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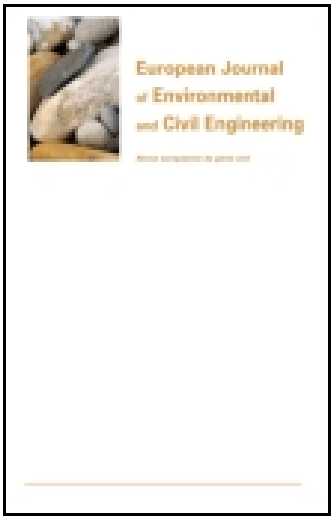
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We have focused on the test conditions influence on accelerated degradation of cementitious materials using ammonium nitrate. PH-buffering and renewal of the leaching solution were studied. PH-buffering appeared not to be very important when the renewal pH remains under eight. Renewal appeared to be the most influential feature. Its absence leads to calcium accumulation in the leaching solution inducing aggressiveness fall. Degradation is then less marked in terms of depth, flux and mineralogy. The resulting porosity increase is also smaller.

Nous nous sommes intéressés à l'influence des conditions expérimentales sur la dégradation accélérée au nitrate d'ammonium (6M). Le renouvellement périodique et le maintien du pH de la solution lixiviante ont été étudiés. Il en ressort que le maintien de pH n'est pas important lorsque le renouvellement est effectué jusqu'à pH=8. Le renouvellement est l'élément le plus important. Son absence entraine l'accumulation d'ions calcium dans la solution et la diminution de son potentiel agressif. La dégradation est alors moins marquée en termes d'épaisseur dégradée, de flux lixivié et de minéralogie. L'augmentation de porosité correspondante est aussi plus faible.

Keywords: cementitious materials; accelerated degradation; ammonium nitrate; protocol influence

Mots-clés: Matériaux cimentaires; dégradation accélérée; nitrate d'ammonium; influence du protocole

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1. Introduction

In the framework of radioactive waste geological disposal, concrete structures would likely be in long-term contact with underground water. This problem has been extensively studied for the last decades and a large number of studies involving degradation using deionized water were published. It was shown that ionic diffusion (mainly calcium ions) from the concrete inner solution to the surrounding water is implied as well as hydrates dissolution (portlandite, C-S-H… etc.) This results in porosity opening and severe performance loss (Adenot, 1992; Bentz and Garboczi, 1992; Delagrave, 1996; Faucon, Adenot, Jacquinot, Petit, Cabrillac, & Jorda, 1998). Using deionized water the most influential parameters upon leaching were highlighted (temperature, solution pH and ionic concentrations…) resulting in the proposition of a reference modus operandi

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(Adenot, 1992; Kamali, Gérard, & Moranville, 2003; Planel et al., 2006; Peycelon, Mazoin, & Blanc, 2006; Rozière and Loukili, 2011). The latter intends to control temperature and maintain the chemical conditions within the leaching water (pH control, calcium accumulation mitigation through acid addition and periodical solution renewal).

Beyond the initial background (radioactive waste geological disposal) leaching is now considered as a performance test for durability assessment (Jacquemot et al., 2009; Rozière and Loukili, 2011). The major drawback of such an approach is, however, the very low degradation rate. The use of concentrated ammonium nitrate solutions was then alternatively proposed and proved great acceleration efficiency (Carde, Escadeillas, & François, 1997; Schneider and Chen, 1999; Le Bellégo, Pijaudier-Cabot, Gérard, Dubé, & Molez, 2003). Nowadays accelerated degradation tests are commonly performed to study leaching consequences using a simplified version of the experimental protocol presented above (Carde & François, 1997; Le Bellégo et al., 2003; Peycelon, Gallé, & Le Bescop 2004; Nguyen, Colina, Torrenti, Boulay, & Nedjar, 2007; de Larrard, Benboudjema, Colliat, Torrenti, & Deleruyelle, 2010; Yurdtas et al., 2011). Concrete samples are immersed into a large volume of ammonium nitrate solution (6 mol/L) which is never renewed or when pH reaches a certain (high) value (8.5 or 9.25 as proposed by Tognazzi, Mainguy, Adenot, & Torrenti, 1999 or Heukamp, Ulm, & Germaine, 2001). In so doing it is implicitly assumed that the ammonium nitrate solution aggressiveness is maintained despite the modus operandi simplicity. In this study, this assumption was investigated and the protocol influence was tested through dedicated experiments which were post-processed using geochemistry approaches and tools (which have proven suitability and efficiency for pure-water degradation). The results highlight the great importance of renewal to prevent pH increase and calcium accumulation and mitigate aggressiveness.

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2. Experimental program

2.1. Materials

In this study a hardened cement paste was used in order to ease the characterization of the material mineralogical evolution. The paste formulation is given in Table 1. Prismatic samples (4x4x4cm) were prepared in laboratory (in a single batch) and cured at 20°C under water (with lime) for three months before use.

2.2. Experimental protocol and program

The reference experimental set-up used in this study was inspired from the work of Adenot (1992). The samples were immersed in ammonium nitrate (6M) in a reactor where the temperature was maintained at 25°C using a thermostatic bath. The ratio between the sample exposed surface and the leaching solution volume was equal to 1.365 dm^2/L.

Periodically, the amount of calcium leached out of the sample was measured using ionic chromatography. Using these results the evolution of the cumulated amount of

Table 1. Hardened cement paste formulation.

Component	Type	Qty	Unit
Cement	CEM I 52.5 CP2 Holcim (Dannes)	1122	kg/m^3
Fly ash	Safament KWB	256	kg/m^3
Water	-	542	L/m^3

calcium released by the sample versus time could be determined. This was complemented with the measurement of the sample degraded depth using phenolphthalein projection (dilution at 1%) and X-Ray Diffraction (XRD). In so doing, diffractograms were acquired directly on the solid surface from the exposed surface to the sound core (unaffected by leaching, the degraded zone corresponds to the absence of portlandite). For this purpose, 50-200 μm thick layers were removed in successive steps using a micro-milling device (using a diamond tool).

In order to study the influence of both pH-buffering and renewal, experiments were conducted (all the samples were taken from the same 4x4x16 specimen) using three different configurations derived from the reference protocol described above (for each protocol, one sample was used):

- Protocol #1 – the solution was agitated using a magnetic stirrer (to ensure homogeneity and enhance calcium exchange at the sample-solution interface), but was neither renewed nor pH-buffered.
- Protocol #2 – the solution was agitated using a magnetic stirrer and was periodically renewed (following the square root of time: after one, four, nine, 16 and 25 days) to prevent calcium accumulation and maintain the concentration difference between the samples and the leaching solution. The pH was not buffered (protocol #2 = protocol #1 + solution renewal);
- Protocol #3 – the solution was agitated using a magnetic stirrer, renewed periodically and the pH was buffered by nitric acid addition using an automated microburette (protocol #3 = protocol #2 + pH buffering).

