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Physicochemical equilibria of cement-based materials in aggressive environments—experiment and modeling

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Abstract

Assessment of the integrity of concrete structures during their service life begins by considering the durability of the material in its environment. Experiments have clearly improved the understanding of the degradation mechanisms of concrete, mortars, and cement pastes under various aggressive environments. As far as radioactive waste containers are concerned, leaching by water has to be considered. Leaching experiments of cement pastes by aggressive solutions are shown to result in degradations with different kinetics. Three cement pastes with variable water-to-cement (w/c) ratio (0.25, 0.4, and 0.5) in two solutions (pure water and mineralized water) were investigated by TG/DTA, SEM-EDS, and by application of the NIST (National Institute of Standards and Technology) microstructure models. Leaching kinetics, evolution of the solid skeleton, and pore solution were experimentally studied and successfully modeled, using a reactive-transport approach. The discrepancies between modeling and experimental results highlight the understanding of complex degradation mechanisms. New results on the interactions on the aggressive solution and the cementitious material, through the pore solution, are presented.

Keywords: Cement; Microstructure; Water leaching; Diffusion; Modeling; Reactive transport

1. Introduction

Prof. H.F.W. Taylor wrote in his well-known book, *Cement Chemistry* [1], “Leaching of concrete by percolating of flowing water has sometimes caused severe damage, e.g., in dams, pipes or conduits, and is potentially important for the long-term storage of nuclear wastes.” In fact in this last case, the leaching is related to the behavior of cement minerals. The variation of the chemical composition of the pore solution is the driving force of cement evolution under thermodynamic equilibria. In addition, ionic fluxes result from differences of the ionic composition between the external aqueous environment and the pore solution. Considering that the cement paste porosity is fully saturated with an interstitial solution and that the external environment is an aqueous solution, the ionic fluxes are mainly diffusive [2]. Most results already published have been related to the decalcification of the solid skeleton [3–5]. This paper reports the evolution of the microstructure of a Portland cement under water leaching: experimentally, by transformation of solid minerals and evolution of the pore solution, then by modeling and coupling of the interactions between the pore solution and the external aggressive solution.

2. Experimental study

2.1. Materials

Cement pastes with three water-to-cement (w/c) ratios (0.25, 0.4, and 0.5) were prepared with a Portland cement (CEM I 52.5, European standard) whose chemical and mineralogical compositions are given in Table 1. The mixture with w/c = 0.25 contained superplastizer with a superplastizer/cement ratio equal to 0.3% by mass. Cylinders (70 mm in diameter and 140 mm long) of pastes were stored for 3 months, after 24 h in molds, in a climatic chamber at 100% relative humidity and 20 °C, followed by immersion in lime-saturated water for 2 months.

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Table 1
Chemical and mineralogical (XRD quantitative analysis) composition of the Portland cement

Composition (% in mass)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
23.4	3.05	2.15	67.4	0.70	2.1	0.15	0.1
	C_3S	C_2S	C_3A	C_4AF	Gypsum	Limestone	
	71	13	4	8	3.5	2.5	

2.2. Experiments

2.2.1. Specimen preparation

Prisms (20 × 20 × 30 mm) were cut from the center of the cylinders to avoid edge problems and to get homogeneous specimens for leaching. Samples to be leached by ammonium nitrate were larger in dimensions: 30 × 30 × 20 mm.

2.2.2. Leaching procedure

Among the three aggressive solutions, ammonium nitrate has already been used to accelerate the leaching phenomenon [4,6,7]. The composition of the natural water is given in Table 2.

Five specimens were leached: three with w/c = 0.25, 0.4, and 0.5 in pure water for 114 days, one with w/c = 0.4 in mineralized water for 114 days, and one with w/c = 0.4 in ammonium nitrate solution (480 g/l) for 19 days. Two different leaching protocols were used. A simple protocol for ammonium nitrate consists in putting the sample on an inoxidizable grid in a large container of nonrenewed aggressive solution at 20 °C. Leaching in pure water and mineralized water is performed [7] in a PTFE container of 1-l volume (Fig. 1). Samples are placed on a PTFE grid and stored for a desired period. The aggressive solution in the container is continuously renewed through a water-circulation system regulated by a peristaltic pump at 1 l/day. Each container is equipped with two pipes. One pipe supplies the container with bubbled water using nitrogen gas to avoid any risk of carbonation. The second pipe withdraws the water from the container to recovery tubes. Three containers are placed in a thermostatted chamber at 26 °C. Each container contains one specimen only.

2.2.3. Characterization of sound materials: TG/DTA and porosity measurements

Porosity and portlandite content are two important parameters to be considered when leaching phenomenon and particularly its kinetics are investigated. Porosity influences the ionic diffusivity and leaching kinetics. Portlandite is the first hydrate to be dissolved [2]. Its dissolution increases porosity and ionic diffusivity. Ions diffuse through connected pores. Different equations to calculate the diffusivity of ions as functions of capillary porosity or total porosity have been published [7,8,9]: these types of porosity are relatively easy to identify experimentally.

