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Damage modelling in concrete subject to sulfate attack

N. Cefis, C. Comi

Department of Civil and Environmental Engineering, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milano, Italy.

nicola.cefis@polimi.it, claudia.comi@polimi.it

ABSTRACT. In this paper, we consider the mechanical effect of the sulfate attack on concrete. The durability analysis of concrete structures in contact to external sulfate solutions requires the definition of a proper diffusion-reaction model, for the computation of the varying sulfate concentration and of the consequent ettringite formation, coupled to a mechanical model for the prediction of swelling and material degradation. In this work, we make use of a two-ions formulation of the reactive-diffusion problem and we propose a bi-phase chemo-elastic damage model aimed to simulate the mechanical response of concrete and apt to be used in structural analyses.

KEYWORDS. Sulfate attack; Concrete; Damage; Finite Element Method; Porous Media.

INTRODUCTION

Under particular environmental conditions, some kinds of concrete may be subject to deleterious chemical reactions that cause swelling and micro-cracking, alter the mechanical properties and affect the durability of concrete structures. The chemistry behind different degradation processes in cement based material in aggressive environments has been the subject of a number of publications in the last twenty-five years; a comprehensive up-to-date review can be found e.g. in [1]. The present work focuses in particular on the sulfate attack and the consequent delayed ettringite formation.

There are two kinds of sulfate attack: the internal sulfate attack (ISA) and external sulfate attack (ESA). In the first case, the sulfate ions are already present within the material because of the thermal depletion of primary ettringite due to curing at high temperature or to the excessive heat of hydration developed in massive structures, see e.g. [2, 3]. In the second case, the sulfate is present in the environment and diffuses within the material through the porous microstructure; this happens e.g. in foundations, galleries, stores of radioactive waste in contact with sulfate-rich soils, [4, 5]. In both cases, the reaction between the sulfate and hydrated products of the cement leads to the formation of gypsum and of secondary ettringite, [6-8]. The product formed in the hardened paste exerts an internal pressure resulting in the appearance of micro-cracks and material degradation.

The kinetics of the reactions and, consequently, the severity of the damage depends on environmental factors (species and concentration of sulfate, pH of the solution, humidity, temperature) and intrinsic material properties (chemical composition of the cement paste, in particular aluminates content, pore distribution, diffusivity properties).

The numerical description of these phenomena requires a proper diffusion-reaction model, for the computation of the amount of reaction expansive products and a mechanical model for the prediction of swelling and material damage. In this work we use the coupled model proposed in [7] and further developed in [9] which allows to compute the sulfate molar



concentration and the amount of formed ettringite from a diffusive-reaction equation, taking into account the aluminate depletion due to the reaction.

The ettringite formation implies a volume increase and, once the initial porosity is filled, it induces a volumetric deformation. Several proposals exist in the literature to describe the mechanical consequences on concrete of this swelling. In [7] the volumetric expansion is treated as an eigenstrain and a simple uniaxial stress-strain law is used. In [10] Basista and Weglewski develop a micromechanical model based on the Eshelby solution of the equivalent inclusion method to determine the eigenstrain of the ettringite crystals in cement paste. In [11] a poroelasticity approach is followed and the Mazars' damage model is used to describe concrete microcracking. Idiart *et al.* in [9] present finite element simulations of the phenomenon at the meso-scale, considering concrete as a two phase composite, constituted by aggregates and cement matrix and describe degradation by cohesive-crack interface elements.

In the present work we follow a weakly coupled approach, similar to that proposed in [12, 13] for concrete affected by alkali-silica reaction. In the context of the Biot's theory of porous media, the concrete subject to sulfate attack is represented as a continuous medium consisting of two phases: the solid skeleton of concrete and the expansive products of the reaction. A phenomenological isotropic damage model, [14], describes the material degradation.

The reactive-diffusion model and the mechanical model have been implemented in a finite element code and used to simulate the experimental tests concerning ESA reported in [15, 16].

