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# MODELLING OF THE SULPHATE ATTACK IN CEMENT-BASED MATERIALS

E. Rozière, F. Grondin, A. Loukili and R. El-Hachem

GeM, UMR-CNRS 6183, Centrale Nantes, Nantes Atlantique Universités, France

## Abstract

In this paper, we present a study on the durability of cement-based materials in their environment and for instance on the problems involved in their degradation when they are subjected to sulphate attacks. This problem is prone to many interrogations on the origin of the degradation of concrete under such conditions. We are interested in the ettringite formation during the chemical reaction between aggressive agents and the components of mortar, developing a pressure in the pores of the cement paste. When this pressure is higher than the tensile strength of the material, micro-cracks propagate in the microstructure. It is noted the behaviour of cement-based materials is strongly related to the fine comprehension of the evolution of the microstructure properties. Based on experimental tests, a numerical study is carried out to model the sulphate attacks in mortars tested in laboratory.

## 1. INTRODUCTION

External sulphate attacks are defined by all degradations of concrete in which the agent is the aggressive sulphate ion ( $SO_4^{2-}$ ) and come from the surrounding environment (sea water, soil, groundwater ...). According to the associated cation (sodium, calcium sulphate) and exposure conditions (pH, temperature, concentration), the degradation process can vary. However, it appears that one of the various phases of cement, the tricalcium aluminate ( $C_3A$ ), plays a leading role as a reactant in the formation of expansive products, such as gypsum and ettringite. Indeed, these two products were highlighted in many cases of damage [1] and observed by analysis of the microstructure of degraded cement-based materials [2, 3]. Accelerated ageing tests make it possible to assess the performance of concrete binders (Portland cement, cement compounds, mineral additives) under sulphate attacks. However, even for high sulphate concentrations, such tests are still relatively long: standards provide criteria for 6 months or 1 year (French standard NF P 18-837, American standard ASTM C 1012). The approach of the standards on the composition of concrete remains prescriptive, with limitations on the choice of cement - mainly their  $C_3A$  content - which fails to take advantage of technological advances in the composition of concrete.

The main objective of this study is to move from a resources obligation to a “performance” approach on the durability of concrete [4, 5]. In this context it would be interesting to have

models to adequately describe the degradation process by sulphates, in order to reduce the tests duration and tests constraints. But the literature review is poor regarding the development of models which can determine the mechanical degradation of concrete under chemical attacks as sulphate [6, 7, 8]. And these models are based on a macroscopic behaviour law of concrete. But it seems important to take into account the microstructure properties. Homogenization methods have been developed to determine the macroscopic behaviour law according to the microstructure properties. We can distinguish analytical methods and numerical methods based on a simple [9], respectively rich [10, 11, 12, 13], Representative Elementary Volume.

In this study, an experimental campaign on an accelerated ageing test and a modelling work was conducted. Tested mortars were prepared with two types of cement with different volume of  $C_3A$  and two water to cement ratio (W/C) in order to assess the vulnerability of the binder vs. the compaction. The model Sulfate2, developed by Tixier and Mobasher [7, 8], was used. This model takes into account the sulphate diffusion in the porosity and calculates strains and damage developed by the ettringite formation. Some input parameters were calculated by a multiscale approach [14].

First of all, the numerical approach is presented. Then, applications on mortars are discussed, presenting the strain evolutions and the loss of rigidity of damaged materials.

## 2. THEORY ON THE SULPHATE ATTACKS



Figure 1 : Degradation of mortars samples ( $4*4*16$  cm<sup>3</sup> and  $2*2*16$  cm<sup>3</sup>) submitted to sulphate attacks at 135 days and 150 days [4].

Experimental tests performed on concrete submitted to sulphate attacks have allowed to show the dominant role of  $C_3A$  in their degradation [15]. Indeed,  $C_3A$  react with gypsum ( $C\bar{S}H_2$ ) and water ( $H$ ) to form ettringite ( $C_6\bar{A}\bar{S}_3H_{32}$ ) according to the following relation:



To determine the amount of ettringite formed, it is important to know the volumes of  $C_3A$  and  $C\bar{S}H_2$  present in the cement paste.

During the sulphate attack, we suppose the initial gypsum has been totally consumed. But sulphate ions  $SO_4^{2-}$  ( $S$ ) present in the sulphate solution react with portlandite ( $CH$ ) and form gypsum:



The new ettringite formation will then generate a crystallization pressure in the concrete capillary porosity. The micromechanical approach presented in this paper is based on a calculation of the volume of phases after the hydration of cement. These calculations allow us to assess input parameters in the model Sulfate2 [7].

