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Material and environmental parameter effects on the leaching of cement pastes: Experiments and modelling

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Abstract

Results already published on the leaching of cement pastes have shown that the kinetics depends sensitively on the material and environment. However and because of the variability of the tested materials and leaching protocols, it is difficult to compare these data and quantify the effect of each parameter. In this paper, a large experimental database on the leaching kinetics of cement pastes is built. Four parameters are investigated: type of cement (portland cement, silica fume cement, slag cement, ternary cement with slag and fly ash); water-to-cement ratio (0.5; 0.4; 0.25), temperature (26 °C; 72 °C; 85 °C) and chemical composition of the leaching solution (pure water, mineralised water, ammonium nitrate solution). Firstly, the database is used to calculate the leaching kinetics of the cementitious materials. Secondly, a simplified model predicting the one-dimensional leaching kinetics for other water-to-cement ratios and temperature up to 85 °C is presented.

Keywords: (D) Blended Cement; (B) Microstructure; (A) Temperature; (C) Degradation; (A) Kinetics

1. Introduction

Because of its suitable physicochemical and mechanical properties, cement-based material is envisaged to be largely used in nuclear waste repository. Its low permeability and diffusivity, and its high mechanical strength make it a very attractive material. Moreover, cement has properties that are well suited to containing low-level radionuclides by both physical and chemical processes. However, these properties can be altered with time and environmental conditions. Since some radionuclides have a long service life, more than 300 years, some degradation phenomena, usually ignored for current concrete structures, are taken into account with a special caution. This is the case of leaching by water, which is one of the main degradation process considered in the design of nuclear waste containers.

When a cement-based material is in contact with pure or acid water, ionic transfers occur between the external water and the pore solution which is strongly a basic solution. Variations in the chemistry of pore solution involve dissolution of some cement hydration products, thus increasing the porosity and permeability of the material and decreasing its mechanical properties [1–8]. Portlandite is the first mineral to be dissolved then C–S–Hs are decalcified. The degradation is characterised by several dissolution–precipitation fronts delimiting zones with different physicochemical and mechanical characteristics.

The leaching kinetics is the main leaching parameter considered when engineers and researchers deal with this phenomenon. Several authors have studied experimentally the leaching kinetics of various cement-based materials under different environmental conditions using various leaching protocols. A first attempt has been done in order to quantify the effect of different material and environmental parameters on the leaching kinetics using experimental data in the literature [9]. It has been shown that the kinetics of leaching strongly depends on the characteristics of the material and its environment including the

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leaching protocols. Since the data are issued from different leaching protocols, only a few of them have been explored quantitatively. This study has shown a lack on experimental data dealing with the influence of temperature and mineral additions as slag and fly ash on the leaching kinetics.

In this study, a large experimental database is built. Twelve cement pastes using four cement types and three water-to-cement ratios are leached at three different temperatures and three leaching water compositions. The database is then used to calculate the leaching kinetics of the materials used in this study. Although the temperature should not exceed 50 °C at the hottest points of the concrete, higher temperatures are studied. A simplified model is proposed to predict the one-dimensional leaching kinetics for other water-to-cement ratios at temperature up to 85 °C.

2. Experiments

2.1. Materials and specimen preparation

All the experiments are led on cement pastes. Twelve pastes are prepared at different water-to-cement ratio using four types of cement: named in the European nomenclature CEM I, CEM II/A, CEM III/A and CEM V/A cement types. The CEM I cement is standard OPC cement. The CEM II/A cement is silica fume cement. CEM V/A cement is blastfurnace slag+ pulverised fuel ash cement and CEM III/A cement is blastfurnace cement. The composition of these cements is shown in Table 1. The composition of the different pastes is given in Table 2.

Table 1
Composition of the four cements, in mass percent (data provided by cement producers)

	CEM I	CEM II/A	CEM V/A	CEM III/A
Clinker	97	92	56	37
Slag			22	63
Fly ash			22	
Silica fume		8		
Limestone	3			
Total	100	100	100	
Gypsum	3.5	3	3	
Anhydrite				5.1
SiO_2	22.75	26.3	28.79	28
Al_2O_3	2.7	4.7	10.91	8.3
Fe_2O_3	1.9	2.35	2.85	2.1
TiO_2			0.6	
MnO			0.11	
CaO	67.1	60.5	47.51	50.4
MgO	0.85	1.12	3	6.5
SO_3	2.1	2.4	2.75	3.1
K_2O	0.23	0.82	1.04	0.52
Na_2O	0.15	0.15	0.22	0.39
P_2O_5			0.53	
S^-	<0.01	<0.01	0.18	0.59
Cl^-	0.1	<0.01	0.02	0.19
Insolubles	0.3		16.15	0.4
Total	99.79	100	99.93	
Free CaO	0.55	1.3		0.9

Table 2
Composition of the twelve mixtures (in mass)

Mixture no.	Cement type	Water-to-cement ratio	Superplasticizer-to-cement ratio
1	CEM I	0.5	
2	CEM I	0.4	
3	CEM I	0.25	0.3%
4	CEM II/A	0.5	
5	CEM II/A	0.4	
6	CEM II/A	0.25	0.6%
7	CEM III/A	0.5	
8	CEM III/A	0.4	
9	CEM III/A	0.25	0.7%
10	CEM V/A	0.5	
11	CEM V/A	0.4	
12	CEM V/A	0.25	1%

Cylinders of 70 mm diameter and 140 mm length are prepared using the twelve pastes. After 24 h, they are removed from the molds and stored for 3 months in a climatic chamber at 100% of relative humidity and 20 °C. Then they are stored in lime saturated pure water. Just before leaching experiments, prisms of 20 mm width, 20 mm height and 30 mm length and other prisms of 30 mm width, 20 mm height and 30 mm length are sawn from the center of the cylinders.

2.2. Leaching experiments

Two different leaching protocols are used:

1 — the first one consists on degrading the pastes using continuously renewed water. The leaching protocol, used at EDF/R&D/MMC laboratory [10], consists in a PTFE container of 1 l volume in which one specimen is leached during a fixed time (Fig. 1). The aggressive solution in the container is continuously renewed using a water circulation system with the flow of 1 l/day regulated by a peristaltic pump. Each container is equipped with two pipes. One pipe supplies the container with pure water bubbled using nitrogen gas to avoid any risk of carbonation. This pipe is plunged until approximately 1 cm from the container bottom in order to homogenise the aggressive solution. The second pipe evacuates the water from the container to tubes of recovery. Theses tubes are graduated in order to check the flow of 1 l per day. The second pipe is plunged to approximately 2 cm from the container top. The tested specimens are prisms of 20 mm width, 20 mm height and 30 mm length. The prisms are put on a Teflon grid in order to get a homogeneous degradation on the six faces of the specimen. The containers are placed in a drying oven allowing the passage of the different pipes. Three drying ovens are used; the temperature is maintained at 26 °C in the first one, at 72 °C in the second one and at 85 °C in the third one. Two different water compositions are used: pure water and slightly mineralised water with chemical composition given in Table 3.

