport properties of the material. A comprehensive overview of the various types of chemical reactions that can occur in reactive porous solids is first presented in Ref. [12], and specific problem related to the numerical modeling of ionic diffusion mechanisms are also discussed in Ref. [13]. Refs. [14,15] treat the influence of chemically

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induced microstructural alterations on material transport properties. Long-term durability of concrete life under severe marine conditions is predicted using both laboratory testing and numerical modeling [16]. The numerical model STADIUM is applied to the diffusion of ions and moisture. The effects of dissolution/precipitation reactions on the transport mechanism are taken into account in Ref. [17]. Migration tests are used to estimate the diffusion coefficients of cement-based materials. Results indicate that the diffusion coefficients depends only slightly on the concentration level and chemical make-up of the upstream cell solution [18].

A 2D model of the diffusion of sulfate ions in cement composite is proposed in our previous papers [19,20]. There, simultaneous effects—pore filling and liquid push out of the pores, are also treated. Considering one- and two-dimensional cases, relations needed to find the average velocity of solution motion in the capillaries and along the coordinate axes are derived in Ref. [20]. However, the assumptions of 1D and 2D models limit the capabilities of the theoretical studies.

2. Model of nonsteady 3D diffusion

Objects of modeling are transfer processes, which take place when a prismatic specimen of cement stone is immersed in a vessel, filled with solution of sodium sulfate. Before immersion, the specimen is kept for some time in drinking water—aged for 28 days . The vessel volume is assumed to be large enough, and diffusion does not change the concentration of sulfate ions in the solution which remains constant. Owing to the concentration driving force, ions enter the liquid that fills material pores. Pores are formally treated as capillaries (microcapillaries), shaped as straight circular cylinders and with symmetry axes parallel to the coordinate axes [20]. As a result of the occurring heterogeneous chemical reaction, chemical products precipitate on capillary walls and partially fill capillaries. Capillary filling and volume decrease yield liquid push out. This process is directed from the specimen internal area and to the solution; that is, its direction is opposite to that of diffusion.

Geometrical center O of the specimen 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 and L_3, respectively (Fig. 1).

Consider an element with dimensions dx, dy, dz and the balance of inflowing and outflowing mass. Then, the following 3D nonsteady equation of transfer of sulfate ions into the area is obtained:

$$\frac{\partial c}{\partial t} = L_x c + L_y c + L_z c - k(1 - k_z q)^2 c, \tag{1}$$

where spatial operators $L_x c$, $L_y c$ and $L_z c$ express balance of diffusive and convective mass flux along coordinate axes, x, y and z, respectively. These operators have the form:

$$\begin{aligned} L_x c &\equiv \frac{\partial}{\partial x}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial x}\right) - \frac{\partial}{\partial x}\left(V_x c\right), \\ L_y c &\equiv \frac{\partial}{\partial y}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial y}\right) - \frac{\partial}{\partial y}\left(V_y c\right), \\ L_z c &\equiv \frac{\partial}{\partial z}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial z}\left(V_z c\right). \end{aligned} \tag{2}$$

The last term in the RHS of Eq. (1) is a source term, which models the heterogeneous chemical reaction between capillary walls and sulfate ions in the solution. The term accounts also for change of the reacting surface, due to capillary filling. Quantity c (x,y,z,t) in Eqs. (1) and (2) is the concentration current value, and $q(x,y,z,t)$ is the quantity of chemically reacted ions at point (x,y,z) and at moment t. k is rate constant of the heterogeneous chemical reaction and k_z denotes coefficient of capillary filling. The effective coefficient of ion diffusion in the whole volume, accounting for pore filling [19,20], is:

$$D_{\mathrm{eff}} = D(1 - k_z q)^2, \tag{3}$$

where

$$D = k_{\mathrm{diff}} \exp[\beta(c(x,y,z,t) - 0.5c_0)] \tag{4}$$

Denominator k_{diff} in Eq. (3) 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 material porosity and grain structure, and for capillary shape. Constant

