Experimental and numerical study on the effect of sulfates on calcium leaching of cement paste

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ABSTRACT: This paper presents some experimental and numerical results obtained on cement paste samples immersed in water with sulfate ions (15 mmol/l). Experimental results include the continuous monitoring of calcium loss and sulfate consumption within the cement paste, SEM, XRD and EDS analysis of the solid constituents of the cement matrix (Ettringite, Portlandite, Gypsum) within the leached (calcium depleted) thickness of the samples. Modeling of the combined diffusion transport problem with local equilibrium of the complex chemical system is then used to estimate the quantities of solid constituents which precipitates in the porous network during the external sulfate attack. The mechanical consequences (cracking) of ettringite or gypsum precipitation are then simulated via finite element analysis. The mechanical model is based on the orthotropic damage theory and accounts for the chemo-mechanical couplings resulting from calcium leaching (chemical softening and damage).

1 INTRODUCTION

This study is concerned with the assessment of the durability performance of concrete in nuclear waste containment. Calcium leaching of cement paste under de-ionized water, considered as the reference scenario of chemical degradation in this context, is characterized in particular by the dissolution of Portlandite and Calcium Silica Hydrates, leading to the diffusion of calcium ions towards the outside medium [Adenot 1992]. Former studies on chemical degradation of cementitious materials have focused successively on cement paste [Adenot 1992], mortars [Bourdette 1994, Tognazzi 1998], and concretes [Badouix 1999], with, in the latter case, a particular emphasis on the effect of carbonates on the overall leaching kinetics. Phenomenological models aiming at describing the combined diffusion transport problem with local chemical equilibrium have been developed for calcium leaching under deionized and carbonated water. Current research efforts tend to focus on the effect of sulfate ions on long-term chemical degradation of cementitious materials. In this respect, this paper presents some experimental results performed on cement paste samples, aiming at clarifying the physico-chemical processes occurring during an external sulfate attack combined with calcium leaching.

Calcium leaching in de-ionized water leads to a significant degradation of the mechanical properties of concrete (material strength, Young's modulus).

Modeling the mechanical behavior of calcium depleted materials requires therefore to account for the strong chemo-mechanical couplings (chemical softening and damage), as shown by several authors [Carde 1996, Gérard 1996, Ulm 1999]. In itself, sulfate attack of cementitious materials can also lead to significant mechanical damage (cracking), related to the precipitation of secondary phases within the porous network, such as ettringite and/or gypsum. Evaluating the long-term behavior of cement paste in sulfated environment requires therefore to model the effect of precipitates on the solid skeleton of cement paste without neglecting the chemo-mechanical damages induced by calcium leaching. In this paper, the modeling of the combined diffusion transport problem (sulfates, calcium, sodium, ...) with local chemical equilibrium during an external sulfate attack is presented, together with the chemo-mechanical analysis of cement paste samples, based on the orthotropic damage theory [Lemaitre & Chaboche 1988].

2 EXPERIMENTAL PROGRAM

2.1 *Materials*

To obtain results in short times and enhance the phenomena, a non sulfate-resistant cement was chosen, the CPA-CEM I 52.5 R NF from Calcia (Couvrot factory). Its high SO_3 (3.9%), Gypsum (5.7%) and C_3A (10.5%) contents together with a high surface

Table 1. Chemical composition (in % of mass) of CPA-CEM I 52.5 R cement.

CaO	SiO2	Al2O3	SO3	Na2O
64.4	20.4	5.2	3.7	0.1

area (S_{Blaine} = 440 m^2/kg) ensured its reactivity to sulfates.

Cement paste samples (with a water/cement ratio of 0.4) were cast in cylindrical moulds (7 cm diameter * 10 cm height), kept in sealed bags until demoulding after 48 hours. Curing conditions at 100% relative humidity and constant temperature 20°C lasted for 28 days. Cylinders were cut in slices of 4, 8, 16 and 32 mm thick and then kept in sealed bags in nitrogen atmosphere to avoid any carbonation. Curing conditions are chosen such that partial leaching of alkalis and carbonation are avoided.

2.2 Experimental set-up

After the curing period, the samples were immersed in water containing a solution of Na_2SO_4. The sulfate concentration (15 mmol/l) was chosen according to the following criteria : avoid any precipitation of gypsum in the solution and in the cement paste, obtain experimental results and cracking in short delays (a few months), keep concentration close to realistic site conditions for nuclear waste storage.