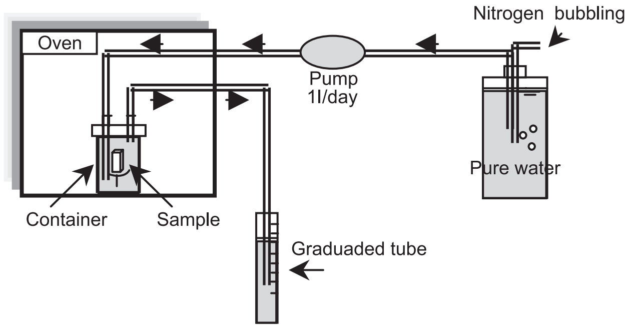

Fig. 1. Leaching protocol used in this study [7].

In this study, the water-filled porosity was determined by means of three weight measurements of saturated and dried samples and portlandite content. The drying temperature was fixed at 105 °C. Table 3 gives the water porosity for the three w/c ratios studied. Portlandite (CH) contents of the three cement pastes were determined from TG/DTA thermograms. Three powdered samples from the sound zones of the three leached specimens were scanned from room temperature to 1100 °C at a scan speed of 10 °C/min with a 60-min stop at 100 °C. Argon gas was used during the thermal tests to avoid carbonation. Table 4 gives the calculated values of CH content for the three cement pastes.

2.2.4. Leaching kinetic measures

After the leaching test, the degraded samples were covered by an epoxy resin and then cut from the surface to the center in order to observe and to measure the leached depth under a binocular microscope (Fig. 2). The leached zone is easily distinguished from the sound zone by its brightness. The accelerated effect of ammonium nitrate on the leaching kinetics is also clearly illustrated.

The leached depth for the different samples increases with w/c in pure water (Table 5). This is due to an increase in capillary porosity that itself increases ionic diffusivity through the material and thus the leaching kinetics. The specimen with w/c ratio of 0.25 is the most leach resistant due to its low porosity and its low portlandite content. For specimens with w/c ratio of 0.4, the leaching kinetics seems

Table 2
Chemical composition of the natural mineralized water

Chemical composition (mg/l)								pH
Ca	Si	Mg	Na	K	Cl	SO_3	HCO_3	
11.5	31.7	8.0	11.6	6.2	13.5	8.1	71	7

Table 3
Experimental water-filled porosity

Paste	Experimental value (%)
w/c = 0.25	25
w/c = 0.4	39
w/c = 0.5	44

Table 4
Experimental CH mass content calculated from thermal analysis

Paste	Experimental CH mass content (%)
w/c = 0.25	16.5
w/c = 0.4	19.6
w/c = 0.5	20.5

to be strongly influenced by the composition and nature of the aggressive solution. The leached depth for ammonium nitrate solution is 6.8 mm for 19 days of degradation, whereas for pure water this depth is 1.5 mm after 114 days of leaching, but only 0.3 mm for mineralized water.

Several authors have already shown that leaching by either pure water or nitrate solution is governed by a diffusion mechanism; one-dimensional leaching kinetics are proportional to the square root of time [2,3,4,9]. This expression is the consequence of the experimental observation of sharp dissolution fronts, one-dimensional degradation tests, and consideration of only one diffusive species in the model. A diffusion equation expressed in a semi-infinite medium has a semianalytical solution. The expression of an isoconcentration evolution is thus possible and depends on time, diffusion concentration, and degradation depth. Within the cement paste, in regard to one ion, subsaturation leads to the dissolution of one solid. As long as this solid persists within the composite, the concentration of the ion cannot be less than the equilibrium concentration. By writing the expression of the equilibrium concentration, the depth of the dissolution front, x, can be expressed by $x = a\sqrt{t}$, where a is a kinetic constant and t the time.

Although this result is not applied to the case of carbonated mineralized water [10], for both pure water and ammonium nitrate solution the evolution of the leached depth (x_l) far from sample edges, where-one dimensional degradation is realistic, is linear vs. the square root of time. Leaching kinetic parameters, a, of the cement pastes with w/c = 0.25, 0.4, and 0.5 are calculated and given in Table 6. These kinetic parameters enable the leached depth to be predicted after any period of leaching. Particularly, the kinetic parameter corresponding to the ammonium nitrate protocol predicts the leached depth of the cement paste with w/c = 0.4 after 114 days of leaching by the following calculation: $x = 1.56\sqrt{114} = 16.7\ \text{mm}$. This value is 11 times higher than that obtained with the pure water protocol, and for the same material leached during the same period. Considering the leaching time instead of the leached depth, the acceleration factor is equal to 121 = 11 × 11, because of the square root of time simplified kinetic equation.

Table 5
Experimental leached depth for the five specimens

Aggressive solution	Leaching period (days)	Leached depth (mm)		
		w/c = 0.5	w/c = 0.4	w/c = 0.25
Pure water	114	1.8 ± 0.1	1.5 ± 0.1	0.8 ± 0,1
Mineralized water	114	–	< 0.3	–
Ammonium nitrate solution	19	–	6.8 ± 0.5	–

2.2.5. EDS X-ray microanalysis

EDS X-ray microanalyses were carried out on specimens with w/c = 0.4 leached by the three aggressive solutions. The surface was polished and then coated with carbon. Calcium and sulfur energy profiles were scanned along different lines, starting from the sound zone to the external layer, which was in contact with water. Two different lines per specimen were scanned in the case of pure and mineralized waters, but only one in the case of ammonium nitrate solution. For a comparative study, all measurements were done with the same experimental conditions and at a fixed accelerating voltage of 10 kV. Each measure corresponds to the mean energy obtained on a 200 × 150-μm surface in the case of pure and mineralized water or on a 300 × 225-μm surface in the case of ammonium nitrate solution. Fig. 3 presents the relative energy profiles of elements, which were calculated by dividing the measured energy by that of the sound zone. Fig. 3 shows the following.