### 3. PRESENTATION OF THE MODEL

#### 3.1 The macroscopic model

The model Sulfate2 developed by Tixier and Mobasher has been retained in this work. The model is based on the finite difference method. The diffusion of the sulphate solution in the concrete porosity is calculated according to the Fick's law:

$$\frac{\partial U}{\partial T} = D \frac{\partial^2 U}{\partial X^2} - kU \quad (3)$$

With  $U$  the sulphate concentration,  $D$  the diffusion coefficient and  $k$  the solubility rate constant of reaction between sulphates and aluminates. The volume strain is deduced from the calculation of the volume change of the cement paste phases:

$$\varepsilon_V^0 = C_{ar} \sum_P \left( \frac{\Delta V}{V} \right)_P \quad (4)$$

With  $C_{ar}$  the concentration of aluminates which have reacted and  $P$  the product phase. By considering the ettringite formation in the capillary porosity, it is assumed that the volume change of ettringite does not alter the porosity as long as its volume is less than the porosity. The volume strain is written as follow:

$$\varepsilon_V^t = \varepsilon_V^0 - f\phi \quad (5)$$

With  $f$  the capillary porosity which can be totally filled by ettringite.

In the model Sulfate2, damage is taken into account for the calculation of the diffusion coefficient of concrete during the degradation. We suppose two zones in the material: a damaged area ( $D(w)$ ) and a healthy area ( $D_2$ ) [7]:

$$D(w) = w(D_1 - D_2) + D_2 \quad (6)$$

With  $D_1$  the maximum diffusion value chosen equal to 10 times  $D_2$ .

#### 3.2 Calculation of the input parameters

The model Sulfate2 needs some input parameters which can be obtained by experimental tests or numerical calculations. We focus in this section on some parameters which are influent on the degradation.

The volume of  $C_3A$  is given in the cement mixture and its hydration degree  $\xi_i$  can be measured or calculated. The Arrhenius law is retained [16]:

$$\tau_i \frac{d\xi_i}{dt} = \tilde{A}(\xi_i) \quad (7)$$

With  $\tau_x$  the characteristic time associated and  $\tilde{A}(\xi_i)$  the normalized affinity.

To determine the mechanical properties of mortar before its degradation, we apply a multiscale approach. We consider a representative elementary (REV) volume  $V$  formed by a

matrix  $V_m$  and several types of inclusions  $V_i$ , supposed to be spherical and with the same size. The elastic properties of concrete are calculated by applying the self-consistent method before immersion in a sulphate solution. We obtain the homogenized compressibility modulus  $k^{\text{hom}}$  and the homogenized shear modulus  $\mu^{\text{hom}}$  for an isotropic medium by solving the following equation system:

$$\sum_i \frac{f_i(k_i - k^{\text{hom}})}{1 + \alpha(k_i - k^{\text{hom}})/k^{\text{hom}}} = 0$$

$$\sum_i \frac{f_i(\mu_i - \mu^{\text{hom}})}{1 + \beta(\mu_i - \mu^{\text{hom}})/\mu^{\text{hom}}} = 0$$
(8)

With

$$\alpha = \frac{3k^{\text{hom}}}{(3k^{\text{hom}} + 4\mu^{\text{hom}})} \quad \text{and} \quad \beta = \frac{(6k^{\text{hom}} + 2\mu^{\text{hom}})}{5(3k^{\text{hom}} + 4\mu^{\text{hom}})}$$

With  $f_i = V_i/V$ ,  $k_i$  and  $\mu_i$  the volume fractions, the compressibility and the shear moduli of each phases present in the material respectively. The volume of each clinker of cement  $V_i$  can be calculated according to the hydration degree [17]:

$$V_i(t) = V_i^0 (1 - \xi_i(t))$$
(9)

With  $V_i^0$  the initial volume of clinker  $i$ . In the same way, the volume of the residual water is equal to:

$$V_w(t) = V_w^0 - \sum_i V_w^i \xi_i(t) = V_w^0 - \sum_i V_i^0 \frac{\rho_c}{\rho_w} \cdot \frac{n_w M_w}{n_i M_i} \cdot \xi_i(t)$$
(10)

With  $V_w^0$  the initial volume of water,  $V_w^i$  the volume of consumed water to hydrate the cement phase  $i$  of molar mass  $M_i$ ,  $M_w$  the molar mass of water and  $n_w/n_i$  the mole number of water consumed to hydrate one mole of cement phase of the apparent density  $\rho_c$ . The volume of hydrated phases can be calculated according to the volume of elements which have reacted as for the following chemical reaction:  $n_1^R V_1^R + \dots + n_n^R V_n^R \rightarrow n_1^P V_1^P + \dots + n_m^P V_m^P$ . And we can write:

$$V_k^P(t) = \sum_l \left( V_l^0 \frac{n_k^P M_k \rho_c}{n_l^R M_l \rho_k} \right) \xi_l(t) \quad k = 1, m$$
(11)

With  $n_k^P/n_l^R$  the mole number of reactant  $R$  of molar mass  $M_l$  consumed to form one mole of product  $P$  of molar mass  $M_k$ .  $\rho_k$  and  $\rho_c$  are the bulk density.

