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CALCIUM LEACHING IN CEMENT MATRICES**

INS Preprint No. 1203

Feb 2012



# COMPUTATIONAL 3D SIMULATION OF CALCIUM LEACHING IN CEMENT MATRICES

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## Abstract

*Calcium leaching is a degradation process consisting in the progressive dissolution of the paste by the migration of calcium atoms to the aggressive solution. It is therefore, a complex phenomenon involving simultaneously several crystalline phases and dissolution and diffusion processes. During this work a new program for the simulation of the degradation process in three dimensions was developed. The program decouples the transport and chemical reaction equations and solves them separately. Transport equations are solved by the Finite Element Method using an algorithm that enables the description of multi-ionic solutions on arbitrary domains. The chemical algorithm accounts for the degradation of portlandite and the CSH gel which are the main constituents of ordinary Portland cement matrices. The program was used to simulate accelerated calcium leaching by a 6M ammonium nitrate solution, in order to test it. The obtained output was a three dimensional representation of the matrix and the values calcium concentration of each particular pixel of the structure at different time steps. This not only makes possible to study the calcium to silicon ratio, porosity and elastic properties of each particular phase as a function of time but also as a function of the position within the matrix.*

## 1. INTRODUCTION

Calcium leaching of the cement paste is a degradation process consisting in the progressive dissolution of the cement paste as a consequence of the migration of calcium ions to the aggressive solution. It is therefore a typical example of a dissolution process in a porous matrix where some of the mineral phases of the paste dissolve in the interstitial pore solution. The kinetics of the process is therefore

controlled by coupled dissolution and diffusion processes. The degradation rate depends to a great extent in the nature of the aggressive solution. Under natural conditions, such solution is generally water with low ion content. However, water is replaced in most experimental works by a more aggressive solution such as 6 M ammonium nitrate [1]. Under such conditions calcium leaching takes place so fast that the process can be considered to be diffusion controlled.

The main effect of calcium leaching is an increase in the porosity of the cement matrix. The reasons for this are the degradation of portlandite and the CSH gel. However, each of them loses calcium by means of very different mechanisms. The former dissolves completely in the aggressive solution increasing leaving a hole/pore in its place. By contrast, the latter solely undergoes a porosity increase in the range of gel porosity. In both cases there is a reduction of the mechanical performance of the paste that can be measured in terms of compressive strength and elastic modulus.

Several attempts have been made to model calcium leaching of cementitious materials [2-5]. One of the difficulties for doing so arises from the multi-phase nature of the cement matrix, since the mechanism of calcium loss and the equilibrium calcium concentration are different for each of these phases. As a consequence, they have different dissolution rates depending mainly on their calcium to silicon ratio [5]. The most common approaches to overcome these difficulties consist on either limiting the number of phases considered or using a continuous equilibrium formulation based on Berner's diagram [6]. The values of average porosity, strength and velocity of the degradation front provided by these models are reproduced well by experimental results.

The objective of this work was the development of the necessary tools to simulate, in three dimensions, calcium leaching of the cement matrix at the level of the microstructure. This includes the construction of a cement matrix microstructure attending to various parameters like the mineralogy of the cement and the water to cement ratio, followed by the degradation of the individual phases making up the cement matrix.

## **2. THE MODEL**

### **2.1 Construction of the matrix**

The construction of the cement matrix was carried out using an updated version of Hymostruc 3D [7]. This program simulates cement hydration and formation of structure in Hardening-Cement-Based materials. The input data are the water to cement ratio, some physicochemical properties of the cement, some geometrical considerations (dimensions of the structure, number of pixels, etc.) and certain information about the hydration products (size of portlandite particles, calcium to silicon ratio of the gel, etc). The hydration process can be extended from a few hours to many days and the structure is a cube with a size of up to 100 microns. The

number of pixels per micron can be varied between 1 and 20 with the processing time and the size of the output files varying accordingly.

## 2.2 Degradation code

For the implementation of the degradation code four reactive phases were considered: portlandite and the three types of CSH gel, inner product (IP-CSH), outer product (OP-CSH) and overlapping (OL-CSH). The CSH gel was described in all cases by Richardon's model [8] which assumes that the gel is made of portlandite and a calcium silicate hydrate with calcium to silicon ratio one. Therefore, the whole degradation process down to calcium to silicon ratio one can be explained solely in terms of portlandite's dissolution. The only differences between phases are portlandite's concentration and the porosity.