- For a specimen leached by pure water, a gradual decrease in the relative energy of calcium occurs from the external edge to a depth of 1.5 mm. This depth value corresponds to the leached depth measured under a binocular microscope. The first hydrate to be dissolved is portlandite [2]; thus, it can be assumed that the depth of 1.5 mm corresponds to the front of portlandite dissolution. Similar decrease in calcium content is observed for ammonium nitrate. However, for carbonat-

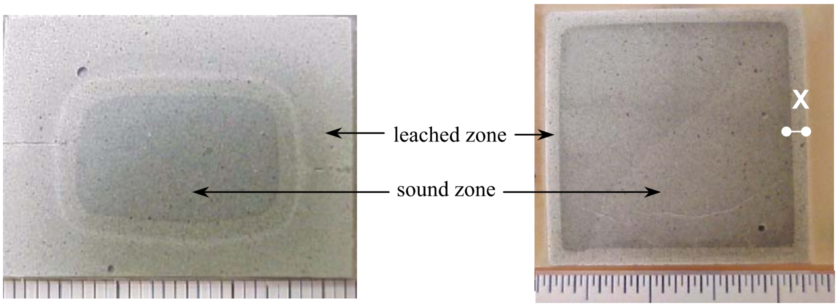

Fig. 2. Photographs of specimens with w/c = 0.4 leached by ammonium nitrate during 19 days (left) and by pure water during 114 days (right).

Table 6
Experimental leaching parameter *a* as a function of w/c ratio and aggressive environment

Aggressive environment	w/c	*a* (mm day$^{-1/2}$)
Pure water	0.25	0.075
Pure water	0.4	0.140
Pure water	0.5	0.169
Ammonium nitrate	0.4	1.56

ed mineralized water, little decalcification of the external layer occurs. This is due to the positive effect of carbonation; the formation of calcite microcrystals decreases the porosity of the external zone and, consequently, the diffusivity of ions from the aggressive water. This protective layer significantly reduces leaching. Thus, pure water can be considered as very aggressive for cement-based materials.

- For a specimen leached by pure water, a gradual decrease in sulfur signal occurs to a depth of 1.5 mm. Sulfur in solid phases is totally dissolved in the external zone, 0.5 mm thick, which corresponds to a total dissolution of ettringite and monosulfoaluminate. However, an increase in sulfur retained in the solid is observed at greater depth, before reaching the portlandite dissolution front. The leached depth seems to be higher than that either measured under a binocular microscope or given by the portlandite dissolution front. The increase in sulfur is probably due to the fixation of this element on solid phases or the formation of a sulfur-rich phase such as gypsum or ettringite. In the case of ammonium nitrate, as well as for the specimen leached by pure water, a gradual decrease in sulfur relative energy is observed. However, the thickness of the zone where sulfur is almost totally dissolved represents only 1/6 of the total leached depth compared to 2/6 for pure water. Leaching in ammonium nitrate solution gives less decrease in sulfur than in pure water. In the case of mineralized water, a slight decrease in sulfur is observed in the external layer.

3. Modeling

3.1. Presentation and objectives of the modeling

Calcium leaching kinetics and degradation fronts vary as functions of the water composition used as an aggressive solution, i.e., pure water, mineralized water, and NH_4NO_3 solution [7,10]. To understand the evolution of a Portland cement paste subjected to calcium leaching at the microstructural scale, we are developing a model based on the interactions between the solid constituents of the cement paste and the internal pore solution and, on the other hand, the pore solution and the external aggressive environment. Physical and chemical laws, based on thermodynamics, are used to implement the model.