## 4. APPLICATIONS ON MORTARS

### 4.1 The experimental conditions and the material mixture

A degradation test has been performed on three mortar mixtures (Table 1). Mortars have been immersed in water with a high sulphate concentration (0,312 mol/L). The volume of the cement paste of these three mortars has been kept constant. Two mortars have a water to cement ratio W/C=0.5 and two types of cement Portland have been used:

- CEM I 52.5 R with a high volume of  $C_3A$  (10.6%), which usually varies between 2 and 11% for usual cement,
- CEM I 52.5 PM ES with a volume of  $C_3A$  equal to 2.1%, which is guaranteed resistant against sulphates.

The third mortar has been prepared with a cement having a high volume of  $C_3A$  and  $W/C=0.65$ .  $W/C$  has been chosen higher to observe the influence of a low compaction.

Table 1: Mortar mixtures

(kg/m <sup>3</sup> )	M2	M3	M9
Normalized sand 0/2 mm	1494	1490	1490
Cement :			
CEM I 52.5 R		497	420
CEM I 52.5 PM ES	498		
Water	249	248	273
W/C	0,50	0,50	0,65
Volume of $C_3A$ (%)	2,1	10,6	10,6

For each mortar mixture, six specimens of sizes  $2 \times 2 \times 16$  cm<sup>3</sup> have been prepared and removed from the mould after 24 hours. Then, they have been stored in water for 14 days and after that they have been dried at 40°C for 14 days. After returning to the ambient temperature (20°C), three specimens have been saturated with a solution with 30 g/L (0312 mol/L) of sodium sulphate ( $Na_2SO_4$ ) renewed every 30 days, and three specimens have been saturated with water as witnesses specimens. The deformation of specimens has been obtained from measurements of the length with a deformer.

#### 4.2 Results and discussion

Results of the calculated strains of mortars are compared with experimental measurements in figures 2, 3 and 4. Calculations of the elastic modulus of the damaged material are presented in figure 5. Evolutions of axial strains calculated by the model Sulfate2 are correlated with those of the experimental measurements. It is still important to note that these results require a setting of the capillary porosity fraction completed by ettringite (the coefficient  $f$ ). This parameter has an important role in the calculation of strains [8]. Calculations of the Young's modulus vs. time have not been compared with experimental measurements. One can observe the loss of rigidity of the material in figure 5.

Experimental studies have helped out that additional water in concrete leads to the hydration of residual clinker of the cement paste that had not yet hydrated and thus enables a healing of the damaged material [18]. This has the effect of a resumption of the rigidity of the material. We suppose this phenomenon happens with the filtration water of the sulphate solution. Developments are in course to take into account the evolution of the stiffness of the material which can re-hydrate [14].

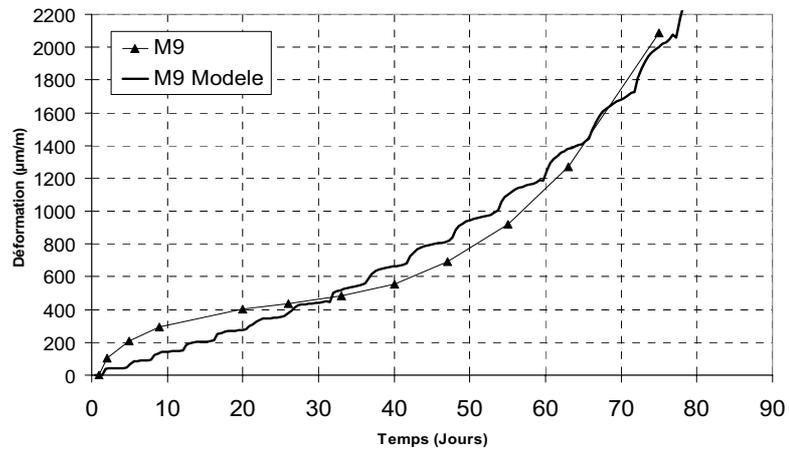


Figure 2: Comparison between calculated results and experimental measurements of strains of M9