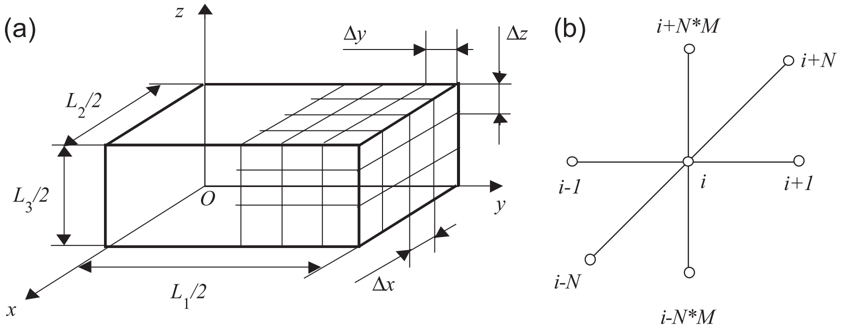

Fig. 1. Coordinate system and discretization scheme.

β is a fitting parameter, while c_0 is a concentration characteristic value—concentration of the solution where specimen is immersed and kept for a definite period of time. V_x, V_y and V_z in Eq. (2) denote the average velocity of the liquid flow in the capillary, along axes x, y and z.

Denote the interface surface "water solution–cement stone" by S, giving there the value of solution concentration as a boundary condition. In accordance with Fig. 1, this condition is given on planes $x=L_1/2$, $y=L_2/2$ and $z=L_3/2$:

$$c(x,y,z,t)|_S = c_0, \begin{cases} x = L_1/2, & 0 \le y \le L_2/2, \quad 0 \le z \le L_3/2, \\ y = L_2/2, & 0 \le x \le L_1/2, \quad 0 \le z \le L_3/2, \\ z = L_3/2, & 0 \le x \le L_1/2, \quad 0 \le y \le L_2/2. \end{cases} \tag{5}$$

Due to symmetry, the problem is solved in 1/8th of the area, having symmetry conditions on planes $x=0$, $y=0$ and $z=0$:

$$\frac{\partial c}{\partial x} = 0, \qquad x = 0, \quad 0 \le y \le L_2/2, \quad 0 \le z \le L_3/2,$$

$$\frac{\partial c}{\partial y} = 0, \qquad y = 0, \quad 0 \le x \le L_1/2; \quad 0 \le z \le L_3/2,$$

$$\frac{\partial c}{\partial z} = 0, \qquad z = 0, \quad 0 \le x \le L_1/2; \quad 0 \le y \le L_2/2. \tag{6}$$

Initial ion concentration within specimen volume is taken to be zero, because the specimen is previously kept in drinking water, i.e.,

$$c|_{t=0} = c(x,y,z,0) = 0. \tag{7}$$

The quantity of chemically reacted ions $q(x,y,z,t)$, at a moment t and at a point with fixed coordinates (x,y,z), can be found by integrating the concentration value at that point, taken as a function of time t.

$$q(x,y,z,t) = \int_o^t kc(x,y,z,\tau)\mathrm{d}\tau \tag{8}$$

Coordinate components of the liquid velocity, participating in Eqs. (1) and (2), can be found by using the procedure described in Ref. [20]. Consider velocity component V_x, for fixed values of the other two coordinates y and z. Then, the following integral along the capillary is to be solved in the interval $[0,x]$.

$$V_x = \int_{\eta=L_1/2-x}^{\eta=L_1/2} -2kk_z(1-k_zq)c \, \mathrm{d}\eta. \tag{9}$$