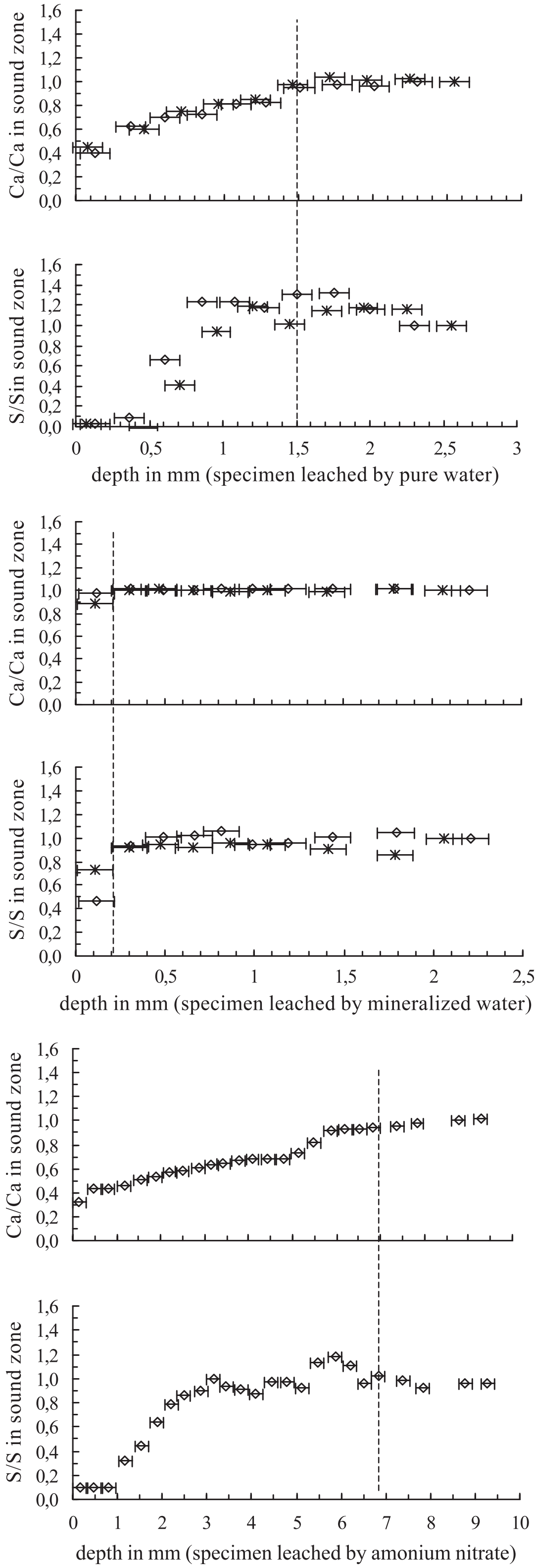

Fig. 3. Relative energy profiles of calcium and sulfur obtained by EDS X-ray microanalysis along different lines perpendicular to the sample surface in contact with aggressive solution as pure water, mineralized water (Table 2), and ammonium nitrate (480 g/l).

The first interaction concerns relationships between ions in the pore solution and solids constituting the material. At a given time, for a specific ion, and in regard to one solid, a pore solution concentration lower than equilibrium tends to dissolve this solid to reestablish equilibrium. Conversely, supersaturation tends to precipitate a solid. In this paper, all references to the cement paste always consider a diphasic system composed of a solid skeleton and a pore solution. Thus, for the cement paste, a change in the pore solution composition may either dissolve or precipitate some solid constituents until a new thermodynamic equilibrium is reached.

The second interaction deals with differences in the ionic composition between the external aqueous environment and the pore solution, resulting in a source of ionic fluxes. Considering that the cement paste porosity is fully saturated with pore solution and that the external environment is always an aqueous solution, these ionic fluxes are mainly diffusive.

By simultaneously modeling and coupling these two interactions in a system composed of a cement paste and an external aqueous environment, it seems possible to represent the evolution of the microstructure of a Portland cement paste subjected to an external chemical attack.

3.1.1. Main equations and numerical resolution strategy

If these two interactions are coupled, it is possible to write a reactive-transport equation for all diffusive ionic species, as is often used in geochemical approaches like KIRMAT (KInetic Reactions and MAss Transport) [11], but rarely applied to concrete durability studies. In our diffusive problem, the evolution of the concentration c_i^{f} of the ith ion in solution can be written as [Eq. (1)]

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

where D_i^{f} is the apparent diffusion coefficient of the ith ion within a representative elementary volume (REV), and $\sum_{j=1}^{J} c_{ij}^{f*}\Gamma_j$ is the reactive term that represents the contribution of the J reaction speeds Γ_j, multiplied by the stoichiometric coefficient $c_{ij}^{\mathrm{f}*}$, of the ith constituent in the jth reaction. An expression of the jth reaction speed Γ_j can be deduced from a classical first-order kinetic law [Eq. (2)],

$$\Gamma_j = k_{\mathrm{d}_j} S_j \left(1 - \frac{Q_j}{K_j}\right) \tag{2}$$

where k_{d_j} is a dissolution or precipitation kinetic constant, S_j the reactive surface of the jth solid constituent, K_j the equilibrium constant at specified thermodynamic conditions, and Q_j the product of activities of all the ions involved in the equilibrium with the jth solid. Thus, the reaction term in Eq. (1) reflects nonlinear relationships between ions.

Expressed in a three-dimensional Cartesian system, a diffusion equation without a reactive term has no analytical solution. Furthermore, a reaction term, which involves nonlinear couplings with other ions, is difficult to solve directly. A numerical resolution, at specific time steps, becomes necessary. Using the hypothesis that the cement paste system follows the local equilibrium approximation, we consider that at each time and in each physical region, reaction rates are infinitely higher than diffusion speeds. Consequently, reactions are instantaneous in regard to diffusive phenomena. The applicability of this approach has been shown [12]. This hypothesis is often used in geochemical models because of the simplification of the numerical resolution of the reactive-transport equation. Indeed, if decoupling the reaction term from Eq. (1) is allowed, the numerical resolution of the reactive-transport equations comprises two phases. Furthermore, the greater the mesh composing the study domain, the longer and more time-consuming the diffusion calculations become. In addition, separating the two calculations gives a second advantage. If the cement paste system reaches a local chemical equilibrium in each time step, it is possible to limit the number of diffusive species and use a speciation calculation to determine the concentration of all ionic species within the pore solution. In our study, diffusive species considered are the principal ones: calcium, silica, aluminum, sulfate, sodium, and potassium. Transport calculations consider as total concentration of a given species the sum of concentrations of species present for all ions in the pore solution. The first four species are involved in dissolutions or precipitations of the main solid constituents present in a Portland cement paste: C-S-H, portlandite, ettringite, and calcium monosulfoaluminate. Alkaline ions (Na^+, K^+) are also taken into account because of their presence during the cement hydration process. Iron is a minor species and so is considered to have the same chemical behavior as aluminum. Consequently, this species is implicitly taken into account in aluminum content.