Several specimens are tested using this protocol. Twelve samples corresponding to the twelve cement pastes are

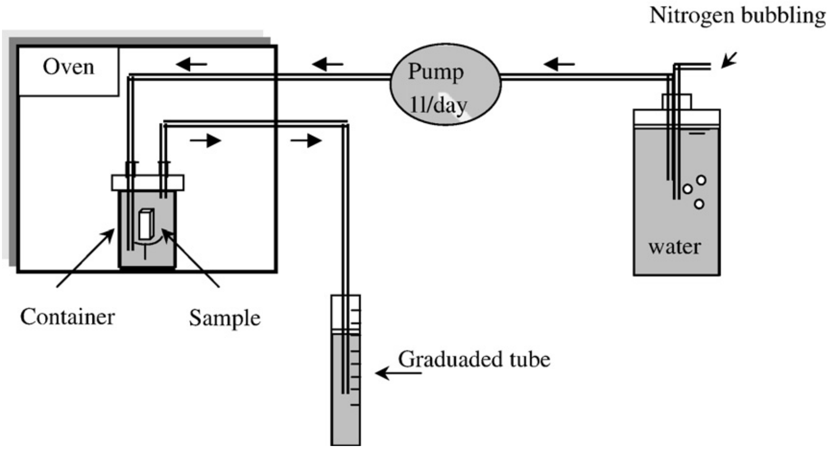

Fig. 1. Scheme describing the leaching protocol using a renewed water.

leached by pure water at 26 °C and others at 85 °C during 114 days. Pastes with water-to-cement ratio equal to 0.4 are also tested at 72 °C using pure water. Other specimens are leached by mineralised water at 26 °C and 85 °C. In order to investigate the evolution of the leaching depth with time at high temperature, other specimens are leached by pure water at 85 °C for different leaching durations.

2 — the second leaching protocol is an accelerated test using ammonium nitrate solution. It consists on conserving during a fixed time the specimens in a big box containing a large amount of the aggressive solution as shown in Fig. 2. The tested specimens are prisms of 30 mm width, 20 mm height and 30 mm length. The prisms are put on a grid in order to get a homogeneous degradation on the six faces of the specimen. In order to avoid carbonation, nitrogen bubbling is used. Eleven specimens were leached using this protocol during 19 days at 20 °C.

2.3. Leached depth measurements

After the leaching test, the specimens are removed from the containers and impregnated with an epoxy resin in order to consolidate and preserve the surface layer. Then the covered samples are cut into two parts. The cut surfaces are then observed using a binocular magnifying glass and scanning electron microscope (SEM) in order to measure the leached depth.

As shown in Fig. 3, the specimen leached by pure water during 114 days presents an easily identified degraded depth delimited from the sound zone by a front. This remark is checked for the three different leaching temperatures but also for the two other aggressive solutions; mineral water and ammonium nitrate solution as shown in Fig. 4. The leached depth for specimens degraded by pure water and ammonium nitrate seems to be itself composed of different zones delimited by various fronts. The leached depths of the different pastes leached in pure water at 26 °C and 85 °C and in ammonium nitrate solution at 20 °C are given in Fig. 5.

The effect of temperature on the leached depth is illustrated in Fig. 6. The degraded depth of specimens leached by mineralised water at 26 °C is given in Table 4, at 72 °C and 85 °C, its value is respectively less than 1 mm and 2 mm for CEM I paste with *w/c* of 0.4. The evolution of the leached depth with time for specimens degraded in pure water at 85 °C is presented in Fig. 7.

2.4. Calcium hydroxide content measurements

For cement pastes leached by pure water at room temperature, the leached depth is given by the dissolution front of portlandite [1]. In order to check if this phenomenon is also true at high temperature (85 °C) for pure and mineralised waters, portlandite content in both sound and leached zones is measured using thermogravimetric analysis. TGA is conducted on different specimens at a heating rate of 10 °C/min under a nitrogen atmosphere (1 bar). The samples are not submitted to any crushing or drying operation prior to thermal measurements. Fig. 8 gives the measured calcium hydroxide content for the different cement pastes before leaching tests according to water-to-cement ratio.

Table 3
Chemical composition of the mineralised water

Chemical composition (mg)/l								pH
Calcium	Silica	Magnesium	Sodium	Potassium	Chloride	Sulphate	Bicarbonate	
11.5	31.7	8.0	11.6	6.2	13.5	8.1	71	7

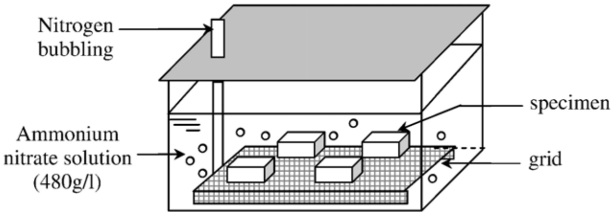

Fig. 2. Scheme describing the accelerated leaching protocol using ammonium nitrate solution.

After leaching tests, TGA is carried out on different specimens with *w/c* equal to 0.4: specimens leached at 85 °C in pure and mineralised waters and a specimen leached at 20 °C in ammonium nitrate solution. TGA results are presented in Fig. 9.

3. Discussion on the experimental results

The first result highlighted by experiments is that the leaching of the different pastes; in ammonium nitrate solution or pure water or mineralised water and at room temperature or 85 °C is characterised by the presence of an easily identified leached zone. This latter is delimited from the sound material by portlandite dissolution front. The leached depth is composed of several zones delimited by different fronts. Its value depends strongly on the water-to-cement ratio, the type