3. Experimental results

Figure 1 presents the leaching solution pH-evolution as a function of the square root of time for the hardened cement pastes (influence of renewal and pH-buffering). It is a good illustration of the differences between the three protocols. The initial ammonium nitrate solution pH is equal to 6.3. For protocol #1 (neither renewal nor pH buffering)

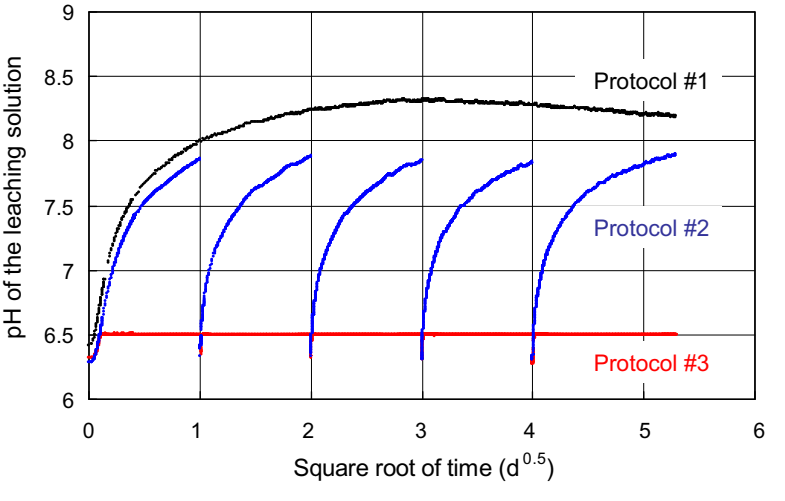


Figure 1. Hardened cement pastes degradation: pH evolution of the leaching solution for the three test configurations.

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the pH shows a sharp increase in the early age caused by the hydroxyls released by the hardened cement paste. After a few days the pH reaches around 8.3, this value stays stable all along the test duration. For protocol #2 (protocol #1 + renewal), the pH evolves as for protocol #1: rapid increase to reach 7.8 after one day. The solution is then entirely renewed and a new leaching sequence begins: the pH increases until the next replacement (note that at each renewal the pH value is almost the same: 7.8). The solution refills are performed after one, four, nine, 16 and 25 days respectively. In the case of protocol #3, (protocol #2 + pH buffering) in addition to the periodical solution renewal (following the same time schedule as in protocol #2), the solution pH is buffered at 6.5 by nitric acid addition.

Figure 2 presents the evolution of the calcium cumulated amounts for the three protocols versus the square root of time. For the two most elaborated protocols (protocols #2 and #3) the evolutions overlap and follow a straight line whereas protocol #1 (without renewal and pH buffering) deviate from this straight line after four days of leaching. This phenomenon origin is discussed in part 4.

The resulting degraded depth was measured using phenolphthalein projection and XRD (the degraded zone is characterized by portlandite absence). A typical example of the resulting diffractogram evolution within the samples is shown in Figure 3 (for protocol #3).

In this case and after 28 days of leaching, the portlandite characteristic diffraction peaks are only visible far from the exposed surface: the degraded depth then appears to be larger than 8mm. Table 2 summarizes the results obtained using phenolphthalein projection and XRD for the three different protocols. Both techniques give very similar results. Moreover in accordance with the cumulated calcium leached amount (Figure 2), the samples submitted to protocols #2 and #3 exhibit the same degraded thickness (8.8mm using phenolphthalein and 8.4–8.6 using XRD) whereas the sample leached using protocol #1 presents a smaller degraded thickness (7.0mm using phenolphthalein).

Among all the experimental conditions tested, the periodical renewal of the leaching solution appears to be the most influential one: when the solution is not renewed the

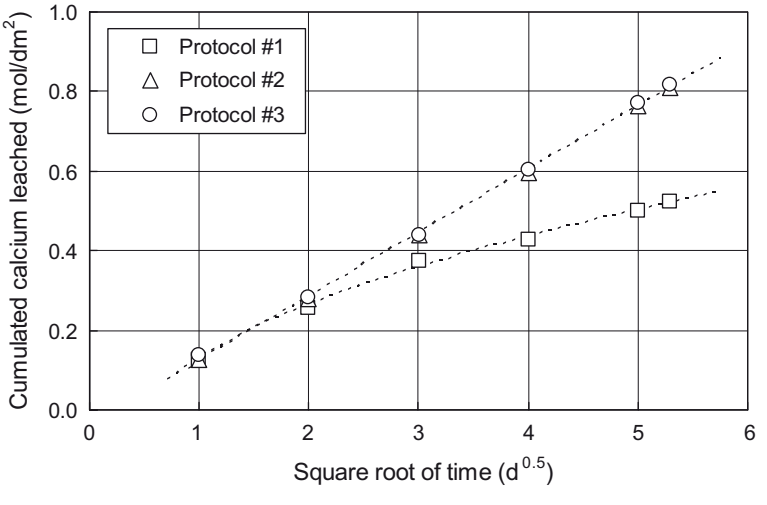


Figure 2. Cumulated amount of calcium leached depending on the test conditions (the dotted lines are only guides for the eyes).

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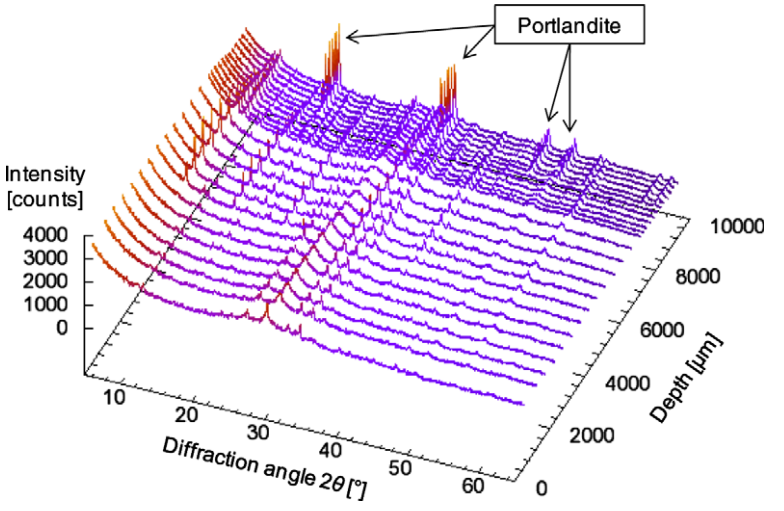


Figure 3. Diffractogram evolution within the hardened cement paste after 28 days of leaching using protocol #3 (renewal and pH-buffering).

