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The Effect of Sulfate Ion Diffusion on the Structure of Cement Stone

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Abstract

This paper studies sulfate ion diffusion into cement stone. The penetration of SO_4 ions into the material is followed experimentally by keeping cement paste specimens in an aqueous solution of 0·515% Na_2SO_4 for different periods of time. The depth of sulfate ion penetration is estimated by solving a non-steady equation of mass transfer, considering chemical reactions which take place in the material and experimentally determining the diffusion coefficient. Material structural response to sulfate diffusion is indirectly followed by determining the change in time of the cement stone compression strength and total porosity. © 1997 Elsevier Science Limited

Keywords: Sulfate diffusion, sulfate attack, compression strength, porosity.

OUTLINES OF THE PROBLEM

It is known that air or water pollution affects significantly the strength and durability of cement-based structures, and aggressive agents present in polluted air or water cause material corrosion. We consider here the mechanism of sulfate diffusion into cement stone and related effects of corrosion and damage. A number of results on this topic have been published and a lot more research is to be done, since the complex problems of diffusion–corrosion–structure changes of the material still need further elucidation—see, for example, Refs 1–4, and many others.[1–4] Sulfate attack on cement/concrete for different periods of time is considered in the literature, regarding various concentrations of the sulfate aqueous solution.[3–7] We study diffusion of sulfate ions into cement stone when the material is immersed and kept for different periods of time in a low concentration of sodium sulfate—a 0·515% Na_2SO_4 aqueous solution, which is characteristic for Bulgarian local ground waters. Such a concentration is equivalent to a content of 0·0362581 mol/l of Na_2SO_4 and at this level gypsum and ettringite are formed as products of the chemical reactions which take place in the material.[3]

To estimate the behaviour of a cement/concrete structure element, undergoing sulfate attack and related corrosion effects, we need:

to solve the direct non-steady problem of sulfate ion diffusion into a solid porous body for a known diffusion coefficient D, when accounting for the chemical reactions which take place in the material; note that the formation of a new phase does not depend on the current concentration at a definite point, but on the quantity of chemically reacted ions from the start of the process onwards;

to estimate the depth of the reacted zone where ions have penetrated and reacted with some cement constituents to form sulfate-containing compounds (gypsum and ettringite, mostly); these products fill the pores which results in material expansion, stressing and subsequent damage/fracture.

We tackle here the first problem, i.e. non-steady diffusion of sulfate ions into a cement paste specimen, accompanied by chemical reactions. The specimen is kept for different periods of time in a water solution of sodium sulfate. Our aim is to calculate the sulfate distribution within the specimen, considering free sulfate ions and newly formed sulfate-containing compounds. Determining the isolines of constant concentration and how the latter decreases through the specimen, we could estimate the thickness of the reacted zone. We consider the diffusion coefficient D as time dependent, determined on the basis of data on the change in time of cement stone porosity.

As for how the chemical compounds affect the cement structure and mechanical properties, we estimate these effects indirectly by experimentally following the change in time of cement stone porosity and compression strength.

THEORETICAL ASSUMPTIONS

Basic equations

The experimental scheme is given in Fig. 1. A rectangular cement paste prism $100 \times 10 \times 6$ mm is immersed and kept in a 200 ml aqueous solution of Na_2SO_4 at room temperature. We consider plane diffusion, since the specimen height H is much larger than the other dimensions. We denote by l_1 and l_2 the cross-section dimensions along the axes x and y. Due to symmetry, $0 \leq x \leq 0{\cdot}5{*}l_1$ and $0 \leq y \leq 0{\cdot}5{*}l_2$.

We assume that a non-steady equation of mass transfer is valid for the whole region. As noted, we consider the chemical reactions taking place in the material during diffusion. Then the diffusion equation can be written in the following form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{dx}\left(D\frac{\partial c}{\delta x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) - k_r c \qquad (1)$$

where c is the ion concentration in the specimen, D is the effective diffusion coefficient and k_r is a coefficient, expressing the rate of the chemical reactions which take place in the material.[8,9] The diffusion problem formulated above is a common one and its solution, for known D and k_r, presents no difficulty. What is essentially important, however, is the appropriate determination of the coefficients D and k_r for each specific case. We assume here that the diffusion coefficient D is non-steady and that it is proportional to the variation of the material porosity in time, where porosity depends on the quantity of reacted ions. Such an assumption is substantial, since it, although implicitly, accounts for the occurring material structure changes and related stress and damage/fracture effects.