During the experiments, the pH and temperature were kept constant, equal respectively to 7 (nitric acid at a concentration of 1 mol/L was added automatically to the solution to regulate the pH) and 20°C. To avoid any carbonation of the samples during the tests, nitrogen gas is injected continuously in the solution. Cylindrical slices of 4, 8, 16 and 32 mm were immersed in the solution and protected from lateral degradation, such that the external attack occurs in one direction only, perpendicular to the circular faces (see Figure 1).
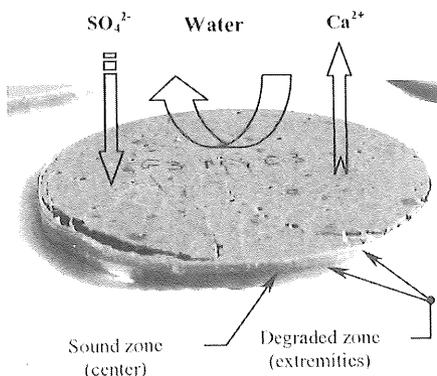
Figure 1. Sulfate attack with calcium leaching of a CPA-CEM I cement paste sample

In order to maintain constant experimental conditions during the tests, the sodium sulfate solution was renewed at regular intervals, in connection with the quantity of added nitric acid (which is also correlated to the quantity of leached calcium from the cement paste).

3 EXPERIMENTAL RESULTS

To understand the underlying chemo-physical processes occurring during the combined sulfate attack – calcium leaching, information was required concerning : the ionic quantities and their diffusion inward and outward from the cement paste, the solid compounds initially in the cement paste or formed during the test. To this end, chemical analysis of the sulfate sodium solution at regular intervals provided some insight on the outward fluxes of calcium and hydroxyl ions and the inward flux of sulfate ions. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer microanalysis (EDS) were used to determine the mineralogy of the degraded (defined as the calcium depleted thickness of the sample) and sound zones. The results of these analysis are presented hereafter.

3.1 Chemical analysis of the leachant.

Figure 2 shows the cumulated quantities of OH^-, Ca^{2+} and SO_4^{2-} ions obtained by ionic chromatography, as a function of the square root of time.

The slopes of the fluxes are respectively of 8.3 mmol/m^2/$s^{0.5}$ for OH^-, 3.7 mmol/m^2/$s^{0.5}$ for Ca^{2+} and 1.3 mmol/m^2/$s^{0.5}$ for SO_4^{2-}. Calcium and hydroxyl ions result mainly from the dissolution of Portlandite ($Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2\ OH^-$) and to a lesser extent from the calcium depleting of Calcium Silicate Hydrates (CSH). The consumption of sulfates between two renewing of the sodium sulfate solution represents about 10% of the initial content of the solution. As for the leaching process in de-ionized water, the ratio between hydroxyl and calcium fluxes is close to 2. The slope of the calcium flux is also similar to that obtained for leaching in pure water (4.7 mmol/m^2/$s^{0.5}$).

3.2 Mineralogy of the leached zone

The mineralogy of the leached zone was assessed by scraping progressively the samples from the external surface to the sound part. With this technique, it was possible to analyze by XRD the solid compounds within slices of less than 100 μm thick.

By using this methodology at different times, the complete mineralogy of the degraded material is obtained, together with the evolution of precipitation fronts (ettringite AFt, gypsum), and dissolution fronts (Portlandite). The resulting profiles obtained
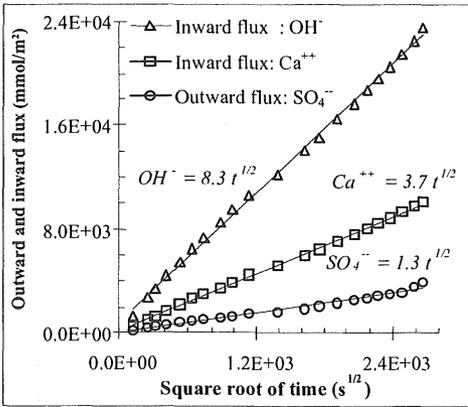
Figure 2. Inward and outward fluxes of calcium, hydroxyl and sulfate ions

on samples subjected to combined sulfate attack – calcium leaching for 5, 10 and 12 weeks are presented in Figure 3.

The profiles of Figure 3 show the existence of three zones. Zone 3 in which the cement paste contains Portlandite ($Ca(OH)_2$) in important quantities. This allows to define as for calcium leaching in de-ionized water a sound zone (where no calcium depletion has taken place) and a degraded thickness. The latter reaches 1.3 mm after 12 weeks testing.