The parameter that governs diffusion processes is the diffusion coefficient. In this work, the diffusion coefficients were assumed to be :

$$D = D_{Bulk} \times P \quad (1)$$

Where  $D_{Bulk}$  is the bulk diffusion coefficient of a given chemical specie in each of the phases considered or water. The values of  $D_{Bulk}$  were obtained from the experimental values available in the literature [9].  $P$  is the relative porosity of the phase, with a value of one when the pixel is part of a capillary pore. Initially, all pixels containing a particular phase have the same porosity and therefore the same diffusion coefficient. However, as soon as the degradation process begins porosity can vary considerably from pixel to pixel and so does the diffusion coefficient.

Due to the aforementioned aggressiveness of the solution, the timescales of the transport and chemical processes differ by several orders of magnitude. Therefore, transport and reaction decouple, so that the basis of the code are the Nernst-Planck equation to describe the transport, and a direct reaction model to account for the chemical reactions. Consequently, the aggressive solution has to enter the pixels containing hydration products in order to degrade them. The (Poisson-)Nernst-Planck equation system has the form

$$\nabla \left( D_i(x) \nabla u_i(x,t) + \frac{z_i F}{RT} \nabla \phi(x) u_i(x,t) \right) = \frac{\partial u_i(x,t)}{\partial t} \quad (2)$$

$$\sum_i z_i u_i(x) = \Delta \phi(x)$$

$$\int_{\Omega} \nabla \left( D_i(x) \nabla u_i(x,t) + \frac{z_i F}{RT} \nabla \phi(x) u_i(x,t) \right) v_j(x) dx = \int_{\Omega} \frac{\partial u_i(x,t)}{\partial t} v_j(x) dx, \quad \forall v_j \in H_1(\Omega)$$

$$\int_{\Omega} \left( D_i(x) \nabla u_i(x,t) + \frac{z_i F}{RT} \nabla \phi(x) u_i(x,t) \right) \nabla v_j(x) dx = \int_{\Omega} \frac{\partial u_i(x,t)}{\partial t} v_j(x) dx, \quad \forall v_j \in H_1(\Omega)$$

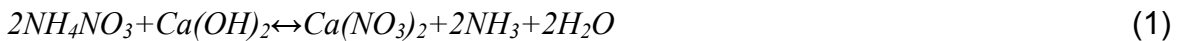
$$\int_{\Omega} (u_i(x, t_n) v_j(x) dx) + \int_{\Omega} \left( D_i(x) \nabla u_i(x, t_n) + \frac{z_i F}{RT} \nabla \phi(x) u_i(x, t_n) \right) \nabla v_j(x) dx = \int_{\Omega} u_i(x, t_{n-1}) v_j(x) dx, \quad \forall v_j \in H_1(\Omega)$$

Since no outer field is present, there is no charge splitting to be expected and species are regarded without explicit dissociation, thus making each species charge neutral. Since the solution of the Poisson Equation is now always trivial, the transport operator of the three species may be split and the resulting smaller systems can be solved much faster than one combined system.

The implementation of the transport is then carried out via a finite element method, rewriting the differential equation into its weak form regarding its space discretization and using an implicit Euler scheme to advance time [10].

With portlandite and CSH cells predefined with initial concentrations in the voxels, the aggressive solution is added by specifying Dirichlet boundary conditions, simulating that the model sample at hand is placed in an equilibrated reservoir of ammonium nitrate. Initially no reaction product is present.

The chemical algorithm accounts for the degradation of portlandite and the CSH gel which are the main constituents of ordinary Portland cement matrices. Within this work it is assumed that the only possible chemical reaction was



As a consequence, only three different species can be present in the pore solution: ammonium nitrate, calcium hydroxide and calcium nitrate. The reaction equation is implemented on the basis functions of the weak formulation as well, by comparing and computing, the reaction results from the respective coefficients wherever portlandite is present. A backward reaction does not need to be calculated due to the separation from equilibrium.

### 3. TESTING OF THE PROGRAM

An ordinary Portland cement matrix was created to test the degradation code. The specimen was cubic with a size of ten microns. The paste was prepared at a calcium to silicon ratio of 0.5. Curing time was 29 steps which correspond to approximately 26 days in real-life. The obtained structure was pixelated so that each pixel consisted solely of one of the following phases: pore solution, portlandite, IP-CSH, OP-CSH and OL-CSH. The geometry of the pixels was cubic with a size of  $0.25 \mu\text{m}$ .

