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A BIPHASE MODEL FOR CONCRETE SUBJECT TO SULFATE ATTACK

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Abstract. In the present paper we focus on the numerical simulation of degradation in concrete due to the development of secondary ettringite in the hardened material (delayed ettringite formation or DEF). This chemical reaction, causing expansion and microcracking of the material, can occur due to an external or internal sulfate attack. A chemical-diffusion model allows for the computation of the amount of expansive products of the reaction. The concrete affected by DEF is then represented as a two-phase material made of a solid skeleton and an expanding phase, which exerts a pressure capable of damaging the concrete surrounding the reactive sites. The model is validated on the basis of experimental data on cement mortar specimens reported in the literature.

1 INTRODUCTION

The delayed ettringite formation is one of the phenomena which may cause swelling and severe microcracking in concrete. This expansive chemical reaction takes place between the reacting calcium aluminates of the cement paste and the sulfates (already present in the material or coming from the environment) and can occur in massive structures where the temperature at early age is large [1] and/or in concrete structures in contact to external sulfate solutions (e.g nuclear waste deposits or tunnels in contact with sulfate-rich soils [2]). In those situations, the durability analysis requires two main ingredients: a proper diffusion-reaction model, for the computation of the amount of expansive reaction products, and a mechanical model for the prediction of swelling and material degradation.

In [3] a detailed formulation of the reactive diffusion model is provided, while a simplified empirical relation is used to compute the damage of the material. In [4] a meso-mechanical approach, describing micro-cracks formation with zero-thickness interface elements, coupled with a diffusion-reaction analysis is proposed.

In this paper we implement the formulation of the reactive-diffusion problem developed in [3] to compute the sulfate and aluminates concentrations and the amount of formed ettringite. Following a weakly coupled approach, similar to that proposed in [5], [6] for concrete affected by the alkali-silica reaction, the ettringite content is assumed as the input variable for a subsequent chemo-elastic damage analysis. In the framework of the Biot's theory [7], the material is represented as a two-phase medium: the solid skeleton and the expansive reaction products. The mechanical degradation is described by a phenomenological isotropic damage model.

The reactive-diffusion model is first applied to compute the ettringite formation in cement mortar specimens subject to external sulfate attack and the influence of the depletion of aluminates on the sulfates diffusion is studied. Then, to assess the capability of the chemo-damage model to account for the influence of different stress conditions on the expansion induced by the DEF, the tests reported in [8] on restrained specimens cured at high temperature and subject to internal sulfate attack are simulated.

2 REACTION-DIFFUSION MODEL

When concrete is in contact with sulfate solutions, sulfate ions diffuse into the cement paste and different chemical reactions can occur. According to several Authors (see e.g [3], [9]) the most relevant reactions can be divided into two sets: first the penetrated sulfates react with the available portlandite to form gypsum ($C\overline{S}H_2$), then the gypsum reacts with the different calcium aluminate phases of the cement paste to form ettringite $C_6A\overline{S}_3H_{32}$ (using the usual cement chemistry notation $C \equiv CaO, A \equiv Al_2O_3, \overline{S} \equiv SO_3, H \equiv H_2O$).

As proposed in [3], all the chemical reactions leading to delayed ettringite formation are lumped in a single expression as

$$C_{eq} + q \cdot \overline{S} \longrightarrow C_6A\overline{S}_3H_{32} \tag{1}$$

where $C_{eq} = \sum_{i=1}^{3} \gamma_i P_i$ is an equivalent grouping of the reacting calcium aluminates ($P_1 = C_4AH_{13}, P_2 = C_4A\overline{S}H_{12}, P_3 = C_3A$) and q denotes the weighted average stoichiometric coefficient of the sulphate phase. Coefficients γ_i are defined as the ratio between the molar concentration c_i of each aluminate phase per unit volume of solid (mol/m^3) and the total aluminate content

$$\gamma_i = \frac{c_i}{\sum_{i=1}^{3} c_i} \tag{2}$$

During the process of delayed ettringite formation the calcium aluminate concentration decreases and this phenomenon affects the diffusion process of sulfates. A coupled diffusion-reaction approach allows to compute the molar concentration $s = s(\mathbf{x}, t)$ of sulfate $\overline{S}$ and the molar concentration $c_{eq} = c_{eq}(\mathbf{x}, t)$ of calcium aluminate C_{eq}, $\mathbf{x}$ being the spatial coordinate and t the time.