Here $D(t)$ can be written as

$$D(t) = k_{dif} P(t)/P_0 \qquad (2)$$

where $P(t)$ is the total material porosity, experimentally determined as dependent on time, P_0 is the initial porosity and k_{dif} is a proportionality coefficient. The dependence $P(t)$ is followed experimentally and can be given approximately by the following linear relation, based on the experimental data — Fig. 2

$$P(t) = \begin{cases} P_0 + (P_1 - P_0) * t/T_1 \\ 0 \leq t \leq T_1 \\ P_1 + (P_2 - P_1) * (t - T_1)/(T_2 - T_1) \\ T_1 \leq t \leq T_2 \\ P_2 + (P_3 - P_2) * (t - T_2)/(T_3 - T_2) \\ T_2 \leq t \leq T_3 \\ P_3 \\ T_3 \leq t \end{cases}$$

However, there still remains a problem of how to determine k_{dif} and k_r, the coefficient of chemical reaction rate in eqn (1). We use in this

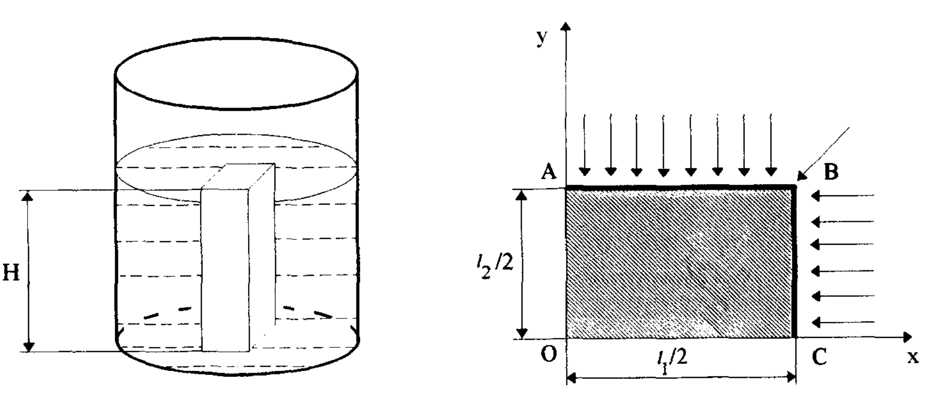

Fig. 1. Scheme of the experiment.

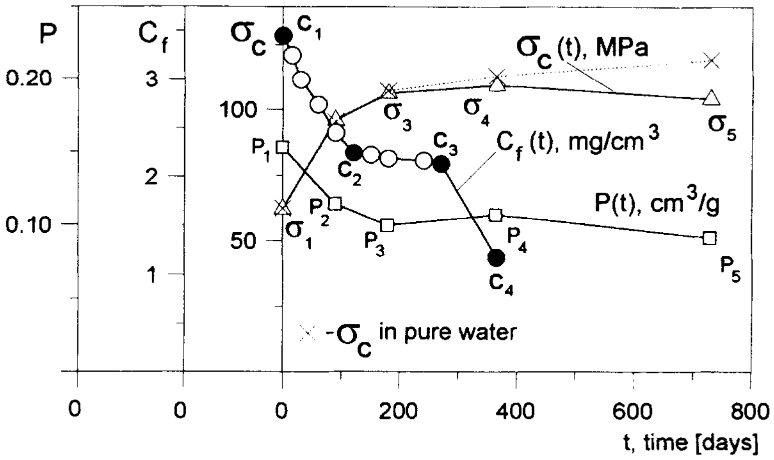

Fig. 2. Change in time of the characteristics $P(t)$, $C_f(t)$ and $\sigma_c(t)$.

study averaged values for k_{dif} and k_r, found on the basis of data obtained by Barovski *et al.*[10]

Initial and boundary conditions

We assume as an initial condition that the ion concentration is constant at zero time:

$$c(x,y,0) = c_0. \tag{3}$$

Table 1. Mineral composition of SRP cement, type 35 (% 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

