Modelling the mechanical evolution of a chemically degraded cement paste at the microstructure scale

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ABSTRACT: Cement-based materials in aqueous environments are subjected to evolutions that concern both the solid skeleton and the pore solution of the cement paste. Moreover these two elements strongly interact themselves. A physico-chemical approach is developed to represent these interactions within a cement paste. A finite-element model supplements this approach and evaluates mechanical properties of a chemically degraded cement paste. This approach is successfully applied to a pure water leaching and represents its influence on the Young modulus of a cement paste.

1 INTRODUCTION

Concrete, a building material, is studied at different length levels. As far as the durable conception of a building is concerned, studies must be focused at different scales. Studies at the structure level concern the mechanical conception with respect to its resistance to loading or seism. At the microstructure scale studies mostly concern the durable behavior of the material versus the time.

Experimental approaches and numerous models have clearly enhanced the understanding and behavior of cement-based materials subjected to an external aggressive environment. Quite often, the composition of the aggressive solution used in accelerated tests, like pure water for leaching experiments, is really different from that of natural aggressive environments. Results from these studies can not be easily applied to real structures and an extrapolation has to be made, by evaluating new parameters. As an example, an experimental accelerated leaching of cement pastes with three aggressive environments (pure water, mineralized water and ammonium nitrate solution) has shown different kinetics and different dissolution phenomenology (Kamali, 2003) in function of the aggressive solution.

In order to propose a tool for understanding the chemical behavior of a cement paste in a specific environment, we are developing a model based on general physical and chemical laws. The identification of phenomena involved in chemical degradations tends towards an approach based on the competition between two interactions: first, between the aggressive external environment and the internal solution contained in the capillary porosity of the cement paste, and secondly, between this pore solution and the mineral phases of the solid cement skeleton.

In this paper, the objectives and structure of our modelling are first presented. Secondly, a pure water leaching is modeled. Finally, some mechanical properties of the leached cement paste are evaluated. The main ideas were to define a link between mechanics and chemical degradations of cement pastes through a general thermodynamical approach.

2 PRESENTATION OF THE MODELLING

2.1 *General considerations*

Most chemical degradations of a cement-based material as mortar or concrete can be characterized by the evolution of the cement paste microstructure. Considering the aggregates as non porous, the whole porosity of a cement-based material is completely located within the cement matrix. Chemical degradations occur by dissolutions or precipitations of solid species when the thermodynamical equilibrium of the system has been lost. The pore solution is an electrolyte

containing calcium, silicon, aluminum, sulfur, and alkaline ions. The chemical equilibrium gives pH a 13.5 value. Most natural aqueous environments do not have such a chemical composition. So, ionic exchanges occur due to the gradient concentration between the external environment and the porous network. Mass exchanges result in local unbalances which are the source of localized transformations of solid species as dissolution if the solution is undersaturated or precipitation if the solution is supersaturated, this in order to recover a thermodynamical equilibrium.

Our approach is based on the coupling effect of the ionic diffusive transport within the microstructure from the external aqueous environment, and reactions of dissolution and precipitation, due to local chemical unbalances, related to the ion transport. This approach has already been described in detail in (Guillon & al., 2003, Guillon & al., 2003b).

2.2 *Relative equations of the physical and chemical phenomena*

The physical and chemical phenomena, in a Representative Elementary Volume (REV) of the cement paste, can be expressed by the evolution of the concentration c_i^f of the ith ion:

$$\frac{\partial c_i^f}{\partial t} = div\left(D_i\ \overrightarrow{grad}\left(c_i^f\right)\right) + \sum_{j=1}^{J} c_{ij}^* \Gamma_j\ , \qquad (1)$$

where D_i is the apparent diffusion coefficient and $c_{ij}^*\Gamma_j$ is the kinetic contribution of the jth reaction.

The expression (1) is a classical reactive-transport equation and is often used in geochemical approaches where considered problems are mostly one-dimensional and transport phenomena simultaneously involve diffusion and advection. Here, diffusive transport in a water saturated porous network is considered in a three-dimensional study in order to visualize the evolution of the microstructure.

