STRENGTH OF CEMENT BASED COMPOSITES AS DEPENDENT ON MATERIAL DETERIORATION DUE TO SULFATE ATTACK

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ABSTRACT. The study proposes an assessment of the strength change of cement stone (hardened cement paste) subjected to sulfate attack. Thin cement stone specimens being immersed and kept in water-sulfate solutions of different concentration are considered. The diffusion of sulfate ions into the material is experimentally and numerically assessed. Material strength changes due to pore filling with products of the running chemical reactions and resulting structure modification are followed. Good agreement with the experimental evidence is found.

KEY WORDS: Cement stone, composite, sulfate corrosion, diffusion, porosity

1. Introduction
As is known, sulfate corrosion is one of the unfavorable effects that cement-based materials undergo. It is due to the attack of sulfate ions and chemical compounds contained in industrially polluted air or water. Moreover, local mineral waters are also known for their aggressive “appetite” to cement based structures owing to the substantial contents of various malignant agents. Yet, we may state that the external sulfate attack is not completely understood, although that mathematical modeling is helpful in this respect. As noted in [1], [2] however, it cannot provide guidance to the resistance of cement based material to sulfate aggression, since the responsible mechanisms are varied and uncertain. On the other hand, more and profound studies of the phenomenon are needed set as a prerequisite by the vast construction activities running in areas where air and water pollution is significant, and the resulting chemical aggression on structures should not be disregarded. The present study is a continuation of our efforts to elucidate from theoretical and experimental viewpoint those effects. We propose a theoretical-experimental approach to corrosion of cement stone undergoing sulfate attack, which has more or less proved its plausibility, [3], [4]. For that purpose we solve numerically the subsequent diffusion boundary value problem and experimentally follow material
deterioration in time, recording resulting strength change and phenomenologically assessing the subsequent change of material structure.

2. Theoretical model of sulfate ions diffusion into the material

Consider sulfate attack on thin cement-stone specimens immersed in water solution of \( \text{Na}_2\text{SO}_4 \) as shown in Fig. 1 and assume 1D diffusion of sulfate ions into the material, [1].

The basic equation of the model reads:

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left( D_{\text{eff}} \frac{\partial c}{\partial z} - \frac{\partial}{\partial z} (Uc) - k(1 - k_zq)^2 c \right)
\]

where \( D_{\text{eff}} \) is the effective diffusion coefficient which has the form

\[
D_{\text{eff}} = D(1 - k_zq)^2,
\]

and \( D \) is the diffusion coefficient of the type

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

Here \( c \) is ion current concentration, \( c_0 \) is the solution initial ion concentration, \( U \) is the velocity of liquid motion within a material capillary, \( k(1 - k_zq)^2 \) expresses capillary filling with ions and chemical products and diffusion hamper, \( k_{\text{diff}} \), \( k_z \) and \( \beta \) are model parameters and \( z \) is the coordinate axis as show in Fig.1. The initial condition has the form \( c(z,0)=0 \), while the boundary condition specifies the solution sulfate concentration at the cement stone/liquid interface \( \Gamma \) (Fig. 1), i.e. \( c_\Gamma = c_0 \).

For a capillary whose symmetry axis coincides with \( z \), the quantity of chemically reacted ions \( q \) for fixed \( z \) and the sulfate solution average velocity \( U \) read

Fig. 1. Experimental set up
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(4) \[ q(z,t) = \int_{\tau}^{t} k c(z,\tau) d\tau, \quad U = \int_{\eta=z}^{\eta=L} -2k_k(1-k_q) c \, d\eta \]

The relations (1) - (4), together with the initial and boundary conditions, pose a non-steady boundary value problem. It is solved using an implicit difference scheme. The algorithm used is described in detail in [4]. The solution of the initial boundary value problem is reduced to the solution of a difference value problem for a linearized system of algebraic equations with a diagonal and weakly filled matrix, completing the algorithm by a numerical procedure for the calculation of the quantity of chemically reacted ions \( q \). The model is employed to disclose a number of phenomena observed during sulfate diffusion within a hardened cement paste.