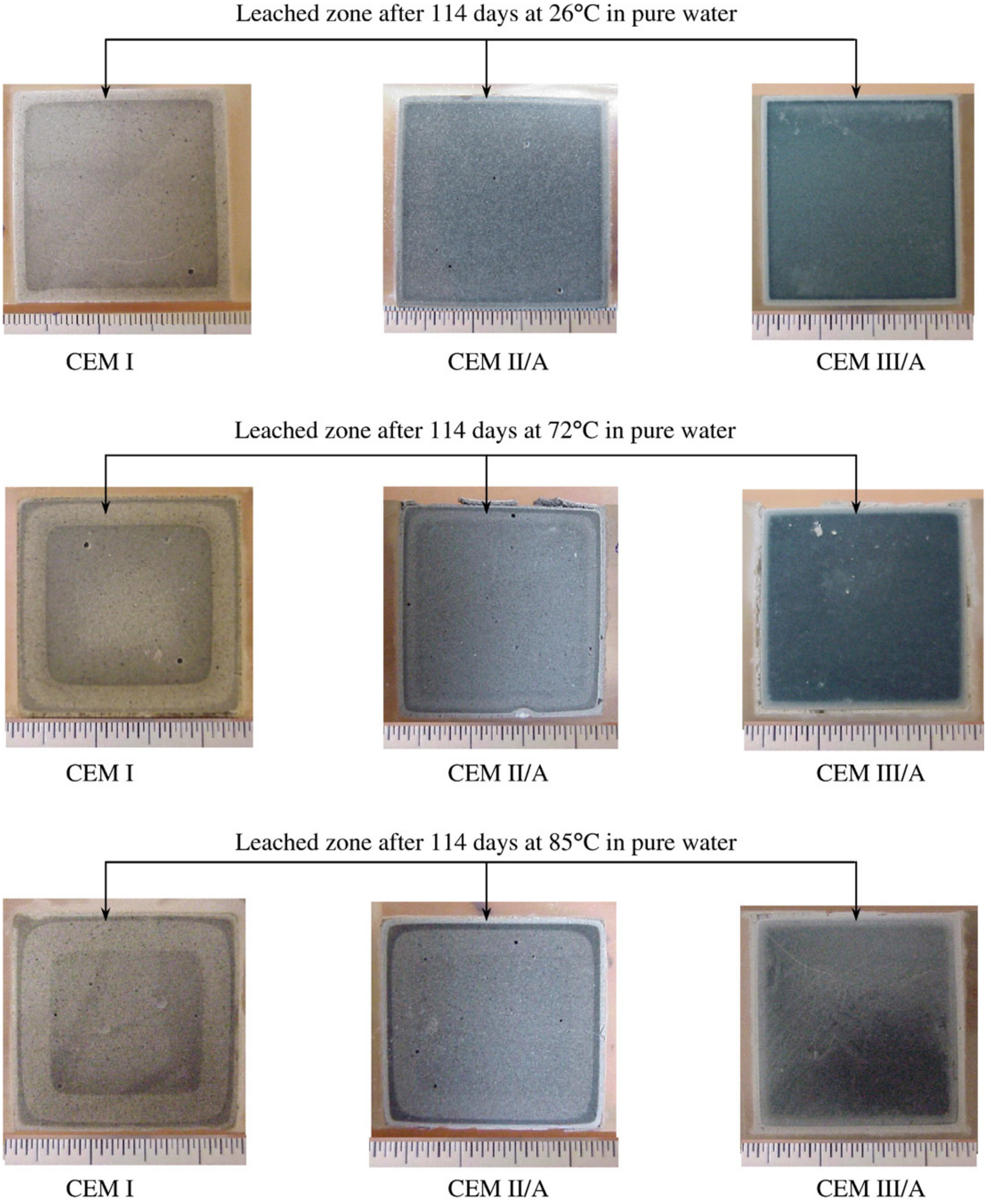

Fig. 3. Photos of the specimens with $w/c = 0.4$ leached during 114 days in pure water showing the presence of a leached depth with different zones delimited by fronts.

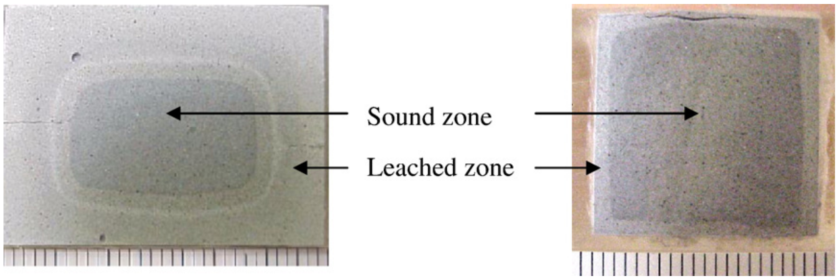

Fig. 4. Photos of CEM I paste specimen with *w/c* = 0.4 leached during 114 days in mineral water at 85 °C (right) and CEM V/A paste specimen with *w/c* = 0.4 leached during 19 days at 25 °C (left) in ammonium nitrate solution showing the presence of a leached zone.

of cement, the temperature and the composition of the leaching water.

3.1. Influence of water-to-cement ratio

The experimental results, as shown in Fig. 5, confirm that the leaching kinetics increases with the rise of water-to-cement ratio by increasing the porosity and consequently the ionic diffusivity through the material. However this increase is more significant for pastes with water-to-cement ratio under 0.4. This can be explained by the evolution of diffusion coefficient with water-to-cement ratio. In fact, according to some experimental results in literature, it can be noted that diffusion coefficient also increases significantly on the same way with water-to-cement ratio for values under 0.4 (Table 5).

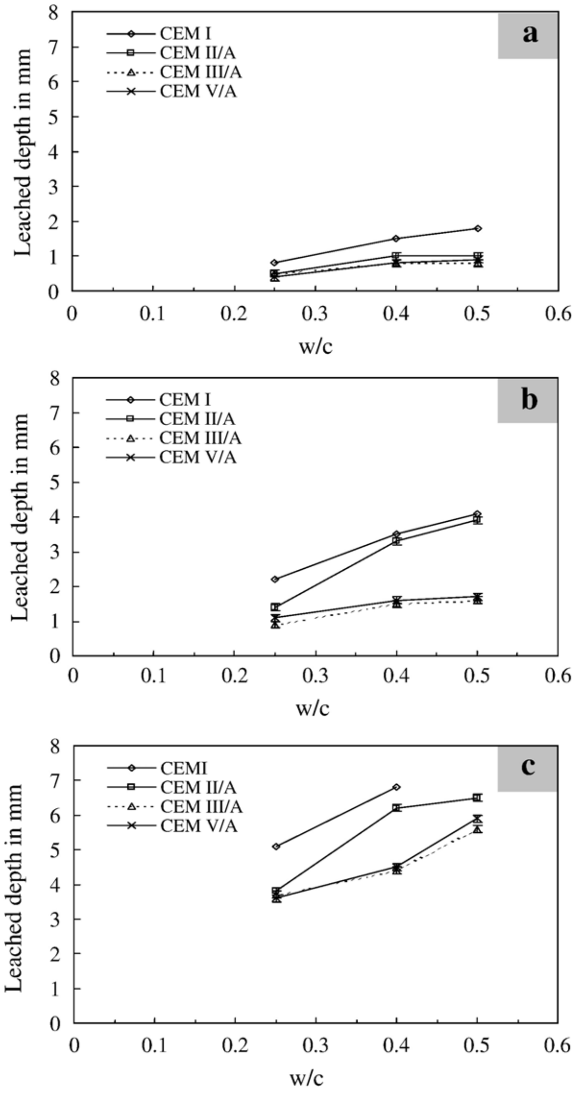

Fig. 5. Leached depth of specimens degraded in pure water; (a) at 26 °C during 114 days (b) at 85 °C during 114 days and (c) in ammonium nitrate solution at 20 °C during 19 days.