Assuming Fick's law of diffusion and denoting by D_s the diffusion coefficient for the sulfate concentration and by k the rate of take-up of sulfates one obtains the following governing system

$$\frac{\partial s}{\partial t} = \mathrm{div}\left(D_s(\mathrm{grad}\,(s))\right) - k\ c_{eq}\ s \tag{3}$$

$$\frac{\partial c_{eq}}{\partial t} = -\frac{k\ c_{eq}\ s}{q} \tag{4}$$

Note that no diffusion term is present in the second equation since aluminate can not move in the cement paste.

To integrate the system of differential equations (3)-(4), one should specify proper boundary conditions for the sulfate concentration s and initial conditions for both sulfate and aluminate concentrations.

A simpler formulation can be obtained neglecting the aluminate depletion caused by the ettringite formation. In this case c_{eq} is assumed constant and only equation (3) should be considered with a linear reaction term, corresponding to a first-order chemical reaction

$$\frac{\partial s}{\partial t} = \mathrm{div}\left(D(\mathrm{grad}\,(s))\right) - \bar{k}\ s \tag{5}$$

with $\bar{k} = kc_{eq}$.

3 CHEMO-DAMAGE MODEL

In the framework of the Biot's theory [7], the cement mortar or the concrete affected by delayed ettringite formation is represented as a two-phase medium: the solid skeleton and the reaction products. The total stress $\boldsymbol{\sigma}$ is then given by the sum of the effective stress $\boldsymbol{\sigma}'$ acting on the solid skeleton and the pressure p exerted by the expansive products

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}' - bp\mathbf{1} \tag{6}$$

The mechanical response of concrete skeleton is described by an elastic model with isotropic damage D relating the effective stress to the total strain $\boldsymbol{\varepsilon}$. The internal pressure is linked via the Biot's modulus M and the Biot's coefficient b to the total volumetric deformation ε_v and to the volumetric expansion ζ due to ettringite formation

$$\boldsymbol{\sigma}' = (1-D)\boldsymbol{d} : \boldsymbol{\varepsilon}; \qquad p = (1-D)[-bM\varepsilon_v + M\zeta] \tag{7}$$

The time evolution of the internal expansion ζ is computed through the diffusion-reaction model described in the previous section. Assuming that ettringite is the only reaction product governing the expansion under stress free conditions, from (6) and (7), denoting by K the skeleton bulk modulus, one obtains

$$\zeta = \frac{K + Mb^2}{Mb}\varepsilon_v^{chem} \tag{8}$$

The volumetric strain ε_v^{chem} is obtained from the amount of reacted calcium aluminate $c^{reac} = c_{eq}^0 - c_{eq}$ (i.e. the difference between the initial amount and the one obtained from (3)-(4) at the considered time) and the volume change associated with it

$$\varepsilon_v^{chem} = c^{reac}\alpha - f\Phi_0 \tag{9}$$

where f is the fraction of capillary porosity that has to be filled before any expansion occurs, Φ_0 is the initial porosity and α accounts for the volumetric change due to the lumped reaction (1)

$$\alpha = \sum_{i=1}^{3} \frac{\Delta V_i}{V_i} m_i \gamma_i = \sum_{i=1}^{3} \left(\frac{m^{ettringite}}{m_i + a \cdot m^{gypsum}} - 1\right) m_i \gamma_i. \tag{10}$$

In the above equation $m_i, m^{ettringite}$ and m^{gypsum} are the molar volumes $[m^3/mol]$ of the aluminate phase P_i, of the ettringite and of the gypsum, respectively, and a is the stoichiometric coefficient involved in the reaction.

As in [5], the activation of the damage in concrete depends on the macroscopic stress tensor and on the pressure through an "inelastic effective stress" defined as $\boldsymbol{\sigma}'' = \boldsymbol{\sigma} + \beta p \mathbf{1}$ with $\beta \leq b$. The activation of the damage is governed by the loading-unloading condition:

$$f_D \leq 0; \qquad \dot{D} \geq 0; \qquad f_D \dot{D} = 0; \tag{11}$$

The damage activation function f_D depends on the first invariant of the inelastic effective stress tensor I_1 and on the second invariant of the inelastic effective deviatoric stress tensor J_2

$$f_D(\boldsymbol{\sigma}'') = J_2 - a_1 I_1^2 + a_2 I_1 h(D) - a_3 h(D)^2 \leq 0; \qquad h(D) = (1 - D^{a_4})^{0.75} \tag{12}$$

where $h(D)$ is the softening function and $a_j,\ j = 1, 4$, are non-negative parameters to be calibrated through experimental data.

4 NUMERICAL MODELLING OF SULFATE ATTACK

To compute the mechanical response of mortar and concrete specimens affected by DEF we developed a weakly coupled numerical approach in the Matlab environment.