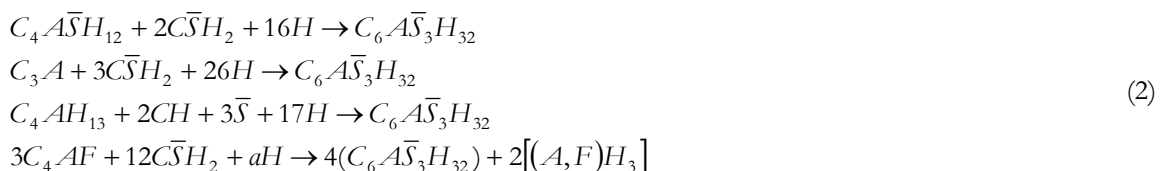
CHEMO-TRANSPORT MODEL

The reactions that take place inside the concrete when in contact with sulfate solutions are briefly reviewed in this section. The usual cement notation will be used: $C \equiv \text{CaO}$; $A \equiv \text{Al}_2\text{O}_3$; $\bar{S} \equiv \text{SO}_3$; $H \equiv \text{H}_2\text{O}$. Driven by a concentration gradient, the sulfates present in the environment penetrate into the material and, reacting with the calcium hydroxide (CH) and with the calcium silicate hydrates ($C-S-H$ gel), form gypsum $C\bar{S}H_2$. The gypsum thus produced reacts with the calcium aluminates which are present in the cement paste, forming ettringite $C_6A\bar{S}_3H_{32}$ [6-7].

The set of chemical equations that describe the gypsum formation are



The reactions between the gypsum and the aluminates P_i ($P_1 = C_4A\bar{S}H_{12}$ mono-sulphoaluminate, $P_2 = C_3A$ unreacted tricalcium aluminate, $P_3 = C_4AH_{13}$ tetra-hydrated aluminate and $P_4 = C_4AF$ alumino-ferrite) read respectively:



As proposed in [9], the reactions (2) can be lumped in a single reaction



where C_{eq} is the equivalent grouping of calcium aluminates

$$C_{eq} = \sum_{i=1}^4 \gamma_i \cdot P_i, \quad \gamma_i = \frac{c_i}{\sum_{i=1}^4 c_i} \quad (4)$$

c_i is the molar concentration of the single species of calcium aluminate P_i and $q = 2\gamma_1 + 3\gamma_2 + 3\gamma_3 + 4\gamma_4$ is the stoichiometric weighting coefficient of the sulfate phase.

The molar concentration $s(\mathbf{x}, t)$ of sulfate \bar{S} , varying in space \mathbf{x} and time t , can be computed taking into account the diffusion process and the consumption of sulfates due to the ettringite formation, through the following reactive-diffusion equation, D_s being the diffusion coefficient for the sulfate concentration and \bar{k} the rate of take-up of sulfates:



$$\frac{\partial s}{\partial t} = \text{div}(D_s(\text{grad } s)) - \bar{k} s \quad (5)$$

During the process of delayed ettringite formation also the calcium aluminates concentration $c_{eq} = c_{eq}(\mathbf{x}, t)$ decreases and the phenomenon affects the diffusion process of the sulfates. A more accurate description can be obtained by considering a second order chemical reaction in a two-ions formulation and computing the evolution of both the concentration of sulfate and aluminates from the following system:

$$\begin{cases} \frac{\partial s}{\partial t} = \text{div}(D_s(\text{grad } s)) - k c_{eq} s \\ \frac{\partial c_{eq}}{\partial t} = -\frac{k}{q} c_{eq} s \end{cases} \quad (6)$$

Note that no diffusion term is present in the second equation since aluminates can not move in the cement paste. To integrate the system of differential Eq. (6), one should specify proper boundary conditions fixing the sulfate concentration s or its normal gradient and initial conditions for both sulfate and aluminate concentrations.

The simplified single-ions formulation (5) is obtained for $\bar{k} = k c_{eq}$, with c_{eq} constant. The two-ions formulation (6) predicts a faster penetration of the sulfate with respect to the one-ion formulation (5), since the depletion of aluminates reduces the sulfate consumption due to the reactive term $k c_{eq} s$ in (6a) and thus results in a higher diffusion.

In the present work the two-ions formulation has been implemented.