Table 2. Hardened cement paste degraded thickness after 28 days depending on the test protocol (estimated using either XRD and/or phenolphthalein).

		Degraded depth (mm)	
	Experimental protocol	**Phenolphthalein**	**XRD (portlandite)**
1	Stirring	7.0	–
2	Stirring, renewal	8.8	8.4
3	Stirring, pH buffering, renewal	8.8	8.6

leached calcium cumulated amount and degraded depth are found to be lower than with renewal. In order to gain information on the phenomena involved, a modelling/simulation approach was chosen. One the main advantages of such an approach is to give a fine mineralogical evolution description within the degraded zone (much more accurate than the one obtained using XRD).

4. Numerical simulations

In a first time the pH influence was checked to explain the similarity between the results of protocols #2 and #3. The numerical tool CHESS (van der Lee, de Windt, Lagneau, Goblet, 2003) was used to describe the ammonium nitrate aggressiveness reduction due to leaching. From a practical point of view portlandite was gradually added to a virtual 6M ammonium nitrate solution (theoretical pH≈4.4). To account for the high ionic strength (equal to 6.0) of the ammonium nitrate solution, the B-dot activity model (Helgeson, 1969) was chosen. It is known to be accurate up to several molal (typically 3M) for simple electrolytes such as NaCl (Bethke, 1996). Note that the ionic strength correction for more concentrated solutions can be described by the semi-empirical model proposed by Pitzer (1991). Yet it cannot be used in this study due to the lack of experimental data. The reader must keep in mind that due to the high ionic strength

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of the ammonium nitrate solution, the results presented hereafter should be taken in a qualitative way. Figure 4 shows that the solution aggressiveness (that is to say ammonium concentration) continuously decreases when pH increases: the major variations can be seen between 8 and 11 pH. The three open circles correspond to the pH at which the solutions are renewed: 7.8 for this study; 8.5 for Tognazzi et al. (1999) and 9.25 for Heukamp et al. (2001).

In this study the difference between protocols #2 & #3 is pH-control between two consecutive renewals (Figure 1) resulting in pH increase from 6.3 to 7.8. The aggressiveness reduction (ammonium concentration decrease) is then very low: less than 3%. This explains why both protocols yielded the same results. Yet renewal at higher pH leads to significant aggressiveness reduction (about 13% and 50% for Tognazzi et al. [1999] and Heukamp et al. [2001] respectively). From a practical point of view pH-control does not appear to be necessary to ensure solution aggressiveness stability as far as the renewal pH does not exceed 8.0 (for which the ammonium concentration reduction is about 5%). Beyond this value the solution aggressiveness falls (from 95% down to 20% of its initial value for pH=8.0 and 10.0 respectively). In the same time, the total calcium concentration (accounting for speciation) increases which participates in the reduction of calcium transport motion and the corresponding degraded depth reduction between protocol #1 and protocols #2 & #3.

The accelerated leaching tests were simulated using the reactive transport code HYTEC (Van der Lee et al., 2003). HYTEC is a finite volume code in which transport is coupled to chemistry (dissolution/precipitation, using CHESS) through a sequential iterative process. Diffusion is the only transport mechanism considered in this study and is coupled with chemistry thanks to the following set of equations:

$$\frac{\partial pC_i}{\partial t} = div[D_e(p)\overrightarrow{grad}(C_i)] - \frac{\partial pS_i}{\partial t}$$

where p is the porosity; D_e is the effective diffusion coefficient [m^2/s]; C_i is the concentration of the ionic species i (in solution) [mol/L] and S_i is the concentration of

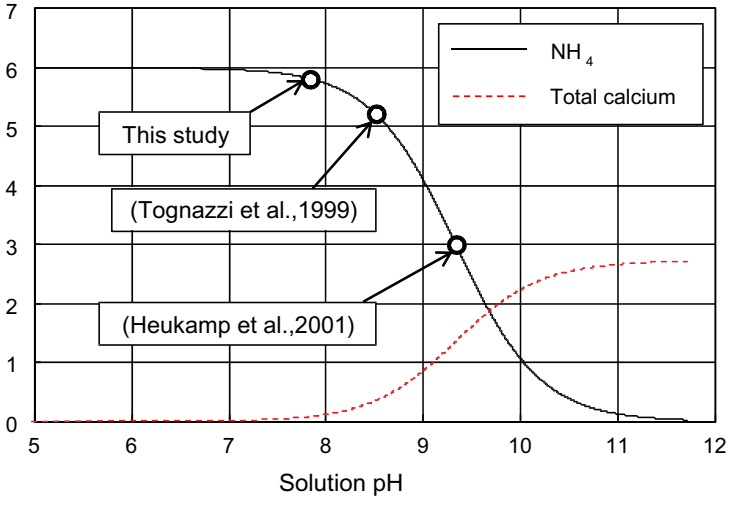


Figure 4. Theoretical neutralization of 6M ammonium nitrate solution by portlandite addition (using CHESS).

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the mineral containing the species *i* (solid phase) [mol/L of paste]. Following the work of Buil, Revertégat, & Oliver (1992) it is also assumed that the solid is always in equilibrium with the inner solution (all the chemical reactions are considered instantaneous compared to diffusion). As before the B-dot activity model was used to account for the high ionic strength. The microstructural evolution influence (induced by the dissolution and precipitation phenomena) on diffusive transport is accounted using Archie's law:

$$D_e(p) = D_e(p_0)\left(\frac{p - p_c}{p_0 - p_c}\right)^{\alpha}$$

where $D_e(p)$ is the effective diffusion coefficient [m^2/s] for the arbitrary porosity p; p_0 is the porosity of the sound material; p_c is the critical porosity under which diffusion is inhibited and α is a positive coefficient. The values used in the simulations are reported in Table 4.

Starting from the elemental composition of the dry mix CEM I + fly ash the mineral composition of the hardened cement paste is evaluated using the geochemical software CHESS in association with the thermodynamic database 'chess.tdb' modified to include 'cemdata2007' information (Lothenbach et al., 2008). In so doing Fe_2O_3 and Al_2O_3 were considered as a unique species; this allowed both to be precipitated in the same phases without distinction (hydrogarnet and ettringite in our case).

