

SULFATE-INDUCED DEGRADATION OF CEMENT STONE

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ABSTRACT

The study treats sulfate ion transport in cement stone and resulting material degradation. Those phenomena are essential for the safety assessment of concrete containers for nuclear waste disposal, for the rehabilitation of civil and industrial constructions, for preserving ancient cultural heritage etc. The process is studied theoretically and experimentally, and a survey of various experimental approaches is made. A diffusion model is designed, considering change of the material structure- void filling with ions and precipitants, liquid push-out of capillaries etc. Long-term experiments of cement stone saturation with sulfate ions are performed and material degradation is registered. Specimen degradation is explained, considering liquid motion within the material pores, which accompanies the transfer process.

INTRODUCTION

Cement-based composites have been always in researchers' focus, since they constitute the basic material for building industrial and civil constructions. Consider the unfavorable effect of air, water and soil pollutants on ecology and on structure durability. Regard also the strict requirements for safety of nuclear waste containers, means of protecting industrial and civil constructions, means of preserving ancient cultural heritage etc. Then, the assessment of the mechanism of chemical corrosion of cement-based composite materials becomes crucial. The work presents a survey of some experimental and theoretical studies of sulfate attack on cement stone, performed by our research group. The interest to sulfate aggression is verified by the fact that sulfates are common pollutants of environment, and local mineral waters are sulfate-containing, too. The results seem useful in following damage of cement-based structures which undergo sulfate attack and in assessing structure durability.

specimens in solutions of different sulfate concentration. The results are shown in Fig. 2 and discussed in detail by Gospodinov, Kazandjiev et al (1996).

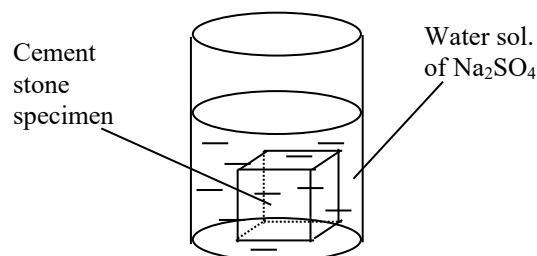


Figure 1. Scheme of specimen immersion in sulfate solution

EXPERIMENTAL STUDIES OF SULFATE ATTACK ON CEMENT STONE

Consider sulfate degradation of cement stone. Sulfate attack develops in time and to model it, one needs to perform long-term experiments of saturating cement stone specimens with sulfate ions. The scheme of specimen saturation is shown in Fig. 1. Cement-stone prisms and/or plates are immersed in water solution of Na_2SO_4 and kept there for a definite period of time. Note also that the concentration of the solution is different, so that its effect on material degradation can be assessed. Material is sulfate resistant cement 35, type "Devnya", whose chemical composition is given in Table 1. Material compression strength is found after keeping the

Table 1. Mineral composition of SRP cement, type 35 Devnya, (% by weight)

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

As said, Fig. 2 illustrates change of the compression strength in time, which displays local maximums and minimums. One

can explain this effect by material saturation with ions and chemical products, resulting in formation of micro-voids, i.e. in strength decrease. Then, subsequent void filling with compounds, i.e. subsequent material strengthening follows etc. The process seems to be periodical and reflects the change of material structure due to the sulfate attack. As said, the results are important for the assessment of the modification of cement stone structure. It is assumed that due to the sulfate attack, the specimen divides into two layers - an external, corrupted one and an intact internal core of cement stone. Moreover, using the approach given in (Mironova, 1997; Gospodinov et al 1998; Gospodinov et al 1999), one can find the elasticity modulus of the corroded material, knowing in advance that of the cement stone. Fig. 3 shows specimen division into layers.

