Available online at www.sciencedirect.com
ScienceDirect
Cement and Concrete Research 36 (2006) 1583 – 1594
Cement and Concrete Research

Ground water leaching resistance of high and ultra high performance concretes in relation to the testing convection regime

C. Alonso *, M. Castellote, I. Llorente, C. Andrade

Institute of Construction Sciences "Eduardo Torroja", CSIC, C/ Serrano Galvache s/n, 28033 Madrid, Spain

Received 3 April 2006; accepted 4 April 2006

Abstract

The stability of concrete in contact with water is an issue of great concern if long-term service-life is needed. High and ultra high performance concretes have been developed to enhance the durability of concretes structures, but the great differences in composition and microstructure of these concretes with regard to the traditional concrete mean that previous experience may be inapplicable.

Ground water leaching resistance of high and ultra high performance concretes has been studied employing two leaching methods based on different convection regimes of the leachant: Tank Water Test (TWT) and Running Water Test (RWT). The leachability of calcium has been used to monitor leaching.

1. Introduction

Hardened cement paste is a porous material whose solid phases are in equilibrium with an alkaline interstitial solution. When cementitious materials are in prolonged contact with water, which generally has a near-neutral nature, the soluble components of the hydrated paste dissolve and leach. This selective dissolution induces a change in the equilibrium solid/liquid and then in the subsequent modification of solid phases: concrete is thus vulnerable to the deterioration associated with water. Stronach and Glasser [1] give a diagram of stability of $CaO–SiO_2–H_2O$ system in aqueous solutions containing different ions.

Leaching of concrete by long-term contact with both still and flowing water has sometimes caused severe damage, e.g., of dams or pipes. Environmental compatibility of concrete is a very relevant issue for this century, but becomes even more important if long-term structural life is needed, for instance for nuclear waste storage. Two main applications of cementitious materials for the storage of radioactive wastes are: 1) use of concrete as an engineering barrier to contain the waste (physical barrier) and 2) use of cementitious materials that chemically react with wastes, stabilising them as part of the solid phases.

Cement is considered to show high capacity to fix hazardous components, either heavy metals or radioactive wastes [2–5]. This ability depends on both the chemical and physical composition of cement matrix, but in both cases the leaching of soluble materials from the cementitious compounds will result in the consequent decrease of confinement properties. In addition, extensive leaching will finally result in loss of mechanical properties [6], although experimental evidence is seldom found in literature [2], except that of crack formation in the degraded zone.

The solid hydrates of cement paste are more persistent at pH above 12–13, but at lower pHs the hydrated phases are no longer remain stable and dissolve. The pore solution of a typical Portland cement paste is highly alkaline, so that the leaching process starts by removing alkalis (Na^+ and K^+), followed by dissolution of portlandite and subsequently by the leaching of calcium from silicates, e.g., C–S–H [7–9]. Aluminate phases are also affected, dissolution/precipitation processes of AFm, ettringite and calcite are observed [4,10], and aluminium might be incorporated in the C–S–H gel. Silica gel formation has also been detected in the outer layer of cement paste exposed to leaching in deionised water.

---

* Corresponding author.
E-mail address: mcalonso@ietcc.csic.es (C. Alonso).

0008-8846/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2006.04.004

The main hydrates in cement paste contain calcium; C–S–H comprises 70% of total solid. Decreases in the CaO/SiO_2 ratio of C–S–H are observed due to leaching [3]. In the degraded zone, between surface and unaffected concrete, there is a continuous decrease in calcium concentration. The concentration of silica species in the pore solution remains very low whatever the concentration of Ca [1,4].

Several experimental studies had been performed to elucidate the leaching mechanism of C–S–H [4,9–12]. In a critical review by Taylor [13], C–S–H is considered to be a complex solid. C–S–H has a variable CaO/SiO_2 ratio, ranging from 0.66 to approximate 2; some C–S–H exhibit the typical structure of tobermorite and jennite, with variable chain lengths formed from silicate tetrahedra. In the first stages of hydration dimers of silicate form, which polymerise with time giving longer chain lengths. The leachable calcium is located in the silicates interlayer. Aluminium may substitute Si in regions of low Ca/Si but only in the bridging tetrahedral.

When cement paste is put in contact with an aqueous solution two phenomena take place simultaneously: a) The transport of mass by diffusion, and b) chemical reactions of dissolution and precipitation. If the kinetics of the chemical reactions are slower than diffusion then the first controls the leaching, but if chemical reactions occur rapidly the leaching flow will be controlled by diffusion; that means proportional to the square root of time [3,4]. Diffusion takes place across a solid–liquid interface, and a diffusion front appears where local chemical equilibrium is usually assumed to have been achieve [14,15].

Leaching may be a slow process; 5 to 10 mm leached depth having been found in concretes exposed for 100 years submerged in still natural water [16]. This is in part due to the hydration of anhydrous grains of cement during leaching, which leads to a densification of the material and new portlandite is formed from in-situ hydration [16].

Numerous leaching tests have been developed to study the leaching rate and mechanisms of concrete and of wastes mixed with concrete that are placed in landfill [17–19,2,15,20–22]. Some of the tests methods are focused to the confinement ability of the cement paste to retain the waste [17–19], others consider the leaching of the concrete and its stability in aqueous media [2,15,20,22].

Leaching tests have to reproduce the leaching mechanisms of the concrete exposed to the specific scenarios they simulate. There is no agreement about the leaching method used concerning the regime of contact with the leachant, or even its composition. For instance, tests using acid media as the leaching agent have been employed [2,15,19], as has deionised water [15], water with chlorides [7], or even bubbling of CO_2 through the demineralised water [2]. Deionised water [15,18] can give information on the degradation stages, but in comparison with natural waters it may be considered too aggressive. Bubbling of CO_2 makes the testing method more representative, as this component is usually present in real conditions [2]. The lower pH of the CO_2-bubbling test provides a marked degree of acceleration, but the leaching mechanism is affected due to the precipitation of calcite in the degraded zone [2]. Natural waters contain ionic species (such as, Ca^{+2}, Si^{+4}, Cl^{-}, $SO_4^{=}$, even Mg^{+2} and alkalis, Na^{+}, K^{+}, and also HCO_3^{-}) that may also affect the leaching process. Obviously the hardness of the waters affects the leaching resistance of concretes [23].

Moreover, all tests considered above function in a closed system or with a periodic renewal of the leachant, with some of them under controlled conditions at the outset system, that is: at constant pH; at a fixed ionic content in the solution in contact with the concrete [2,15].

Leaching tests working in an open system and using running water are rarely found in the literature ([15,22] being exceptions, using deionised water as leachant). In addition, most of the studies are related to the water leaching resistance of cementitious materials: C_3S, cement paste or traditional concretes with or without additions.

Few studies have been made using ultra-high performance pastes [22], although diffusion is important in leaching. Therefore the decrease of porosity is one of the aims of high performance concretes (HPC) in order to achieve longer durability. HPC concretes use low w/c ratios, high content of cement and, in many cases, high proportions of mineral additions such as silica fume. The persistence of anhydrous grains of cement is very typical in HPC. All these factors may affect their leaching resistance.