Assuming that ettringite is the only reaction product governing the expansion of the concrete, the volumetric strain of chemical nature ε_v^{chem} is obtained from the amount of reacted calcium aluminates $c^{rac} = c_{eq}^0 - c_{eq}$ (i.e the difference between the initial aluminates molar concentration and the current one) and the volume change associated with the reaction. For any of the individual reactions described above, Eq. (2), the volume change for unit volume associated to the formation of one mole of ettringite can be calculated as in [7]:

$$\frac{\Delta V_i}{V_i} = \frac{m_{ettringite}}{m_i + a_i m_{gypsum}} - 1 \quad (7)$$

where m_i , $m_{ettringite}$ and m_{gypsum} are the molar volumes (m^3/mol) of the aluminate phase, of the ettringite and of the gypsum, respectively, and a_i is the stoichiometric coefficient involved in the reaction. To obtain the overall volume change per unit volume one has to multiply the change related to one mole by the number of reacted moles $m_i c_i^{rac} = m_i (c_i^0 - c_i)$ and then take the sum of the contributions coming for the different aluminates. Using the lumped formulation (3) one finally obtains

$$\varepsilon_v^{chem} = \left\langle \alpha (c_{eq}^0 - c_{eq}) - f \Phi_0 \right\rangle \quad \text{with} \quad \alpha = \sum_{i=1}^4 \frac{\Delta V_i}{V_i} m_i \nu_i \quad (8)$$

In the above equation $\langle \bullet \rangle$ denotes the positive part of \bullet and $f \Phi_0$ is a fraction of the initial porosity Φ_0 , introduced to take into account the fact that the reaction products partially fill the initial porosity, without producing any macroscopic expansion.

MECHANICAL BEHAVIOR OF CONCRETE

The mechanical response of the material to the chemical expansion expressed by Eq. (8) is computed in this work by a poroelastic-damage model. Within the framework of the Biot's theory [17], the concrete is described as a two-phase material: the homogenized skeleton phase, including cement paste and aggregates, and the expansive phase of the products of the reaction. The total stress σ is the sum of the effective stress acting on the solid skeleton σ' and of the stress on the reaction products phase, p being the pressure at the microscale, b the Biot's coefficient related to the concrete porosity and $\mathbf{1}$ the unit second-order tensor:



$$\boldsymbol{\sigma} = \boldsymbol{\sigma}' - b p \mathbf{1} \quad (9)$$

The effective stress on the concrete skeleton is related to the total strain $\boldsymbol{\varepsilon}$ by an elastic law with isotropic damage D , \mathbf{d} is tensor of the elastic properties of the homogenized skeleton:

$$\boldsymbol{\sigma}' = (1 - D) \mathbf{d} : \boldsymbol{\varepsilon} \quad (10)$$

The pressure of the expansive phase depends on the volumetric deformation ε_v and on the volumetric expansion ζ due to ettringite formation, M being the Biot's modulus

$$p = (1 - D) [-b M \varepsilon_v + M \zeta] \quad (11)$$

The expansion term ζ can be related to ε_v^{chem} for the unconstrained material by the Skempton coefficient

$$\begin{aligned} & Mb / (K + Mb^2) : \\ \zeta &= \frac{K + Mb^2}{Mb} \varepsilon_v^{chem} \end{aligned} \quad (12)$$

Only tensile damage is considered in this work and its evolution is governed by the loading-unloading conditions proposed in [14], expressed in term of the inelastic effective stress $\boldsymbol{\sigma}'' = \boldsymbol{\sigma} + \beta p \mathbf{1}$, with β ($\beta \leq b$) a material parameter which tunes the level of material degradation:

$$f_D \leq 0; \dot{D} \geq 0; f_D \dot{D} = 0 \quad (13)$$

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

$$f_D(\boldsymbol{\sigma}'') = J_2 - a_1 I_1^2 + a_2 I_1 b(D) - a_3 b(D)^2 \leq 0 \quad (14)$$

where a_1, a_2, a_3 are non-negative parameters to be identified through experimental tests. The function $b(D)$ governs the hardening and softening behavior of the material and its expression is

$$b(D) = \begin{cases} 1 - \left[1 - \left(\frac{\sigma_e}{\sigma_0} \right) \right] \left(1 - \frac{D}{D_0} \right)^2 & \text{for } D < D_0 \\ \left[1 - \left(\frac{D - D_0}{1 - D_0} \right)^{a_4} \right]^{0.75} & \text{for } D \geq D_0 \end{cases} \quad (15)$$

In the above equation σ_e is the elastic limit stress, σ_0 is the peak stress, D_0 is the damage corresponding to the peak stress. The parameter a_4 governs the slope of the softening branch of the stress-strain curve. In the finite-element implementation, the exponent a_4 is used to scale the fracture energy density of the material in such a way that each finite element can dissipate the correct amount of energy, independently of its size. This so called "fracture energy regularization" prevents the occurrence of spurious mesh dependency in the structural global response.

