

# DAMAGE OF CONCRETE IN CHEMICALLY AGGRESSIVE ENVIRONMENT: A MICROMECHANICAL MODEL

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## ABSTRACT

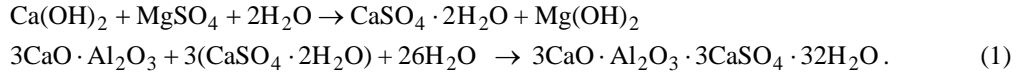
A micromechanical model is proposed to simulate the deformation process of hardened concrete exposed to chemical corrosion by sulfate ions migrating from the ground water. The model involves several coupled physico-chemical processes such as nonsteady diffusion with reaction, heterogeneous chemical reaction of ettringite formation, expansion of ettringite inclusions, microcracking of heterogeneous matrix (hardened cement paste with ettringite inclusions) and percolation of sulfates through a heavily deteriorated matrix. Fick's second law with a sink term (rate of chemical reaction) is used as a governing equation for diffusion of the sulfate ions. The topochemical reaction of ettringite formation is assumed to be controlled by diffusion of the sulfate ions migrating to  $C_3A$  grains through the increasing ettringite coat. It is shown that the full conversion of the tricalcium aluminate crystal into ettringite is a very fast process. Thus, a first order kinetic equation is assumed for the sink term. The equivalent inclusion method and the Eshelby solution is used to determine the eigenstrain of the expanding ettringite crystal in a microcracked mortar. The cracking mechanism is that of a penny-shaped crack generated by the hydrostatic crystallization pressure in a spherical pore surrounded by an elastic matrix. The dependence of the transport properties is studied in two regimes: the effective medium and the percolation regime. The damage dependent compliance and diffusivity tensors are determined using the Budiansky-O'Connell crack density parameter and the self-consistent method in regions with distributed microcracking. Once a defect cluster emerges the proposed description switches to that of the percolation model and the respective scaling laws for the elastic constants and diffusivity are employed. The final set of governing equations is obtained satisfying the equilibrium, compatibility and the boundary conditions. Having formulated the general damage model of the sulfate corrosion in concrete, an initial value problem is solved of expansion of a mortar specimen immersed in a sulfate solution.

## 1 INTRODUCTION

It is well known that hardened concrete may suffer corrosive damages if exposed to contact with aggressive environments. Among all types of chemical corrosion of portland cement concrete, the external sulfate attack has attracted attention of many researchers due to its frequent occurrence in engineering structures and severe consequences (e.g. Skalny [1]). The sulfate ions are often present in the ground water in corrosive concentrations. Once a structure or foundation is permanently or temporarily immersed in the ground water the sulfate anions diffuse through the pores of concrete and trigger complex chemical reactions with the active components of hardened cement paste. The transport of sulfate ions as well as mechanisms of sulfate expansion have been modeled by many authors in the past (e.g. Gospodinov [2], Tixier [3]). However, there is a lack of sound micromechanical approach to this problem as most of the proposed models treat the damage aspect of the sulfate corrosion within phenomenological setting. The primary goal of this paper is to formulate a comprehensive micromechanical theory of the damage induced by the external sulfate attack. At this stage of model development a rational explanation of the experimentally measured trends is deemed more important than a close fit with a particular set of test data.

## 2 MODEL

The sulfate ions diffuse through the concrete driven by the concentration gradient, encounter on their path calcium dioxide particles, react, form gypsum, and eventually the highly expansive *ettringite* ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ) on the surface of tricalcium aluminate ( $\text{C}_3\text{A}$ ) grains. The ettringite formation will be described below on the example of magnesium sulfate attack:



The first reaction is a through-solution reaction since it proceeds in the aqueous medium filling the pores. The difference in volume between gypsum (reaction product) and  $\text{Ca(OH)}_2$  (reactant) is readily accommodated by the original porosity of mortar and the additional space released by the dissolved  $\text{Ca(OH)}_2$ . The second reaction is often assumed to be of the solid-liquid or topochemical type. It occurs directly on the surface of  $\text{C}_3\text{A}$  crystal and may generate large swelling pressures if the space available locally is not sufficient for undisturbed growth of the ettringite layer.