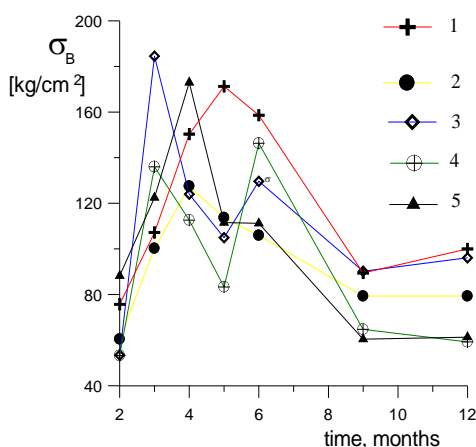


Figure 2 Change of material compression strength in time, depending on the solution concentration – 1-0.5 % Na_2SO_4 , 2 – 1% Na_2SO_4 , 3 – 3% Na_2SO_4 , 4- 5% Na_2SO_4 , 5 – 10% Na_2SO_4 ,

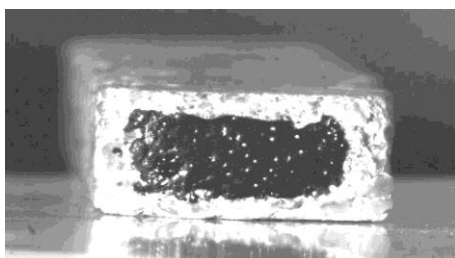


Figure 3. Specimen division into layers. Solution concentration-3%; immersion time – 9 months.

Another effect of structure modification of the cement stone is material swelling due to the sulfate aggression. Data on the change of specimen weight and density are given in Table 2 and are shown in Fig. 4 and Fig. 5, as depending on the solution concentration, while immersion time is 5 years. As seen, material density decreases with the concentration increase. This is an important experimental fact, attributing to the clarification of the modification of the cement stone structure and proving that although voids are filled with chemical products and ions, void formation is prevailing over

their filling. Hence, material is subject to total degradation in some cases, as the experiments show.

Table 2. Change of specimen weight and material density

Solution concentr. C, %	Cement stone density, $[\text{g}/\text{cm}^3]$	Specimen weight G, [g]	Weight difference ΔG , [g]
0	2.317	1.733	0
3	1.762	1.938	0.205
5	1.683	2.658	0.925
10	1.673	4.978	3.244

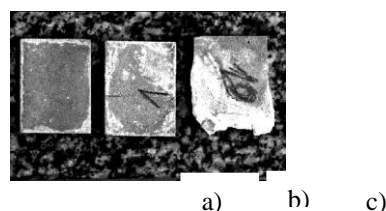


Figure 4. Material swelling and degradation due to the sulfate attack: a)-3% solution of Na_2SO_4 ; b)-5% solution of Na_2SO_4 ; c) 10% solution of Na_2SO_4 ;

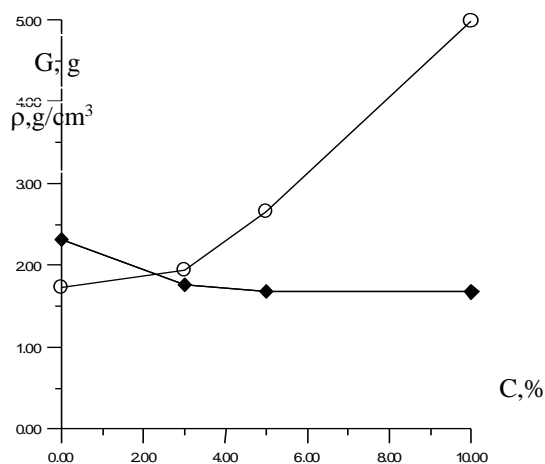


Figure 5. Change of specimen weight G and cement stone density ρ : o - G and \blacklozenge - ρ

Another important phenomenon resulting from material degradation is the formation of disturbances (cracks, voids, pores etc.) within the specimen and on its surface-Fig. 6.

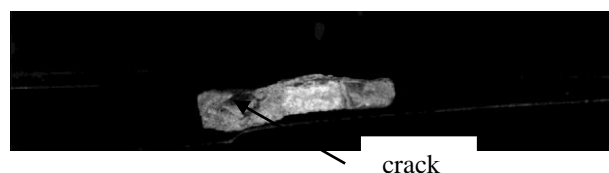


Figure 6. Crack formed on the specimen surface.

THEORETICAL MODEL OF SULFATE DIFFUSION

Their registration is important, since one can thus follow material degradation and change of the construction durability. To estimate the degradation mechanism, Kazandjiev et al (2002) propose a model of reconstructing material cracks, following cement stone immersion in solutions of different concentration.