The program was used to simulate accelerated calcium leaching of the structure by a 6M ammonium nitrate solution. This particular solution was chosen because it is one of the most commonly employed in experimental works [11-13]. The evolution of the calcium concentration, porosity and elastic properties of each particular phase were studied along time. Figure 1 a-d shows the spatial evolution of the degradation fronts towards the inside of the matrix in terms of calcium concentration.

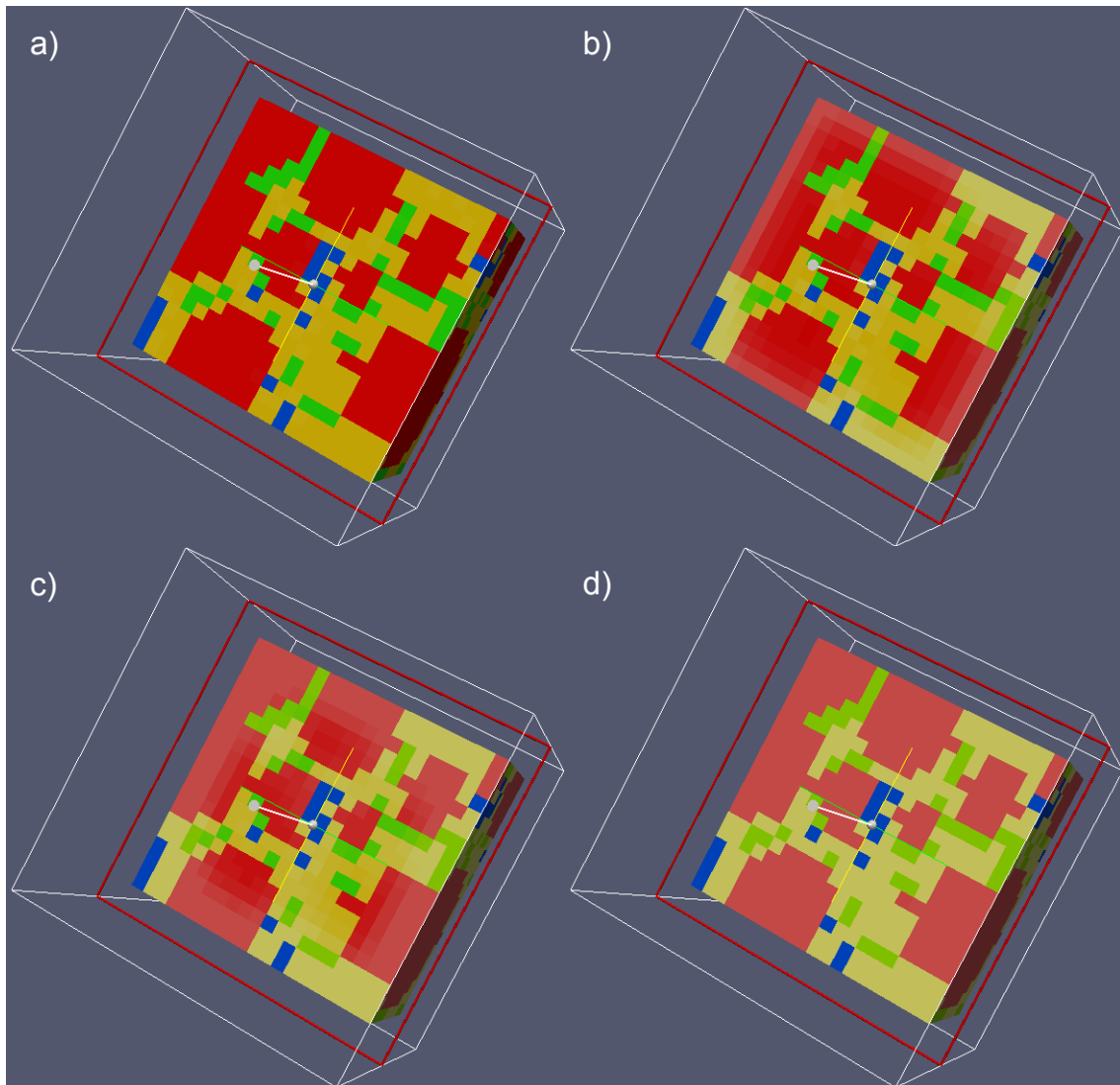


Figure1: Evolution of the degradation front along time. The side of the cube is 10 mm. Inner Product CSH appears in red, Outer Product CSH appears yellow, Overlapping CSH is displayed in green and Porosity is painted blue. For each particular phase darker tones are correspond to greater calcium content.