The kinetics of ettringite formation in the presence of gypsum can be modeled as a steady diffusion process where a spherical  $\text{C}_3\text{A}$  grain with an initial radius  $r_{a0}$  is exposed to constant supply of sulfate ions. As the reaction progresses, a layer of ettringite forms on the outside of the shrinking part of the  $\text{C}_3\text{A}$  grain. Solving the Fick I law while accounting for the stoichiometry of reactions (1) it follows that the rate of ettringite production ( $r_e/r_{a0}$ ) is rapid initially, and gets slower as time elapses (see Figure 1) due to increasing thickness of the ettringite layer. The time necessary to fully convert the  $\text{C}_3\text{A}$  grain into ettringite is very short in comparison to that of diffusion of sulfate ions through hardened concrete. Consequently, it seems reasonable to conclude that the actual rate-controlling mechanism is the diffusion of sulfate ions through hardened concrete, the rate of ettringite production being a secondary effect.

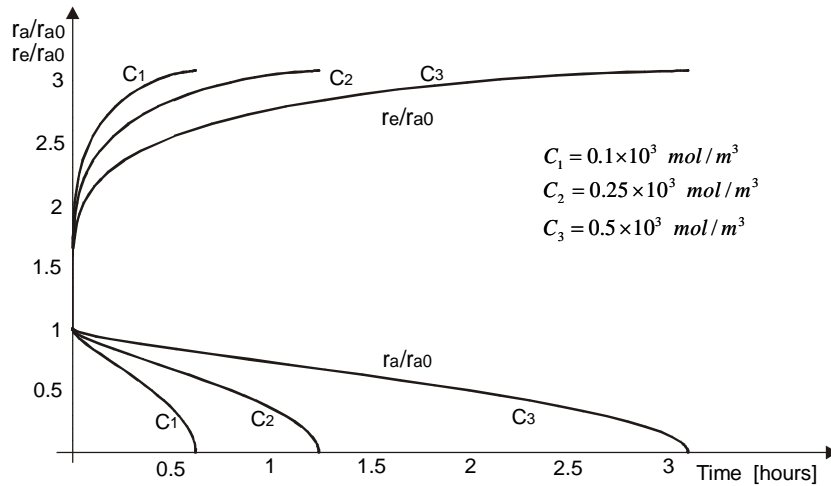


Figure 1: Conversion of  $\text{C}_3\text{A}$  crystal into ettringite (steady diffusion process)

To compute the volumetric strain  $\varepsilon^v$  induced by the expanding ettringite inclusion it is first necessary to determine its current radius  $r_e$  by integrating the kinetic equation of ettringite formation (cf. Pommersheim [4], Basista [5]). The volumetric strain then reads

$$\varepsilon^v = (r_e / r_{a0})^3 - 1 = (d - 1) \left[ 1 - (r_a / r_{a0})^3 \right], \quad d = d_a / (1 - \phi_e) d_e, \quad (2)$$

where  $d_a$ ,  $d_e$  are the molar densities of  $C_3A$  and ettringite, respectively and  $\phi_e$  is the porosity of the ettringite layer. The maximum expansion takes place when the whole  $C_3A$  grain is consumed ( $r_a = 0$ ), and is thus given by  $\varepsilon_{\max}^v = d - 1$ . Since the ettringite has different elastic properties than the surrounding matrix (hardened cement paste), the total eigenstrain within the ettringite crystal (inhomogeneity in Mura's nomenclature, [6]) consists of two terms

$$\varepsilon_{ij}^{**} = \varepsilon_{ij}^* + \varepsilon_{ij}^{eq} = \frac{1}{3} \varepsilon^v \delta_{ij} + \varepsilon_{ij}^{eq}, \quad (3)$$

where  $\varepsilon_{ij}^*$  is the inclusion own eigenstrain (free expansion strain) while  $\varepsilon_{ij}^{eq}$  is the equivalent eigenstrain resulting from the disparity in elastic constants between the matrix and inclusion. The thermal expansion strain associated with heat released during the topochemical reaction (1) is neglected here. If there is no external loading the expression (3) takes the following form (Basista, [5])

$$\varepsilon_{kk}^{**} = \frac{3(1-\nu)K^*}{(1+\nu)K^* - (4\nu-2)K} \varepsilon_{kk}^* = \beta(\omega) \varepsilon_{kk}^*, \quad (4)$$

where \* refers to the ettringite inclusion while the non-indexed moduli denote the effective continuum,  $\omega = N \langle a^3 \rangle$  is the Budiansky-O'Connell crack density parameter. In the present model the SCM estimates were used for  $K$  and  $\nu$ , (Basista, [5]).