Zone 2 in which Portlandite co-exist with Ettringite (AFt) and Gypsum ($CaSO_4,2H_2O$). This zone is localized and of reduced thickness (15% of the total degraded thickness after 12 weeks testing) with respect to Zone 1 where ettringite (AFt) appear to be qualitatively the dominant phase. The thickness of Zone 1 reaches 50% of the total degraded thickness after 12 weeks.

According to these results (5, 10 and 12 weeks), the position of the Portlandite dissolution front

seems to evolve linearly with the square root of time, showing that calcium leaching in a sulfated environment is governed by diffusion processes, as it is the case for calcium leaching in de-ionized water [Adenot 1992]. By linear regression, a slope of 0.145 mm/j$^{0.5}$ was obtained. Similarly, the size of the AFt zone (Zone 1) evolves linearly with the square root of time, with a slope of 0.067 mm/j$^{0.5}$.
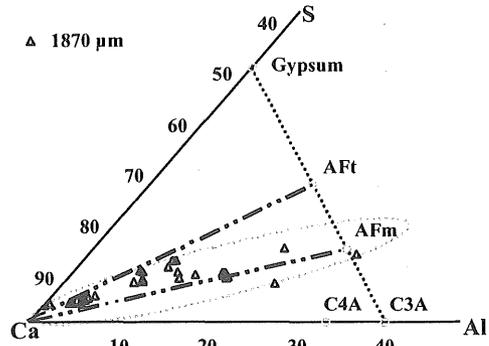
Figure 4. Cement paste composition before testing, obtained from EDS micro-analysis

3.3 Correlation between mineralogy and cracking

Every 100 µm, local analysis on lines parallel to the external surface have been performed with the EDS technique to confirm these results. Again Portlandite was found predominantly in the previously defined "sound zone". Monosulfoaluminate AFm was also detected in this zone (see Figure 4), which was not possible with XRD owing to its reduced quantity. As shown latter, AFm (C_4ASH_{12}) plays a non-negligible role in the overall degradation process. EDS also confirmed the coexistence of AFt, Gypsum and Portlandite between the sound zone (Zone 1) and the AFt precipitation zone (Zone 3).

Figure 3. Identification by XRD analysis of the solid compounds in the degraded zone of the cement paste samples at different times
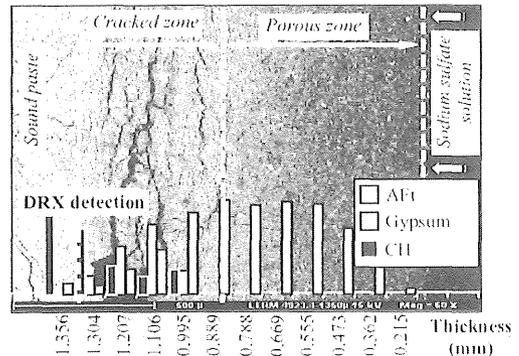
Figure 5. SEM picture of the CPA cement paste sample after 12 weeks testing

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A picture of the degraded zone obtained by SEM analysis is given in Figure 5, together with the XRD profiles for the sample tested during 12 weeks. The superposition shows obviously that major cracks occur in Zone 2 where Portlandite, Gypsum and AFt were detected. More refined SEM analysis showed that the porosity of this part was significantly reduced with respect to that of the sound zone (Zone 3). On the contrary, the porosity of Zone 1 where AFt was the dominant phase seems to increase significantly, owing to calcium leaching. No cracks were observed in this part, in spite of the important quantity of AFt detected by XRD.

4 MODELING OF THE COUPLED CHEMICAL-TRANSPORT PROBLEM

The modeling of the coupled diffusion transport / chemical problem was performed with the code CASTEM2000. The solution is obtained by solving iteratively and independently the chemical and transport problems. The chemical system is assumed to remain in local equilibrium, which implies that precipitation and dissolution processes occur instantaneously. By minimizing Gibb's energy and enforcing the mass balance equations, the chemical composition is obtained. The transport problem is then solved using a finite volume formulation. The diffusion coefficient and porosity remain constant within the material.