In the present work, leaching tests are applied to high and ultra high performance concretes, HPC and UHPC respectively. The influence of contact water regime has been taken into account using a Tank Water Test (TWT) based on ANSI standard [17] and a specifically developed leaching test using a continuous flow of water, the Running Water Test (RWT) [24]. The leachant employed in both methods has been groundwater, specifically a natural commercialised water chosen for its ionic content and stability in composition. Comparisons between both leaching methods are made with respect to the leachability of calcium from the different concretes.

2. Experimental

2.1. Materials

2.1.1. Concrete samples preparation

Concrete cylinders of 110×210 and 75×150 mm were prepared. Seven concrete mixes: 3 High Performance Concretes (HPC), 3 Ultra High Performance Concretes (UHPC) and 1 Reference Concrete have been tested. The identification of the concretes and dosages are given in Table 1, for UHPC and Table 2 for HPC and reference concrete.

UHPC are special patented concretes and were cured during 48 h in 100%RH and 20 °C, plus 48 h at 90 °C and at 95%RH, and 48 h at 90 °C in dry air. The HPC samples were cured for 28 days immersed in limewater.

2.1.2. Leaching agent

Natural ground water (Granitic Water, GW) was employed as leaching agent. The chemical composition determined at the laboratory is given in Table 3. The bicarbonates, identified in

Table 1
UHPC characteristics

	Unit	ANL MST D1 (AMSD1)	ANL MST D2 (AMSD2)	ANL 940U D1 (AD1)
Type I low alkali content sulphate resisting Cement	kg/m^3	759	695	737
Silica fume from zirconium metal industry	kg/m^3	247	104	–
Silica fume	kg/m^3	–	–	239
Quartz flour	kg/m^3	228	104	221
Sand	kg/m^3	1086	1390	1054
Total water	kg/m^3	129	146	154
Plasticizer	kg/m^3	33	30	32
Water/binder ratio		0.2	0.24	0.24

Table 3
Chemical composition of natural ground water (GW) employed for leaching tests

Ionic species	Concentration (mmol/l)
Calcium	0.84±0.04
Sodium	0.55±0.03
Magnesium	0.27±0.005
Potassium	0.023±0.003
Bicarbonates	2.9±0.05
Sulphates	0.114±0.05
Chlorides	0.39±0.01
Silicium	0.35±0.005
pH	7.91±0.3
Conductivity (mS/cm)	0.337±0.02

equilibrium with the atmosphere CO_2, are analysed by acid–base titration, silicon by colorimetric method and calcium, magnesium, sodium, potassium, chloride and sulphate by ion chromatography. This type of natural water has the advantage, in comparison with deionised water, that the tests are more representative of a real exposure condition for long-term water resistance studies.

2.2. Protocol of leaching tests

Two type of leaching tests were selected based on the interest of testing different convection regimes of the leaching water, those selected were: 1) Continuous running water test (RWT), using a constant flow, and 2) Tank water test (TWT), with periodic renewal of the water. The tests were made under thermostatic control at 20±2 °C.

2.2.1. Running Water Test (RWT)

A special leaching device was designed for RWT, described in [24]. The method works in an open system, similar to a leaching column with a continuous flow, as indicated in Fig. 1a. A separate leaching device was employed for each type of concrete. The specimens were disks or slices of concrete of 110 mm ϕ and 6 mm depth, in order to control the real surface of concrete exposed to leaching and the volume of the specimens. Each leaching device contains five concrete disks in series. First the water contacts with one surface of the slice (part a), and then with the other (part b), before flowing to the next slice. Every 3 months the concrete slice located at the fourth position in each leaching device is removed and a new concrete disk is introduced and located at the beginning of the device (column). The other four slices change their position in the device every 3 months, while the fifth is maintained fixed in order to be removed at the end of experiment (18 months in present case).

The water flows upwards at a rate of 7 ml/h. Once the chamber in contact with face (a) is filled, the leachant passes to the next chamber, in contact with face (b) filling also in the upward direction. The dead volume of water for each leaching chamber was 9.5 ml. A modified device was designed for testing reference concrete, DB 110, that includes only 4 slices of 10 mm depth.

Periodic sampling of the leachate was made. The evolution in the leaching water of Ca^{+2} is the parameter of interest considered in present paper. Analyses of $CO_3^{=}$ and HCO_3^{-} were also performed for the full balance of the calcium leached. Besides, the complete ionic analysis of the leaching system was made, including: Conductivity, pH, Ca^{+2}, $CO_3^{=}$, HCO_3^{-}, Si^{+4}, Na^{+}, K^{+}, Mg^{+2}, Cl^{-}, $SO_4^{=}$, Fe^{+3} and Al^{+3}.

Table 2
HPC characteristics and reference concrete

	Unit	Reference concrete DB 110	DB 111	DB 112	DB113
Type II cement containing 20% fly ash	kg/m^3		–	–	509
Type I low alkali content sulphate resisting cement	kg/m^3	397	454	531	–
Silica fume	kg/m^3		91	27	25.5
Calcareous aggregates; 0–2 mm	kg/m^3	441	413	417	417
Calcareous aggregates; 2–5 mm	kg/m^3	367	344	348	348
Calcareous aggregates; 5–8 mm	kg/m^3	331	310	313	313
Calcareous aggregates; 8–16 mm	kg/m^3	698	654	661	661
Total water	kg/m^3	171	153	156	150
Plasticizer	kg/m^3	–	5.2	5	7.17
Water/binder ratio		0.43	0.28	0.28	0.28

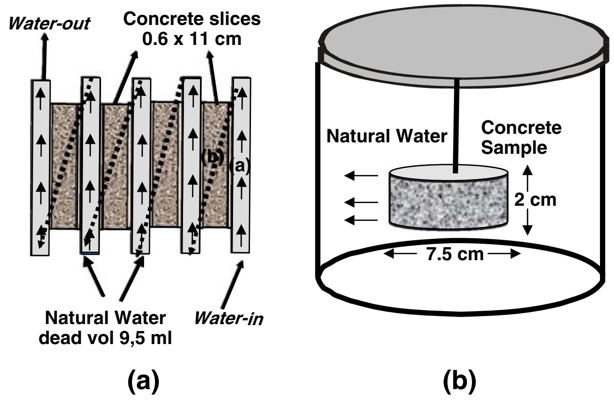

Fig. 1. Leaching arrangement: a) Running Water Test (RWT), and b) Tank Water Test (TWT).

2.2.2. Tank Water Test (TWT)

The TWT follows the standard ANSI/ANS-16.1-1986 [17], “Measurement of the leachability of solidified low-level radioactive wastes by short-term test procedure”, commonly used in testing cementitious materials for the nuclear industry.