The cement paste could then be described using only four different minerals: portlandite (CH), jennite (C-S-H with C/S = 1.67), hydrogarnet ($C_3AS_{0.8}H_{4.4}$) and ettringite ($C_3A \cdot 3\overline{S} \cdot H_{32}$). Assuming that all the anhydrous compounds are converted into hydrates (that is to say complete hydration) it is easy to determine the concentration of each mineral as well as the total porosity (Table 3). Nonreactive minerals were added up to 8% (volume fraction) to force the paste total porosity to be equal to 29% as measured experimentally. The interstitial solution pH is controlled by portlandite equilibrium (12.5) since alkalis are not accounted in this study. They are assumed to be leached during the curing period.

The paste initial composition validity as well as the hydration degree assumption was checked through portlandite amount comparison between the simple hydration

Table 3. Simplified composition of the non-degraded hardened cement paste.

Compound		Concentration		Volume fraction
		mol/L (paste)	mol/L (solution)	
Portlandite	CH	3.81	13.20	12.6%
Jennite	$C_{1.67}SH_4$	3.55	12.30	27.7%
Hydrogarnet	$C_3AS_{0.8}H_{4.4}$	0.78	2.70	11.6%
Ettringite	C_3A 3CS H_{32}	0.16	0.55	11.5%
Nonreactive mineral		–	–	8.0%
Total porosity				28.6%

Table 4. Archie's law parameters used for the simulations.

Parameter	$D_e(p_0)$	p_c	p_0	A
Value	3.7×10^{-12} m^2/s	0.05	0.29	3.5

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model and the value measured using Thermo-Gravimetric Analysis (TGA). The good similarity between both (3.81 and 3.85 mol/L of paste for the model and TGA respectively) validates the approach and the assumptions used. The different compounds taken into account to describe in a simplified way the degraded zone mineralogy are given below:

- tobermorite ($C_{0.83}SH_{1.3}$) as an intermediate stage of jennite degradation;
- gypsum ($C\overline{S}H_2$) as an intermediate stage of sulfate-based phases degradation;
- amorphous silica gel (SiO_2) as the ultimate stage of jennite degradation;
- amorphous aluminum hydroxide ($Al(OH)_3$) as the ultimate stage of aluminate-based phases.

Following the results presented above, it was considered that the tests performed using protocols #2 & #3 led to the same results and only two different simulations were conducted. In the first one, constant chemical conditions over time were applied at the interface between the concrete and the leaching solution (pure ammonium nitrate at 6 mol/L, pH = 6.5 and no calcium ions). This simulation describes the tests performed using the protocols #2 and #3.

The second simulation corresponds to the test performed using the protocol #1. Initially the chemical conditions in the leaching solution are the ones presented above, but they are left to evolve freely (in relation to the species amounts released by the paste and the resulting dilution within the leaching solution). In this simulation, the exposed surface to solution volume ratio was the same as in the experiment. The paste sample was described using a 1D mesh with 150 volumes (each of them being 100 μm large). The temperature used for the simulations is 25°C and leaching was described up to 28 days.

From a practical point of view, the parameters p_c and α of Archie's law were fixed to usual values (Trotignon et al., 2007; de Windt and Devillers, 2010) and the diffusion coefficient of the sound paste $D_e(p_0)$ was fitted to reproduce the experimental degraded

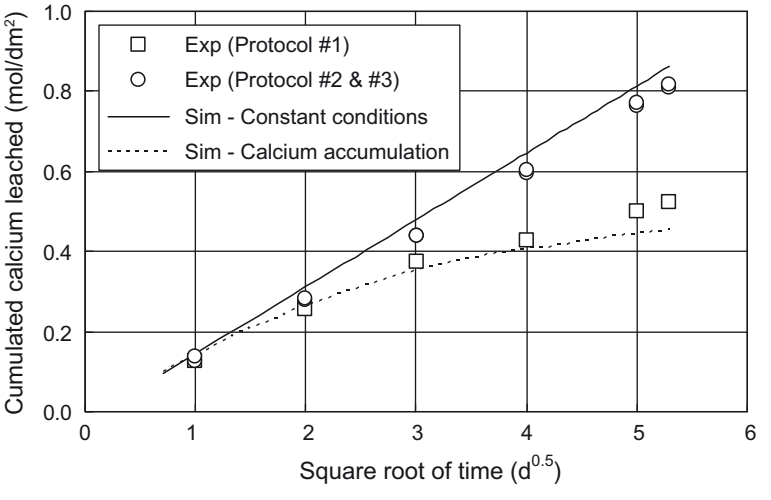


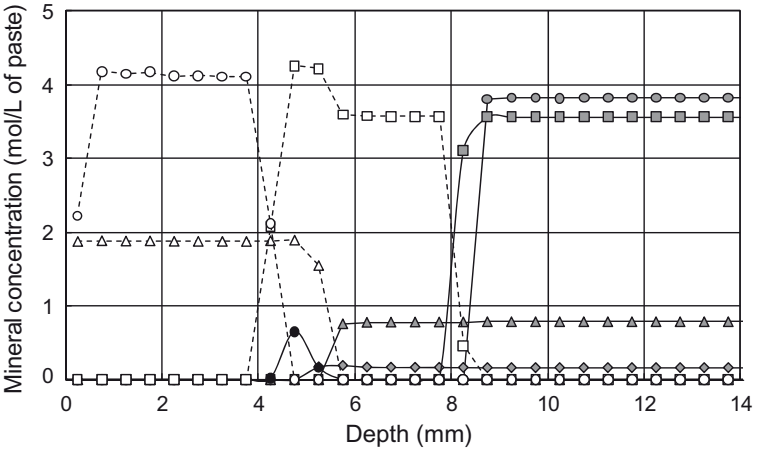
Figure 5. Comparison between the experimental (symbols) and the simulated (curves) cumulated amounts of calcium leached.