3.1.2. Presentation of the study domain

In order to numerically solve the reactive-transport equations in regard to our strategy, it is necessary to explain the study domain [13].

Let us consider a parallelepiped domain subdivided into cubic cells. These cells can represent either a volume of cement paste or an aggressive external solution. The aggressive solution is considered as an aqueous solution; its chemical composition is known and defined by the total concentration of all considered diffusive species. A variable composition with time of the aggressive solution is possible but is normally kept constant. The cells representing the cement paste are deduced from microstructures generated by the three-dimensional hydration model CEMHYD3D developed at NIST (National Institute of Standards and Technology) [14,15]. Knowing the anhydrous cement chemical composition and its granularity, this microstructural model builds a three-dimensional digital image representative of the solid constituents within a cement paste during its hydration. In this work, the building process is arbitrarily stopped when the calculated portlandite content reaches the value determined by TG experiments. The microstructure generated is a 100-μm-size cube composed of 1-μm cubic pixels: either a cement hydrate, an anhydrous constituent, or a capillary pore. This microstructure size justifies the choice of cell dimensions in our study domain. The pore solution composition is then numerically determined in order to be in chemical equilibrium with solid phases within the digitalized microstructural image of the cement paste.

Fig. 4 shows the study domain. In the *x* direction, the first two cells are aggressive solutions, whereas the others are cement pastes. Boundary conditions are the following: no fluxes crossing the two surfaces perpendicular to the *x* direction and periodic conditions for the four other surfaces. The equations constituting the model are developed and solved numerically in three dimensions. In this study, in order to simulate the leaching experiments presented subsequently, a one-dimensional problem is considered with all cells identical in a section perpendicular to the *x* direction, i.e., the chemical aggression direction.

3.1.3. Numerical expression of the modeling

The reactive-transport system of equations is numerically solved in three stages: (i) ionic diffusion, (ii) chemical reaction calculations, and (iii) the calculation of transport parameters, from the volume balance of dissolved or precipitated solid species.

First, transport equations are expressed for each diffusive species. The equations are formulated using a finite volume scheme [16]. In each cement paste cell and for a given species, the evolution of the total concentration of this species is equal to the sum of the fluxes between this cell and its six neighbors. Each cement paste cell is characterized by its capillarity porosity, determined in the model by the sum of all pore pixels within the microstructure. This porosity, ϕ, allows us to deduce the apparent diffusion coefficient D of a solution species in the cement paste cell as a function of the diffusion coefficient in an aqueous solution, and in regard to Garboczi and Bentz's relation [17] for pastes of pure hydrated C_3S, or for OPC with and without silica fume by Bentz et al. [8] [Eq. (3)]

$$\frac{D}{D_o} = \frac{0.004}{\beta} + \frac{0.03}{\beta}\phi^2 + 1.7H(\phi - 0.17)(\phi - 0.17)^2, \qquad (3)$$

where β is a parameter function of the added silica fume, equal to 1.00 in an OPC without silica fume, H is the Heavyside equation, and 0.17 is a mean porosity percolation value obtained from hydrated CEMHYD3D digital images.

This relation is deduced from a statistical study of porosity percolation of microstructures generated by CEMHYD3D and is available for a given relative diffusivity of C-S-H and a 1-μm-size pixel. This expression needs to be adjusted for other pixel sizes [18].

The diffusive flux between two cells is expressed by a concentration gradient at a given time step in these two cells and the diffusion coefficient expressed at the boundary of these cells. This latter can be deduced from coefficients within the two considered cells using a mass conservation relation [19]. For a given cell and its neighbor in the x direction this boundary diffusion coefficient is expressed as [Eq. (4)]

$$D_{x+\Delta x/2} = \frac{2D_x D_{x+\Delta x}}{D_x + D_{c+\Delta x}}. \qquad (4)$$

Considering a time step Δt, the six total fluxes exchanged between the considered cell and its six neighbors are expressed using a Crank–Nicholson scheme able to accommodate relatively large time steps required in durability studies. Here, the time step chosen is 3600 s, resulting from a compromise between (i) computation time, (ii) simulated time, (iii) cell size, and (iv) numerical stability. This semi-implicit scheme is known to be unconditionally stable and convergent whatever the chosen time step [16]. This scheme writes a linear system equation between concentrations in all cells at the $t + \Delta t$ instant as a function of the concentrations at the t instant. For each diffusive species and for each time step, the diffusive calculation consists in evaluating the solution vector by using a conjugate gradient algorithm [16].