Because the introduced origin of the coordinate system is specimen symmetry center, velocity is zero for $x=0$ and maximal for $x=L_1/2$. Velocity direction coincides here with the positive direction of axis Ox. For specified values of y within the interval $[0,L_2/2]$ and z within the interval $[0,L_3/2]$, velocity component V_x is found by calculating integral (9). Note that $L_1/2-x$ is lower integration limit here, and $L_1/2$ is upper integration limit. Thus, velocity $V_x(x,y,z,t)$ at each point of the area under consideration can be found. Velocity field $V_y(x,y,z,t)$ is obtained in the same manner, where the lower integration limit is $L_2/2-y$ and the upper integration limit is $L_2/2$, while velocity field $V_z(x,y,z,t)$ is found for lower integration limit $L_3/2-z$ and upper integration limit $L_3/2$.

3. Numerical solution

The equation of transfer (1) and (2), together with the boundary conditions (5), (6) and the initial condition (7), formulate the initial nonsteady boundary-value problem. It is completed by integral relations (8) needed to find the quantity of chemically reacted ions, as well as by integral relations of type (9), needed to find liquid velocity field in the capillaries. An implicit difference scheme to solve numerically the formulated diffusion problem is used. The discretization scheme is partially shown in Fig. 1a. Starting from the coordinate origin, N, M and L number of sections are introduced along the three coordinate axes x y z, respectively, and those sections are perpendicular to the subsequent coordinate axis. The cross point of three arbitrary sections, perpendicular to each other, is a grid knot. Knots general number is $N \times M \times L$. Spatial grid steps along axes x, y and z are

$$\Delta x = \frac{L_1}{2(N-1)}, \quad \Delta y = \frac{L_1}{2(M-1)}, \tag{10}$$

$$\Delta z = \frac{L_1}{2(L-1)},$$

respectively. When numbering knots, the first one of them coincides with the origin of the coordinate system. Let i_x, i_y and i_z are numbers of sections, shown in the discretization scheme (Fig. 1) and perpendicular to axes x, y and z.

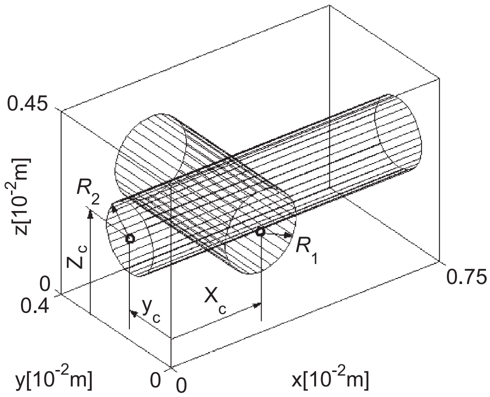

Fig. 2. Schematic representation of the inert filler subarea in 1/8th of the specimen volume.

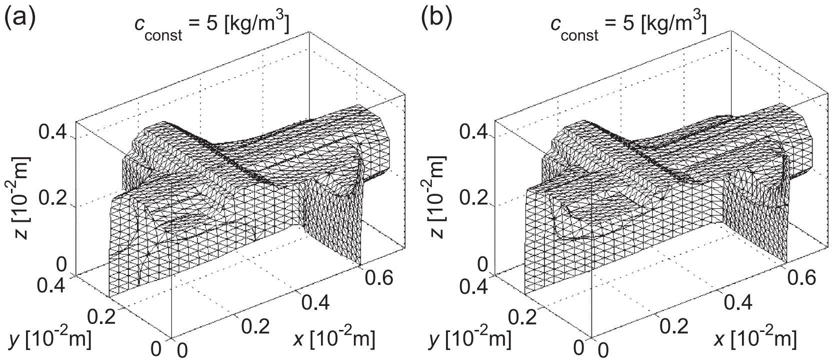

Fig. 3. Isosurfaces for concentration c_{const}=5 (kg/m^3); (a) after 3 months of specimen immersion; (b) after 6 months of specimen immersion.