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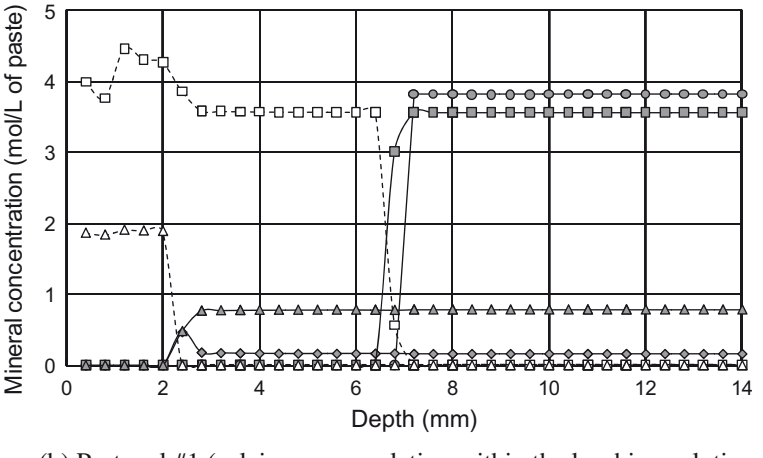
depth (at 28 days). A unique value ($3.7x10^{-12}$ m^2/s) could be obtained for both simulations (Table 4). In order to validate the simulations, it was verified afterwards that the cumulated calcium leached amounts obtained in both simulations are in good agreement with the experiments (Figure 5).

The mineralogical profiles for the two simulations after 28 days of leaching are presented on Figure 6 (the interface paste-solution is located at x = 0). In a first time, one can verify that the degraded depths obtained do correspond to the ones measured experimentally (the sound zone can be identified by the presence of portlandite). In a second time, one must note the difference of mineralogical evolution within the degraded zone between both configurations.

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(a) Protocols #2 & #3 (constant chemical conditions within the leaching solution)



(b) Protocol #1 (calcium accumulation within the leaching solution

Figure 6. Theoretical mineralogical profile after 28 days of leaching (using HYTEC): (a) constant chemical conditions within the leaching solution (protocols #2 & #3 – renewal and pH buffering); and (b) calcium accumulation (protocol #1). Key: —o—Portlandite; —▫—Jennite; —◇—Ettringite; —△—Hydrogarnet; ···▫···Tobermorite; —•—Gypsum; ···o···Silica Gel; ···△···Alumina Gel.

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It is well-known that leaching leads to the apparition of several zones of different mineralogy (Adenot, 1992; Adenot, Gérard, & Torrenti, 1999; Bernard, Kamali-Bernard, & Prince, 2008). In this study, when constant chemical conditions are applied three main different layers can be observed (this is of course a rough description of the mineralogical evolution: note that five zones could be detected with a more accurate observation as proposed by Adenot et al., 1999 and Bernard et al., 2008). The first corresponds to the first degradation stage (between 5.5 and 8.5 mm). It consists in partial decalcification and is characterized by portlandite and jennite dissolution and precipitation of tobermorite. The second one (between 4 and 5.5 mm) consists in ettringite dissolution and the consequent precipitation of amorphous aluminium hydroxide. Note that a small amount of gypsum can be found in this layer. The third layer (between 0 and 4mm) corresponds to the ultimate degradation stage. It consists in a calcium-depleted layer which is only composed of amorphous compounds (silica gel and aluminium hydroxide).

The precipitation of amorphous compounds could not be proved experimentally for protocols #2 and #3, but it was supported by XRD results (not presented in this article). The C-S-H relatively sharp peak (at 29.2°) disappearance as well as the development of a large amorphous bulge between 20° and 35° were observed in the degraded zone close to the sample surface. Also note that for protocols #2 & #3 gypsum could be detected using XRD at a depth equal to 4.2mm (Figure 7). This observation was confirmed using Scanning Electron Microscopy: a sulphate-rich zone was observed (Figure 8) and the presence of gypsum was supported by Energy-Dispersive X-Ray Spectroscopy (EDS). This zone could be located between 4.0 and 4.6mm. These

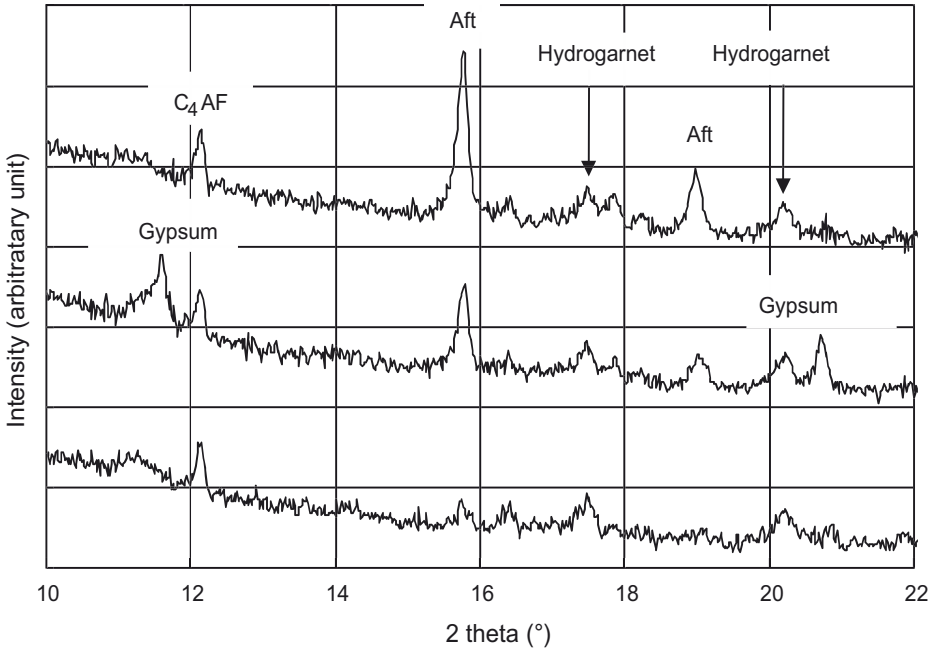


Figure 7. X-ray diffractograms acquired in the degraded zone for protocol #2, the corresponding depths are 3.74, 4.24 and 4.72 mm from bottom to top. Note the presence of gypsum at 4.24 mm.

findings (gypsum presence as well as the corresponding depths) are in good agreement with the first simulation results (using constant chemical conditions). This gives confidence in the approach and assumptions used.

Without leaching solution renewal (protocol #1, Figure 6[b]), the mineralogical evolution within the degraded zone is simpler than shown above. The first layer (between 2 and 7mm) consists in portlandite and jennite dissolution and tobermorite precipitation. Note that when hydrogarnet is dissolved, ettringite precipitates (concentration increases) due to the increase of sulphate availability. The last layer (between 0 and 2mm) is only composed of amorphous aluminium hydroxide and tobermorite. In this case tobermorite remains stable in the ultimate layer in contact with the leaching solution in contradiction with the first simulation results.