Second, reaction calculation occurs in each cell. The evolution of the total concentrations of diffusive species induces chemical unbalances: the pore solution is no longer in thermodynamic equilibrium. Dissolutions and precipitations of all solid species occur immediately. In order to calculate a new equilibrium in each cell, additional equations have to be included:

- mass conservation for all species; during the reaction calculation phase the content of one given species is

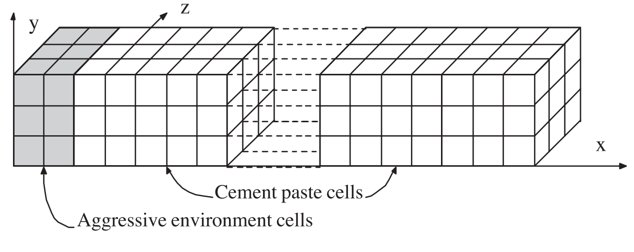

Fig. 4. Study domain used in the modeling. Each cell represents either the aggressive environment or a cement paste cell, composed of a microstructure generated by the CEMHYD3D model and the pore solution.

constant and is subdivided into a solid part and an ionic solution part;
- the mass action laws that determine for each solid an equilibrium relationship with the ions involved;
- the electroneutrality of the pore solution; this equation is used to determine the pH value of the pore solution.

All these equations form a nonlinear system and are evaluated by iterations using the Newton–Raphson algorithm [16]. In each iteration, ionic activities are evaluated with the Debye–Hückel model. This reactive calculation scheme is done with the PHREEQC speciation code [20] and a modified thermodynamical database based on PHREEQC default one in order to add Portland cement hydrates. Thermodynamical data have been found in the literature [21–24]. The C-S-H chemical behavior is simplified by using two silicate hydrates: the first with a C/S ratio equal to 1.65, i.e., $C_{1.65}SH_{2.45}$, and the second, $C_{1.1}SH_{1.9}$, with a C/S (calcium-to-silica) ratio equal to 1.1. In such an approach, the C-S-H decalcification is ruled by a linear combination of the two C-S-H, similarly as in Ref. [2]. Some anhydrous constituents may be present in the microstructures, depending on the w/c ratio. They are considered here as chemically inert because the modeling of their influence is not finalized yet. Thus, predictions of the modeling can only be compared on fully hydrated materials, as in most leaching models [2,3].

Given the total concentration of all species in the pore solution and all solid content, PHREEQC calculates the mass of each solid that dissolves or precipitates until a new thermodynamical equilibrium is reached. The last step in the numerical resolution of the reactive-transport equation is to calculate in each cell the new capillarity porosity in order to evaluate a new apparent diffusion coefficient using Eq. (3).

Thus, due to the resolution strategy, the modeling consists of a succession of one-time, stepwise diffusion calculations until a solid phase has totally dissolved. Diffusive species profiles and profiles of solid phases evolve as a function of the diffusion time step chosen. A numerical study has shown a range of time steps where evolutions of solid phases are linear. Nevertheless, as solid species contents spatially evolve in the material there cannot be an abrupt dissolution front as observed in experiments.

3.2. Leaching simulations

To model the leaching experiments, two principal studies gathering three simulations have been made with this reactive-transport approach. Using the CEMHYD3D model, three different initial microstructures representing three different hydrated cement pastes of the CEM I 52.5 Portland cement used in experiments have been generated. The variable parameter was the w/c ratio (= 0.25, 0.4, and 0.5). The aggressive environment was pure water with a constant chemical composition. To simplify the transport problem in the model, diffusion values of solution species have been considered constant; the only parameter affecting the diffusion constant was the value of the capillarity porosity as expressed in Eq. (3).

3.2.1. Qualitative comparison of pure water leaching degradations

First, the CEMHYD3D microstructure of a w/c = 0.4 Portland cement paste has been used to study the zoning phenomena developed in the course of leaching. Fig. 5 shows the evolution of pH and total calcium in the pore solution vs. depth of the material at different simulated times. Because of the presence of alkali ions, the initial composition of the pore solution is characterized by having a pH close to 13.3 and a total calcium concentration equal to 1.3×10^{-3} mol l^{-1}. After beginning the simulation, the pH value goes down, whereas calcium concentration rises with time until it reaches 20×10^{-3} mol l^{-1}. This stage corresponds to the replacement of all ions released by the cement paste, due to diffusive fluxes, by dissolution of some solid species, alkali ions excepted because they are not replaced. When all alkali ions have leached, a new chemical equilibrium appears within the cement paste, characterized by a pH close to 12.5 and a total calcium concentration equal to 20×10^{-3} mol l^{-1}.

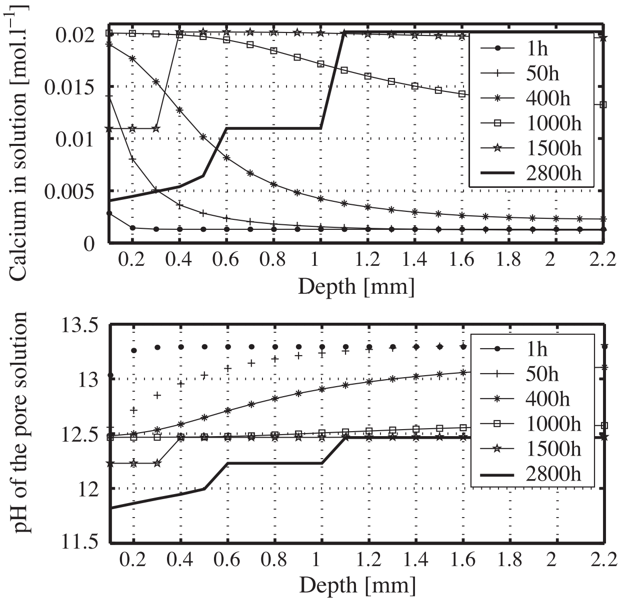

Fig. 5. Calculated pH and total calcium profiles within the cement paste at different time steps.