Equation 1 is expressed for all diffusive species. This so created system is a non-linear system of differential equations. The expression of an analytical or a semi-analytical solution is not possible. Our numerical strategy consists first in expressing by time-steps and in specific locations the evolution of diffusive ionic concentrations and secondly in separating the reactive term of the equation 1 in order to consider a two-phase numerical resolution.

2.3 *Representative Elementary Volume*

The reactive-transport modelling is done with a three-dimensional mesh representing both the cement paste system and the aggressive external environment. Figure 1 shows the study domain. Each cell is a *100μm* width cube. The cement paste cells are deduced from digital microstructures generated by CEMHYD3D model (Bentz, 1997, Bentz, 2000), in which a pore solution composition is calculated in order to equilibrate the cement paste system. Aggressive environment cells are aqueous solutions defined by their chemical composition.

CEMHYD3D "digital microstructures" are 100μm width cubes composed of 1μm pixels. This model first generates a 3D image of anhydrous cement, given its granularity and chemical composition. Then, some algorithms based on cellular automatons "hydrate" this 3D image representing the cement hydration process. Each 1μm size pixel can represent either a solid constituent of the cement paste, like C_3S, C_2S, C-S-H, or the porosity. The visualization of the cement microstructure during its hydration is so directly possible with this 3D representation.

2.4 *Hypothesis relative to the calculations*

Three principal aspects have to be developed here.

1- The study domain is a three dimensional mesh in which all reactive-transport equations are evaluated by time-steps. In order to simplify the calculations the Local Equilibrium Approximation (LEA) is formulated. As dissolution or precipitation reaction speeds are considered infinitely faster than diffusion process, LEA implies that the thermodynamic system composed of the solid skeleton and pore solution within the cement paste always follows a succession of infinitesimal equilibriums. So, the decoupling of reactive calculation in equation 1 is possible and this calculation occurs, in all cells, and reaches a new chemical equilibrium after the unbalance introduced by the transport phenomena.
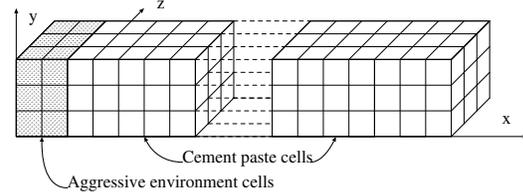

Figure 1: study domain used in the modelling. Each cell represents either the aggressive environment, of a cement paste cell, composed of a microstructure generated by CEMHYD3D model and the pore solution

2- As diffusion calculations can be really time-consuming in large meshes, species considered in transport calculations are total species, and represent for a given species (i.e. calcium) the sum of the concentration of all ions constituting this species; the principal and its complexes forms (i.e. for calcium: Ca^{2+}, $CaOH^+$, $Ca(OH)_2^0$…).

3- The apparent diffusion coefficient which appears in equation 1 is usually expressed in function of the porous network characteristics and the diffusive species considered. As diffusive species are chosen to be the total species and not specific ions, a simplification of the transport calculation is made by giving to all species the same diffusion characteristics. This can be justified by the fact that:

- The pore solution is an electrolyte and the mobility of ions is gratefully influenced by the presence of other ions. Though, mobility characteristics of ions are given for infinitely diluted aqueous solutions, and not directly applicable to the pore solution.

- The determination of a "mean diffusion coefficient" can be made if mobility of all ions constituting the species, and their relative concentrations are all known. This really complicates the study.