The test consists of a procedure in which the leachant is sampled and replaced at designated intervals. The procedure permits the accumulation of sufficient data in a reasonably short time for quality assessment purposes. The data obtained from this standard are expressed as a material parameter of the leachability of the specific leached species. This parameter is called the “Leachability Index”. Fig. 1b shows a schematic drawing of the leaching arrangement employed. The sample must have a well-defined shape, mass and volume. The preferred test specimen geometry is cylindrical and it shall have a length to diameter (L/D) ratio in the range of 0.2 to 5. Cylindrical samples with a diameter of 75 mm and a length of about 20 mm were used for the present study (L/D = 0.27). The dead volume of water was 1400 ml. The test does not prescribe that a fixed value of the pH be maintained of the leachant in contact with concrete.

In this test the leachate is sampled and entirely replaced at designated time intervals. The water solution is sampled and replaced after cumulative leach times of 2, 7 and 24 h from the initiation of the test. Subsequent leachate sampling and leachant replacements shall be made at 24 h intervals for a further 4 days. Three additional leaching intervals of 14, 28 and 43 days extend the entire test to 90 days. For the interest of present work, a further renewal of leached water was made every 6 weeks, up to a total leaching period of 12 months.

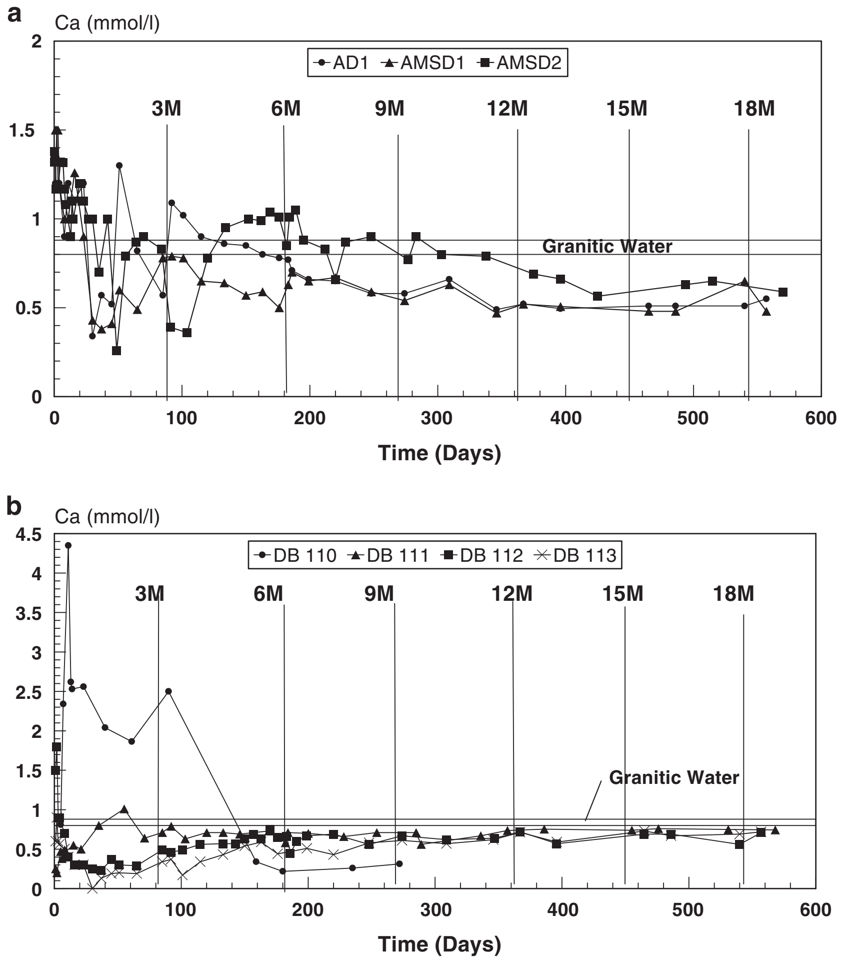

Fig. 2. a) Evolution of calcium concentration in the leached solution of UHPC after RWT. b) Evolution of calcium concentration in the leached solution of HPC after RWT.

Under these conditions the mass-transfer equations permit the calculation of an effective diffusivity of the concretes by the expressions given in the standard [17]. If they are applied to the amount of calcium leached from the concretes, the “effective diffusivity of Calcium, D_{nsCa}” is obtained from (Eqs. (1) and (2)). The “Leachability Index of Calcium, L_{iCa}” is obtained using the (Eq. (3)).

$$D_{\mathrm{nsCa}} = \pi \left[\frac{a_n/A_0}{(\Delta t_n)} \right]^2 \left[\frac{V}{S} \right]^2 T \qquad (1)$$

D_{nsCa}	effective diffusivity of Calcium, cm^2/s
V	volume of specimen, cm^3
S	geometric surface area of the specimen from measured dimensions, cm^2
T	leaching time representing the “mean time” of the leaching interval, s
a_n	activity of calcium released from the sample during leaching interval n
A_{o}	total activity of calcium at the beginning of the first leaching interval, 30 s.

$$T = [1/2(t_n^{1/2} + t_{n-1}^{1/2})]^2 \qquad (2)$$

$(\Delta t)_n = t_n - t_{n-1}$, duration of the n leaching interval, s.

The Leachability Index of Calcium from the tested concretes is obtained through (Eq. (3)):

$$L_{\mathrm{iCa}} = \frac{1}{10} \sum_{10}^{1} \left[\log(\beta / D_{\mathrm{nsCa}}) \right]_n \qquad (3)$$

Constant $\beta = 1.0\ \mathrm{cm}^2$ s.

D_{nsCa} is the effective diffusivity of Calcium calculated from the test data using above (Eq. (1)).

L_{iCa}	Leachability index of calcium. A mean of 10 determinations (L_n) for calcium is given.

3. Results

3.1. Calcium leached from running water test (RWT)

The type of water used in this study (Granitic-Water, GW) contains a certain amount of Calcium, which varies around 0.84 ± 0.04 mmol/l. In Fig. 2 the calcium concentrations in the leachates are given for the different concretes, HPC (Fig 2a) and UHPC (Fig. 2b). The content of Ca introduced by the GW is plotted in the figure.

The general trend deduced is a decrease of the amount of Ca leached with time, although cycling processes (up and