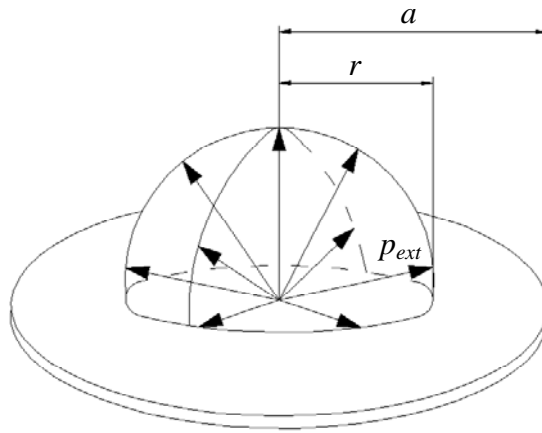


Figure 3: Penny-shape microcrack due to ettringite swelling pressure.

The expanding inclusion exerts uniform radial pressure in the surrounding matrix. Its maximum value is attained when the reaction (1) is completed, and is equal to

$$p_{ext} = \frac{-E(\nu+1)(1-2\nu^*)K^*(d-1)}{E(4\nu-2)(1-2\nu^*)-E^*(1-2\nu)(\nu+1)}. \quad (5)$$

Assuming that a small notch exists around the spherical ettringite crystal (Figure 3), the stress intensity factor at the penny-shape crack perimeter is

$$K_I = \frac{p_{ext}}{\sqrt{\pi a}} \left( a - \frac{a^2 - r^2}{2r} \ln \left| \frac{a+r}{a-r} \right| \right). \quad (6)$$

Spatial and temporal distribution of sulfate ions in the hardened concrete is governed by a diffusion-reaction equation (Fick's II law) with the initial and boundary conditions as follows:

$$\frac{\partial c}{\partial t} = \nabla \cdot (\mathbf{D} \nabla c) - 3kc, \quad c(x,0) = 0; \quad c(-w_0,t) = c(w_0,t) = c_0; \quad \partial c / \partial x(0,t) = 0, \quad (7)$$

where  $c$  is the sulfate concentration,  $c_0$  its initial value,  $\mathbf{D}$  the effective diffusivity tensor,  $k$  the reaction constant,  $w_0$  the half-width of a prismatic specimen. Eq (7) has been solved numerically using the FEM. In Figure 4 exemplary solutions of the diffusion-reaction equation (7) are depicted as concentration profiles for different values of  $D$  and  $k$ . The curve marked with  $D = D(\omega)$  represents solution of eqn (7) coupled with the microcracking mechanism shown in Figure 3. The computations were performed for distributed damage, i.e. the SCM estimates were used for  $E(\omega)$ ,  $\nu(\omega)$ ,  $D(\omega)$  and no microcrack clustering was yet accounted for.

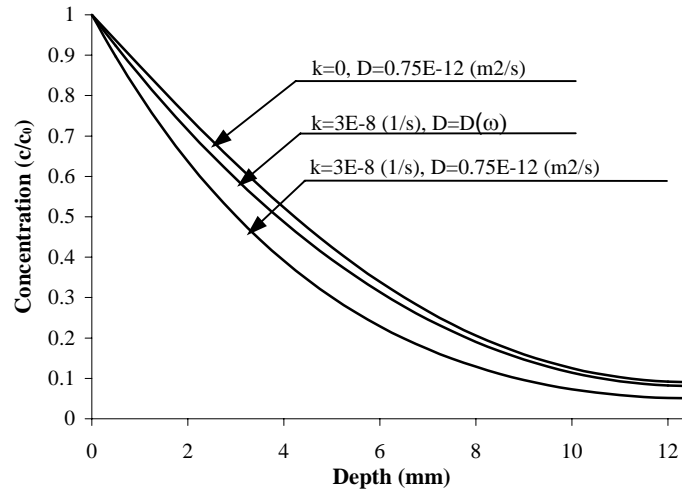


Figure 4: Sulfate concentration profiles for varying diffusivity and reaction constant;  $D = D(\omega)$  denotes solution coupled with the microcracking model of Figure 3.