3. Experimental set up

To follow experimentally the diffusion of sulfate ions into cement stone and the change of material porosity, we performed appropriate experiments. Thin cement-stone specimens, with dimensions 0.2 x 1 x 2 cm, were first immersed and kept in water for 28 days, until water filled their pores. Then, they were immersed and kept for 5, 10, 15, 20, 25 and 28 days and 6, 12, 24, 36, 48 and 60 months in water sulfate solutions with different concentration of Na\(_2\)SO\(_4\) - 1%, 3%, 5%, 8% and 10%. The material used for sample preparation was sulfate resistant cement, type PC - 35 – DO -SU Devnya according to the Bulgarian Standard, and the water/cement ratio was w/c = 0.30. The samples thus fabricated and exposed to sulfate attack were subsequently subjected to three-point bending till fracture, and the material bending strength \( \sigma_B \) was found. Note that 6 cement stone plates for each solution and for each given period of time were tested. The model parameters were:

- \( k_{\text{diff}} \) - coefficient of ion diffusion in the water solution;
- \( \beta \) - fitting parameter participating in Eq. (11);
- \( k \) - constant of the chemical reaction rate;
- \( k_z \) - coefficient of pore filling.

Data for the material bending strength were collected and processed using 2D spline interpolation. The surface \( \sigma_B(t,c) \) is plotted in Fig. 2. Local extremums of \( \sigma_B(t,c) \) are seen in the figure, as diffusion runs in time. For comparatively low concentration of the sodium sulfate - about 1%, there are four local maximums of \( \sigma_B(t,c) \) corresponding to immersion times ~ 1÷3, 18, 30 and 60 months. They can be assumed as resulting from the phase transformation and precipitation of the products of the chemical reaction on the capillary walls, yielding growth of the specimen effective cross section. Note also that the first maximum is the largest one. This can be interpreted as resulting from the lower sulfate concentration of the solution, where pressure on the capillary walls is not so large to yield material cracking but is large enough to guarantee ions penetration, material reaction with the sulfate, capillary filling with chemical products diminishing capillary cross sections and finally-material strengthening.
Then, drop of $\sigma_B(t,c)$ follows in time, since material durable exposure to sulfate aggression yields capillary pressure increase over the critical limit, resulting in crack formation and material weakening/fracture, expressed by the “gorge” in the plot. Next, the newly formed cracks and capillaries are again filled with chemical products resulting in second although smaller material strengthening and another local maximum of $\sigma_B(t,c)$. As a third step, $\sigma_B(t,c)$ starts diminishing, since old cracks grow, new ones occur and the material again weakens. The process proceeds periodically in time with expressed ups and downs of $\sigma_B(t,c)$ recorded, till final material destruction.
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Similar is the behavior of $\sigma_b(t, c)$ for other sodium sulfate concentrations. Fig. 3 shows the curve $\sigma_b(t,c_{\text{=}5\%})$ plotted for concentration of 5% of sodium sulfate. The plot is extracted from the general $\sigma_b(t,c)$ diagram in Fig. 2. Yet, maximums of $\sigma_b(t,c_{\text{=}5\%})$ are smaller as compared to those of $\sigma_b(t,c_{\text{=}4\%})$, which proves that the material strengthening is not so large. Pursuant to the above considerations, this is due to the earlier material deterioration resulting from the stronger aggressive agent (the water solution is with larger sulfate concentration). A circle borders the initial section of the plot in Fig. 3.

4. Results and analysis

We stress here on finding the moment of entire ions penetration into the material as the sulfate aggression goes on. For that purpose we solve numerically the diffusion problem (1) – (4). Plots of the sulfate ions concentration $c$ and the material chemically reacted quantity $q$ as depending on the time of specimen immersion $t$ are shown in Fig. 4.a, b and Fig. 4.c, d for time of immersion 30 days. Due to symmetry, the plots show results recorded within margins “liquid/solid interface-sample middle surface”.