Obviously, $1 \le i_x \le N$, $1 \le i_y \le M$ and $1 \le i_z \le L$. A number of grid knot, for fixed values of i_x, i_y and i_z, is given by the following relation:

$$i = i_x + (i_y - 1)N + (i_z - 1)NM. \tag{11}$$

Thus, the last knot would have number $N \times M \times L$ and coordinates ($L_1/2$, $L_2/2$, $L_3/2$). Spatial operators (2) are approximated on the pattern shown in Fig. 1b. Approximation accuracy is assessed by means of $O(h^2)$, where h=max(Δx, Δy, Δz). Time derivative in Eq. (1) is approximated as

$$\frac{\partial c}{\partial t} \cong \left[c(x_i, y_i, z_i, t) - c(x_i, y_i, z_i, t - \Delta t)\right] / \Delta t, \tag{12}$$

where Δt is discretization step of time.

Thus, the difference value problem, for a given time t, is reduced to the solution of a linearized system of ($N \times M \times L$) algebraic equations, which has a diagonal and weakly filled matrix. System matrix has seven nonzero diagonals and is nonsymmetric with respect to the main diagonal. Before performing calculations at the next time step, components of the liquid velocity are calculated. The algorithm is completed for that purpose with a numerical procedure for the calculation of integrals of the type (9) along the three coordinate axes. In cases of numerical modeling of volume subareas with completely different conductivity—inert filler, for instance, grid knots where liquid velocity is zero along some of the coordinate axes must be additionally found. These are knots on the line, starting from the symmetry plane and ending at the boundary “cement composite–inert filler” (Fig. 2). Velocity component at those knots, parallel to the knot line, is obviously zero. A procedure of prescribing subarea boundaries is included in the algorithm.

Due to problem nonlinearity, an internal iteration process is used. After attaining a previously prescribed accuracy, distribution of chemically reacted ions for the current time is found and then the next time step is considered.

Numerical results are found for the following values of dimension and dimensionless constants, as given in Refs. [6,7]:

- coefficient of ion diffusion in the water solution k_{diff}=0.361×10^{-13} m^2/s
- fitting parameter participating in Eq. (11): β=0.291 m^3/kg
- constant of the chemical reaction rate: k=0.305×10^{-7} s^{-1}
- coefficient of pore filling: k_z=0.05 m^3/kg.

The above values are obtained for specimens, molded of cement paste of sulfate-resistant Portland cement 35, type

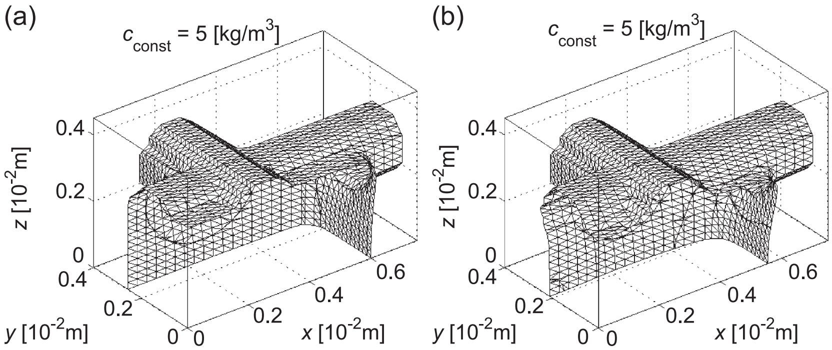

Fig. 4. Isosurfaces for concentration c_{const}=5 (kg/m^3); (a) after 3 months of specimen immersion; (b) after 6 months of specimen immersion. Liquid push out is disregarded.