3.2. Influence of mineral additions

Fig. 5 shows that for the same water-to-cement ratio, the leached depth is lower for cement with mineral additions. This effect is more significant for pastes containing a high content of mineral additions: CEM V/A and CEM III/A. Two combined effects can explain the benefit results due to the additions of slag, fly ash and silica fume:

- Mineral additions decrease the ionic diffusivity of cement-based materials. According to various researchers [13,14], this is due to the pore size distribution. These systems contain less capillary porosity than portland cement paste. Table 6 gives the effective diffusion coefficient of chloride ions in CEM I, CEM II/A and CEM V/A pastes with *w/c* equal to 0.5. These values were obtained experimentally from steady state electrical migration test [10]. This test has already been described in detail [2]. One can remark that diffusion coefficient of chloride in CEM I paste is 7.5 times higher than that of CEM II/A. This factor is in a good agreement with other data in the literature [15]. This remark can explain the important difference in the leached depth values obtained when these two pastes are leached by pure water at 26 °C.
- Mineral additions decrease the portlandite content of cement paste because less clinker is used and pozzolanic reactions happened. The leaching of portlandite increases the ionic diffusivity in the leached zone, which will contribute to increase the leaching kinetics. This effect can explain the significant difference in the leached depth of CEM II/A and CEM V/A pastes although their diffusivities are quite similar.

3.3. Influence of temperature

Fig. 6 clearly shows that the leaching kinetics increases with temperature. This increase is more important at temperature above 70 °C and mainly for CEM I and CEM II/A cements. The

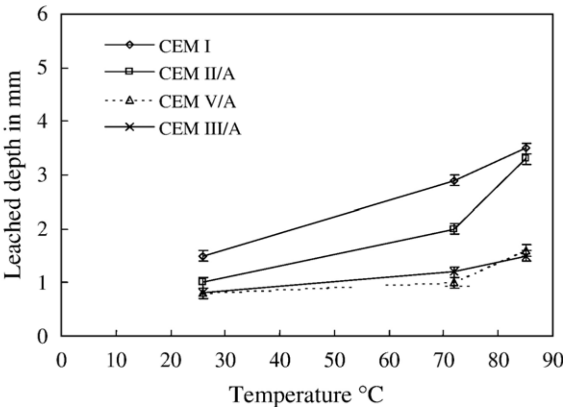

Fig. 6. Leached depth of specimens with $w/c=0.4$ degraded in pure water at different temperatures during 114 days.

leaching depth of portland cement with *w/c* equal to 0.4 is 2.3 times higher at 85 °C than at 26 °C. This factor is reduced to 1.9 for CEM III/A paste. CEM II/A pastes (*w/c* equal to 0.4 and 0.5) behave differently at 26 °C and 85 °C. At 25 °C, they perform closely to CEM III/A and CEM V/A pastes for the same water-to-cement ratio. However, at 70 °C, there is an abrupt slope modification, which could be related to either C–S–H and/or sulfoaluminates (CEM II contains more alumina than CEM I). At 85 °C, the leached depth is closed to that of portland cement paste. This result cannot be generalized to all cements with silica fume. The amount of silica fume is an important parameter that can modify the diffusivity of the material and consequently its leaching kinetics. At 26 °C as at 72 °C and 85 °C, CEM III/A and CEM V/A pastes present a high resistance to leaching by pure water comparing to portland cement paste.

The observed accelerating effect of temperature on the leaching kinetics is mainly due to three phenomena. Firstly, temperature increases ionic diffusivity. Secondly, temperature accelerates dissolution kinetics of most of cement paste minerals; except portlandite for which the solubility decreases with temperature. Thirdly, temperature creates significant changes in cement paste microstructure involving an additional porosity. It influences the stability of some hydrates: ettringite for example is unstable at temperature above 70 °C. The crystal structure of high temperature C–S–H contains more polymerized silica tetrahedra. The silanol–siloxane polymerization $2\ \mathrm{Si{-}OH} \rightarrow \mathrm{Si{-}O{-}Si} + \mathrm{H_2O}$ resulting in H_2O liberation creates porosity [16]. The additional porosity due to changes in the microstructure depends on several parameters among them temperature and ettringite, C–S–H and alkali content.

Table 4
Leached depth of specimens with $w/c=0.4$ leached in mineralised water during 114 days at 26 °C

Maximum leached depth in mm		
CEM I	CEM II/A	CEM V/A
0.3	0.3	0.25

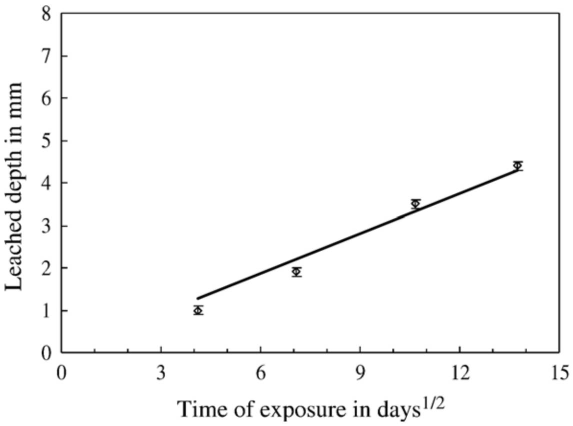

Fig. 7. Leached depth of portland cement paste with $w/c=0.4$ degraded in pure water at 85 °C according to the square root of the exposure time.

3.4. Influence of the chemical composition of the aggressive solution

Experimental results show that the leaching depth strongly depends on the chemical composition of the leaching water. For portland cement paste with *w/c* equal to 0.4 leached during 114 days in pure water and at room temperature, the leached depth is 4.5 times smaller than that obtained on the same material in ammonium nitrate solution during 19 days. However it's at least 5 times less when mineralised water is used. Pure water seems to be very aggressive comparing to the mineralised water. This remark is also true at high temperature (85 °C).

The presence of ions in the leaching water modifies strongly the kinetics of leaching. The presence of ammonium nitrate ions increases drastically this kinetics while the presence of calcium ions decreases it. Moreover, carbonate ions in the

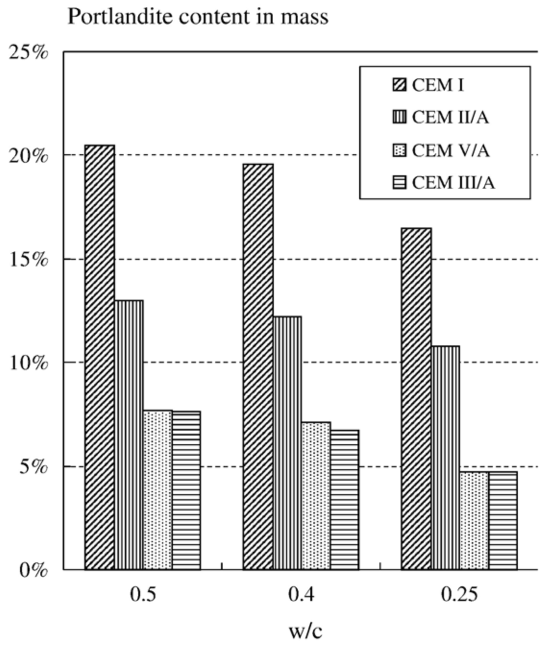

Fig. 8. Calcium hydroxide content measured by TGA.