As a conclusion, the diffusion coefficient D taken for equation one is specific for each cell and its value is deduced from the water diffusion constant D_0, and from a function of the capillarity porosity ϕ within the cells. Its expression is deduced from (Bentz & al., 2000):

$$\frac{D}{D_0} = \frac{0.004}{\beta} + \frac{0.03}{\beta}\phi^2 + 1.7H(\phi-0.17)(\phi-0.17)^2 . \quad (2)$$

In expression (2) β is a parameter expressing the silica fume content. As we consider the behavior of a Portland cement, its value is zero in our modelling

2.5 *Numerical resolution of the system of equations*

Equation 1 without the reactive term is a classical diffusion equation expressed in a three dimensional Cartesian system. All equations for all diffusive species are linearly independent. A finite volume scheme is chosen. Diffusive fluxes are expressed at the boundaries of the cells, which imply to write the "diffusion coefficient" of theses boundaries from a mass conservation relation (Martys, 1999).

$$D_{x+\Delta x/2} = \frac{2D_x D_{x+\Delta x}}{D_x + D_{x+\Delta x}} , \quad (3)$$

In order to consider large time-steps in compatibility to durability studies, a Crank-Nicholson scheme has been chosen. This semi-implicit scheme is known to be unconditionally stable and convergent whatever the time-step chosen (Press & al., 1992). In our studies, the time-step value is 1800 seconds, which nears the stability time-step for an explicit scheme. For a given species, the solving of the diffusion calculation implies to write a linear system expressing the concentration in all cells at the next time-step in function of the concentrations in the previous time-step. This system is evaluated by iterations using a conjugate-gradient algorithm (Press & al., 1992).

After the transport calculations, reactive calculations occur. The mass of phases in the solid skeleton which dissolve or precipitate to reach a thermodynamical equilibrium is calculated. In all cement paste cells, mass-action laws, mass conservations and electro neutrality of the pore solution are the whole equations expressed. All these relations tend to write a non-linear system of equations in which some coefficients like ionic activities are variable in function of the ion concentrations in the pore solution. A modified Newton-Raphton algorithm (Press & al., 1992) evaluates, with few iterations and systematic correction of the activity coefficients, a thermodynamical equilibrium between the solid skeleton and pore solution. This calculation is made with the PHREEQC speciation code (Parkhust & al., 1999), which uses this resolution strategy and the Debye-Hückel model for evaluating ionic activities.

2.6 *Concluding remarks about the modelling strategy*

Our reactive-transport approach is able to reproduce the evolution of the microstructure of a hydrated cement paste due to its interactions with an external aggressive solution. Given a "digital" cement paste generated by CEMHYD3D model and composition of the aggressive environment, the model applies a succession of transport and reactive calculations reproducing, first, the interactions between the external environment and the internal pore solution, and secondly, the interactions between the evolutive pore solution and the solid cement phases. The transport calculation is made globally, at the mesh scale, while reaction calculations are carried out locally, in all cement paste cells.

3 APPLICATION OF THE MODELLING TO WATER LEACHING

In this application, three digital microstructures of Portland cement pastes with variable water-to-cement ratio (w/c) are generated by CEMHYD3D model. The "digital hydration" process is done until portlandite content reaches the same value obtained in experiments with DTA measurements with real cement pastes of the same w/c ratios (Kamali, 2003). The aggressive environment is considered to be pure water, with pH = 7.

Figure 2 shows the evolutions of pH and total calcium in the pore solution within the cement paste from the interface solution-solid surface, at different simulated times, and for w/c =0.4. The simulation starts at pH = 13.3 due to the presence of alkaline ions in the pore solution The total calcium concentration equals 1.3mmol/l. Transport phenomena induce ionic transfers from the pore solution to the external environment, especially alkaline ions which are not replaced in the pore solution by dissolutions of solid species. When all alkaline ions have left the solid, a new chemical equilibrium appears at pH = 12.45 and calcium concentration near 20.2mmol/l. At this stage, the dissolution or precipitation of solid species becomes faster, and after a sufficient time, new equilibriums appear in the depth of the material,
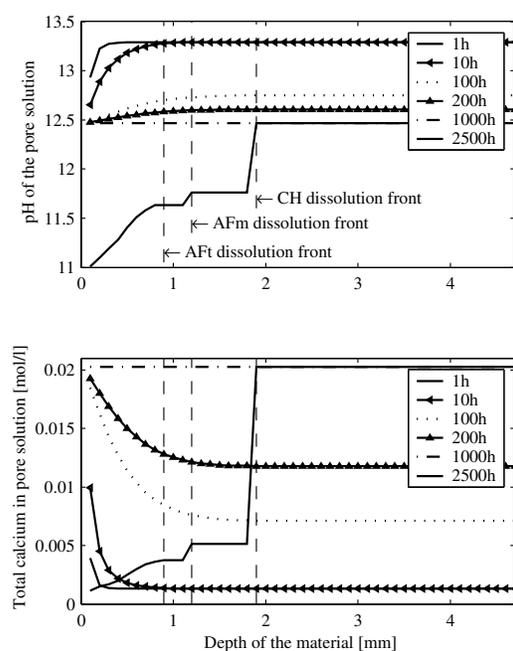
when some solid species have been totally dissolved. The first hydrate to dissolve is portlandite, followed by monosulfoaluminate, then ettringite, and finally C-S-H.