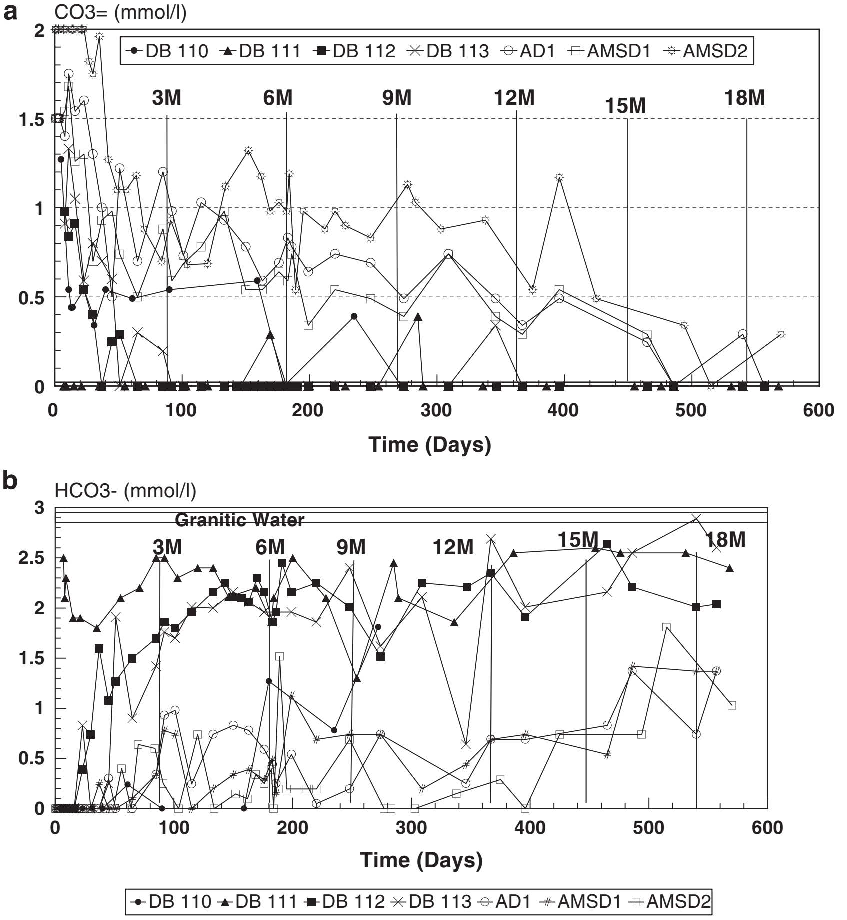

Fig. 3. a) Carbonate concentration in the leachates of RWT for all concretes. b) Bicarbonate concentration in the leachates of RWT for all concretes.

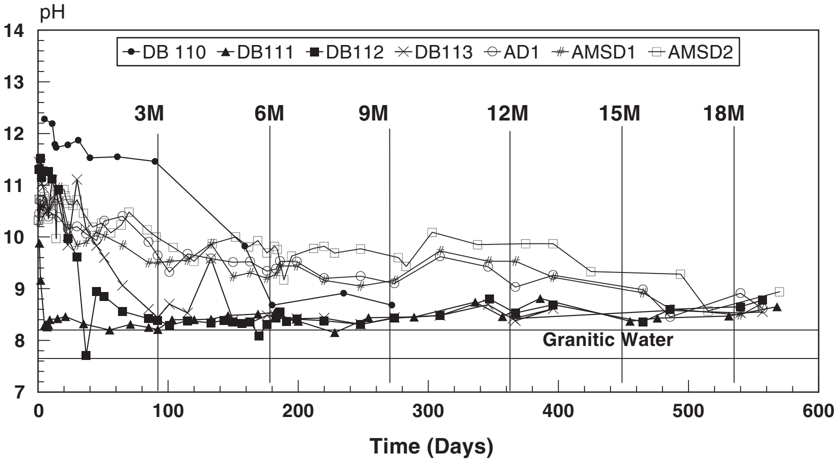

Fig. 4. pH of the leachates in RWT in all concretes.

down) of the concentration of Ca in the leacheates are significant until around 200 days with UHPC (Fig. 2a). After 12 months of leaching the concentration of Ca leached is quite stabilised below that of the Ca content in GW. The cycling in the leaching of Ca is less significant with HPC (Fig. 2b), where concentrations are below that of granitic water after the first month of leaching. An exception is the reference concrete that leaches higher concentration of Ca during the first 3 months than any other concrete, but after 6 months stabilises below the others.

The cycling behaviour of $[Ca^{+2}]$ in the leacheates is attributed to the presence of HCO_3^- in the GW (2.9 mml/l). An equilibrium between $[HCO_3^-]\Leftrightarrow[CO_3^=]$ in function of the pH of the leachate should take place, so that, analyses and changes in concentration of both ions in the leachates are included in Fig. 3a and b. The pH evolution of the leachates is shown in Fig. 4 where the pH of the GW is also indicated. The pH values of the leached solutions are alkaline at the beginning of the test ($pH > 10.5$) but evolve to neutralisation. The leachates remain more alkaline for longer periods with UHPC than with HPC. At the beginning of the test, practically all HCO_3^- is transformed into $CO_3^=$ due to the high pH of the leachates. The $[CO_3^=]$ decreases faster with time for HPC than for UHPC (Fig. 3a). On the contrary, the $[HCO_3^-]$ increase progressively with time, but more slowly with UHPC, whose leachates are more alkaline (Fig. 3b).

3.2. Calcium leached from the Tank Water Test (TWT)

The concentration of Calcium in the leachates is given in Fig. 5 for TWT. The values of calcium concentration leached from all concretes are below that of the Ca introduced by the granitic water, even during the first time intervals of leaching. The cycling evolution noticed with RWT is less significant in TWT, in fact, the amount of calcium leached remains below that using the RWT.

One particular difference with the TWT with respect to the RWT is that the pH value of the leachates is from the beginning, around that of the granitic water ($pH \cong 8 \pm 0.2$), as represented in Fig. 6. The pHs are similar for all concretes, but in HPC higher scatter is noticed in the first intervals of leaching renewal. Also the content of carbonates is negligible, while the bicarbonates concentration in the leachates is very high (>2 mmol/l), nearly the amount introduced with the GW, as indicated by Fig. 7.

4. Discussion

In general authors agree that when ground water is in contact with concrete, the main process leading to the leaching is the

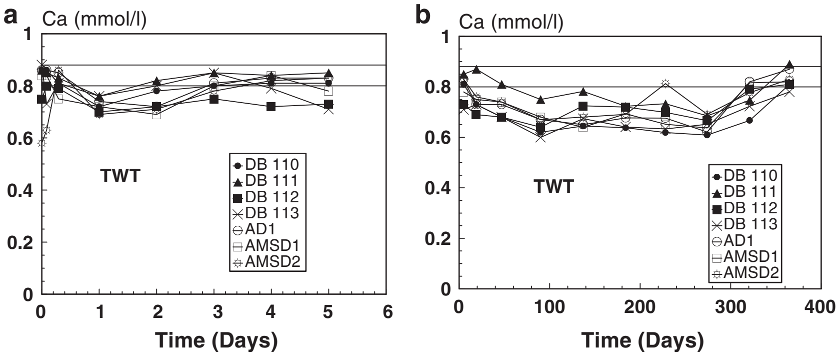

Fig. 5. Calcium concentration in leachates of TWT for all concretes: a) 5 days of leaching, b) total length of test.