RESULTS

The numerical solution of the diffusion-reaction problem and of the subsequent chemo-damage problem are obtained by an ad-hoc developed finite element code.

Fracture energy pseudo-regularization is adopted. The finite element internal length for the constant strain tetrahedral elements is assumed to be the cubic root of the volume.

To validate the approach proposed in this paper we simulate the external sulfate attack experiments on mortar prism reported in [15] and also simulated in [16]. The experimental campaign was carried out on $25 \times 25 \times 285$ mm³ mortar prisms immersed in a solution with 35.2 mol/m³ of Na₂SO₄. Simulations of the reaction-diffusion process were performed in 3D considering three symmetry planes and solving the two ions formulation (6). The reaction and diffusion parameters used

in the simulation are: $D_s = 0.07 \text{ mm}^2 / \text{day}$ and $k = 8 \times 10^{-5} \text{ m}^3 \text{ mol} / \text{day}$. A constant sodium sulfate concentration is imposed at the outer surfaces and no flux is allowed through the symmetry planes. The initial concentration of equivalent aluminates, reported in [16], is 100 mol/m^3 .

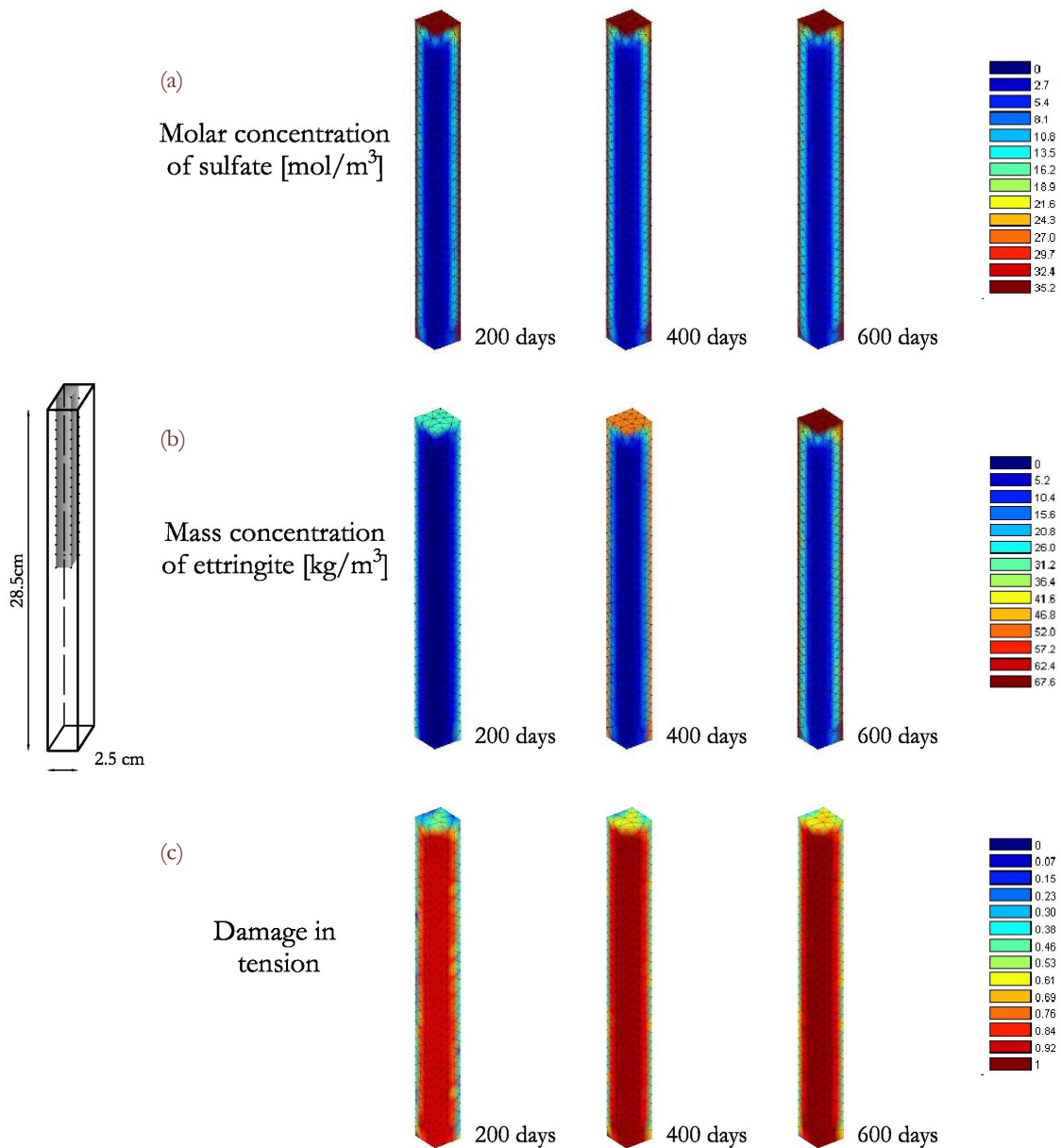


Figure 1: External sulfate attack on a mortar specimen: a) sulfate concentration, b) ettringite concentration and c) damage for three different exposure times (200, 400, 600 days).