A remarkable point is that although the pH evolution within the material is sharp when a hydrate is totally dissolved, the solid species within the material do not proceed in the same way. So zoning of hydrates is not as pronounced as previously modeled (Adenot, 1992, Gerard, 1996). Indeed, in order to compensate ion depletions, dissolutions or precipitations of different solid species occur simultaneously which implies that at a given position, two hydrates can dissolve. As an example, portlandite and monosulfoaluminate are both dissolving in the same zone, as shown in (Moranville & al., 2003).

The evolutions of cement pastes with w/c=0.25 and 0.5 follow the same phenomena as observed in the w/c=0.4 cement, but with different kinetics. As degradation phenomena are kinetically controlled by diffusion processes, most studies use a square root of time equation to model the evolution of a dissolution front, $x = a\sqrt{t}$. A relative comparison with experiments (Kamali, 2003) at the instant when portlandite is totally dissolved, for the three water-to-cement ratios, shows close results, as shown in table 1.

Table 1: comparison of kinetic constant ratios between experiments and modelling for different w/c ratios

Kinetic constant ratio	Modelling Position 1	Modelling Position 2	Leaching experiments
$a_{(w/c=0.4)}/a_{(w/c=0.25)}$	1.50	1.70	1.84
$a_{(w/c=0.4)}/a_{(w/c=0.5)}$	0.86	0.79	0.82

4 MECHANICAL PROPERTIES OF A LEACHED CEMENT PASTE

4.1 *Microstructural evolutions due to chemical reactions*

In every time-step, dissolutions or precipitations occur to reach a thermodynamical equilibrium. In each cell the quantity of solid phases and the capillarity porosity change versus time. At given instants corresponding to the finite-element calculations, an algorithm randomly dissolves or precipitates some solid pixels. So, the digital representation of the microstructure evolves. Similarly to NIST microstructure models, some algorithms are developed to create an image file in a given section of the 3D microstructure. In order to simplify the visualization, colors can represent

Figure 2: pH and total calcium profiles within the cement paste at different time-steps

2D digital section of cement pastes, before and after the chemical degradation due to leaching

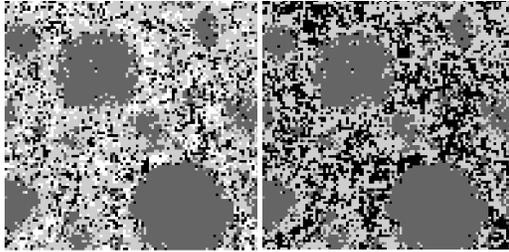

Figure 3: first section of the sound w/c=0.25 cement paste (left) and after total dissolution of portlandite (right)
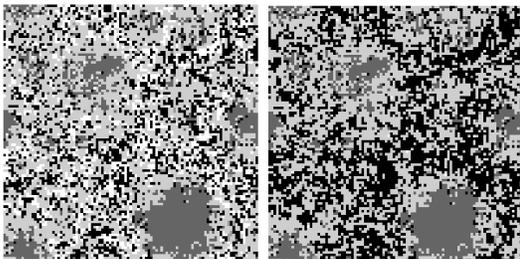