Immersion time: 1 – 5 days, 2 – 10 days, 3 – 15 days

\[ C [kG/m^3] \]

\[ x \times 10^{-2} [m] \]

\[ \text{Immersion time: 1 – 5 days, 2 – 10 days, 3 – 15 days} \]

\[ a) \]
Immersion time: 4 – 20 days, 5 – 25 days, 6 – 30 days

Immersion time: 1 – 5 days, 2 – 10 days, 3 – 15 days
Immersion time: 4 – 20 days, 5 – 25 days, 6 – 30 days

d)

Fig. 4. Distribution of $c$ and $q$ within the material; 5% concentration of $\text{Na}_2\text{SO}_4$

To account for the depth of penetration of the aggressive agent into the material, it seems reasonable to follow most of all the behavior of $q$. This is so, since it reflects the largest degree of filling the material capillaries with chemical products as a result of the running chemical reactions between the cement stone and the sodium sulfate. As discussed above, the material may strengthen to a certain degree thanks to the deposition of a layer of chemical compounds on the capillary wall, specimen compaction and cross section increase. Then, the material may weaken due to subsequent pressure increase within the capillaries and resulting material cracking.
Schematically, the progress of this process is shown in the above Fig. 5. Note the sequence 1-5. At first, the material initially kept in clear water for 28 days, is then immersed in the sulfate solution and deposition of a layer of chemical compounds on the capillary walls starts (position 2 in the figure). The layer develops in time until capillary final obstruction and subsequent material cracking and fracture take place (positions 3-5).

As said, the above strengthening-weakening periodicity of the cement stone may be mostly linked with the chemically reacted quantity $q$, since it is the main factor of material structure modification due to the sulfate aggression. For that purpose we follow in time the depth of formation of the layer of chemical compounds within the initially “virgin” material capillaries (Fig.5), analyzing the distribution of $q$ within the sample for 5% sulfate concentration. We consider the coordinates of the cross points of the curve $q(t)$ with the abscissa of the coordinate system as shown in Fig. 4.b (points A, B, C, D, E and F), taking them as limits of the depth of penetration of chemically reacted ions within the cement stone for each time interval specified in the figure, in contrast to the sulfate ions floating in the water that fills the capillaries. The plot of that depth limit as dependent on the immersion time $t$
is shown in Fig. 6.a. Fig. 6.b shows magnification of area A (relation $\sigma_B(t)$) encircled in Fig. 3.

The juxtaposition of the two plots shows that:
- diffusion runs for about 1 month (30 days); for that time the curve $q(t)$ crosses the abscissa at a point lying on the sample symmetry axis, i.e. $q$ has spread over the specimen thickness covering the total capillary length (see curve 6 and point F in Fig. 4.d, as well as case 4 in Fig. 5 and the corresponding point $A_q$ in Fig. 6.a). At the same time, $\sigma_B$ grows as shown in Fig. 6.b, reaching the corresponding point $A_\sigma$, and the material strengthens;
- having reached the capillary bottom (curve 6 in Fig. 4.d), $q$ proceeds growing and filling the capillary (case 5 in Fig. 5). Yet, $\sigma_B$ increases for some time reaching maximum $\sigma_{max}$ in Fig. 6.b, and then drops. This is due to the internal
pressure exercised by chemically reacted quantity $q$ on the capillary walls, while pressure becomes large enough to cause material cracking and weakening.

Those considerations yield the conclusion that the proposed theoretical-experimental study of the diffusion transport in porous mineral composites outlines a more or less plausible picture of the related phenomena. Thus, one can get a better idea on material response to sulfate aggression, and the results may prove useful in assessing the reliability of cement based structures subjected to sulfate attack.

REFERENCES