After depletion of alkali, the calcium leaching rate increases due to the increased gradient of calcium concentration between the external environment and the pore solution. From the sound zone (at the right of Fig. 5) to the aggressive environment, the first sharp drop of pH (from 12.5 to 11.8) and, simultaneously, calcium (from

20×10^{-3} to 5×10^{-3} mol l^{-1}) in solution corresponds to a new chemical equilibrium when the total dissolution of portlandite occurs. The volume evolution with time of the main solids composing the first cement cell (Fig. 6) confirms that calcium hydroxide is the first solid species to totally dissolve. The second abrupt drop of pH and calcium concentration can be attributed to total dissolution of AFm. Focusing on solid species evolution (Fig. 6), as soon as portlandite has totally dissolved in a cell, dissolution of $C_{1.65}SH_{2.45}$ and precipitation of $C_{1.1}SH_{1.9}$ occur, illustrating the decalcification of C-S-H. Then, AFt total dissolution results in further drop of pH and decreased calcium concentration.

Looking at hydrate profiles (Fig. 7), the reactive-transport modeling highlights the zoning phenomenology observed in previous experiments or modeling [2,3,7,10]. However, complementary information is given by this approach and shows a precipitation of ettringite in the zone where AFm is dissolving. This precipitation of AFt is possible only in the presence of supplementary calcium ions in the pore solution. These results are in agreement with recent experiments [2,7] but were not taken into account in models that considered calcium as the only diffusive species [3]. It appears that, for example, sulfate ions that leave the solids to diffuse into the external solution will be replaced within the pore solution by dissolving sulfated solids, calcium monosulfoaluminate, and ettringite principally, but also remaining gypsum. This calcium sulfate may be present in our digital images of microstructures because the hydration is incomplete at the given time when the CEMHYD3D building process is stopped. This especially occurs in digital images with low w/c ratios, similar to that found in reactive powder concrete [5].

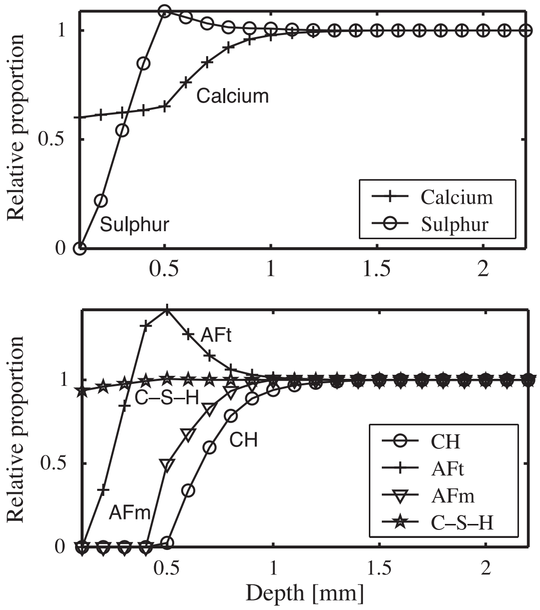

Fig. 7. Relative quantities of solid species and hydrates vs. depth of the material determined by the model, after 1286 h of simulated pure water leaching on a w/c = 0.4 Portland cement paste. The value 1 refers to the initial value, before chemical aggression, i.e., sound material.

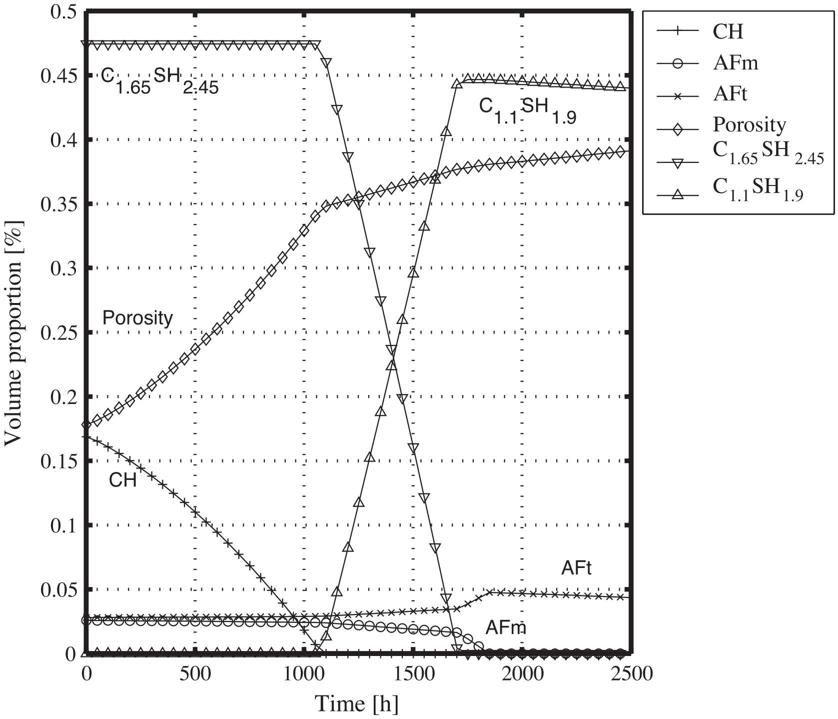

Fig. 6. Evolutions with time of the volume proportion of the main hydrates in the first cement paste cell calculated by the model, for pure water leaching simulations on a w/c = 0.4 Portland cement paste.