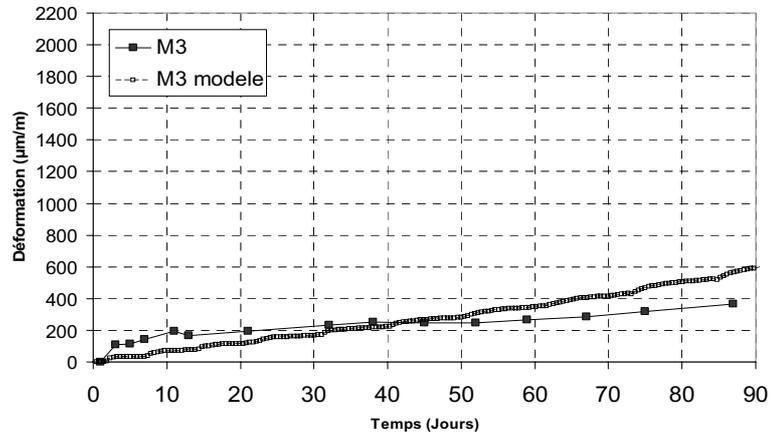


Figure 3: Comparison between calculated results and experimental measurements of strains of M3

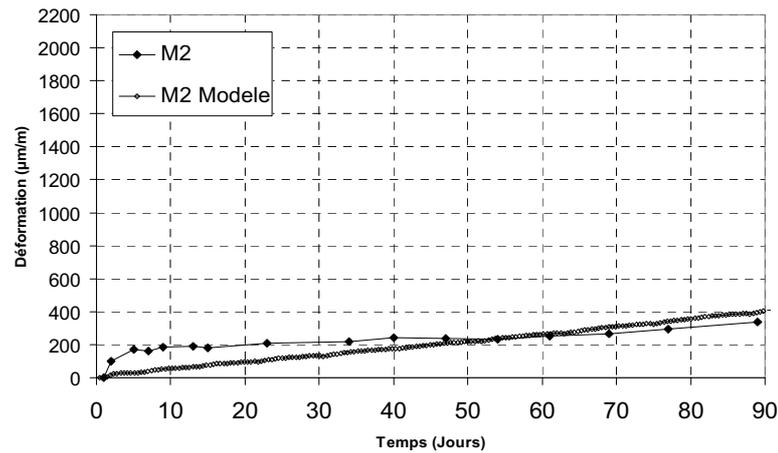


Figure 4: Comparison between calculated results and experimental measurements of strains of M2

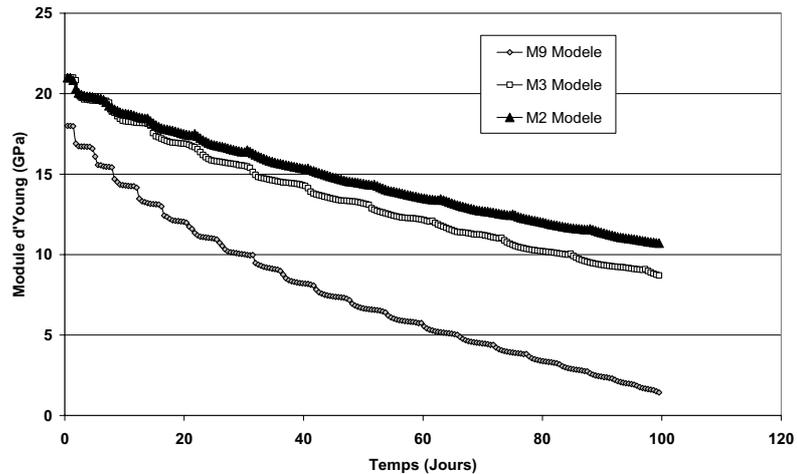


Figure 5: Calculated results on the evolution of the Young modulus vs. time

## 5. CONCLUSIONS

Experimental studies on the durability of cement-based materials under sulphate attacks are very long (6 months to 1 year). The determination of the evolution of strains and the rigidity modulus under these conditions is costly in time because it requires regular measurements of concrete samples (or mortar). It is therefore necessary to develop a numerical tool to calculate the properties of concrete under sulphate attacks in order to have an initial assessment of results. In this work, we have presented a first approach to the calculation of these properties. The results obtained with the model Sulfate2 are quite satisfactory, but this model requires the determination of the capillary porosity fraction in which the crystallization pressure of the ettringite formation is influent on the strain. The model does not take into account either the resumption rigidity of the material which can be re-hydrated with supplementary water of the sulphate solution. However, it helps to evaluate the axial deformation of the material until the degradation. That is relatively difficult in experimental tests. In order to take into account the resumption of rigidity a model is in validation course. This model, based on the homogenization methods, allows to calculate the rigidity modulus according to the cement hydration.

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