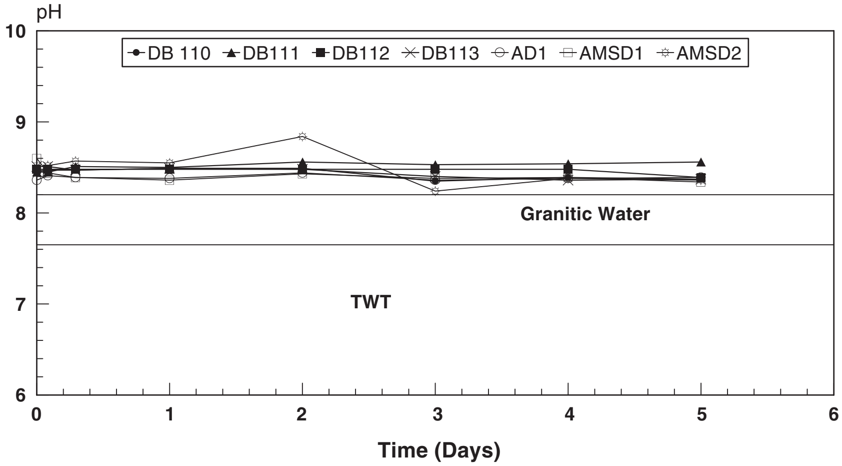

Fig. 6. pH of leachates in TWT for all concretes.

neutralisation of the pore solution and subsequent decalcification of the solid phases [1–4,7,8,14,15,25,26]. All consider that the leaching mechanism of concrete occurs in a sequence of stages:

1. Leaching of the more soluble elements such as alkalis hydroxides, Na^+ and K^+, initially present in high pH (~13.5), which falls rapidly to around 12.5 as these phases, are removed.
2. The next step shows a slow fall of the pH from 12.5 to around 11.5, as a consequence of portlandite dissolution.
3. When portlandite has fully dissolved, the pH falls to approximately 10.5, due to the progressive dissolution of the calcium–silicate–hydrate (C–S–H) gel phases.
4. A final stage takes place from pH around 10.5 until pH = 7, the pH buffering of the C–S–H gel is exhausted and other cement phases such as hydrogarnet, ettringite and hydrocalcite are dissolved.

Alteration of these stages may occur due to modifications in the leaching system employed, i.e., changes in the chemical composition of the leachant agent (acid, deionised water, carbonated water or ground water), the concrete quality (type and quantity of cement in concrete), type of leaching test (the contact regime of the leaching agent with concrete surface).

4.1. Influence of chemical composition of water in the leaching of HPC and UHPC

In systems where the leachant agent is deionised water, if the isolation from the atmospheric CO_2 is guaranteed, the isolated analysis of the concentration of calcium in the leachate is sufficient to know the amount of calcium leached from the concrete. However, with granitic water the amount of calcium introduced and the content of bicarbonates can modify the leaching of calcium and therefore the amount of Ca leached.

In a system like the one used in the present work, where addition of carbonates plus bicarbonates is made, values below the initial concentration introduced in the granitic water in the form of bicarbonates is found, due to the precipitation of calcite [2]. The amount of calcium precipitated needs to be calculated to know of the real calcium leached from the concretes. In

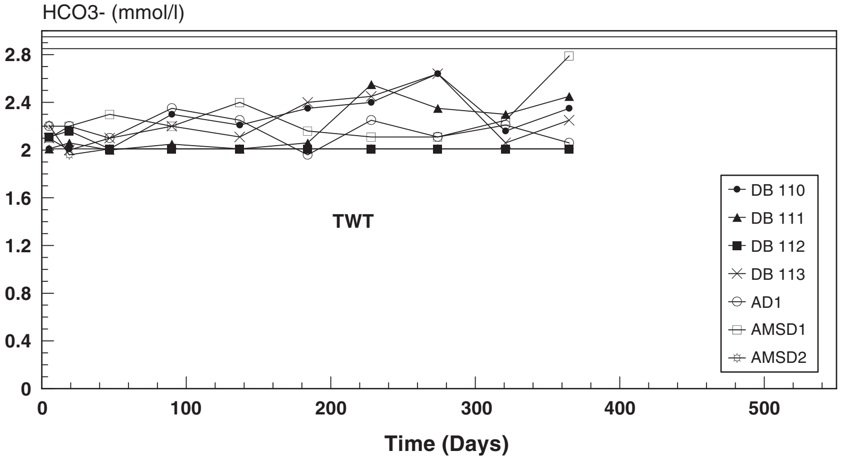

Fig. 7. Bicarbonate concentration in leachates of TWT for all concretes.

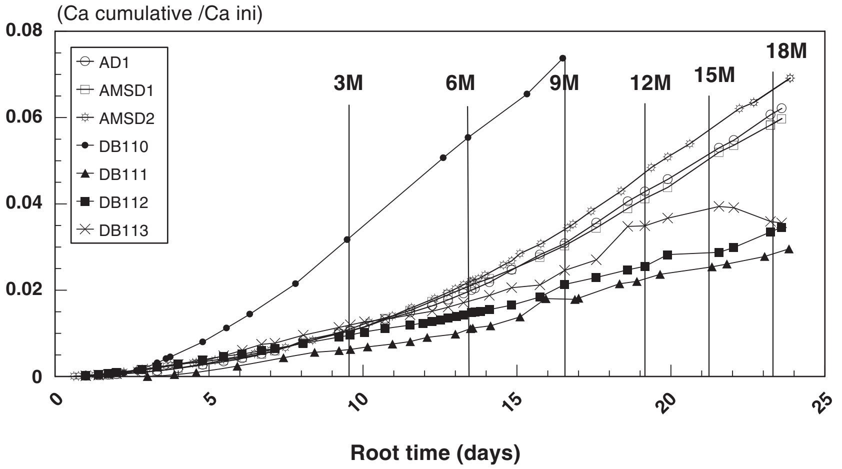

Fig. 8. Cumulative Calcium leached from RWT for all concretes.

present tests the total amount of calcium released from the concretes has been obtained using the (Eq. (4)):

$$[\mathrm{Ca}^{+2}]_{\mathrm{leached}} = ([\mathrm{Ca}^{+2}]_{\mathrm{leachates}} - [\mathrm{Ca}^{+2}]_{\mathrm{granitic\ water}}) + ([\mathrm{HCO}_3^-]_{\mathrm{granitic\ water}} - [\mathrm{HCO}_3^-]_{\mathrm{leachates}} - [\mathrm{CO}_3^=]_{\mathrm{leachates}} \quad (4)$$

From this calculation, the comparison between different concretes is possible, once the amount of calcium leached has been normalised to the initial calcium content in the different specimens. In Fig. 8 the $\mathrm{Ca}_{\mathrm{cumulative}}/\mathrm{Ca}_{\mathrm{initial}}$ curves of UHPC and HPC are plotted. From these curves it can be seen that a higher amount of calcium is leached from UHPC than HPC in the RWT. The reference concrete leaches the highest amount of calcium for the same period of leaching, nearly 7% by weight of cement after 9 months of leaching.

Fig. 8 also shows that up to 18 months of leaching, there is a continuous increase in accumulated Ca. After this period of leaching all UHPC lixiviate nearly 6% of the initial content of Ca, while HPC ranges from 3% to 4%, varying with the type of concrete, the smallest amount of Ca leached was from concrete DB 111.

Provided that part of the calcium leached precipitates on the surface of the specimen or even on the walls of the container, correction with precipitated carbonates has also been made in the values of leached Ca in the TWT. In order to make the correction, it has been assumed that the difference between carbonates and bicarbonates in the leachate and the amount initially present in the granite water has precipitated in the form of calcium carbonate. This kind of calculation is not specified in the standard [17] of this testing method, which does not consider any subsequent precipitation of the released species (as the standard only considers deionised water).