Figure 4: first section of the sound w/c=0.4 cement paste (left) and after total dissolution of portlandite, monosulfoaluminate and ettringite (right)
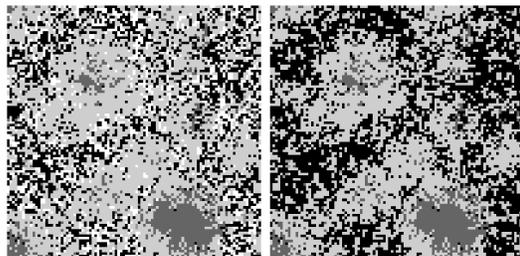

Figure 5: first section of the sound w/c=0.5 cement paste (left) and after total dissolution of portlandite, monosulfoaluminate and ettringite (right)

different phases focusing precisely on considered chemical degradations.

In figures 3 to 5, the same color correspondence is used. Black corresponds to the capillarity porosity, dark grey are anhydrous constituents, medium grey both ettringite and monosulfoaluminate, light grey is C-S-H and finally white is portlandite.

Figure 3 represents the evolution in a given section of the microstructure of a w/c = 0.25 cement paste. Left section is the intact microstructure and the right one is the partially leached microstructure, when all portlandite has been totally dissolved and replaced by porosity. Figures 4 and 5 show the same evolutions but with w/c = 0.4 and w/c = 0.5 cement pastes. All these images of sections are

generated at different stages of the chemical degradation.

The three figures above permit to visualize the influence of the microstructure repartition on the mechanical behavior of the cement paste. In low w/c cements, remaining anhydrous constituents tend to act as rigid micro-aggregates. In the other hand, the porosity repartition is not homogeneous, which can cause mechanical percolation problems when degradation becomes important. Indeed, porosity surrounds hydrated cement grains, and the more important the dissolution of hydrates is, the more porosity is, and the less the physical and mechanical percolation of hydrates is.

4.2 *Micromechanical calculation strategy*

A 2D elastic finite-element model is developed in order to calculate the homogenized Young modulus of the chemically degraded cement paste, and from the digital image of the microstructure. A section of the image, like those shown figures 3 to 5, is used as the mesh for the finite-element model, which represents 100*100 elements. Each element corresponds to a solid phase and has its own mechanical characteristics, taken from the literature. These characteristics are reminded table 2.

Table 2: Elastic moduli taken in the finite-element computations

Phase	Young modulus [GPa]	Reference
C_3S	135	(Velez & al., 2001)
C_2S	130	//
C_3A	145	//
C_4AF	125	//
Portlandite	36	(Velez & al., 2001b)
C-S-H (C/S>1)	31	//
C-S-H (C/S<1)	20	//
Ettringite	50	(Zohdi & al., 2002)
AFm	40	//

Using CASTEM 2000 finite-element code (Castem, 1995), a displacement is imposed in one boundary and the resulting boundary forces are used to calculate the homogenized Young modulus. 2D computations are relatively fast, only two minutes are necessary for a calculation, which is a real advantage when a precise following of the mechanical degradation is required.

Calculations are done in two different parallel sections of the cell nearest to the aggressive environment every 50 reactive-transport cycles, until the chemical degradation is considered sufficient. The number of finite-element computations corresponding for the cement pastes
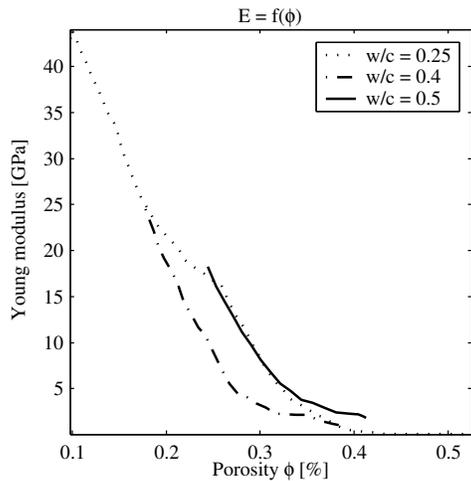
Figure 6: evolutions for the three w/c ratio cement paste of the Young modulus in function of the capillarity porosity

is 20 for w/c=0.5, 40 for w/c=0.4 cement and 105 for w/c=0.25.