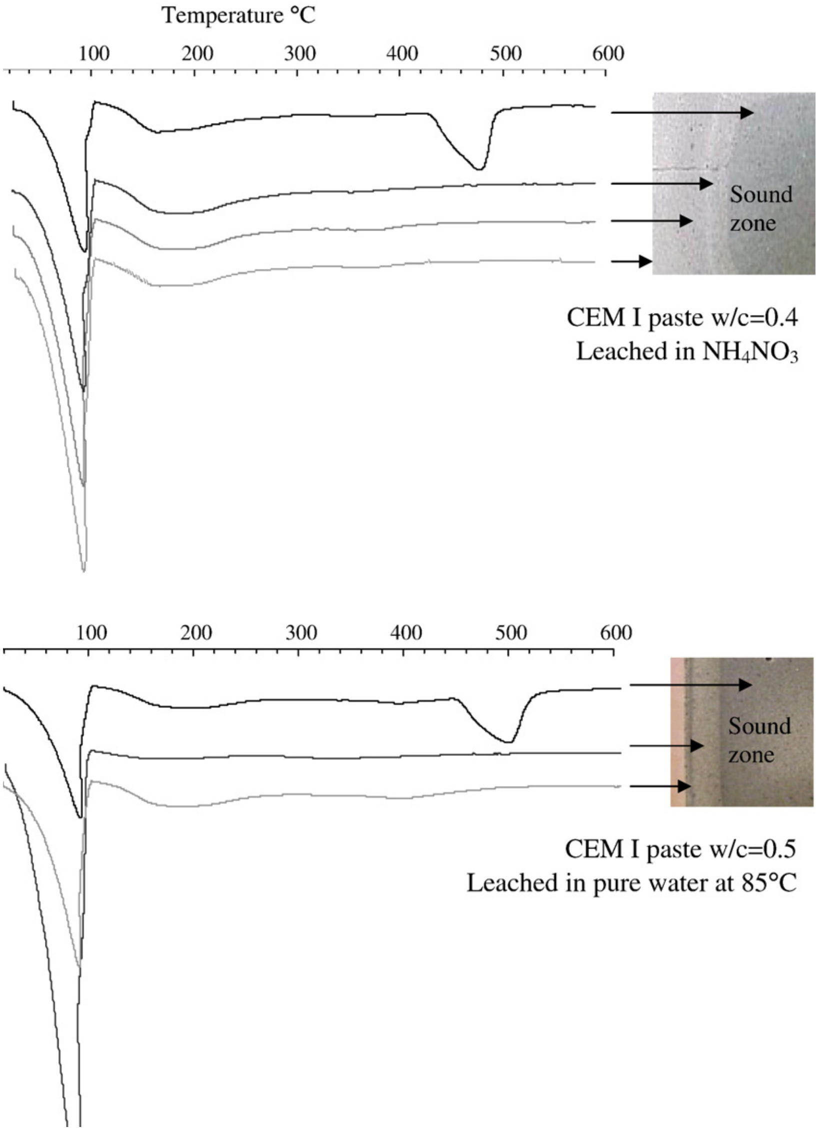

Fig. 9. DTG curves showing the presence of portlandite in the sound zone, identified by a peak in the temperature range 450–520 °C and its absence in the leached zones.

leaching solution react with calcium ions supplied by portlandite and C–S–H to form less soluble carbonates $CaCO_3$. The precipitation of calcium carbonates at the surface and in the cement paste porosity results in a decrease in the diffusivity of the material. The external zone becomes a protective layer, which will control the leaching kinetics

Table 5
Effective diffusion coefficient of Tritium according to water-to-cement ratio

w/c	Effective diffusion coefficient of Tritium m^2/s	Source
0.45	$9.8\ 10^{-12}$	[11]
0.4	$5.0\ 10^{-12}$	[12]
0.25	$5.4\ 10^{-13}$	[12]
0.25	$6.3\ 10^{-13}$	[11]

Table 6
Effective diffusion coefficient of chloride in CEM I, CEM II/A and CEM V/A pastes with *w/c* equal to 0.5 [10]

Paste	Effective diffusion coefficient of chloride ions m^2/s
CEM I	$2.4\ 10^{-12}$
CEM II/A	$3.2\ 10^{-13}$
CEM V/A	$2.6\ 10^{-13}$

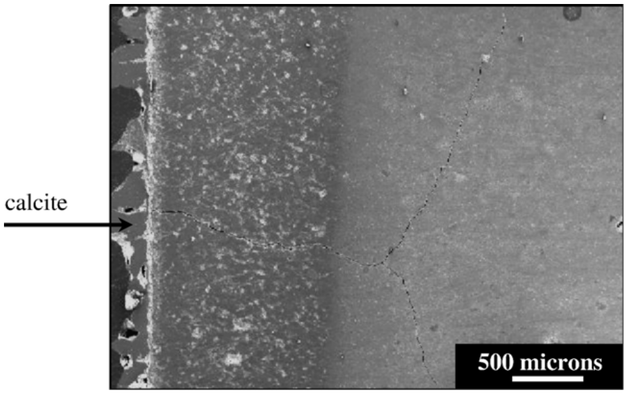

Fig. 10. SEM images showing the presence of calcium carbonate at the surface layer of portland cement paste leached by mineralised water at 85 °C.

(Fig. 10). Also, the presence of ions such as sodium should significantly modify the stability domains of the different hydrates like ettringite [17].

4. Simplified modelling

Several authors have already shown that leaching by either pure water or ammonium nitrate solution at room temperature is governed by a diffusion mechanism and consequently one-dimensional leaching kinetic is proportional to the square root of time [1,3,6]. The depth of the dissolution front of portlandite, L_d, far from sample edges where one-dimensional degradation is checked, can be expressed by $L_d = a \times t^{1/2}$, where a is a kinetic constant and t the time. This expression seems to be suitable for the leaching by pure water at high temperature, at least up to 85 °C as shown in Fig. 7. However, this result could not be generalized to the case of carbonated mineralised water, which involves more complicated phenomena.

Leaching kinetic parameter, a, of the twelve cement pastes is calculated and given in Table 7. This kinetic parameter enables the leached depth to be predicted after any period of leaching in pure water at 26 °C, 72 °C and 85 °C and in nitrate ammonium solution at 20 °C.

In order to predict the leaching depth for other water-to-cement ratios and other temperatures up to 85 °C, a simplified model based on the experimental data developed in this study is proposed. The model assumes that the rate of leaching follows a square root of time and the leached depth is expressed as follows:

$$L_d = a \times t^{1/2} \tag{1}$$

with L_d (mm), t (day), a: constant parameter.