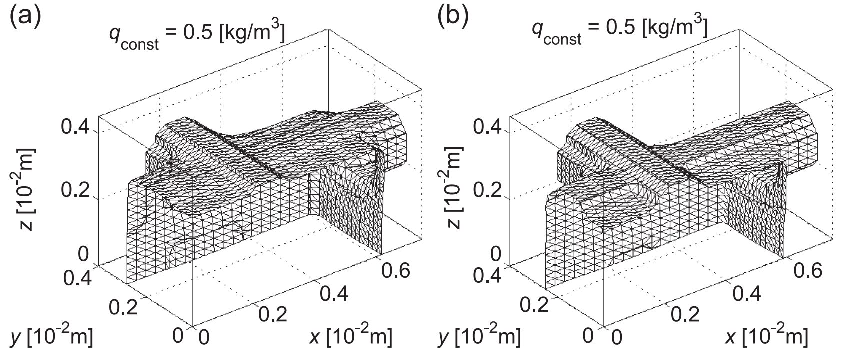

Fig. 5. Isosurfaces of chemically reacted ions; (a) after 3 months of specimen immersion; (b) after 6 months of specimen immersion.

"Devnya", according to the Bulgarian standard. Ref. [20] gives the cement mineral composition.

4. Results and discussion

Basic numerical results are found for a prismatic specimen, kept in 3% water solution of sodium sulfate. Content of sulfate ions in the solution is 20.282 kg/m^2. Calculations, illustrated in Figs. 3–7, are performed under those conditions. Solution sulfate concentration is assumed to remain constant in time. Specimens have the following dimensions: $L_1=1.5\times10^{-2}$ m, $L_2=0.8\times10^{-2}$ m and $L_3=0.9\times10^{-2}$ m. To illustrate the capabilities of the 3D model and those of the numerical algorithm, it is assumed that two cylindrical bodies of inert filler are located in 1/8th of the specimen volume. Note that there is no diffusion transfer into the bodies, and ion concentration is zero within them. Body radii are $R_1=1\times10^{-2}$ m, $R_2=0.85\times10^{-2}$ m, and body symmetry axes are parallel to the coordinate axes x and y, respectively, lying in the plane $z_c=2.5\times10^{-2}$ m. The distance between those axes and the other two coordinate axes are $x_c=2.5\times10^{-2}$ m and $y_c=1.5\times10^{-2}$ (Fig. 2).

Calculations are performed for 3 and 6 months of specimen immersion in the solution. Fig. 3a and b shows isosurface corresponding to the ion concentration within the specimen $c_{const}=5$ (kg/m^3). The effect of inert filler subarea on isosurface shape is clearly visible.

Fig. 4a and b shows the same results for comparison, but disregarding liquid push out of the capillaries. Then, the surface corresponding to a concentration of 5 (kg/m^3), especially for immersion time of 6 months, has penetrated deeper within the specimen.

Because distribution of the quantity of chemically reacted ions gives an idea of cement stone corrosion, Fig. 5a and b shows isosurface, corresponding to the quantity $q_{const}=0.5$ (kg/m^3), for specimen immersion of 3 and 6 months, respectively. The process of sulfate corrosion can be assessed by regarding the shape and location of those surfaces.

Fig. 6a and b shows the same isosurfaces as shown in Fig. 5, but disregarding the effect of liquid push out.

Convective ion transfer, directed opposite to diffusion transfer (Fig. 4), essentially affects the results. Its influence can be estimated by means of the velocity field of liquid push out of the capillaries, along axes x, y and z—Fig. 7a, b, c and d shows the liquid full-velocity field.

Areas where there is no liquid motion along one of the coordinate axes are present, because capillaries in those areas touch with one end the symmetry plane, and with the other end—the surface that envelopes area of zero permeability. Then, liquid motion is impossible and there is no convective transfer. It can be concluded that inert filler, with