Taking into account multiple diffusive species also justifies the fact that two solids can dissolve simultaneously; for example, portlandite and AFm, and thus does not, in this modeling, create an abrupt dissolution front, contrary to already published results [2,3].

The comparison of relative EDS X-ray analysis profiles (Fig. 4) and relative solid species profiles obtained by the modeling (Fig. 7) show some similarities. The calcium profile has the same evolution after total dissolution of the portlandite. As the total dissolution front is not marked in the modeling, the gap of calcium content due to the dissolution is progressive; this is contrary to experiments. This establishment is, in part, a consequence of the numerical resolution strategy that decouples diffusive and reactive calculations but can also be interpreted by noting that partial dissolution and precipitation can occur simultaneously within the material.

3.2.2. Comparison of leaching kinetics between experiments and reactive-transport modeling

For the second study, the original CEMHYD3D cement paste microstructures with three different w/c ratios have been used to study the influence of w/c content on portlandite dissolution front kinetics. Table 7 gives the calculated volume proportions of the principal hydrates in the three cement pastes.

A comparison of the instant when the portlandite dissolution front reaches a specific position between the reactive-transport modeling and experiments has been made. To differentiate real time in experiments and simulated time, comparisons have been made in functions of the CEM I w/c = 0.4 kinetic parameter $a_{\mathrm{w/c}=0.4}$, in order to only characterize the influence of the w/c ratio.

Results in Table 7 show that the ratios of the kinetic constants determined by the model are close to those found experimentally. The maximum 20% deviation, acceptable with regard to the general formulation of the model, is mainly due to the interactions between multiple diffusive species and evolution of the apparent diffusion coefficient that increases as solid species dissolve. Consequently, because the diffusion coefficient is not taken as constant, the diffusive problem cannot be solved with a square root of time equation. Here, our model, which takes into account the transport property evolutions, is able to predict similar degradation kinetics as in pure water leaching experiments, and especially to characterize the w/c ratio effect.

Table 7
Comparison of kinetic constant ratios between experiments and modeling for different w/c ratios

	Modeling		Leaching experiments
	$x = 100$ μm	$x = 200$ μm	
$a_{(\mathrm{w/c}=0.4)}/a_{(\mathrm{w/c}=0.25)}$	1.50	1.70	1.87 = 0.140/0.075
$a_{(\mathrm{w/c}=0.4)}/a_{(\mathrm{w/c}=0.5)}$	0.86	0.79	0.82 = 0.140/0.169

4. Conclusions

This leaching study has been approached both by experiments and modeling.

The degradation of three cement pastes in three aggressive solutions was experimentally studied by microanalysis and TG/DTA. The leaching kinetics appears to be influenced by w/c ratio and is strongly dependent on the nature and composition of the aggressive solution. Pure water is more aggressive than carbonated natural mineralized water. This last one carbonates the surface layer and decreases both leaching kinetics and leaching depth, x, which is five times lower than for pure water. The ammonium nitrate leaching protocol as described in this paper accelerates leaching time by a factor of 121 and multiplies leaching depth by 11.

Leaching kinetics related to ammonium nitrate and pure water as solvents for Portland cement pastes with different w/c ratios enable altered depths to be predicted, as kinetics are mainly controlled by the simplified square root of time equation. Indeed, the pure water leaching modeling has shown the applicability of this law, considering a certain deviation due to the evolution of capillarity porosity.

The reactive-transport modeling highlights the following complementary information.

- The w/c ratio has the same influence on the evolution of leaching as in experiments, although kinetic phenomena are different between simplified laws and our modeling, which takes into account all the ions in solution.
- Using only the general laws and thermodynamical equilibrium constants already published, we find that our reactive-transport model confirms the zoning, as observed and analyzed by microscopy. Nevertheless, the dissolution fronts are not as sharp as considered previously because several cement minerals can dissolve or precipitate simultaneously. For example, the model predicts a precipitation of ettringite in the zone where both portlandite and calcium monosulfoaluminate are dissolving. That prediction is in agreement with some experimental observations but is not taken into account in classical models. Experimental results are in agreement with these calculations. Indeed, sulfur EDS X-ray microanalysis indicates a change in sulfate solid distribution within the farthest zone from the aggressive solution, i.e., in the zone previously considered to be sound. Consequently, the leached depth determined by the total portlandite dissolution front seems to underestimate the depth to which reaction penetrates.

Work in progress is related to the development of the C-S-H chemical behavior in order to enhance our understandings of the leaching mechanism and improve the predictions of species profiles and their comparison with SEM profiles. A second improvement relates to the influence of anhydrous constituents, here considered as inert inclusions.

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