First the reactive-diffusion problem is numerically solved by the finite element method to compute the history of sulfate and aluminate concentration and the corresponding ettringite formation and volumetric expansion at each point. Both s and c_{eq} are modeled in terms of nodal values, using four-nodes tetrahedrons.

Then a non-linear mechanical analysis is performed to compute strains, stresses and damage at each point for given variation of ettringite content.

In this weakly coupled approach the diffusivity D_s is assumed as a constant, neglecting its decrease due to the filling of the pore during ettringite formation and its increase due to damage development.

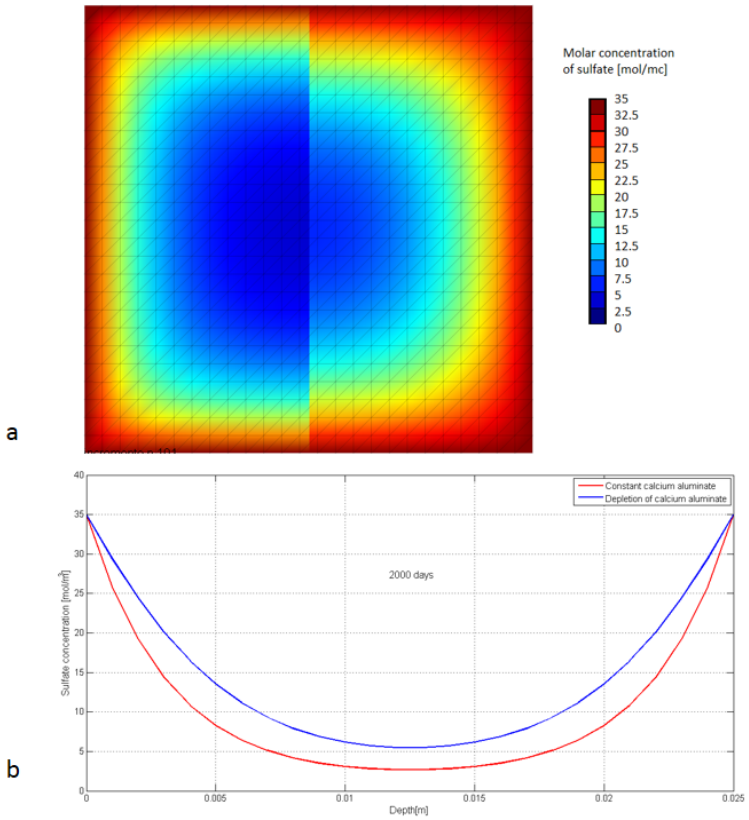

Figure 1: a) Molar concentration of sulfate in the cross section of the specimen at 2000 days (rigth part: considering depletion of aluminates, left part: neglecting depletion of aluminates), b) profiles of molar concentration of sulfate along the middle line.

4.1 External sulfate attack

We first focus on the study of the process of diffusion and reaction of sulfate and we simulate the external sulfate attack experiments on mortar prisms performed in [10] and also considered by [9]. The experimental campaign was carried out on $25 \times 25 \times 285 mm^3$ mortar prisms immersed in 5% Na_2SO_4 solution made of CEM I 52.5R. Simulations of the reaction-diffusion process were performed in 3D considering three symmetry planes and considering the depletion of alluminates, and thus solving the two ions formulation (3)-(4), or neglecting it and thus solving the single ion equation (5).

The reaction and diffusion parameters used in the simulation are the same as in [9] $D = \ 1.7 \times 10^{-1}\ mm^2/day$ and $k = 8 \times 10^{-5} m^3\ (mol/day)$. A constant sodium sulfate concentration is imposed at the outer surfaces and no flux is allowed through the symmetry planes. Figure 1a shows the comparison between the two-ions and single-ion solution in terms of contour plot of the sulfate concentration in the middle section of the specimen (rigth part: considering depletion of aluminates, left part: neglecting depletion of aluminates), figure 1b displays the two different concentration curves along the mid-line of

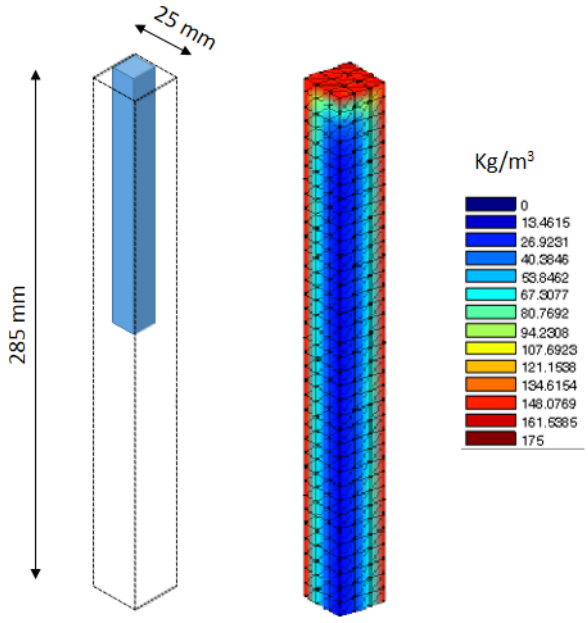

Figure 2: Ettringite distribution at 2,000 days considering depletion of aluminates.