In fact the dependence of elastic constants and diffusivity on the randomly nucleating microdefects should be studied in two distinct regimes: the distributed microcracking regime and percolation regime. To account for the diffusion through the matrix containing penny-shaped microcracks and the percolation through the spanning cluster of microcracks, a parallel connection between the two transport phenomena was postulated in Krajcinovic [7], i.e.

$$D = D_0 \left( 1 + \frac{32}{9} \omega \right) + D_p, \quad (8)$$

where:  $D_p = D_0 \frac{(\omega - \omega_c)^2}{\omega - \omega_{ec}}$  for  $\omega_c < \omega < \omega_{ec}$  or  $D_p = 0$  for  $\omega < \omega_c$ , or  $D_p = \infty$  for  $\omega > \omega_{ec}$ .

In eqn (8)  $\omega_c$  stands for the conduction percolation threshold at which a spanning cluster traverses the specimen forming a worm-hole, while  $\omega_{ec}$  stands for the elastic (rigidity) percolation threshold at which the cluster transecting the volume makes the material macrostiffness vanish and the diffusion becomes practically instantaneous. As for the elastic moduli, the SCM estimates are valid for dilute density of microcracks. Once microcracks clusters start to emerge, the proposed approach switches to that of the percolation model, the main task being the determination of elastic percolation threshold and the scaling law for the elastic modulus (see Krajcinovic [7] for details).

Having determined the local stress and strain fields around ettringite inclusions as well as the effective elastic moduli, the macrostrains were mapped on the macrostresses according to

$$\boldsymbol{\varepsilon} = \mathbf{S}(\omega) : \boldsymbol{\sigma} + f \boldsymbol{\varepsilon}^{**} \quad (9)$$

where  $\mathbf{S}(\omega)$  is the effective compliance tensor reflecting the ettringite buildup and microcracking,  $f$  is volume density of ettringite inclusions,  $\boldsymbol{\varepsilon}^{**}$  the total eigenstrain tensor defined in eqn (3),  $\boldsymbol{\sigma}$  is the compressive stress due to the beam-column action of the elastic matrix. In addition to the equations listed so far, the governing set involves the equilibrium, compatibility and boundary conditions for a particular initial boundary-value problem.

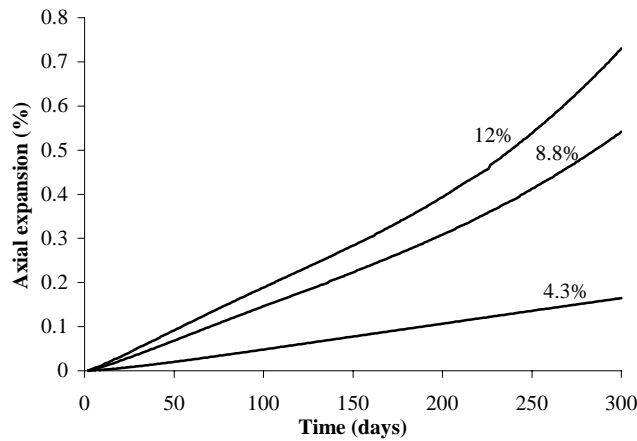


Figure 4: Expansion of mortar specimens in sulfate solution for different  $C_3A$  contents.

The proposed model was implemented numerically to compute the expansion of a mortar prismatic specimen immersed in a mixed solution of magnesium and sodium sulfates of equal concentration 0.176 mol/l. It is a symmetric initial boundary-value problem with one-dimensional diffusion of sulfates. The objective of this numerical example was to determine the overall linear expansion of the specimen vs. time. The obtained results are depicted in Figure 4 for different amounts of  $C_3A$  in the cement. These curves reproduce qualitatively the experimentally observed behavior of the mortar specimens under external sulfate attack (cf. Ouyang [8]). However, the present model is still being refined to arrive at a modeling tool with quantitative predictive capabilities.

### 3 CLOSING REMARKS

A micromechanical model has been developed for the progressive damage in hardened concrete induced by the external sulfate attack. This is a multifield model combining transport of sulfate ions, a topochemical reaction on the surface of active compounds of hardened concrete, stress and strain fields due to expanding inhomogeneities (ettringite crystals), microcracking of elastic matrix and percolation. The governing equations have been implemented numerically using the FEM and applied to reproduce expansions of mortar specimens exposed to constant concentration of sulfates.

### 4 REFERENCES

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