The parameter a is modelled as a product of weight independent functions f, i and j (Eq. 2). Function f corresponds to the influence of water-to-cement ratio, function g to the influence of temperature and function j to the influence of the leaching protocol.

$$a = e \times f(w/c) \times i(T) \times j(\mathrm{Prot}) \tag{2}$$

with e: constant value.

In order to build the weight functions, a protocol of reference and a reference material are defined. The pure water leaching protocol is chosen as the reference protocol. The selected reference material is the portland cement paste with a water-to-cement ratio equal to 0.4. It is a traditional material that was studied by several authors in France. In these reference conditions, the value of the various weight functions is equal to 1 (Eq. 3). Thus, a is equal to e.

$$f(w/c = 0.4) = i(T = 26°C) = j(\mathrm{Prot} = \text{pure water protocol}) = 1. \tag{3}$$

According to the experimental values obtained in this study, the leached depth of the reference paste after 114 days of leaching using the protocol of reference is equal to 1.5 mm for CEM I, 1.0 mm for CEM II/A, 0.8 mm for CEM V/A and 0.8 mm for CEM III/A. According to Eqs. (1) and (2), the constant e is equal to 0.140 for CEM I, 0.094 for CEM II/A, 0.075 mm for both CEM V/A and CEM III/A.

In order to build the function f, the experimental data where only the parameter w/c varies are used. The L_d-to-reference L_d ratios allows to approach the function f according to the following equation:

$$\frac{L_d(w/c)}{L_d(w/c = 0.4)} = \frac{e \times f(w/c) \times i(T) \times j(\mathrm{Prot}) \times t^{1/2}}{e \times f(w/c = 0.4) \times i(T) \times j(\mathrm{Prot}) \times t^{1/2}} = f(w/c). \tag{4}$$

The L_d-to-reference L_d ratio values obtained from the experimental data are plotted according to w/c and a suggested expression of the function f is given in Fig. 11.

Table 7
Leaching kinetic parameter a calculated from the experimental database developed in this study

Type of cement	w/c	Aggressive water	Temperature °C	a (mm/day$^{1/2}$)
CEM I	0.5	Pure water	26	0.169
	0.4		26	0.140
	0.25		26	0.075
	0.5		85	0.384
	0.4		85	0.328
	0.25		85	0.206
	0.4		72	0.272
CEM II/A	0.5	Pure water	26	0.094
	0.4		26	0.094
	0.25		26	0.047
	0.5		85	0.365
	0.4		85	0.309
	0.25		85	0.131
	0.4		72	0.187
CEM V/A	0.5	Pure water	26	0.084
	0.4		26	0.075
	0.25		26	0.037
	0.5		85	0.159
	0.4		85	0.150
	0.25		85	0.103
	0.4		72	0.094
CEM III/A	0.5	Pure water	26	0.075
	0.4		26	0.075
	0.25		26	0.047
	0.5		85	0.150
	0.4		85	0.140
	0.25		85	0.084
	0.4		72	0.112
CEM I	0.5	NH_4NO_3	20	–
	0.4		20	1.560
	0.25		20	1.170
CEM II/A	0.5	NH_4NO_3	20	1.491
	0.4		20	1.422
	0.25		20	0.872
CEM V/A	0.5	NH_4NO_3	20	1.354
	0.4		20	1.032
	0.25		20	0.826
CEM III/A	0.5	NH_4NO_3	20	1.285
	0.4		20	1.009
	0.25		20	0.849

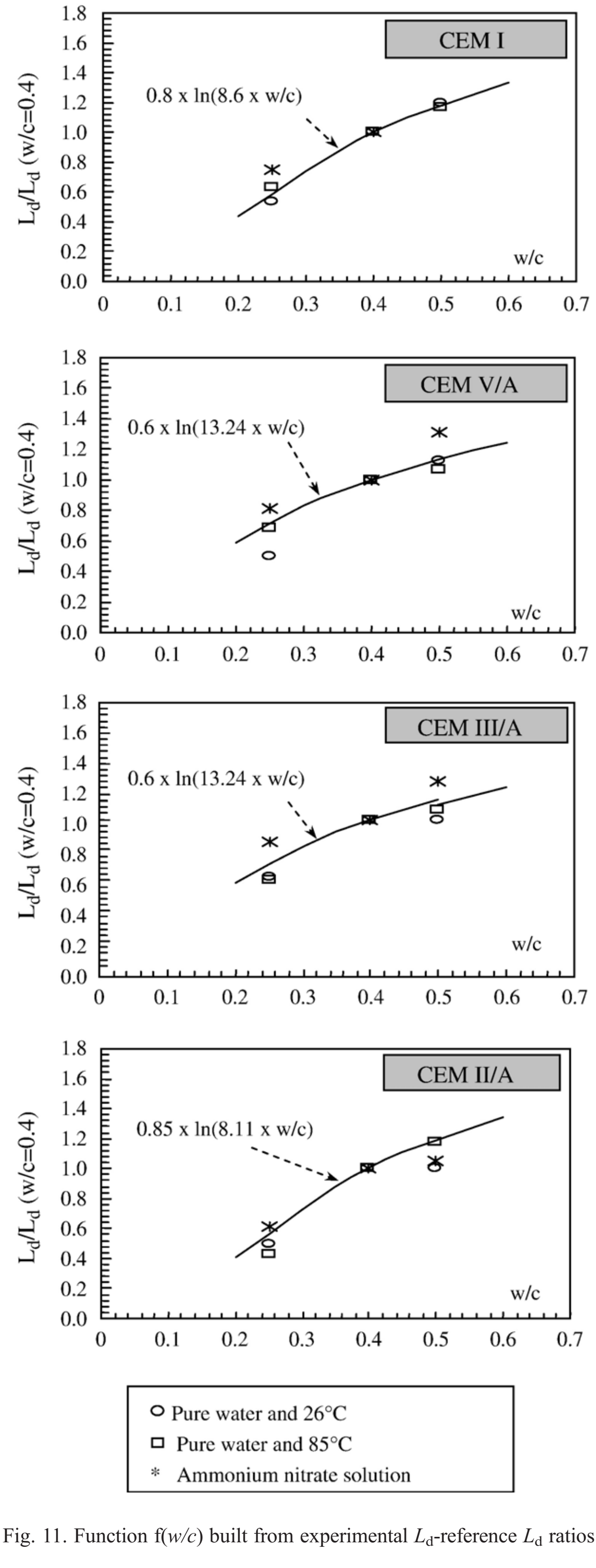

Fig. 11. Function f(*w/c*) built from experimental L_d-reference L_d ratios.