Fig. 7.a shows a reconstructed crack, accounting for the different concentration of Na_2SO_4 , while Fig. 7.b – its location within the cement stone specimen. The estimation is qualitative but enables one to assess the mechanism of cement stone corruption. The reconstruction is done, involving cracks formed under solution sulfate concentration of 3%, 5% and 10% and using 3D pattern recognition.

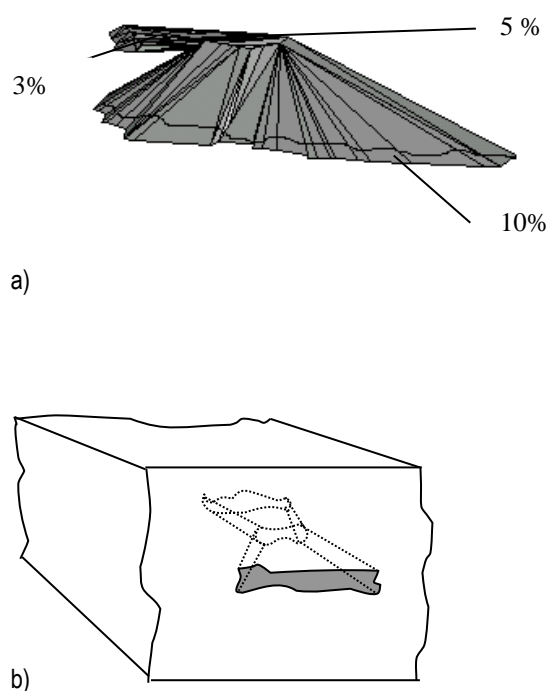


Figure 7. Reconstruction of a crack in cement stone specimen regarding the solution sulfate concentration; a) actual crack reconstruction; b) crack location

Modelling of corrosion due to ion aggression on cement composite is studied in (Atkinson, Haxby et al, 1988) and (Ratinov and Ivanov, 1977). Theoretical models are based on the diffusion equation, disregarding the heterogeneous chemical reaction occurring between the ions and the composite matrix. Diffusion of weak electrolytes in a porous medium is considered in (Sherwood, Pigford et al, 1982) and (Zaykov, Yordanskiy et al, 1984). The 1D steady case of pore filling in a catalyst and its effect on the reaction rate is considered in (Matros, 1982). A 2D model of the diffusion of sulfate ions in cement composite is proposed in (Gospodinov, Kazandjiev et al, 1999) and (Mironova, Gospodinov et al, 2002). We refine the model of ion transport, following several successive steps - account for material porosity, account for ion transport and accompanying chemical reactions and further account for the liquid push out of the cement stone capillaries. This is shown in (Mironova, Gospodinov et al, 2002) and (Kazandjiev, Gospodinov et al, 2002). Hence, we consider here 3D model of sulfate ion diffusion in a prismatic specimen of cement stone, which gives plausible results and generalizes 1D and 2D models, designed so far. Before immersion, the specimen has been kept for some time in drinking water. 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. They are formally treated as capillaries, shaped as straight circular cylinders and with symmetry axes parallel to the coordinate axes. As a result of the occurring heterogeneous chemical reaction, chemical products precipitate on the walls of the capillaries, partially filling them. Capillary filling and volume decrease yields liquid push out of the capillaries. This process is directed from the specimen internal area to the solution, i.e. its direction is opposite to that of diffusion.

Thus, the following balance equation for an elementary volume of the area is considered, which generalizes the 1D and 2D transfer processes:

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

where the spatial operators $\text{div}(\)$ and $\text{grad}(\)$ read

$$\text{div}(\) \equiv \sum_{i=1}^R \frac{\partial}{\partial x_i}(\)_i \quad (2)$$

$$\text{grad}(\) \equiv \sum_{i=1}^R \mathbf{j}_i \frac{\partial}{\partial x_i}(\)_i$$

and $R \in [1, 2, 3]$ is the spatial dimensions of the area considered. $x_1 = x$; $x_2 = y$; $x_3 = z$. The last term in the RHS of equation (1) is a source term, which models the heterogeneous chemical reaction between the capillary wall material and the sulfate ions in the solution. The term accounts also for the change of the reacting surface, due to capillary filling. Quantity $c(x_1, \dots, x_R, t)$ in equations (1)-(2) is the concentration current value, while $q(x_1, \dots, x_R, t)$ is the quantity of chemically reacted ions at point (x_1, \dots, x_R) and

at moment t . k is the rate constant of the heterogeneous chemical reaction and k_z denotes the coefficient of capillary filling. The effective coefficient of ion diffusion in the whole volume, accounting for pore filling is:

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

where

$$D = k_{\text{diff}} \exp[\beta(c(x_1, \dots, x_R, t) - 0.5c_0)] \quad (4)$$

The denominator k_{diff} in Eq. (4) 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, and for the capillary shape. Constant β is a fitting parameter, while c_0 is a concentration characteristic value - the concentration of the solution where the specimen is immersed and kept for a definite period of time. Projections V_i , $i = 1, R$, of velocity V in eq. (2) denote the average velocity of the liquid flow in the capillary, along axes x_i , $i = 1, R$.

The value of the solution concentration is given as a boundary condition on the interface surface "water solution - cement stone". Due to symmetry of the areas considered, symmetry conditions are given on boundaries $x_i = L_i / 2$, $i = 1, R$.

The initial ion concentration within the specimen volume is taken to be zero, since the specimen is previously kept in drinking water.

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

$$q(x_1, \dots, x_R, t) = \int_0^t k c(x_1, \dots, x_R, \tau) d\tau, \quad (5)$$

Consider the velocity component V_i , for fixed values of the other coordinates x_m , $m \neq i$. Then, the following integral along the capillary should be solved in the interval $[0, x_i]$.

$$V_i = \int_{\eta=U}^{\eta=G} -2kk_z(1 - k_z q)c d\eta, \quad (6)$$

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

Since the origin of the coordinate system is the symmetry center of the specimen, the velocity is zero for $x_i = 0$ and maximal for $x_i = L_i / 2$. The velocity direction coincides here with the positive direction of axis Ox_i . V_i is found by calculating the integral (6). Note that the lower integration limit here is $L_i / 2 - x_i$, and the upper integration limit is $L_i / 2$. Thus, one can get the velocity $V_i(x_1, \dots, x_R, t)$ at each point of the area under consideration. Velocity components $V_m(x_1, \dots, x_R, t)$, $m \neq i$, $m \in [1, \dots, R]$ are obtained in the same manner.

NUMERICAL SOLUTION

The equation of transfer (1)-(2), together with the boundary conditions and the initial condition, pose the initial non-steady boundary-value problem. It is completed by the integral relations (5) needed to find the quantity of chemically reacted ions, as well as by integral relations of type (6), needed to find liquid velocity field in the capillaries. An implicit difference scheme to solve numerically the formulated diffusion problem is used. The difference value problem, for a given time t , is reduced to the solution of a linearized system of algebraic equations, which has a diagonal and weakly filled matrix. The algorithm enables one to model numerically volume sub-areas with completely different conductivity - inert filler, inclusions, reinforcement etc. Due to problem non-linearity, an internal iteration process is used.

The numerical results are found for the following values of the dimension and dimensionless constants, as given in (Mironova, Gospodinov et al, 2002):

-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):

$$\beta = 0.2917 \text{ m}^3/\text{kg};$$

-constant of the chemical reaction rate:

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

- coefficient of pore filling:

$$k_z = 0.05 \text{ m}^3/\text{kg}$$

Those values are obtained for specimens, molded of cement paste of sulfate resistant Portland cement 35, type "Devnya" - see Table 1.

RESULTS AND DISCUSSION

As outlined above, the experimental evidence proves a number of mechanisms that develop in the cement stone - change of the material structure due to pore filling with ions and precipitants, liquid push out of the material capillaries, cement stone loosening due to the subsequent formation of material voids, resulting change of the material compression strength etc. One can plausibly account for these effects by using the model of ion transport (1)-(4) and relations (5) and (6).

The basic numerical results are found for a prismatic specimen, kept in 3% water solution of sodium sulfate. The content of the sulfate ions in the solution is 20.282 kg/m². The solution sulfate concentration is assumed to remain constant in time. We consider at first ion transport in a cement stone bulk without and with an arbitrary inclusion. The calculated isolines of sulfate concentration are given in Fig. 8 and Fig. 9.