Preliminary results are presented in the two following paragraphs.

4.3 *Influence of the porosity on elastic properties of a cement paste*

Figure 6 shows the calculated evolutions of the Young modulus in function of the capillarity porosity in a given section, and for the three water/cement ratios. These evolutions show a strong influence of the porosity on the Young
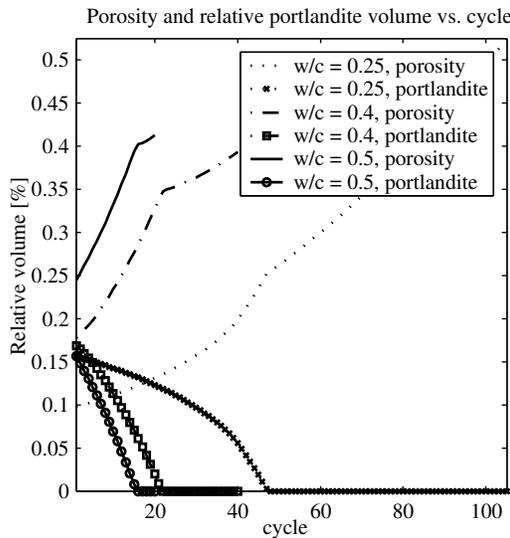

Figure 7: evolutions of the volume percentages of porosity and portlandite in the three cement pastes.

modulus. The three cement pastes, in the same range of porosities, have quite the same evolution of the Young modulus. Focusing on the Young modulus, this study highlights former studies which concluded that mechanical properties of cement pastes are strongly influenced by their porosity (Powers, 1960).

Furthermore, for all leached cement pastes, when capillary porosity reaches 45% in volume, the Young modulus can be considered as negligible. Our interpretation is that there is no more mechanical percolation in the mesh constituted by the section. This 45% porosity value is in agreement with former 2D studies of percolation (Babalievski, 1995, Garboczi & al, 1999). Nevertheless, this does not mean that for the whole cell the percolation situation is the same because of the 3D network of the solid skeleton.

Figure 7 shows the evolution of relative volume versus "simulated time" for the porosity and portlandite in the cell where mechanical calculations are computed. In the three leached cements, the porosity evolution brutally changes in kinetic when all portlandite is dissolved. The confrontation of figures 6 and 7 permits to determinate the mechanical influence of the portlandite dissolution on the Young modulus of a cement paste.

4.4 *Mechanical loss properties of leached cement pastes*

For w/c=0.25, the total dissolution of portlandite tend to have a 25.1% porosity. The initial porosity corresponding to the intact microstructure is 9.5%. The corresponding loss of the Young modulus is equal to 61%. Results for w/c=0.4 or w/c=0.5 are sensibly different: respective capillary porosities after total dissolution of portlandite are 35% and 42%, resulting in respective losses of Young modulus equal to 91% and 83%.
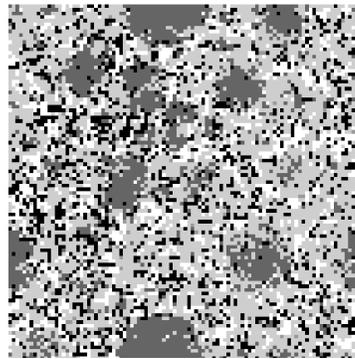

Figure 8: second section of the sound w/c=0.25 cement paste

These differences are interpretable if focused on the mineral composition of the section chosen for the finite-element calculation. Indeed, the spatial repartition of solid phases is not homogeneous and depends particularly on the position of the main anhydrous constituents, which are susceptible not to be completely hydrated.

For the w/c=0.25 cement paste, the solid phases composition of the considered section is quite different from the whole cell, due to the presence of anhydrous cement grains. Portlandite content is 14% instead of 15.6% for the whole cell before leaching. The mechanical study of another section, also taken randomly, gives respectively a portlandite volume ratio of 15.4%. Figure 8 represents the digital image of the intact second section of the w/c=0.25 cement paste. Also, anhydrous volume proportion is 32%, 20% and 25% for the first, second section and whole cell respectively. The Young modulus of this second section before leaching is equal to 34.8 GPa instead of 42.9 GPa, which corresponds to a 20% variation. This variation is in relationship with the heterogeneous aspects and properties of cement-based materials observed at local scales. In order to translate this heterogeneous aspect and to improve the precision of mechanical calculations, a probabilistic approach of the section choice is envisaged in further development of the modelling, because of its better relevance for heterogeneous materials, compared to deterministic approaches.