the cross section. It can be seen that the predicted penetration front of sulfate is higher in the case of the two ions formulation: the depletion of aluminates reduces the sulfate consumption due to the reactive term $k\ c_{eq}\ s$ in equation (3) and thus results in a higher diffusion. Figure 2 shows the ettringite distribution obtained in the simulations at 2,000 days of exposure considering depletion of aluminates.

4.2 Mechanical response of the specimens subjected to internal sulphate attack

To validate the proposed chemo-mechanical model we simulated the experimental tests presented in [8]. Those tests were performed on mortar prism in which 3.1% of Na_2SO_4 was added to the mixture water. The specimens where cured at high temperature to allow for DEF; then some of them were placed in restraint devices in order to compare the expansion under stress-free and loaded conditions. In this case an internal sulfate attack occurs, the sulfate concentration is homogeneous in space and varies in time due to the reaction with the aluminates. The concentrations of sulfate and aluminates can still be computed from (3)-(4), dropping the diffusion term. The comparison between the experimental curves and numerical simulations is shown in Figure 3 in terms of radial and longitudinal strains (blue: free expansion, red: restrain bars $\oslash = 2mm$, black: restrain bars $\oslash = 5mm$). The model is able to correclty simulate the reduction of the asymptotic longitudinal expansion due to the compressive stress acting on the restrained specimens. The real strain evolution at early stages of the reaction is smoother than the one predicted

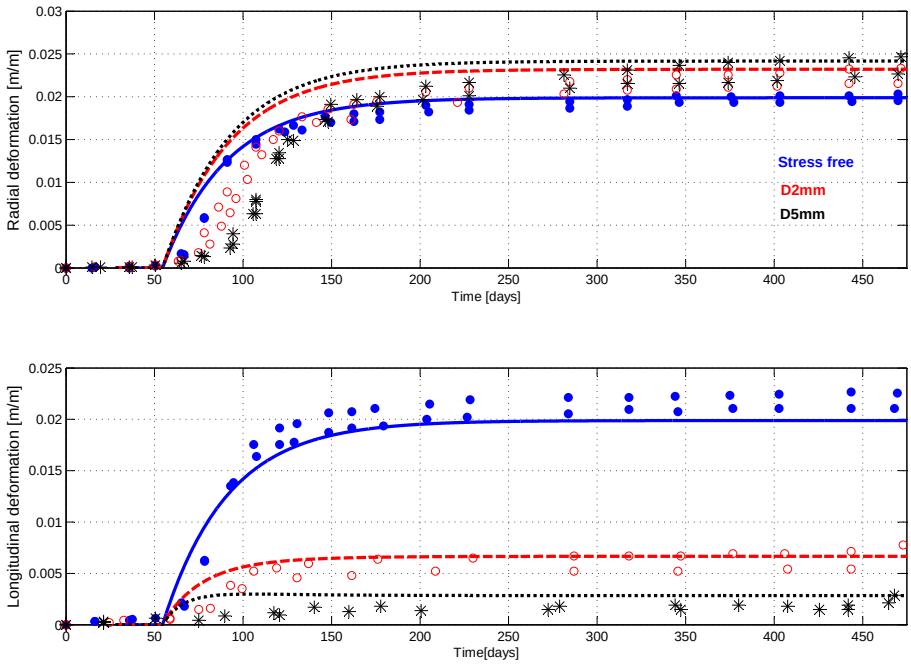

Figure 3: Transversal and longitudinal strains of specimens subject to DEF in stress-free conditions and under restraint: experimental points from [8] and numerical prediction.

by the model. This is probably due to the fact that the material is inhomogeneous at the mesoscale and thus the reaction does not start simultaneously in all points of the specimen.

5 CONCLUSIONS

A weakly coupled approach has been developed for modeling the mechanical effects of sulfate attack in concrete. A reactive-diffusion analysis is first carried out, then a poro-chemo-mechanical analysis is performed starting from the values of ettringite content preliminary calculated. The model has been validated by comparing the results numerically obtained by the proposed formulation with the experimental results reported in the literature for specimens subject to sulfate attack.

The enhancement of the model, in order to include the effect of damage on the diffusivity, is currently under development.

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