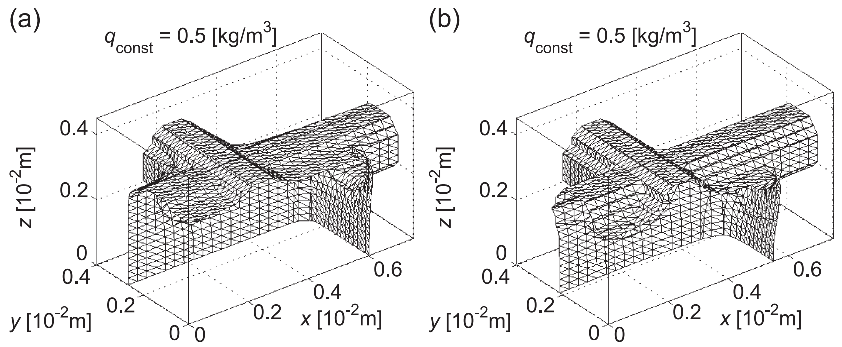

Fig. 6. Isosurfaces of chemically reacted ions; (a) after 3 months of specimen immersion; (b) after 6 months of specimen immersion. Liquid push out is disregarded.

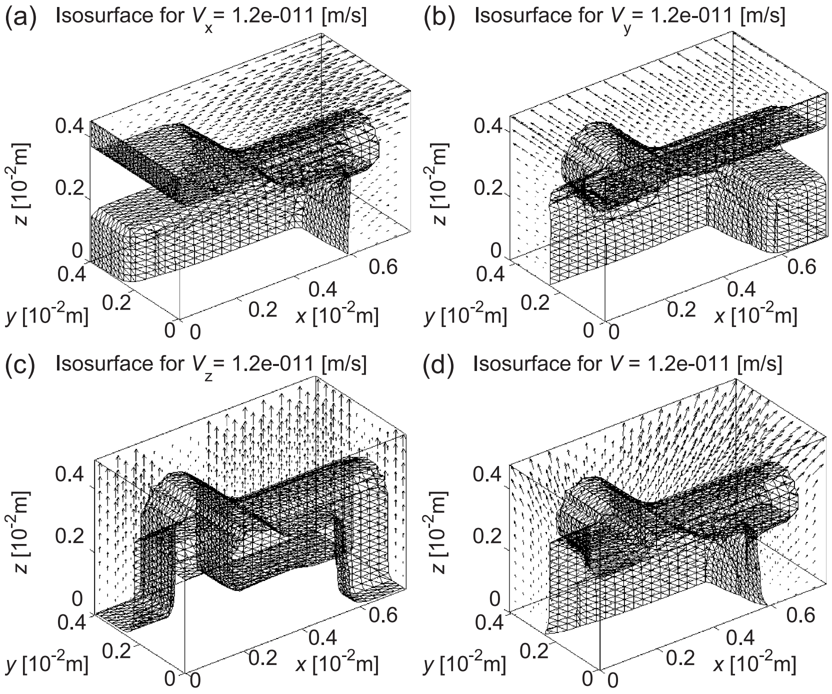

Fig. 7. Velocity field of pushed-out liquid.

its shape and location, significantly affects both mechanisms of ion transfer—diffusion and convection. The numerical algorithm designed provides a possibility to study various cases of areas with zero diffusion permeability, thus comprising a wider class of problems.

Results for corrosion of plates, after 5 years of immersion, are shown in Fig. 8. Note that plate dimensions are L_1=2.2×10^{-2} m, L_2=1.7×10^{-2} m and L_3=0.2×10^{-2} m, and solution concentration is higher—10% of sodium sulfate. Sulfate ion concentration of the solution is 67.166 kg/m^3. Hence, it can be practically assumed that the quantity of chemically reacted ions is uniformly distributed within the whole volume.

One of the specimen dimensions (its thickness) is significantly smaller than the other two dimensions. Hence, the process of ion transfer from the solution and into the specimen could be considered as being one-dimensional diffusion, as assumed in Ref. [20].

However, the use of 1D diffusion model and the subsequent numerical results are insufficient to explain the experimental evidence. As seen, spatial “disturbances” occur on the specimen facial surface and they are shaped as closed concentric furrows. Obviously, ion transfer and accompanying processes have developed along all three coordinate axes; that is, 3D diffusion model should be employed here.