The comparison between figure 8 with figure 3 highlights the visual different solid repartition within the microstructure, confirming the strong influence of portlandite and anhydrous constituents on the elastic behavior of cement pastes. Portlandite acts at short term as a mechanical bond between hydrated cement grains because of its precipitation in the porosity during its early hydration. The dissolution of the portlandite tends to break these links, increasing the "flexibility" of the cement paste. As the remaining anhydrous constituents are three to five times more rigid than hydrates, their presence in the microstructure tends to increase the rigidity of the cement paste.

Results for the same "digital" cement pastes in which portlandite, monosulfoaluminate and ettringite pixels are successively removed, on one hand, and using a three-dimensional finite-element elastic model, on the second hand, have shown that the portlandite dissolution results in a half value of the Young modulus of the cement paste (Kamali, 2003). Our 2D computations show a bigger influence, which is explained by:

- First, the leaching of a cement paste causes simultaneous dissolutions or precipitations of solid species. This implies that when portlandite has totally dissolved, some other species have also partially dissolved.

- Secondly, our finite-element calculations are bi-dimensional. Percolation studies show that the physical percolations of porosity in a 2D or a 3D medium is not the same and is near 45% (Babalievski, 1995, Garboczi, 1999) in 2D and 17% in 3D (Garboczi, 2001). As these limits are different, the elastic losses are different if the problem is studied in two or three dimensions.

5 CONCLUSIONS

Three digital images of Portland cement pastes with variable water-to-cement ratio were studied in regards to their chemical behavior to pure water leaching. A reactive-transport approach based on the interactions between the pore solution and the solid skeleton, and also on the aggressive environment, was developed. This model directly gives the same degradation as that experimentally observed, and in particular highlights the effect of the water-to-cement ratio on global degradation kinetics, and on the order of total dissolution of the main hydrates. Using a "digital" representation of the leached microstructures, a bi-dimensional finite-element elastic model is able to evaluate the homogenized Young modulus of the leached cement pastes. Results highlight the influence of capillarity porosity on the evolution of the Young modulus. Indeed, the three w/c cement pastes have similar evolutions in regards to the porosity content. Results also show the strategic choice of the section to be representative of the whole cell. According to the chosen section, the proportion of minerals like anhydrous constituents and hydrates, and porosity can vary and so influence the calculated value of the homogenized Young modulus. At last, the direct comparison with former 3D finite element calculations is delicate because of the difference of percolation characteristics between 2D and 3D meshes or chemical calculations.

In order to determinate more accurately the elastic properties of a leached cement paste, two orientations are possible. First, an extension of the finite element computations to a 3D mesh representing the whole cell is possible but with one million nodes. Thus a 3D finite element becomes really time-consuming, which causes disagreements when numerous calculations corresponding to different chemical degradation stages are required. A second orientation is the

choice of a strategic section in which the proportion of each phase is the nearest to the whole cell. This orientation however does not fix the problem of the percolation limit. Nevertheless, preliminary results obtained by this bi-dimensional finite-element model are encouraging because of its possible extension. The future evolutions with a probabilistic approach would increase the relevance of the calculations. Also, access to further information is directly possible, like local stresses or stains in minerals, or homogenized values like tensile or compressive strengths.

As a conclusion, the coupling of these two models could study the influence of external chemical attacks on the mechanical behavior of cement paste. A possible direct study can be, for example, the mechanical influence of the penetration of the aggressive ions like SO_4^{2-} or Cl^-. Indeed, such external sulfate ions coming through a cement paste cause the precipitation of minerals, possibly expansive.

6 AKNOWELDGEMENTS

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