The following components are considered in the simulations : Ca, Al, S, Na and Si. Initial quantities in mol/l of cement paste are obtained from the chemical composition of the cement (see Table 1). Concentrations (in mol/l of porous volume) are derived from these quantities. Four minerals can potentially appear or disappear during the calculations : Portlandite, monosulfoaluminate (AFm), ettringite (AFt) and Gypsum. In a first approximation, CSH are not considered. Boundary conditions consist in enforcing constant ionic concentrations at one end of the mesh : 30 mmol/l of sodium ions, 15 mmol/l of sulfate ions, and 0 mmol/l of calcium ions. These
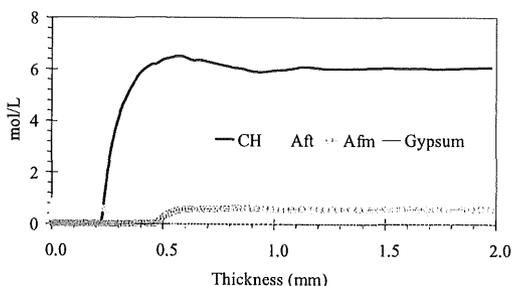
Figure 6. Simulated profiles of concentrations in solid phases after 3 weeks of testing.

values correspond to the theoretical composition of the external solution in contact with the samples during the tests.

As for calcium leaching of Portland Cement pastes in deionized water, the porosity and the diffusion coefficient should evolve considerably due to the dissolution of Portlandite [Richet 1992]. Since the coupled diffusion transport / chemical code could not cope with non constant coefficients, average values were estimated to obtain the experimental degradation kinetics $(0.145 \text{ mm/j}^{0.5})$: porosity of 0.319 and diffusion coefficient of $5.4 \ 10^{-12} \text{ m}^2/\text{s}$.
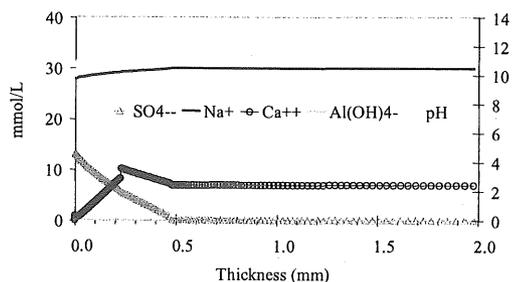
Figure 7. Simulated profiles of concentrations in liquid phases after 3 weeks of testing.

Concentrations in solid and liquid phases after 3 weeks are presented in Figures 6 and 7. Figure 7 illustrates the inward diffusion of Na^+ and SO_4^{2-} ions, together with the outward diffusion of Ca^{2+} and $Al(OH)_4^-$ ions. According to the profiles of Figure 6, AFm plays a major role since it combines with sulfate ions to form AFt. Similar to the dissolution front of Portlandite, a dissolution front for AFm appears in the profiles, to which corresponds also a precipitation front for AFt and a zero concentration in SO_4^{2-} (see Figure 7). The position of this front depends greatly on the initial quantity of AFm in the cement paste. It is however always located in the sound zone (defined as the zone where Portlandite has not been dissolved). The greater the initial quantity of AFm, the greater the quantity of sulfate ions it can combine with, and therefore, since the sulfate ions profile (see Figure 7) decreases almost linearly from the external surface to the sound part of the sample, the closer the AFm dissolution front is from the Portlandite dissolution front.

No Gypsum appeared in the simulations, as it did in the experiments. The precipitation of Gypsum was however obtained for similar calculations performed with smaller initial quantities of AFm and slightly different values for the chemical equilibrium constants than those used by the data base of CASTEM2000. Further efforts are dedicated to a precise understanding of the conditions in which Gypsum appears in the material.

5 MODELING OF THE COUPLED CHEMO-MECHANICAL PROBLEM

The mechanical model is based on the orthotropic damage theory [Lemaitre & Chaboche 1988]. Damage is introduced by defining effective stresses which are then related to elastic strains. Effective microscopic stresses are linked to macroscopic stresses by damage variables. Damage in the model can originate from either excessive macroscopic stresses or local auto-stresses induced by precipitation of a secondary solid phase.