The boundary conditions at the liquid/solid interface are given in the form

$$\begin{aligned} &c(t) = k_c \cdot c_f(t) \text{ for} \\ &x = 0{\cdot}5^* l_1; \\ &0 \le y \le 0{\cdot}5^* l_2 \text{ and} \\ &y = 0{\cdot}5^* l_2; \\ &0 \le x \le 0{\cdot}5^* l_1 \end{aligned} \tag{4}$$

Table 2. Data for $D(t)$ and k_r, SRPC 35 (w/c = 0·30) — Barovsky *et al.*[10]

Time (days)	*D, 10^{-8} (cm^2/s)*	*k, 10^{-7} (1/s)*
60	4·8	2·9
90	3·6	3·1
120	3·1	3·1
180	1·9	2·9

Table 3. Development of C_f, P and σ_c in time

Time (days)	*C_f (mg/cm^3)*	*P (cm^3/g)*		*σ_c (MPa)*	
		In solution	*In water*	*In solution*	*In water*
0	3·465	0·146	0·146	61·9	61·9
15	3·260	—	—	—	—
30	3·010	—	—	—	—
60	2·755	—	—	—	—
90	2·465	0·109	0·111	95·9	95
120	2·260	—	—	—	—
150	2·239	—	—	—	—
180	2·200	0·095	0·093	106·2	106·8
240	2·180	—	—	—	—
270	2·150	—	—	—	—
365	1·195	0·102	0·099	109·2	112·6
730	—	0·087	0·090	104·1	119