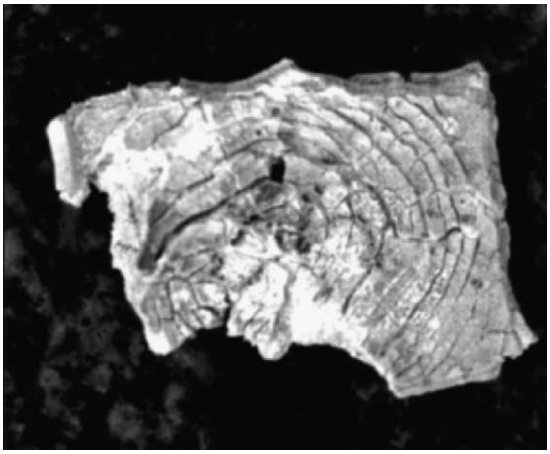

Fig. 8. Corroded specimen after 5-year immersion in 10% solution of sodium sulfate.

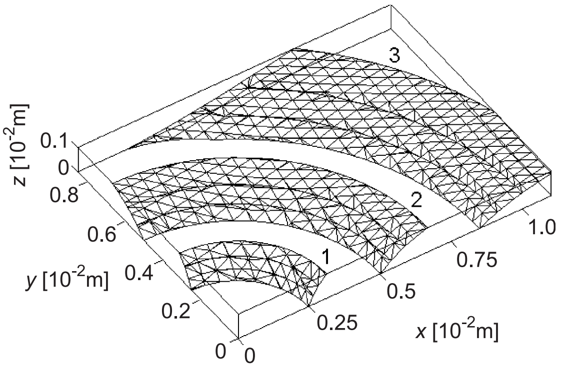

Fig. 9. Isosurfaces of the solution velocity in 1/8th volume of a specimen, immersed for 1 year in a solution with concentration of 10% of sodium sulfate. 1—V=0.889×10^{-10} m/s; 2—V=1.81×10^{-10} m/s; 3—V=3.06×10^{-10} m/s.

Compare the experimental evidence to the calculated isosurfaces of the velocity of liquid motion, for 1 year of specimen immersion—Fig. 9. Then, it can be assumed that those spatial "disturbances" are due to material phase transformations, related to the chemical reaction and to the front of solution motion within the porous structure of the cement stone.

5. Conclusions

The mathematical model, comprising simultaneous processes, such as pore filling and liquid push out of the capillaries, is extended, to study 3D processes of transfer of sulfate ions in cement stone. It gives adequate explanation of some experimental data and allows for a better account for real transfer conditions. The numerical algorithm developed is effective to solve different practical problems and to investigate real processes, which take place in structures or structural elements. Results found for the velocity field of liquid push out of the composite porous structure help to the assessment of how inert filler, located in the volume, would affect convective and diffusion ion transfer. The study gives a relation between experimentally found modifications, taking place in a specimen as a result of sulfate corrosion, and motion of the front of the liquid, pushed out of cement composite capillaries.

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References

[1] A. Atkinson, A. Haxby, J.A. Hearne, The chemistry and expansion of limestone–portland cement mortars exposed to sulfate containing solutions., Safety studies, Nirex Radioactive waste disposal, Harwell Lab., UKAEA, 1988.

[2] V.B. Ratinov, F.M. Ivanov, Chemistry in Civil Engineering, 2d ed., Stroyizdat, Moscow, 1977, in Russian.

[3] T.K. Sherwood, P. Pigford, C.P. Wilke, Mass Transfer, Himyia, Moscow, 1982, Russian translation.

[4] G.E. Zaykov, A.L. Yordanskiy, V.S. Markin, Diffusion of Electrolytes in Polymers, Himyia, Moscow, 1984, in Russian.

[5] Yu.Sh. Matros, Non Steady Processes in Catalytic Reactors, Nauka, Novosibirsk, 1982, in Russian.