Calcium loss from portlandite takes place by means of a dissolution process. This means that there is a net reduction of the volume of the solid phase and, as a consequence, an increment of porosity. In particular, portlandite’s dissolution contributes to the increase of capillary porosity of the cement paste. The evolution of the capillary porosity as a function of the degradation time is presented in Figure 2. The obtained curve can be divided in three different segments. The first one corresponds to the initial stages of the degradation process. At this time, calcium concentration of the aggressive solution is very low and therefore a fast dissolution takes place. The degradation process in this region is therefore driven by the dissolution kinetics. As the concentration of calcium in the pore solution increases the degradation rate is reduced until a linear regime is reached. This is the beginning of the second segment in which the pore solution is saturated of calcium and the kinetics of the degradation process is controlled by the diffusion of the calcium ions towards the outer bounds of the test specimen. Finally, the linear regime takes to an end and the porosity tends to saturation. This third segment is due to the complete dissolution of some portlandite pixels. As portlandite is being exhausted capillary porosity tends to its maximum value which is the sum of the initial porosity plus the initial volume of portlandite.

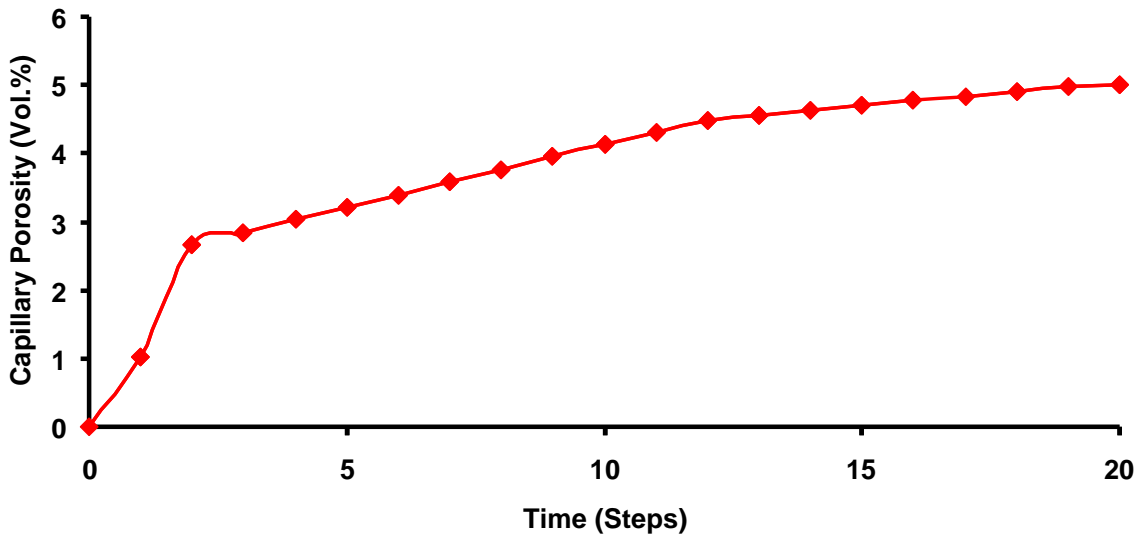


Figure 2: Increase of capillary porosity as a consequence of portlandite’s dissolution.