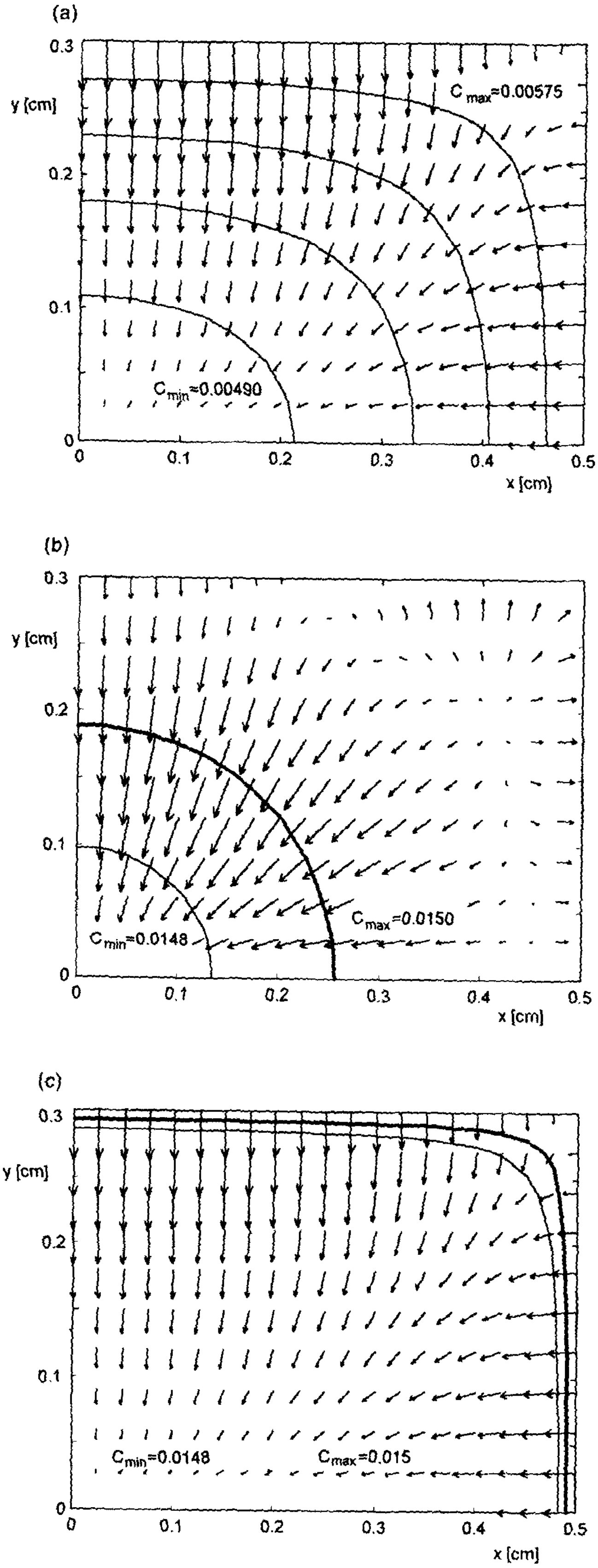

Fig. 3. (a) Isolines of constant concentration, mg/cm^3, time = 365 days, diffusion with chemical reaction. (b) Isolines of constant concentration, mg/cm^3, time = 28 days, diffusion without chemical reaction. (c) Isolines of constant concentration, mg/cm^3, time = 28 days, diffusion with chemical reaction.

where $c_f(t)$ denotes the experimentally found concentration of the liquid phase, while k_c is a coefficient, expressing the interfacial resistance. We assume here that $k_c = 1$, since we do not know its specific value. Finally, conditions of symmetry are assumed to hold for $x = 0$ and $y = 0$.

Numerical solution

The formulated problem is solved numerically as a non-steady difference scheme by using a rectangular grid, but performing an appropriate assembly of the difference functions. This enables one to solve simultaneously the obtained system of linearized algebraic equations at each time step by employing the method of decomposition, without splitting the scheme. The numerical procedure enables one to solve exactly the algebraic equations without additional iterations.

DATA FOR THE PROCESS OF MASS TRANSFER

We consider diffusion into a specimen of cement stone, prepared by using a commercial, sulfate resistant Portland cement 35, type 'Devnya' according to the Bulgarian standard. The cement mineral composition is given in Table 1. The specimen is prepared of a cement paste with water/cement ratio w/c = 0·3. The mix, after solidification in a casing, is aged for 28 days in water. The dimensions of the specimens thus fabricated are 100 × 10 × 6 mm and the specimens are kept for different periods of time in 200 ml of an aqueous solution of 0·515% Na_2SO_4. The initial concentration of the sulfate itself at room temperature is $c_f(0) = c_0 = 3{\cdot}465$ mg/cm, equivalent to a level of 0·0362581 mol/l of Na_2SO_4. The decrease of the solution concentration $c(t)$ in time is followed experimentally and the experimental data are interpolated for intermediate time values — Fig. 2 and Table 2. It is assumed that the quantity of ions lost from the solution is equal to the ion quantity gained by the cement paste specimen.

The change of the material compression strength in time is followed experimentally too and given in Fig. 2. The compression strength $\sigma_c(t)$ is determined using a standard testing procedure, after immersing and keeping the

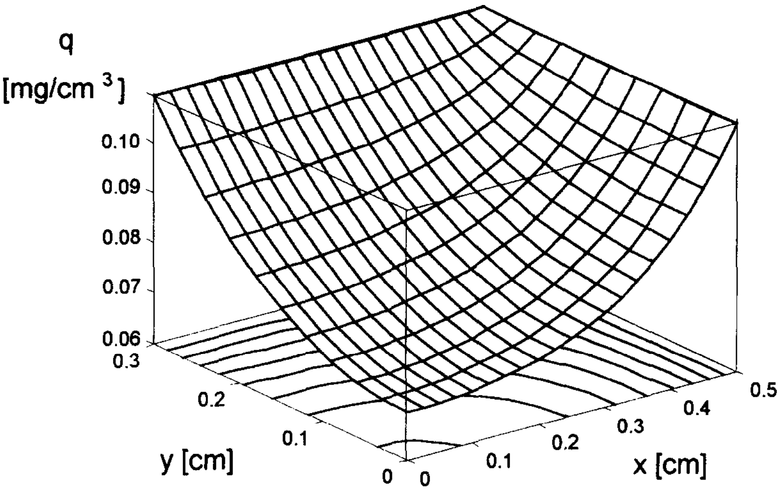

Fig. 4. Distribution of chemically reacted ions q, mg/cm^3, within the specimen cross-section, time = 365 days.

specimens in an aqueous solution of 0·515% Na_2SO_4 for different periods of time. Note that we obtain an averaged value of the compression strength, since there is no sharp boundary between the external layer and the core.