Figure 9(a) presents the calcium content (in the solid phase) evolutions within the degraded samples for both simulations. The amount of calcium remaining in the degraded zone is much higher when the leaching solution is not renewed: for instance the residual calcium concentration in the ultimate layer (the one in contact with the solution) is equal to 0.0 when constant conditions are prescribed and is about 3.5 without renewal. This is consistent with the difference of mineralogy highlighted above (and especially with tobermorite stability in the degraded zone) and also with the experimental cumulated calcium leached evolutions. From a practical point of view, when the

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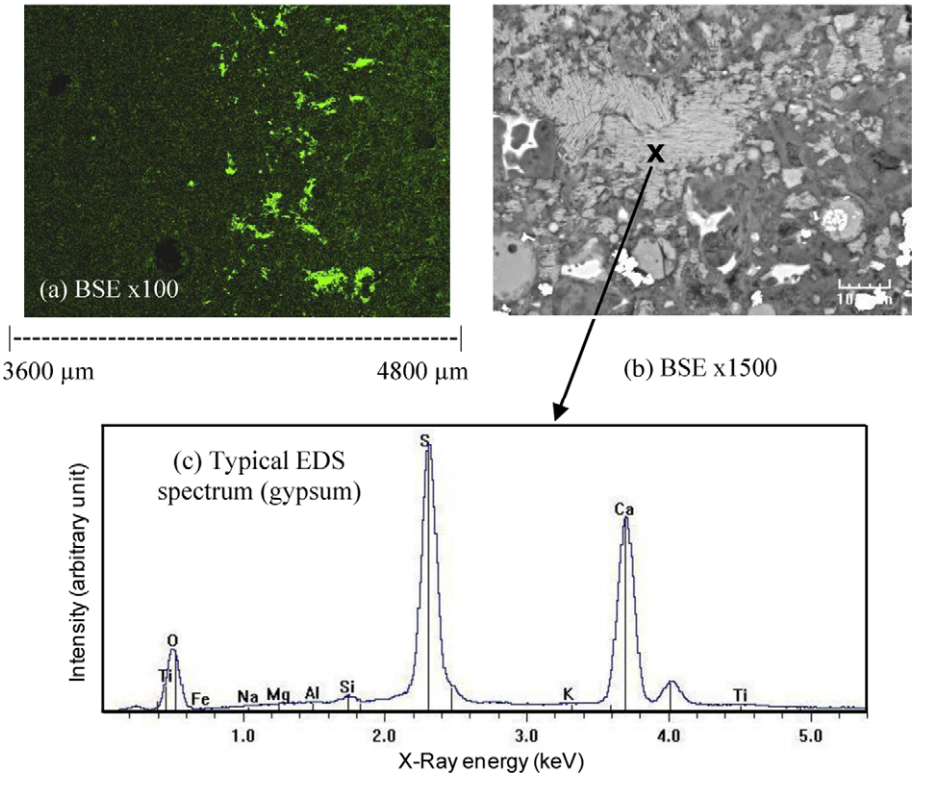
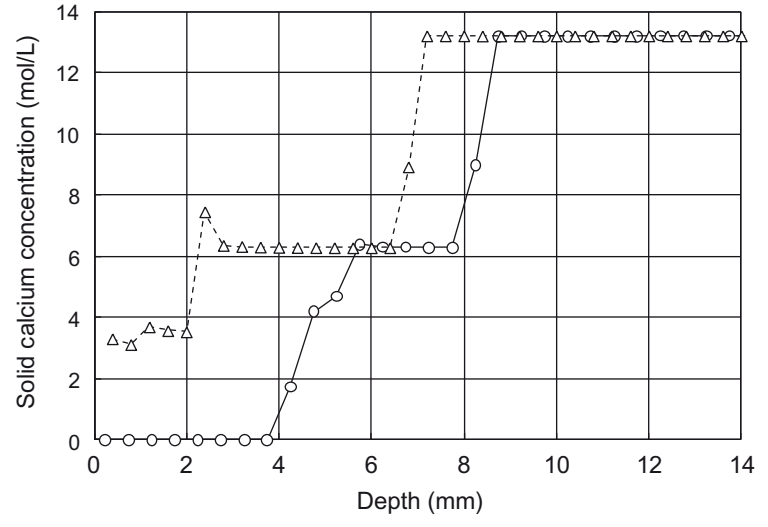
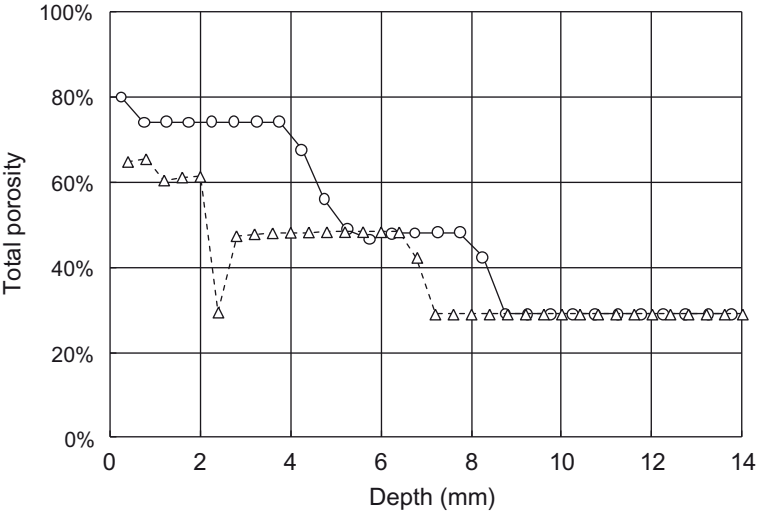


Figure 8. Back-Scattered Electron visualization of the degraded zone: localization and morphology of the sulphate-rich layer within the degraded zone (a); focus on a cluster (b); and typical EDS spectrum of a cluster (gypsum) (c).



(a) Solid calcium concentration



(b) Total porosity

Figure 9. Theoretical evolutions of the: (a) calcium concentration within the solid matrix and (b) total porosity within the hardened cement paste after 28 days of leaching (using HYTEC). Key: —o—Protocols #2 & #3 (constant chemical conditions) and ···▵··Protocol #1 (calcium accumulation within the leaching solution).

leaching solution is not renewed the calcium (and hydroxyl) concentration increases in relation to the leaching behaviour of the sample. Figure 10 presents a compilation of experimental results showing the evolution of the C/S ratio in the solid phase as a function of the calcium concentration in pure-water. The original results were reprocessed in order to account for the calcium solubility increase induced by the concentrated ammonium nitrate (6M) according to the approach proposed by Tognazzi et al. (1999). In practice, to estimate the equilibrium calcium concentration in ammonium nitrate at 6M the corresponding values for pure-water were multiplied by 125.