Fig. 1a depicts the results of the evolution of the molar concentration of the sulfate at three different exposure times $t = 200$ days, 400 days and 600 days. Fig. 1b depicts the corresponding ettringite concentration: because of the penetration of sulfate, the ettringite front advances towards the center of the specimen. Fig. 2 shows the profiles of ettringite concentration at different times as a function of the distance from the center in the mean section of the specimen.

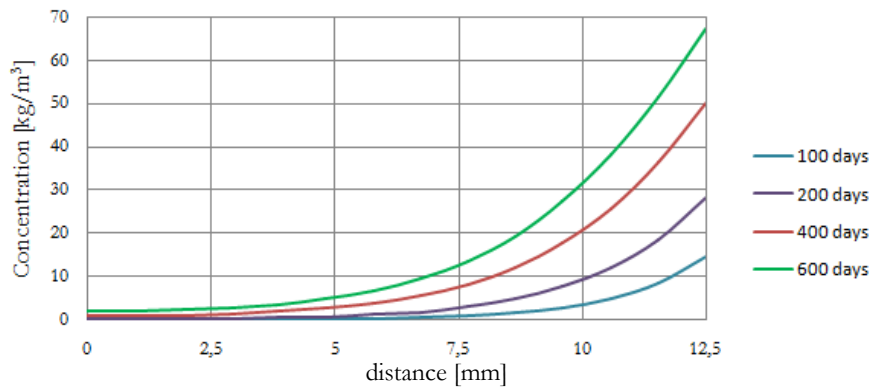


Figure 2: Profiles of ettringite concentration in the central section of the specimen.

The subsequent mechanical analysis allows computing the strains and damage in the specimen. A non-uniform initial porosity has been considered, leading, through Eq. 8, to a non-uniform chemical expansion in the specimen. Assuming a normal distribution with mean value 0.08 and standard deviation 0.02, the porosity of the different finite elements have been extracted by the Marsaglia's algorithm, also called "Ziggurat" algorithm; Fig. 3 displays the obtained pseudo-random distribution.

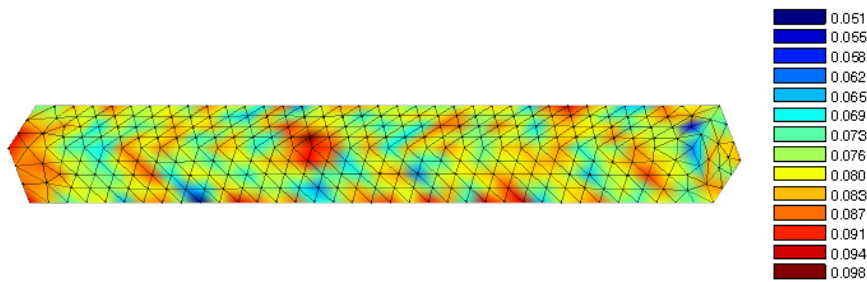


Figure 3: Pseudo-random distribution of porosities within the specimen.

Fig. 4 shows the comparison between the longitudinal expansion obtained in the simulations and the experimental measurements. After the first 150 days, a good agreement is observed. The discrepancy in the early response is due to the fact that full saturation is assumed in the numerical simulation, therefore the initial expansion due to imbibition is not reproduced.