Total porosity $P(t)$ (and P_0) is measured by using a porosimeter, type 'Carlo Erba', on samples of the specimens with volume less than 1 cm^3. The proportionality coefficient k_{dif} in relation (2) has the same dimension as that of the diffusion coefficient D, since $P(t)/P_0$ is non-dimensional. The value of k_{dif}, used in the numerical experiment, is determined on the basis of an averaged value D^{av} calculated by using data for $D(t)$ (see Barovsky *et al.*[10]) and Table 2. The actual k_{dif} is obtained from eqn (2) for $t = 0$, i.e. $k_{dif} = D(0) = D^{av} = 3{\cdot}35 \times 10^{-8}$ cm^2/s. We assume an averaged value ($k^{av}{}_r$) for the coefficient of the chemical reaction rate k_r too, using again data of Barovsky *et al.*[10] (Table 2). Here $k^{av}{}_r = 3 \times 10^{-7}$/s. As noted above the sulfate attack results in the formation of gypsum and ettringite as products of the chemical reactions. These are the compounds which fill the pores of the material and cause structure changes and eventual material damage and fracture.

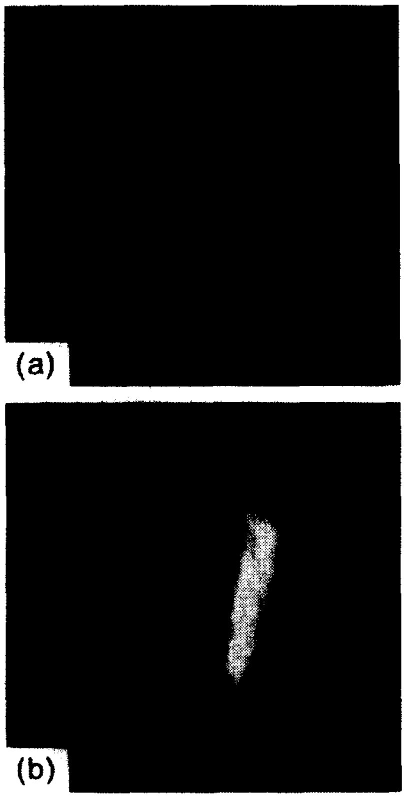

Fig. 5. (a) Cement paste specimen kept for 365 days in a 0·515% aqueous solution of sodium sulfate. (b) Cement paste specimen kept for 365 days in a 5% aqueous solution of sodium sulfate.

RESULTS AND DISCUSSION

The experimental data obtained are given in Table 3 and the calculated characteristics are shown in the corresponding figures.

The calculated front of penetrating ions into the cement stone and the lines of constant concentration are shown in Fig. 3(a), where chemical reactions are taken into account and the time of immersion is 365 days. Figures 3(b) and (c) show, for comparison, results of ion penetration, for time of immersion of 28 days, when chemical reactions are neglected and when these reactions are considered. To obtain the entire quantity of ions, having penetrated at a moment t to a given depth, we need to add to the current concentration of free (non-reacting) ions the integral

$$q(x,y,t) = \int_0^t k_r \cdot c(x,y,\tau)\, d\tau \qquad (5)$$

which gives the quantity of ions linked in chemical products (gypsum and ettringite). It is seen in the figures that if the chemical reaction is not taken into account, the specimen saturation with ions takes place very rapidly—the dense line corresponding to the isoline of $c_{max} = 0{\cdot}015$ mg/cm^3 in Fig. 3(b) (diffusion without a chemical reaction) is located much deeper within the specimen than the same isoline ($c_{max} = 0{\cdot}015$ mg/cm^3) for diffusion with a chemical reaction—Fig. 3(c). Moreover, if the chemical reaction is not considered, an opposite effect, i.e. ion diffusion back from the specimen and into the solution, can be established. This, however, is not in accordance with the experimental result. As is seen in the figures, when chemical reactions are considered diffusion slows down considerably. This is due, as already said, to the formation of gypsum and ettringite which fill the cement stone pores and hamper the ion penetration, causing material expansion and stressing.[3,11] Note that we do not specify here the separate formation and distribution of gypsum and ettringite within the specimen, but estimate generally the total amount of newly formed chemical compounds. Nevertheless, the comparison between Fig. 3(b) and 3(c) gives a plausible picture of the diffusion hamper owing to the sulfate attack and related structure changes.