The function *i* is built in the same way as the function *f* (Eq. 5). Fig. 12 presents the L_d-to-reference L_d ratios according to temperature and the suggested expression of the function *i*.

$$\frac{L_d(T)}{L_d(T=26°C)} = \frac{e \times f(w/c) \times i(T) \times j(\text{Prot}) \times t^{1/2}}{e \times f(w/c) \times i(T=26°C) \times j(\text{Prot}) \times t^{1/2}} = i(T). \quad (5)$$

The ammonium nitrate solution increases the leaching kinetics. We assume that *j*(Prot) has a constant value when the leaching test corresponds to ammonium nitrate protocol described in this study. This value is calculated by using the experimental L_d of the four cement pastes at *w/c* of 0.4 according

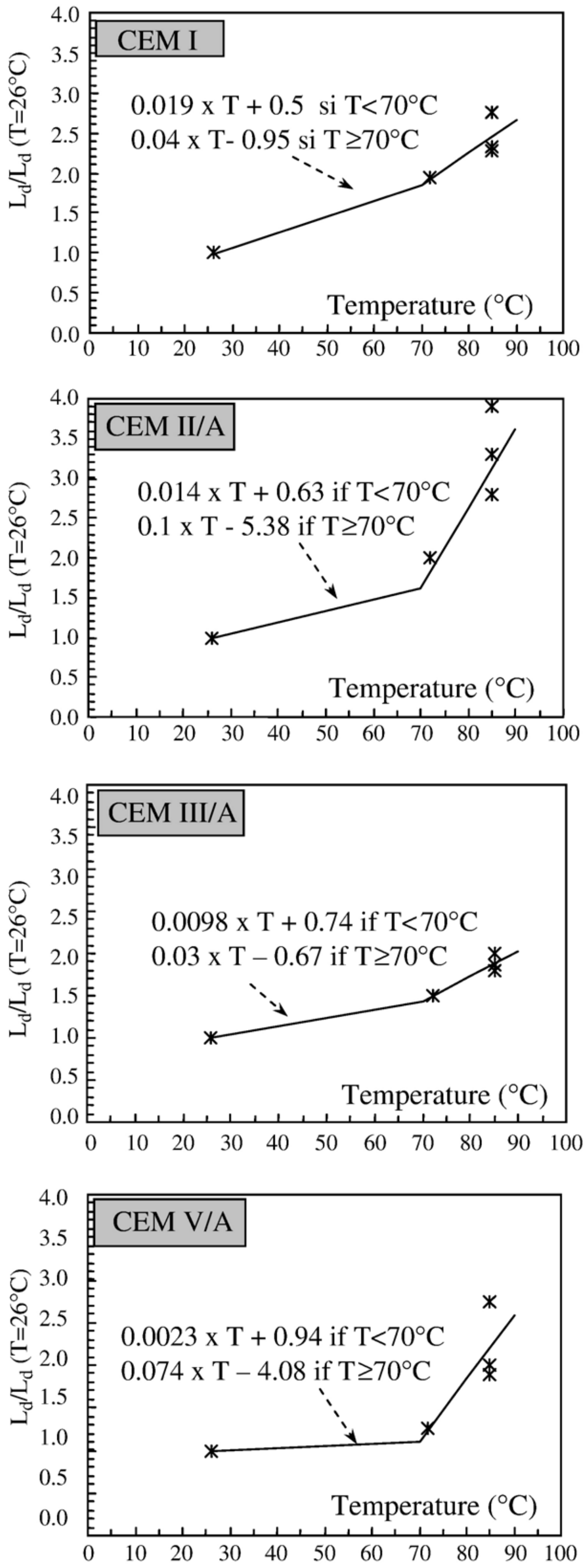

Fig. 12. Function *i*(*T*) built from experimental L_d-reference L_d ratios.

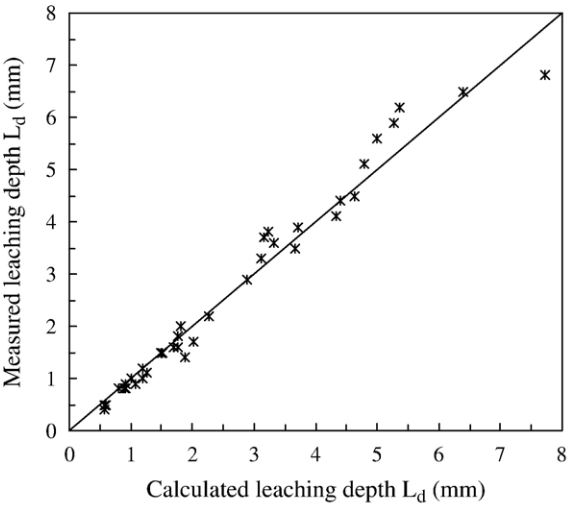

Fig. 13. Measured leaching depth according to the calculated one.

to the Eq. (6). The function *j*(Prot) is assigned the mean value of the four values of *j*(Prot). Thus *j*(Prot=ammonium nitrate solution) is equal to 14.4.

$$\frac{L_d(\mathrm{Prot}=\mathrm{NH_4NO_3})}{L_d(\mathrm{Prot}=\text{pure water})} = \frac{e\times f(w/c=0.4)\times i(20°C)\times j(\mathrm{Prot}=\mathrm{NH_4NO_3})\times 19^{1/2}}{e\times f(w/c=0.4)\times i(26°C)\times j(\mathrm{Prot}=\text{pure water})\times 114^{1/2}}. \tag{6}$$

In summary, the simplified model proposed in this study is described below:

$$\begin{aligned}
&L_d = e\times f(w/c)\times i(T)\times j(\mathrm{Prot})\times t^{1/2}\\
&f(w/c)=\begin{cases}0.81\times\ln(8.592\times w/c) \text{ for CEM I}\\ 0.85\times\ln(8.107\times w/c) \text{ for CEM II/A}\\ 0.6\times\ln(13.236\times w/c) \text{ for CEM V/A and CEM III/A}\end{cases}\\
&i(T)=\begin{cases}\begin{cases}0.019\times T+0.5 \text{ if } T<70°C\\ 0.04\times T-0.95 \text{ if } T\geq 70°C\end{cases} \text{for CEM I}\\
\begin{cases}0.014\times T+0.63 \text{ if } T<70°C\\ 0.1\times T-5.39 \text{ if } T\geq 70°C\end{cases} \text{for CEM II/A}\\
\begin{cases}0.0023\times T+0.94 \ \textit{if}\ T<70°C\\ 0.074\times T-4.08 \ \textit{if}\ T\geq 70°C\end{cases} \textit{for CEM V/A}\\
\begin{cases}0.0098\times T+0.74 \ \textit{if}\ T<70°C\\ 0.03\times T-0.67 \ \textit{if}\ T\geq 70°C\end{cases} \textit{for CEM III/A}\end{cases}\\
&j(\mathrm{Prot})=\begin{cases}1 \text{ if Prot = pure water protocol (described in this study)}\\ 14.4 \text{ if Prot = ammonium nitrate protocol}\\ \qquad\qquad\text{(described in this study)}\end{cases}
\end{aligned} \tag{7}$$

with L_d (mm) and *t* (days).