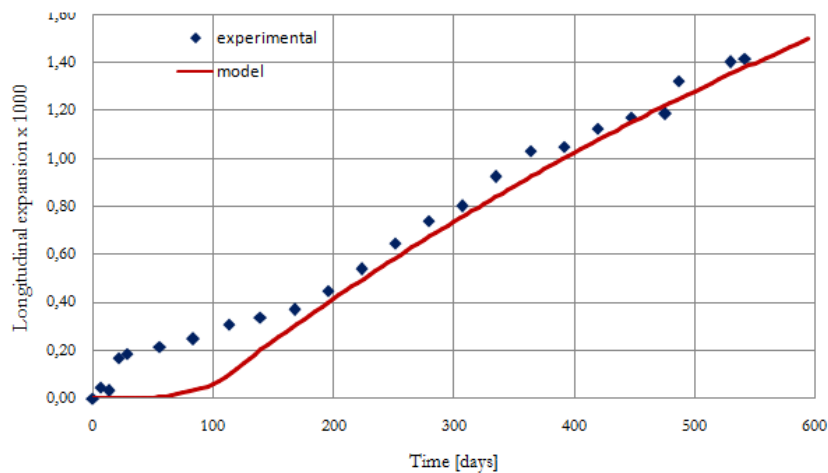


Figure 4: Evolution of longitudinal expansion with time of exposure to a Na_2SO_4 solution: experimental points from [15] and numerical results.



Fig. 1c depicts the evolution of the corresponding damage pattern. Since the chemical swelling reaction starts from the outer skin of the specimen, the central part of the specimen is subject to tensile stresses and undergoes damage. The pattern and the evolution of damage can be better appreciated in Fig. 5 that illustrates the results obtained with a finer mesh on a different geometry, representative of the central portion of the specimen. In the continuum approach here followed, the damage distribution simulates the presence of the cracking pattern experimentally observed, see e.g. [18].

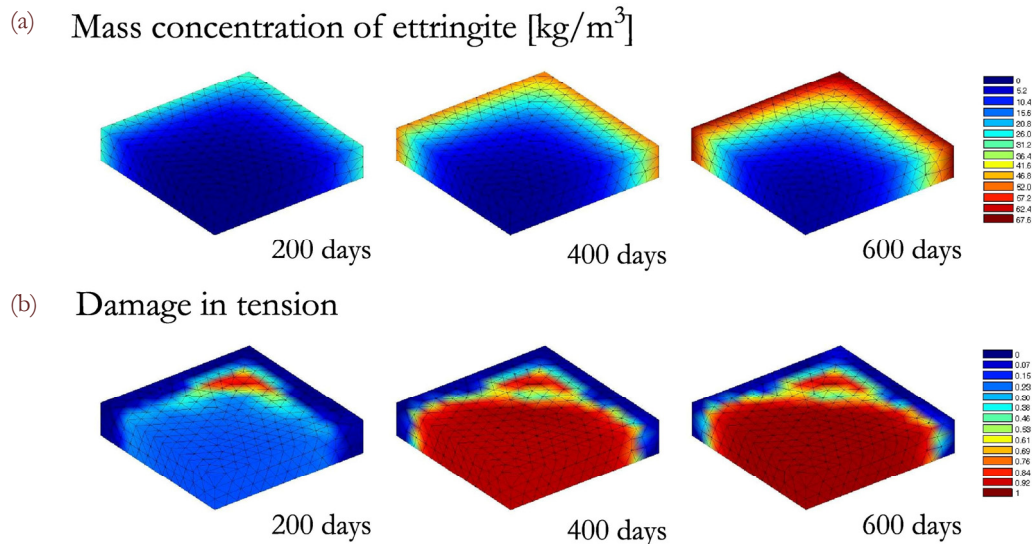


Figure 5: External sulfate attack on a mortar specimen: a) ettringite concentration and b) damage for three different exposure times (200, 400, 600 days)

CONCLUSIONS

The model developed and implemented in this work allows for the computation of the mechanical response of concrete subject to sulfate attack. The weakly coupled approach followed makes the formulation simple enough to be used to effectively compute the response at the structural level. The predictive capabilities of the model have been shown on a preliminary simple example concerning ESA.

A fully coupled formulation in which the effect of damage on the diffusion-reaction problem is taken into account is currently under development.

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