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The calcium in solution accumulation results in a shift of equilibrium between the calcium in solution and in the solid phase (as depicted on Figure 10): the higher the concentration in solution, the higher the C/S ratio in the solid phase. This effect is strongly noticeable for very limited calcium concentration increases: for instance in ammonium nitrate and between 0 and 200 mmol/L (this corresponds to an increase from 0.0 to around 1.5 mmol/L in pure water) the C/S ratio increases from 0.0 to around 0.85. For the experiment conducted using the protocol #1 (neither renewal nor pH buffering) the calcium concentration in the solution after 28 days of leaching was measured to be equal to 250 mmol/L. As a result, the C/S is expected to fluctuate between 0.0 and more than 1.0. Calcium which should be leached in ideal conditions is then retained in the solid in the degraded zone: decalcification is then less effective when the chemistry of the leaching solution is not maintained. For protocols #2 and #3 the calcium concentration reaches about 60 mmol/L at the end of each leaching sequence.

The difference of mineralogy and calcium content in the solid phase for both configurations is important since it impacts the porosity profiles within the degraded zone as presented on Figure 9(b). The more the amount of calcium retained in the degraded zone (that is to say the higher the C/S ratio), the less the porosity increase generated by the mineralogical evolution. In our case, the average difference of total porosity increase between the two configurations (as obtained using HYTEC) is about 12% (absolute value). This fact is important since immersion in ammonium nitrate is usually used to study the impact of degradation on the cementitious materials behavior. In so doing, specimens are immersed into a large volume of solution which is almost never renewed. In that case, calcium concentration in the leaching solution is expected to increase and allow retaining more calcium in the solid phase. This is expected not to yield optimal degradation and is believed to impact the measurements (through differences in

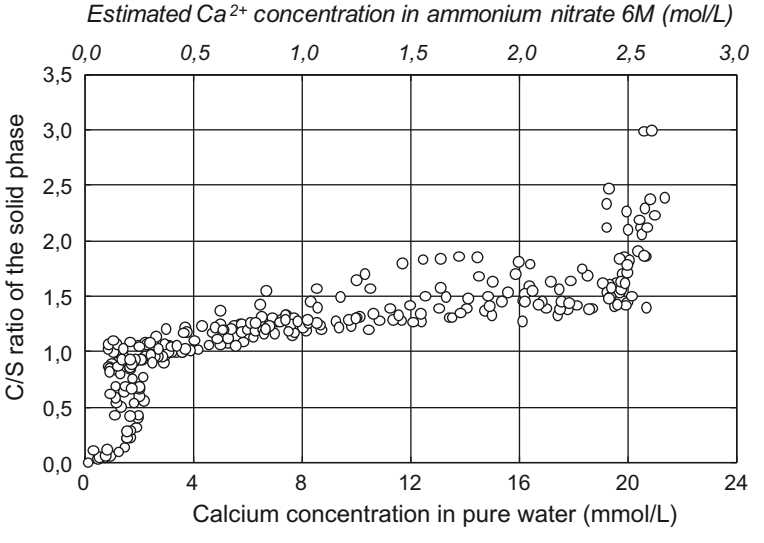


Figure 10. Evolution of the C/S ratio in the solid phase as a function of calcium concentration in solution: compilation of results obtained between 20°C and 30°C (Flint & Wells, 1934; Roller & Ervin, 1940; Taylor, 1950; Kalousek, 1952; Greenberg & Chang, 1965; Fujii & Kondo, 1981; Chen, Thomas, Taylor, & Jennings, 2004).

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microstructure and total porosity for instance). When using ammonium nitrate to accelerate concrete degradation, one should then be very careful and adapt the experimental protocol to the experiment objectives.

5. Conclusion

This work was undertaken to study the test conditions influence on accelerated concrete degradation using ammonium nitrate (namely agitation, pH-buffering and renewal of the leaching solution). Among all of them, pH control showed little influence (as far as the renewal pH remains under 8). For such values the ammonium nitrate aggressiveness reduction remains very negligible (aggressiveness drastically decreases beyond this value). Renewal was found to be the only feature to be really influential. When the leaching solution is not renewed, calcium concentration tends to increase (as well as pH). As a consequence, degradation is less effective than when constant conditions are maintained in the leaching solution: for a given time the degraded depth is less and the mineralogy is also different. More calcium is retained in the solid phase. The resulting porosity opening is expected to be smaller without renewal. When using ammonium nitrate to study the behavior of decalcified cementitious materials (for instance the mechanical one), one should then be very careful and keep in mind that the concrete degradation state and the resulting measurements depend on the test conditions.

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References

Adenot, F. (1992). Durabilité des bétons: caractérisation et modélisation des processus physiques et chimiques de dégradation du ciment (in french). (PhD thesis, University of Orléans, France).

Adenot, F., Gérard, B., & Torrenti, J-M. (1999). Etat de l'art (in french). In Torrenti, Didry, J-P. Ollivier & F. Plas (Eds.), *La dégradation des bétons, couplage fissuration-dégradation chimique*. Paris: Hermès Science Publications.

Bentz, D.P., & Garboczi, E.J. (1992). Modeling the leaching of calcium hydroxide from cement paste: effects on pore-space percolation and diffusivity. *Materials and Structures, 25*, 523–533.

Bernard, F., Kamali-Bernard, S., & Prince, W. (2008). 3D multi-scale modeling of mechanical behavior of sound and leached concrete. *Cement and Concrete Research, 38*, 449–458.

Bethke, C.M. (1996). *Geochemical reaction modeling. Concepts and applications*. Oxford: Oxford University Press.

Buil, M., Revertégat, E., & Oliver, J. (1992). A model of the attack of pure-water or undersaturated lime solutions on cement. In Gilliam & Wiles (Eds.), *The proceedings of Stabilization and solidification of hazardous radioactive and mixed wastes STP 1123* (pp. 227–241). Philadelphia, PA: American Society for Testing and Materials.

Carde, C., Escadeillas, G., & François, R. (1997). Use of ammonium nitrate to simulate and accelerate the leaching of cement pastes due to deionized water. *Magazine of Concrete Research, 49*, 295–301.

Carde, C., & François, R. (1997). Effect of the leaching of calcium hydroxide from cement paste on mechanical and physical properties. *Cement and Concrete Research, 27*, 539–550.