[6] E. Samson, G. Lemaire, J. Marchand, J.J. Beaudoin, Modeling chemical activity effects in strong ionic solutions, Comput. Mater. Sci. 15‘ (3) (1999) 285–294.

[7] E. Samson, J. Marchand, Numerical solution of the extended Nernst–Planck model, J. Colloid Interface Sci. 215 (1) (1999) 1–8.

[8] J. Marchand, E. Samson, Y. Maltais, J.J. Beaudoin, Theoretical analysis of the effect of weak sodium sulfate solutions on the durability of concrete, Cem. Concr. Compos. 24 (3–4) (2002) 317–329.

[9] E. Samson, J. Marchand, J.-L. Robert, J.-P. Bournazel, Modeling ion diffusion mechanisms in porous media, Int. J. Numer. Mech. Eng. 46 (12) (1999) 2043–2060.

[10] E. Samson, J. Marchand, J.J. Beaudoin, Describing ion diffusion mechanisms in cement-based materials using the homogenization technique, Ceme. Concr. Res. 29 (8) (1999) 1341–1445.

[11] J. Marchand, E. Samson, Y. Maltais, Modeling microstructural alterations of concrete subjected to external sulfate attack, Material Science of Concrete—Special Volume: Sulfate Attack Mechanisms, American Ceram. Society, USA, 1999, pp. 211–257.

[12] E. Samson, J. Marchand, J.J. Beaudoin, Modeling the influence of chemical reactions on the mechanisms of ionic transport in porous materials—An overview, Cem. Concr. Res. 30 (12) (2000) 1895–1902.

[13] J. Marchand, E. Samson, Y. Maltais, Modeling ionic diffusion mechanisms in saturated cement-based materials—An overview, in: R.D. Hooton, M.D.A. Thomas, J. Marchand, J.J. Beaudoin (Eds.), Material Science of Concrete—Ion and Mass Transport in Cement-Based Materials, American Ceram. Society, USA, 2001, pp. 97–111.

[14] J. Marchand, Modeling the behavior of unsaturated cement systems exposed to aggressive chemical environments, Mat. Struct. 34 (238) (2001) 195–200.

[15] J. Marchand, E. Samson, Y. Maltais, R.J. Lee, Predicting the performance of concrete structures exposed to chemically aggressive environments—Field validation, 2nd Material Specialty Conference of the Canadian Society for Civil Engineering, Canadian Society for Civil Engineering, Montreal, 5–8 June, 2002, pp. 1–13.

[16] Y. Maltese, E. Ouelett, J. Marchand, E. Samson, Prediction of the long-term durability of lightweight aggregate concrete mixtures under severe marine environment, in: D.A. Lange, K.I. Scrivener, J. Marchand (Eds.), Advances in Cement and Concrete, Proceedings of the ECI conference, Engineering Conferences International, Brooklyn, NY, August 10–14, 2003, 2003, pp. 329–338.

[17] J. Marchand, E. Samson, Y. Maltese, R.J. Lee, S. Sahu, Predicting the performance of concrete structures exposed to chemically aggressive environment—Field validation, Mat. Struct. 35 (254) (2002) 623–631.

[18] E. Samson, J. Marchand, K.A. Snyder, Calculation of ionic diffusion coefficients on the basis of migration test results, Mat. Struct. 36 (257) (2003) 156–165.

[19] P. Gospodinov, R. Kazandjiev, T. Partalin, M. Mironova, Diffusion of sulfate ions into cement stone regarding simultaneous chemical reactions and resulting effects, Cem. Concr. Res. 29 (10) (1999) 1591–1596.

[20] M. Mironova, P. Gospodinov, R. Kazandjiev, The effect of liquid push out of the material capillaries under sulfate ion diffusion in cement composites, Cem. Concr. Res. 32 (1) (2002) 9–15.