Opposite to portlandite, the loss of calcium from the CSH gel is not accompanied by a complete dissolution of the solid phase. In this case, the total volume of the solid phase is not so severely affected although an important increase in porosity takes place. This increment of porosity is bound to a reduction of the mechanical performance which has been the objective of intensive research [12]. Figure 3 shows



the evolution of the elastic modulus of the three CSH phases considered in this work as a function of the degradation time. As can be observed, the initial values of both IP-CSH and OP-CSH fall within the range of values of the High Density CSH available in the literature [14]. Similarly, the modulus of the OP-CSH is initially similar to that of the Low Density CSH (LD-CSH). As the degradation goes on the elastic modulus of all CSH phases are seriously reduced. This tendency is in good agreement with the experimental evidences found in the literature [12]. On the contrary, the values of the elastic modulus found in the literature for asymptotically leach specimens are considerably smaller. This is a consequence of Richardson’s model. Down to calcium to silicon ratio 1 the degradation of the matrix can be explained solely in terms of CSH’s degradation. By contrast, below such value a different mechanism should be proposed for the degradation of the CSH gel. In any case, experimental works rarely show values of calcium to silicon ratio lower than 0.8 what serves to justify the approach made in this work.

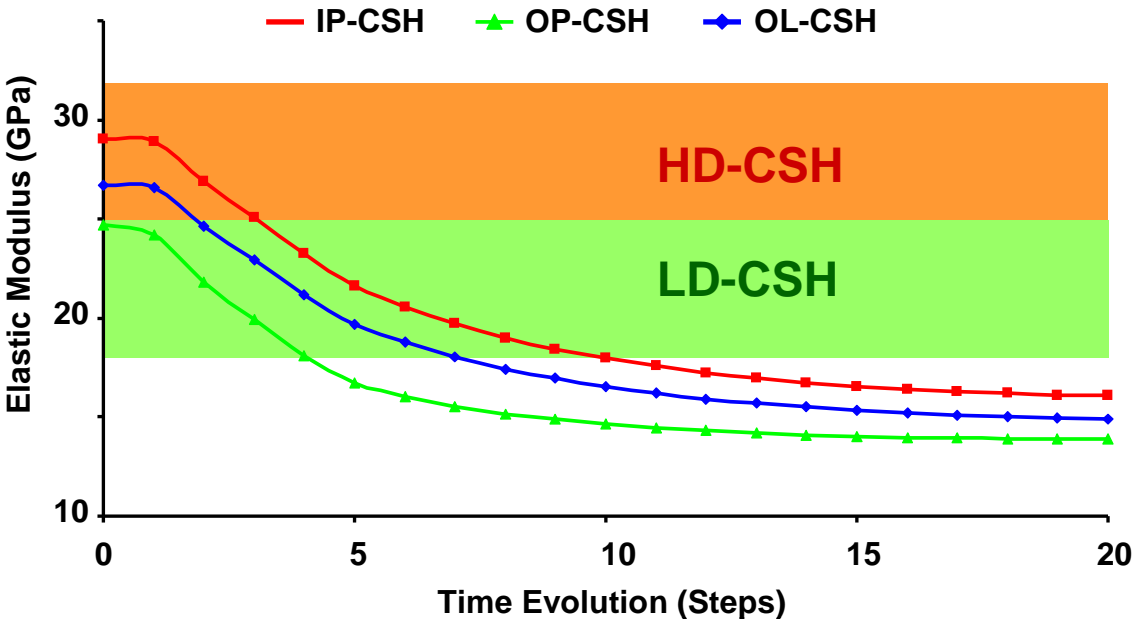


Figure 3: Elastic modulus of the three CSH phases. The shadowed areas represent the typical range of experimental values of the low and high density CSH as obtained from the literature [14-15].

**4. CONCLUSIONS**

The set of tools developed in this work allow the creation of a cement matrix and the subsequent simulation of its degradation by calcium leaching. In this work, the matrix consisted of an ordinary Portland cement mixed at a water to cement ratio of 0.5 and cured for 26 days. However, there are no limitations on any of these

parameters. The employed aggressive solution was 6M ammonium nitrate but any other solution could also be employed. Accordingly, the number of species present in the pore solution was very limited but the degradation program is very flexible in this aspect. Finally, the number of cement hydrates considered was reduced to portlandite and the three types of CSH, although the program allows the introduction of more phases as far as calcium concentration, porosity and diffusion coefficient are provided.

In spite of the approximations made in this work the obtained results are in good agreement with the experimental evidences. Nevertheless, parallel experimental and simulation works will have to be carried out in order to correlate simulation time and real time. In addition, a mechanism to degrade the CSH gel below a value of calcium to silicon ratio one should also be implemented.

## ACKNOWLEDGEMENTS

This work was supported by the European Commission as part of the project: Computationally driven design of innovative cement-based materials "CODICE" (CP-FP 214030-2).

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