Chen, J.J., Thomas, J.J., Taylor, H.F.W., & Jennings, H.M. (2004). Solubility and structure of calcium silicate hydrate. *Cement and Concrete Research, 34*, 1499–1519.

de Larrard, T., Benboudjema, F., Colliat, J.-B., Torrenti, J.-M., & Deleruyelle, F. (2010). Concrete calcium leaching at variable temperature: Experimental data and numerical model inverse identification. *Computational Materials Science, 49*, 35–45.

de Windt, L., & Devillers, P. (2010). Modeling the degradation of Portland cement pastes by biogenic organic acids. *Cement and Concrete Research, 40*, 1165–1174.

Delagrave, A. (1996). Mécanismes de pénétration des ions chlore et de dégradation des systèmes cimentaires normaux et à haute performance (in french). (Ph.D. thesis. Laval University, Canada).

Faucon, P., Adenot, F., Jacquinot, J.-F., Petit, J.-C., Cabrillac, R., & Jorda, M. (1998). Long-term behaviour of cement pastes used for nuclear waste disposal: Review of physico-chemical mechanisms of water degradation. *Cement and Concrete Research, 28*, 847–857.

Flint, E.P., & Wells, L.S. (1934). Study of the system CaO-SiO_2-H_2O at 30°C and the reaction of water on the anhydrous calcium silicates. *Journal of Research of the National Bureau of Standards, 12*, 751–783.

Fujii, K., & Kondo, W. (1981). Heterogeneous equilibrium of calcium silicate hydrate in water at 30°C. *Journal of the Chemical Society, Dalton Transactions, 2*, 645–651.

Greenberg, S.A., & Chang, T.N. (1965). Investigation of the colloidal hydrated calcium silicates II Solubility relationships in the calcium oxide-silica-water system at 25°C. *The Journal of Physical Chemistry, 69*, 182–188.

Helgeson, H.C. (1969). Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *American Journal of Science, 267*, 729–804.

Heukamp, F.H., Ulm, F.-J., & Germaine, J.T. (2001). Mechanical properties of calcium-leached cement pastes. Triaxial stress states and the influence of the pore pressure. *Cement and Concrete Research, 31*, 767–774.

Jacquemot, F., Ammouche, A., Badoz, C., Bertron, A., Bosmet, J., Brédy-Tuffé, P., & Cassat, P., et al. (2009). Leaching performance test assessing durability of concrete exposed to chemical attack. In M. Alexander & A. Bertron (Eds.), *The proceedings of concrete in aggressive aqueous environments, performance, testing and modeling*, (pp. 372–79). Toulouse, France: RILEM Pro 63.

Kalousek, G.L. 1952. Application of differential thermal analysis in a study of the system lime-water. In the proceedings of the *3rd International Symposium on the Chemistry of Cement*, Cement and Concrete Association, London. pp. 296–311.

Kamali, S., Gérard, B., & Moranville, M. (2003). Modelling the leaching kinetics of cement-based materials – influence of materials and environment. *Cement and Concrete Composite, 25*, 451–458.

Le Bellégo, C., Pijaudier-Cabot, G., Gérard, B., Dubé, J.-F., & Molez, L. (2003). Coupled mechanical and chemical damage in calcium leached cementitious structures. *Journal of Engineering Mechanics (ASCE), 129*, 333–341.

Lothenbach, B., Matschei, T., Möschner, G., & Glasser, F.P. (2008). Thermodynamic modelling of effect of temperature on the hydration and porosity of Portland cement. *Cement and Concrete Research, 38*, 1–18.

Nguyen, V., Colina, H., Torrenti, J.-M., Boulay, C., & Nedjar, B. (2007). Chemo-mechanical coupling behaviour of leached concrete. Part I: experimental results. *Nuclear Engineering and Design, 237*, 2083–2089.

Peycelon, H., Gallé, C., & Le Bescop, P. (2004). Effect of an accelerated chemical degradation on water permeability and pore-structure of cement-based materials. *Advances in Cement Research, 16*, 105–114.

Peycelon, H., Mazoin, C., & Blanc, C. (2006). Long term behaviour of concrete: influence of temperature and cement binders on the degradation (decalcification/hydrolysis) in saturated conditions. *European Journal of Environmental and Civil Engineering, 10*, 1107–1125.

Pitzer, K.S. (1991). Ion interaction approach: Theory and data correlation. In K.S. Pitzer (Ed.), *Activity coefficients in electrolyte solutions,* chapter 3 (pp. 75–153). Boca Raton, FL: CRC Press.

Planel, D., Sercombe, J., Le Bescop, P., Adenot, F., & Torrenti, J.-M. (2006). Long-term performance of cement paste during combined calcium leaching–sulfate attack: kinetics and size effect. *Cement and Concrete Research, 36*, 137–143.

Roller, P.S., & Ervin, G. (1940). The system oxide-silica-water at 30°C. The association of silica* ion in dilute alkaline solution. *Journal of the American Chemical Society, 62*, 461–471.

Rozière, E., & Loukili, A. (2011). Performance-based assessment of concrete resistance to leaching. *Cement and Concrete Composites, 33*, 451–456.

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Schneider, U., & Chen, S.-W. (1999). Behavior of high-performance concrete under ammonium nitrate solution and sustained load. *ACI Materials Journal, 96*, 47–51.

Taylor, H.F.W. (1950). Hydrated calcium silicates. Part I. Compound formation at ordinary temperatures. *Journal of the Chemical Society*, paper 726, 3682–90.

Tognazzi, C., Mainguy, M., Adenot, F., & Torrenti, J.-M. (1999). Modélisation de la dégradation chimique. In Torrenti, Didry, J-P. Ollivier, & F. Plas (Eds.), *La dégradation des bétons, couplage fissuration-dégradation chimique,* chapter 7.2 (pp. 156–170). Paris: Hermès Science Publications.

Trotignon, L., Devallois, V., Peycelon, H., Tiffreau, C., & Bourbon, X. (2007). Predicting the long term durability of concrete engineered barriers in a geological repository for radioactive waste. *Physics and Chemistry of the Earth, 32*, 259–274.

Van der Lee, J., de Windt, L., Lagneau, V., & Goblet, P. (2003). Module-oriented modeling of reactive transport with HYTEC. *Computers and Geosciences, 29*, 265–275.

Yurdtas, I., Xie, S.Y., Burlion, N., Shao, J.F., Saint-Marc, J., & Garnier, A. (2011). Influence of chemical degradation on mechanical behavior of a petroleum cement paste. *Cement and Concrete Research, 41*, 412–421.

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