Fig. 9 depicts the cumulative amount of calcium leached after calculating the correction for the carbonates with respect to the initial amount of calcium in the specimens for the TWT. The profile of cumulative Ca curves is very similar for both types of concretes. It is possible to divide the process into two steps: 1) during the first 6 days the rate is higher, and 2) when the renewal of the solution is less frequent, a second slope can be found. The shape of these curves is very much dependent on the periodicity of the water renewal. It can be noticed that HPC leached more Calcium than UHPC in this type of leaching test. DB 110 and DB 111 release the highest Ca for HPC and DB 113 the least. UHPC releases similar quantities, which reverses the classification obtained from RWT.

4.2. Influence of the leaching regime in the leaching process

Following the sequence of stages of the leaching process described above, it can be said that HPC and particularly the reference concrete (DB 110) leached higher amount of Ca at the beginning of the test precisely due to the dissolution of portlandite.

The Running Water Test (RWT) releases higher amounts of calcium than the Tank Water Test (TWT), if comparison of the amount of Ca leached from both methods is made, this suggest that the RWT accelerates leaching more than the TWT. But another important difference between the methods is that the classification of concretes achieved is different. This is of major importance, as it confirms that the type of leaching test used may change the leaching mechanism, as indicated in [2]. Further studies are needed to confirm this hypothesis.

One reason for this difference is found in the pH value of the leachates in contact with the concretes surfaces. The higher alkaline nature of the initial leachates in RWT may favour the precipitation of calcite, that can be removed easily and not be

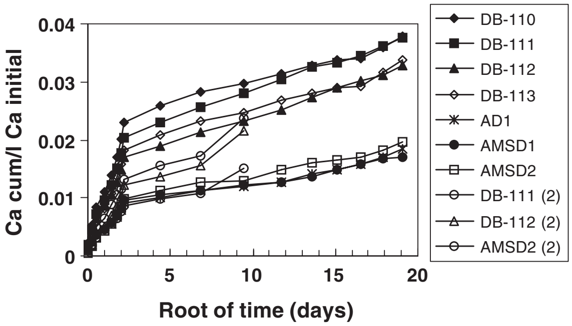

Fig. 9. Cumulative calcium leached from TWT for all concretes.

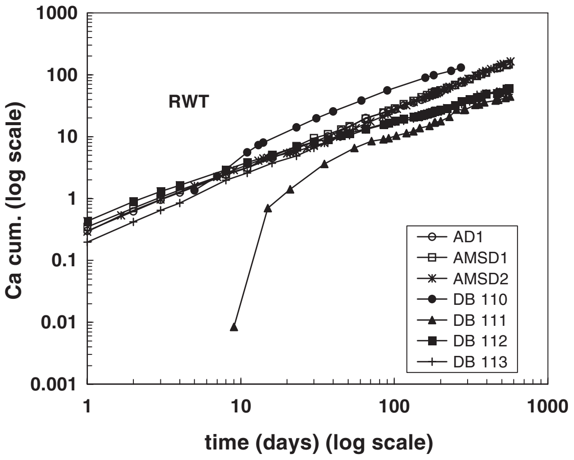

Fig. 10. Log–log fitting of calcium leached from RWT for all concretes.

deposited on the surface of the concretes. This possibility of calcite precipitation is thermodinamicaly less favoured with the TWT,where the pH is nearly that of the introduced water: the higher volume used dilutes the OH$^-$ leached from the concretes. However the longer contact time of water with the concretes allow the precipitation of calcite and sealing of the surfaces. At later stages, when the pHs of the leachates from the RWT are similar to that of granitic water, both methods approximate to the leaching ability of Ca.

The inversion of the classification of concretes depending on the leaching test employed may also be attributed to the fact that UHPCs have high contents of anhydrous particles that react in contact with the leaching water. With the RWT, the water is continuously removed which favours further reaction of anhydrous grains. In the case of TWT the anhydrous grains also react, but the large amount of calcite precipitated on the surface stabilised further reaction and dissolution of anhydrous cement. The reason for the higher leachability of DB 111 in the TWT is not clearly understood and a microscopical observation of the degraded zone will clarify this.

4.3. Correlation between Running Water Test (RWT)/Tank Water Test (TWT)

In dense concretes completely submerged and with no pressure gradient or movement of water, the reaction between water begins to occur at the surface. Then, the dissolution process may follow as a "moving boundary" [27] showing a concentration gradient. The thickness of the degraded zone may grow with the square root of time. If surface erosion takes place due to the movement of the water, the leaching rate will increase.

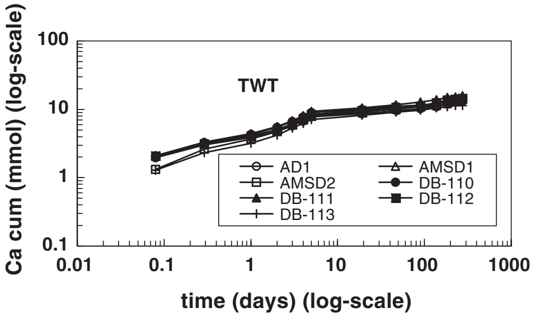

Fig. 11. Log–log fitting calcium from TWT for all concretes.

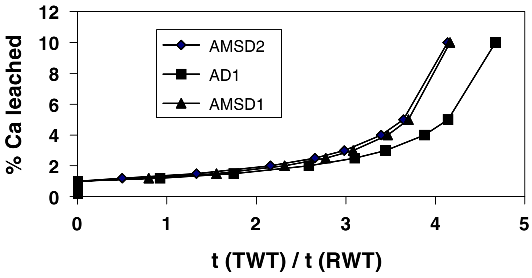

Fig. 12. Correlation between time to degradation from TWT and RWT with respect to % Ca leached for UHPC.

In Figs. 10 and 11, the amount of Ca leached versus time is represented in a log–log scale, for the two types of tests.

The fitted equation used is:

$$\text{Cumulative Ca}_{\text{leach}} = a \times \text{time}^b \tag{5}$$

When using the TWT (Fig. 11), the leaching process of calcium occurs in two stages, independently on the type of concrete used, HPC or UHPC. In all cases slopes, $b = 0.2$, were determined in the first stages of leaching, although slightly higher for HPC. In the second stage of leaching the slopes decrease to values of $b = 0.1$. The r^2 of these fitting were always above 0.94.

If the RWT is used (Fig. 10), one or two slopes of the leaching process are identified depending on the type of concrete tested. The slopes calculated in this case are always higher than those of TWT, indicative of higher aggressiveness for the running water method. For UHPC concretes, one slope was the best fitting for the whole process. The b values are in the order of 1, with an $r^2 > 0.97$. For HPC two slopes are the best fitting of the leaching process. The first stage shows slopes of $b \cong 1$, with $r^2 > 0.97$. The second stage shows slopes of $b > 1$, with $r^2 > 0.98$.