As was said earlier, the quantity of ettringite and gypsum formed due to the sulfate attack is determined by the quantity of reacted ions at a given point, considering the process duration from its start to the considered moment of time and following relation (5). The distribution of the quantity of chemically reacted ions within the specimen cross-section is shown in Fig. 4. It corresponds to the current concentration given in Fig. 3(a) for a period of 365 days. It is clearly seen that the concentration of reacted ions attains its highest value at the cross-section boundary and $q(x, y, t)$ decreases when drifting away from the boundary.

Returning to Fig. 2, where the change of sulfate concentration, porosity and compression strength of the specimens in time is given, the analysis of the line character shows that when porosity decreases in time (section $P_1-P_2-P_3$ of the broken line $P(t)$), material compression strength grows (section $\sigma_1-\sigma_2-\sigma_3$ of the broken line $\sigma_c(t)$). This can be interpreted as a material overall strengthening due to pressure, which the chemical compounds (gypsum and ettringite, mostly) exercise on the pore walls, causing a subsequent material stressing.[4,5,11] During this time interval the quantity of diffusing ions grows (section c_1-c_2 of the broken line $c_f(t)$.

A section c_2-c_3 of the line $c_f(t)$ follows where the quantity of diffusing ions is kept almost constant. In this time interval the total porosity attains a minimum (point P_3 of the curve $P(t)$), while compression strength σ_c is kept almost constant (section $\sigma_3-\sigma_4-\sigma_5$ of the line σ_4). Such a correspondence can be interpreted as a saturation of the pores with chemical compounds and/or ions, and the material attains its maximum strength σ_4.

The growth of total porosity follows (section P_3-P_4 of the line $P(t)$). A comparison between P_3-P_4 and the corresponding section C_3-C_4 of the concentration line in the same figure shows that porosity increases with a much smaller gradient than the gradient, with which the ion concentration decreases. Such a discrepancy can be explained, as said, by specimen microcracking, i.e. a lot of ions have been 'lost' filling the microcracks, but the latter can hardly be registered by the porosimeter we use and porosity value is lower than the expected one. At the same time, compression strength $\sigma_c(t)$, as noted, remains almost constant. The assumption of a micro crack formation can be proved by a comparison between a specimen, being kept for 365 days in a 0·515% solution of sodium sulfate and such, being immersed for the same period of time in a 5% water solution of Na_2SO_4 (Fig. 5). It is seen in the figure that there are no visible macro cracks on the 0·515% cement stone specimen, Fig. 5(a), while such are clearly seen on the 5% specimen (Fig. 5(b)).

Finally, point P_5 of the porosity line follows, corresponding to a time of 730 days. The P_5 value is slightly lower than that of P_4. This can also be interpreted as micro and macro crack filling with ions and chemical products but the process is much slower than that during the first 365 days, since the quantity of ions in the solution has significantly decreased.

Data for the change of the material strength, when specimens have been kept in pure water, are also given in Fig. 2 and Table 3. The comparison between these strength lines shows that the compression strength of pure-water specimens grows, opposite to the compression strength of specimens, being kept in a water sulfate solution. This confirms the interpretation made above. Porosity change in time for specimens being kept in pure water is also followed. These data are given in Table 3.

CONCLUSIONS

The described approach allows for an estimation of the link between the mechanism of sulfate ion diffusion and the subsequent structural and strength changes, occurring in the cement stone—a phenomenon of substantial practical interest. The non-steady diffusion equation is solved after an appropriate choice of the coefficients of diffusion and chemical reaction rate. The phenomena occurring within the material during the process of sulfate diffusion are indirectly followed by an experimental determination of the material total porosity and compression strength for each time step.

We still need, however, data on the specific concentration of gypsum and ettringite. This can be a basis for the estimation of the depth of the reacted zone. Thus, the specimen could be considered as consisting of two layers: an external one affected by sulfate diffusion; and an intact internal core. The account for such a specific structure is of essential importance when determining the strength of cement/concrete structure elements, undergoing the combined effects of diffusion and mechanical loading. These will be the desired further steps of the analysis.

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