This model is applied to calculate the L_d value after 114 days. A comparison between the L_d measured and the L_d calculated using the simplified model is illustrated in Fig. 13.

The simplified model developed in this study is applied to pastes based on CEM I, CEM II/A, CEM V/A or CEM III/A cement and leached using one of the two protocols described before. When the aggressive solution is different from pure water and ammonium nitrate solution, we suggest the use of more phenomenological model based on chemical calculation coupled to transport phenomena [8,18,19]. One can remark that usually the calculations using this type of model need in one hand the knowledge of the porosity and the diffusivity of the sound material and in other hand a long time of computing.

5. Conclusions

A large experimental database on the leaching of cement-based materials is built. Twelve cement pastes with three water-to-cement ratios (0.5; 0.4; 0.25) based on four cements with different mineral additions (silica fume, slag and fly ash) are leached by various aggressive solutions (pure water, mineralised water and ammonium nitrate solution) and at different temperatures (26 °C; 72 °C; 85 °C).

The experimental results show that the leaching of the different pastes whether in ammonium nitrate solution or pure water or mineralised water and whether at room temperature or 85 °C is characterised by the presence of an easily identified leached zone. This latter is delimited from the sound material by portlandite dissolution front.

The results clearly show that the leaching kinetics increases significantly with the water-to-cement ratio and temperature for the different cements with and without mineral additions. However these additions strongly decrease the leaching kinetics. This decrease depends on the type and amount of the mineral addition. CEM III/A and CEM V/A pastes present the lowest leaching kinetics at both room and high temperatures. There is a modified behaviour from 70 °C for all the cements studied and more particularly for CEM II.

The chemical composition of the aggressive solution is probably the most important parameter to be considered. The leached depth can be reduced by a factor more than 5 when mineralised water is used instead of pure water. This is due to the presence of different ions in the aggressive water and particularly carbonates. Thus, pure water is a very aggressive solution compared with a mineralised one.

The experimental leached depth values are then used to calculate the one-dimensional leaching kinetics for the twelve cement pastes in pure water and in ammonium nitrate solution. Then, a simplified model is proposed to predict the one-dimensional leaching kinetics for other water-to-cement ratios at temperature up to 85 °C. It is a simplified model, limited to two aggressive waters: pure water and ammonium nitrate solution. When the aggressive solution has a different chemical composition, we suggest the use of chemical reactive transport model using the real composition of the cement matrix and exact chemical composition of the aggressive solution.

Finally, the experimental database developed in this paper can be useful to validate other models dealing with the leaching phenomenon.

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References

[1] F. Adenot, Durabilité du béton: Caractérisation et modélisation des processus physiques et chimiques de dégradation du ciment, PhD Thesis, Université d'Orléans, France, 1992.

[2] B. Gérard, Contribution des couplages mécanique-chimie-transfert dans la tenue à long term e des ouvrages de stockage de déchets radioactifs, PhD Thesis, LMT-ENS de Cachan, France, and Université Laval, Québec, 1996.

[3] C. Carde, Caractérisation et modélisation de l'altération des propriétés mécaniques due à la lixiviation des matériaux cimentaires, PhD Thesis, INSA Toulouse, France, 1996.

[4] C. Tognazzi, Couplage fissuration-dégradation chimique dans les matériaux cimentaires: caractérisation et modélisation, PhD thesis, INSA Toulouse, France, 1998.

[5] V. Matte, M. Moranville, Durability of reactive powder composites: influence of silica fume on the leaching properties of very low water/binder pastes, Cement and Concrete Composites 21 (1999) 1–9.

[6] C. Le Bellégo, Couplage chimie mécanique dans les structures en béton armé attaquées par l'eau — Etude expérimentale et analyse numérique, PhD Thesis, LMT-ENS de Cachan, France, 2001.

[7] S. Kamali, M. Moranville, Ed. Garboczi, S. Prene, B. Gérard, Hydrate dissolution influence on the Young's modulus of cement pastes, Proceedings of the 5th International Conference on Fracture Mechanics of Concrete and Concrete Structures, Vail, USA, 2004, pp. 631–638.

[8] E. Guillon, Durabilité des matériaux cimentaires: modélisation de l'influence des équilibres physico-chimiques sur la microstructure et les propriétés mécaniques résiduelles, PhD Thesis, LMT-ENS de Cachan, France, 2004.

[9] S. Kamali, B. Gérard, M. Moranville, Modelling the leaching kinetics of cement-based materials — influence of materials and environment, Cement and Concrete Composites Journal 25 (4–5) (2003) 451–458.

[10] S. Kamali., Comportement et simulation des matériaux cimentaires en environnements agressifs: lixiviation et température, PhD Thesis, LMT-ENS de Cachan, France, 2003.

[11] A. Delagrave, Mécanismes de pénétration des ions chlore et de dégradation des systèmes cimentaires normaux et à haute performance, PhD Thesis, Université Laval, Québec, 1996.

[12] C. Richet, Etude de la migration des radioéléments dans les liants hydrauliques: Influence du vieillissement des liants sur les mécanismes et la cinétique des transferts, PhD Thesis, Université Paris XI Orsay, France, 1992.

[13] R.F. F, Significance of porosity measurements on blended cement performance, 1st International Conference on the use of fly ash, silica fume, slag and other mineral by-products, in: V.M. Malhotra (Ed.), Concrete, ACI, SP-79, 1, 1983, pp. 415–433, Montebello.

[14] H. U, Effect of blending components on hydration and structure formation, 8th International Congress on the Chemistry of Cement, Vol. 2, Rio de Janeiro, 1986.

[15] M.D.A. Thomas, M.H. Shehata, S.G. Shashiprakash, D.S. Hopkins, K. Cail, Use of ternary cementitious systems containing silica fume and fly ash in concrete, Cement and Concrete Research 29 (8) (1999) 1207–1214.

[16] M. M, Implications of curing temperatures for durability of cement-based systems, in: K.L. Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-Based Materials, E & FN SPON, London, 1997, pp. 211–218.

[17] W. Wieker, Th. Bade, A. Winkler, R. Herr, On the composition of pore solutions squeezed from autoclaved cement pastes, in: A. Nonat, J.C. Mutin (Eds.), Proceedings of the International RILEM Workshop, Dijon, 1991, pp. 125–135.

[18] D.L. Parkhust, A.C.J. Appelo, User's guide to PHREEQC (version 2)—a computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical reactions, US Geological Survey, US Department of the Interior, Water Resources Investigation, Report 99–4259, 1999.

[19] Jan van der Lee, Laurent De Windt, Vincent Lagneau, Patrick Goblet, Module-oriented modeling of reactive transport with HYTEC, Computers and Geosciences 29 (3) (2003) 265–275.