The main conclusion to point out from data fitting is again that the leaching process is very much dependent on

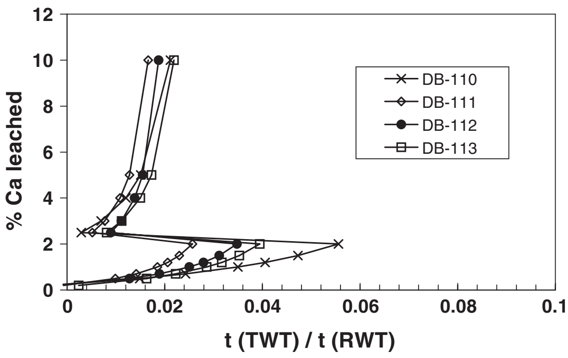

Fig. 13. Correlation between time to degradation from TWT and RWT with respect to % Ca leached for HPC.

Table 4
Values of D_{nsCa} (cm^2/s) and L_{iCa} of the seven concretes obtained from ANSI test

Concrete	D_{nsCa} (cm^2/s) 190 h data	D_{nsCa} (cm^2/s) 90 d data	L_{iCa} 190 h data	L_{iCa} 90 data
DB-110	6.318 E − 11	4.436 E − 11	10.266426	11.171462
DB-111	7.209 E − 11	5.074 E − 11	10.202037	10.762423
DB-112	3.931 E − 11	2.768 E − 11	10.473085	11.02463
DB-113	2.652 E − 11	1.868 E − 11	10.737405	11.358799
AD1	2.863 E − 11	2.01 E − 11	10.662082	11.499518
AMSD1	4.227 E − 11	2.964 E − 11	10.463705	11.204302
AMSD2	2.585 E − 11	1.817 E − 11	10.737762	11.335005

the leaching test and on the type of concrete, and a pure diffusion control is not yet reached in present experimental conditions, as with both methods the law of the square root of time (slope 0.5) is not fulfilled. This result is in agreement with [2].

As commented before, both leaching methods have given different conclusions concerning the classification of long-term water resistance of concretes with respect to the leaching of calcium. The acceleration of degradation is also different. This effect has been pointed out in Figs. 12 and 13 where the percentage (%) of calcium leached is represented versus leaching time in TWT/leaching time in RWT ratio. For UHPC it may be seen that for short ages of leaching, TWT is more accelerated, but at longer ages RWT results are more accelerated.

4.4. Effective diffusivity and leachability index calculated through ANSI test for all the concretes tested

The criteria followed in the ANSI standard [17] to qualify the leachability of species is that, if the leachable species is less than 20% leached from a uniform and regularly shaped solid, its leaching behaviour is diffusion controlled and approximates to that of a semi-infinite medium. Under these conditions the mass-transport equation may be used and permits the calculation of so-called "effective diffusivity of calcium, D_{nsCa}" using Eqs. (1) and (2). The calculation of the leachability Index, L_{iCa}, is possible using the Eq. (3). Both expressions are specific to the amount of calcium leached from the concretes in the test conditions of the present work.

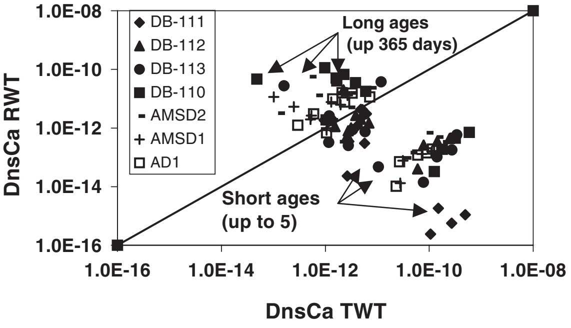

Fig. 15. Comparison of D_{nsCa} for all concretes from TWT/RWT.

The expressions employed for these calculations do not specify the proportion of leachable material of each concrete exposed to leaching, e.g., the cement paste plus anhydrous cement, which is higher for UHPC than HPC. The aggregates may be considered stable and impermeable to water, but the interfacial zone is more permeable and may increases diffusivity and leachability. The proportion and the size of the aggregate influence the interfacial transition zone. The values for D_{nsCa} obtained are referred to the overall concrete under study, but for the same family (HPC and UHPC) the content and size of aggregates are similar (Tables 1 and 2). In fact although UHPC contains 1275–1314 kg/m^3 aggregate and HPC 1721–1837 kg/m^3, D_{nsCa} HPC > D_{nsCa} UHPC, which indicates the capability of the test to differentiate between different type of concretes.

Table 4 shows the values of effective diffusion coefficient, D_{nsCa}, and leachability index, L_{iCa}, of HPC and UHPC calculated for two intervals, 120 h and 90 days in the TWT. As can be seen in Fig. 14 and Table 4 the highest leachability corresponds to DB110 and DB 111 concretes and the lowest to AMSD2.

Fig. 14 shows a comparison of the non-steady diffusion coefficients (D_{nsCa}) for the different concretes after an interval of 120 h of leaching and after 90 days. In all cases these coefficients are higher in the first interval. D_{nsCa} was higher than expected for DB111 with results even higher than the reference concrete, DB 110. Although the test has been repeated for this concrete the leaching of Ca is higher than that of DB 112 and DB 113. UHPC always shows lower D_{nsCa} than HPC using TWT.

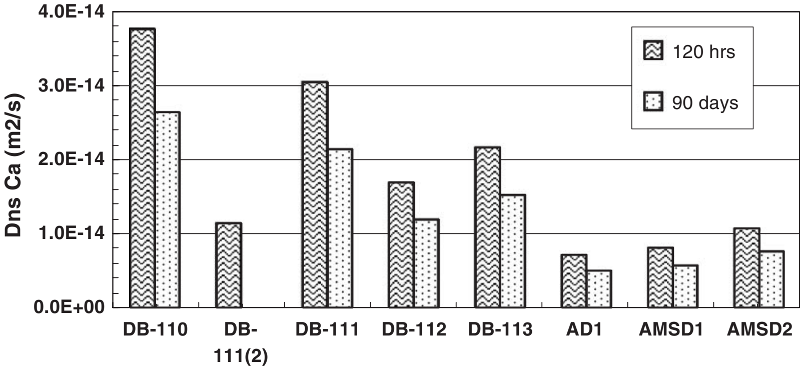

Fig. 14. Non-stationary diffusion coefficient, D_{nsCa}, following ANSI test, of calcium for all the concretes leached in TWT.

D_{nsCa} has also been calculated for the leaching of calcium with RWT. The volume of water considered in this case is that the renewal of water is made every 18 h (which is the time needed to fill the device at the flow of 7 ml/h). The results obtained are compared with those from the TWT and plotted in Fig. 15. Comparisons of D_{nsCa} from both testing methods indicate that TWT is more accelerated at the beginning, but after some time, both methods roughly agree.

This indicates again that the testing conditions are crucial and that obviously control the results of any leaching test. That is, the performance and classification of concretes differ depending on the type of test selected. Without a proper classification of exposure conditions, any testing regime or modelling will lack reliability, and complete correlation will not exist between laboratory and natural exposure conditions.

Attention has to be paid to the rigorous definition of leaching scenarios attending to the leaching regime and to the rate determining parameters of leachability. It is still not possible to select a type of test for the classification of concrete resistance against water aggression. An absolute assessment with long-term predictive purposes is still not available, but long leaching of RWT test are under way for up to 5 years in order to model the leaching process and confirm the predictions from earlier ages.