Application of the model to combined sulfate attack – calcium leaching consist in accounting, on the one hand, for the evolution of the local mechanical characteristics of the material with calcium loss, and, on the other hand, for the precipitation of ettringite within the porosity of the material. Figure 8 and 9 illustrate the first dependency for the elastic modulus and the normalized local cohesion of the material.
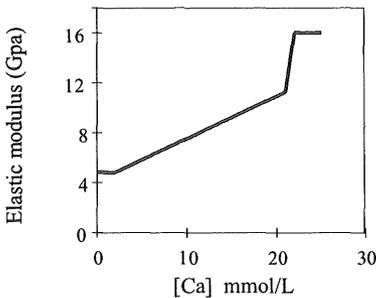
Figure 8. Evolution of the elastic modulus with the calcium ionic concentration.
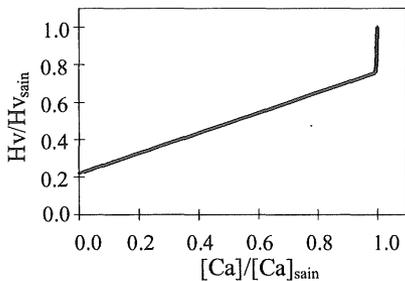
Figure 9. Evolution of the normalized cohesion with the normalized calcium ionic concentration.

Ettringite precipitation is introduced within the damage loading surfaces via an auto-stress tensor σ_r (see Figure 10).
The intensity of the positive part of this auto-stress (tensile stress) is assumed to be proportional to the difference between the volume of formed ettringite
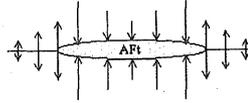
Figure 10. Schematic representation of the stress state in and around the ettringite precipitation front (the precipitation induces local compressive stresses which, in turn, generate tensile stresses in the neighborhood).

(V_{AFt}) and the porous volume (V_p), as described by equation 1.

$$\sigma_r = K\langle V_{AFt} - V_p \rangle \tag{1}$$

The coupling between both type of damage (related to macroscopic stresses or local auto-stresses) is treated according to the weakest link theory. Total strains include an elastic component related to the effective stress tensor and an anelastic component, subdivided in two parts, associated, on the one hand, to macroscopic damage and, on the other hand to damage generated by internal stresses induced by AFt precipitation. This material model was implemented in the Finite Element code CASTEM2000. The global equilibrium equations are solved iteratively using the Newton-Raphson scheme. The local integration of the constitutive equations of the model is performed in the effective stress space. The local convergence is assumed to be reached as soon as the local strain field is compatible with the global strain field. The local resolution relies on a gradient method [Sellier 2000].

This coupled chemo-mechanical approach was used to model the behavior of the samples subjected to a combined sulfate attack – calcium leaching test.
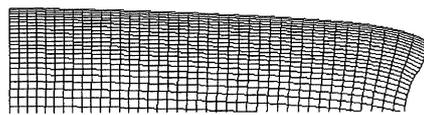
Figure 11. Calculated displacements of the sample subjected to combined sulfate attack – calcium leaching
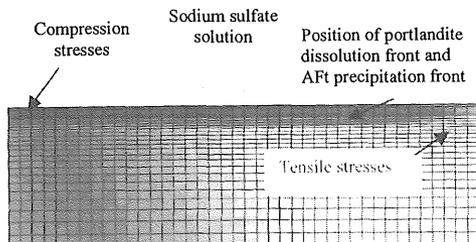
Figure 12. Auto-stresses generated by the internal precipitation of AFt in the calcium depleted part of the sample

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Figure 11 illustrates the global swelling of the sample when subjected to an internal pressure related to AFt precipitation.

Since AFt precipitation was only considered to occur within the calcium depleted part of the material (as shown before, the AFt precipitation front depends on the initial quantity of AFm and could be located within the sound part of the sample), the positive part of the auto-stresses (tensile stresses) is located in the neighborhood of the Portlandite dissolution front. As shown in Figure 12, tensile stresses are mainly generated within the sound part of the sample. This distribution is the consequence of the important decrease of the elastic modulus in the calcium depleted zone. These tensile stresses could lead to cracking, particularly close to the Portlandite dissolution front, as found experimentally (see Figure 5).

6 CONCLUSIONS

In this paper, experimental and numerical results concerning the chemo-mechanical degradation of cement paste samples subjected to a combined sulfate attack – calcium leaching test have been presented. With regards to calcium leaching in pure deionized water, the presence of sulfates does not modify significantly the leaching kinetics. Cracking was observed predominantly close to the Portlandite dissolution front, where XRD analysis showed the co-existence of Gypsum, Portlandite and ettringite.

Numerical analysis of the combined diffusion / chemical problem showed the importance of AFm concerning the location of the ettringite precipitation front. No Gypsum was however obtained in the calculations. Further research concentrates on this point. The chemo-mechanical analysis of the samples demonstrated that internal auto-stresses related to ettringite within the calcium depleted part of the samples could lead to tensile stresses and therefore cracking in the neighborhood of the Portlandite dissolution front, as found experimentally.

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