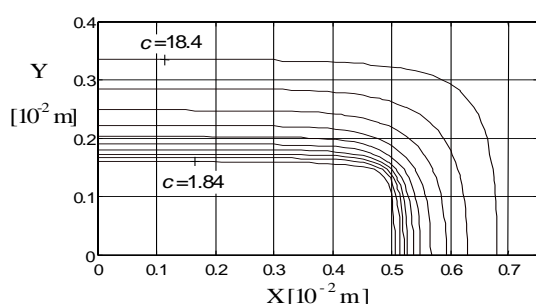


Figure 8. Isolines of sulfate concentration in a cement stone specimen without an inclusion

The comparison of both figures shows that the isolines deform due to the presence of an inclusion. Hence, some effects resulting from the sulfate attack can be established near the inclusion surface, where isolines compact as seen in Fig. 9.

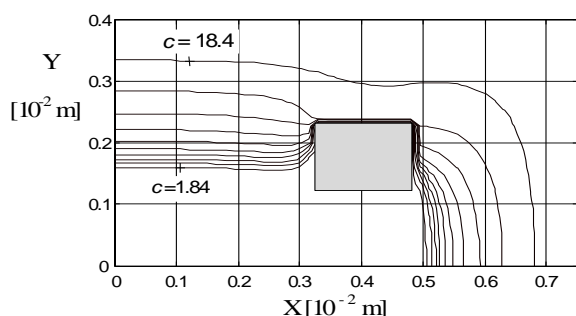


Figure 9. Isolines of sulfate concentration in a cement stone specimen with an inclusion.

Next, to illustrate the capabilities of the 3D model and those of the numerical algorithm, it is assumed that two cylindrical bodies (inert filler or reinforcement) are located in 1/8th of the specimen volume – Fig. 10.

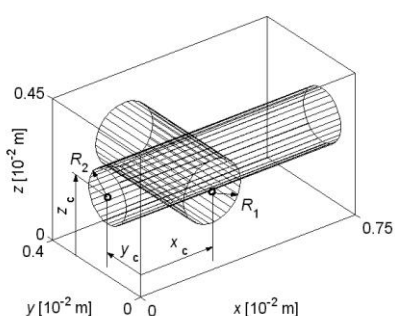


Figure 10. Schematic representation of the inclusion sub-area in 1/8th of the specimen volume

The calculations are performed for 3 and 6 months of specimen immersion in the solution. Fig. 11.a and Fig. 11.b show the isosurface corresponding to ion concentration within the specimen $c_{\text{const}} = 5 \text{ [kg/m}^3\text{]}$. The effect of the sub-

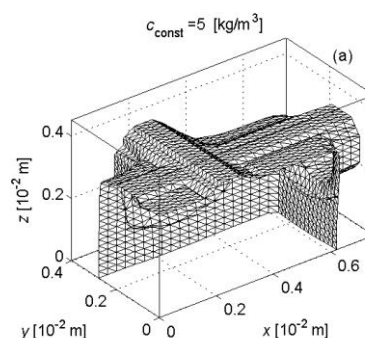


Figure 11.a. Isosurfaces for concentration $c_{\text{const}} = 5 \text{ [kg/m}^3\text{]}$ after 3 months of specimen immersion

area of inert filler on the shape of the isosurface is clearly visible.

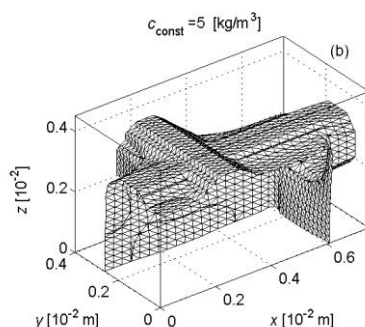


Figure 11.b. Isosurfaces for concentration $c_{\text{const}} = 5 \text{ [kg/m}^3\text{]}$ after 6 months of specimen immersion

CONCLUSIONS

The presented study outlines a mathematical model of ion transfer which comprises simultaneous effects, such as pore filling and liquid push out of the capillaries. It enables one to study processes of transfer of sulfate ions in cement stone, giving adequate explanation of some experimental data and allowing for a better account of the real conditions of mass transfer. The numerical algorithm developed is effective to solve different practical problems and to investigate real processes, which take place in structures or structural elements. The calculation results are in satisfactory agreement with the experimental evidence.

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