5. Conclusions

The following conclusions may be drawn up from present results:a) With respect to the type of leaching method:

1. The use of natural water (GW) as leaching agent needs to take into account the amount of Ca and bicarbonates introduced in the water and the subsequent amount of the calcite precipitated.
2. The leachability of concretes with respect to water aggression depends significantly on the convection and contact regime.
3. Tank Water Test (TWT) was more aggressive in the first stages of contact but the Running Water Test (RWT) leached more calcium in the long-term (18 months in present test).
4. The classification of concrete resistance to leaching depends on the type of test used.
5. Leaching mechanism may be altered due to the convection regime of the water in the test.b) With respect to the type of concrete:

1. The determination of the amount of calcium leached is a good indicator to follow the progression of the attack.
2. Reference concrete leaches more calcium than HPC and UHPC, for the same age of leaching, due to the calcium removed from portlandite dissolution.
3. HPC resulted in more resistance to leaching of calcium than UHPC in a Running Water Test. But, UHPC resists water aggression better than HPC in a Tank Water Test.
4. One part of the calcium leached is precipitated in the form of calcite. This precipitation may contribute to a self-healing and to slowing down the leaching process.

Acknowledgements

The authors are grateful to the EC and to the partners involved in UNICORN project, BE97-4452, for the helpful discussions and are especially grateful to Bouygues and Cement Nordic for the preparation of concretes and to C. Vernet for developing the leaching test and design contribution.

References

[1] S.A. Stronach, F.P. Glasser, Modelling the impact of abundant geochemical components on phase stability and solubility of $CaO–SiO_2–H_2O$ system at 25 °C: Na^+, K^+, $SO_4^=$, Cl^- and $CO_3^=$, Adv. Cem. Res. 9 (6) (1997) 167–181.
[2] M. Andac, F.P. Glasser, Long-term leaching mechanism of Portland cement-stabilized municipal solid waste fly ash in carbonated water, Cem. Concr. Res. 129 (8) (1999) 179–186.
[3] P. Lovera, P. le Bescop, F. Adenot, G. Li, Y. Tanaka, E. Owaki, Physico-chemical transformations of sulphated compounds during the leaching of highly sulphated cement wastes, Cem. Concr. Res. 27 (10) (1997) 1523–1532.
[4] P. Faucon, F. Adenot, J.F. Jaquinot, C. Petit, R. Cabrillac, M. Jorda, Long-term behaviour of cement pastes used for nuclear waste disposal: review of physico-chemical mechanisms of water degradation, Cem. Concr. Res. 28 (6) (1998) 847–857.
[5] S. Goñi, M.S. Hernandez, A. Guerrero, M.P. Lorenzo, Effect of temperature on the leaching performance of a simulated cement based immobilisation system. Calcium and hydroxil behaviour, Constr. Build. Mater. 10 (3) (1996) 171–177.
[6] B. Gerard, G. Pijaudier-Cabot, C. Le Ballego, Calcium leaching of cement based materials: a chemo-mechanics application. Construction materials theory and application. Hans-Wolf Reinhart. Zum 60 Geburtstag. Ed. H von R. Eligehausen, ibiden-Verlag Stutgart (1999) 313–329.
[7] H.F.W. Taylor, Cement Chemistry. Chap 9, Concr. Chem. (1997) 380–383.
[8] A. Hidalgo, C. Andrade, C. Alonso, An accelerated leaching test to evaluate the long term behaviour of concrete in waste disposal, 5th CANMET/ACI Inter. Conf. on Durability of Concrete, June 2000, pp. 373–381, Barcelona.
[9] B. Gerard, Hydrolysis of cement-based materials: a review, 3th Int Bolomey Workshop. Pore solution in hardened cement paste, Aedificatio Pub., 2000, pp. 271–304.
[10] P. Faucon, F. Adenot, M. Jordá, R. Cabrilac, Behaviour of crystallised phases of Portland cement upon water attack, Mat. Struct. 30 (8) (1997) 480–485.
[11] S. Chatterji, Concrete durability and CaO/SiO_2 mole ratio of CSH, Cem. Concr. Res. 25 (5) (1995) 929–932.
[12] R.J. Van Eijk, H.J.H. Brouwers, Study of the relation between hydrated Portland cement composition and leaching resistance, Cem. Concr. Res. 28 (6) (1998) 815–828.
[13] H.F. Taylor, Nanostructure of C–S–H: Current status, Adv. Cem. Based Mater. (1993) 38–46.
[14] F. Adenot, P. Faucon, Modellisation du comportement a long terme des betons utilises dans le stockage des dechets radioactfs, Int. RILEM Conf., Arles, 1996, pp. 277–288.
[15] F. Adenot. Durabilite du beton: Characterisation et modelisation des processus physiques et chimiques de degradation du cement. Doctoral Thesis, Univ. D'Orleans (1992).
[16] B. Lagerblad, Texture and chemistry of historic concrete subjected to prolonged hydration. Workshop on water in cement paste and concrete hydration and pore structure, Nordic Concrete Federation, Skagen, 1999, pp. 148–154.
[17] ANSI/ANS-16, Measurement of the leachability of solidified low level radioactive wastes by short-term test procedure (1986).
[18] NEN 7341, Determination of the availability for leaching from granular to monolithic construction materials and waste materials (1994).

[19] H.A. Van der Sloot, Comparison of the characteristic leaching behaviour of cements using standard (EN 196-1) cement mortar and an assessment of their long-term environmental behaviour in construction during service life and recycling, Cem. Concr. Res. 30 (2000) 1079–1096.

[20] B. Gerard. Contribution of the mechanical, chemical and transport coupling in the long-term behaviour of radioactive waste repository structures. Doctoral Thesis, Univ. Laval (1996).

[21] P. Faucon, B. Gerar, J.F. Jacquinot, J. Marchand, Water attack of a cement paste. Towards an improved accelerated test? Adv. Cem. Res. 10 (2) (1998) 67–73.

[22] V. Matte. Durabilite des betons ultrahautes performance: role de la matrice cementaire. Doctoral thesis, Ecole Sup. of Cachan (1999).

[23] Imre Biczok, Corrosion and Protection of Concrete, translation J. Dócon Asensi, Ed Urmo, Chap. 4 (1968) 198–318.

[24] C. Vernet, C. Alonso, C. Andrade, M. Castellote, I. Llorente, A. Hidalgo, A new leaching test based in running water system to evaluate long-term resistance of concretes, Adv. Cem. Res. 14 (4) (October 2002) 157–168.

[25] G. Sergi. Corrosion of steel in concrete: cement matrix variables. Ph D Thesis. Aston University (1986).

[26] E. Zamorani, F. Lanza, G. Serrini, H. Blanchard, Water leachability of cement forms for medium-level waste immobilization, Nucl. Chem. Waste Manag. 6 (1986) 197–202.

[27] J. Crank, The mathematics of diffusion, Ed. Oxford Univ. (1975).