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Modelling of radionuclide release from a concrete container

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Abstract This study presents numerical simulations of radionuclides (RN) release from a concrete container performed with a chemo-transport model, which describes simultaneously radionuclides (RN) migration in concrete and concrete leaching. The mathematical description of leaching is based on the generalized transport equation of calcium in concrete. The equation is solved numerically using the CAST3M code. 2D simulations of concrete leaching with the possibility to account for the influence of cracking have been performed. A second transport equation has also been implemented in the CAST3M code to determine the extent of radionuclide diffusion in (partially) leached concrete. The radioactive decay and the retention of the RN in concrete are taken into account. Results show that leaching is particularly important for RN having long decay periods. The crack depth appears to be the most important geometric parameter (compared to the crack opening and the crack width) with respect to RN diffusion.

Keywords Concrete · Radionuclide · Release · Leaching · Cracking · Modelling

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Nomenclature

Φ	Porosity ($m^3\,m^{-3}$)
ρ_s	Solid phase mass volume-density ($kg\,m^{-3}$)
C_{ca}	Calcium concentration in the pore solution ($mol\,m^{-3}$)
S_{ca}	Calcium concentration in the solid phase ($mol\,m^{-3}$)
C_{RN}	Radionuclide concentration in the pore solution ($mol\,m^{-3}$)
K_d	Radionuclide distribution coefficient ($m^3\,kg^{-1}$)
D_{ca}	Effective diffusion coefficient of calcium ($m^2\,s^{-1}$)
D_{RN}	Effective diffusion coefficient of radionuclide ($m^2\,s^{-1}$)
D_{HTO}	Effective diffusion coefficient of tritium ($m^2\,s^{-1}$)
t	Time (s)
T	Radionuclide half-life (year)
λ	Radionuclide decay constant (s^{-1})

1 Introduction

In the intermediate-level radioactive waste disposal concepts, it is generally considered that concrete structures (e.g., radioactive waste containers, disposal engineering barriers,...) will be in contact with aqueous solutions over extended periods of time (Harris et al. 1998). It is well known that concrete leaching by pure water or ionic solutions has a significant impact on its microstructural properties (Adenot 1992, Adenot and Buil 1992, Carde et al. 1996, Carde and François 1997, Planel 2002, Bary and Le Bescop 2004), mainly because of the dissolution by water of the calcium hydroxide (portlandite), the aluminate phases (monosulfoaluminate and ettringite) and the C–S–H (Calcium Silicate Hydrates) of the cement paste. Consequently, the initial confinement and mechanical properties of concrete may change considerably (Tognazzi 1998, Carde et al. 1996, Carde and François 1997, Bernard et al. 2003, Heukamp et al. 2003). Since the time scales considered in radioactive waste disposal systems (several thousands of years), many studies have been devoted to the modelling of concrete behaviour when leached by aqueous solutions. This has led to the development of coupled chemo-diffusion models aiming at describing at the macroscopic scale (i.e. at the scale of the material) the dissolution–diffusion processes at hand in leached concrete (Peycelon et al. 2001, Galle et al. 2002, Kamali 2003, Bary and Le Bescop 2004, Maltais et al. 2004).

On the other hand, the focus point of many studies concerned with the safety of radioactive waste disposals has been the evaluation of radionuclide (RN) migration. For example, the transport of radionuclides (RN) by diffusion and advection through the various components of a repository structure (concrete vault, sand, soil, groundwater) has been presented by Nair and Krishnamoorthy (1996). The self-sealing of a confining concrete by calcite precipitation due to the interaction with a groundwater rich in carbonates has been examined by Pfingsten (2002) using diffusion-dominated and advection–dispersion–diffusion scenarii. The RN migration and the alkaline perturbation of the near field environment due to hydrated cement leaching (alkaline plume) have been evaluated by De Windt et al. (2004) for a multi-barrier repository (clay barrier, concrete, stiff clay as host rock). In the study of De Windt et al. (2004), a special attention has been paid to the impact of the excavation-damaged zone (EDZ) by considering first pure diffusion and second advection. To the authors knowledge, the potential evolution of concrete properties due to leaching and cracking, and its impact on RN migration has however never been considered in safety analyses of radioactive waste disposals.

In this paper, simulations of RN release from a (cracked) concrete container are thus performed with a chemo-transport model aiming at describing simultaneously concrete leaching and RN diffusion in concrete. First, the equations of the model and the material parameters are presented. Results from calculations performed with various RN are then detailed.

2 Transport equations and material parameters

2.1 Transport equations

The model is devoted to the simulation of RN migration in (partially) leached concrete. The mathematical description of concrete leaching has already been presented elsewhere in details (Adenot and Aspart 1998, Mainguy et al. 2000). Leaching of hydrated cement is due to concentration gradients between the interstitial solution and the leachant. These gradients generate diffusion of dissolved chemical species through the material. The chemical equilibriums of the system are thus modified. These chemical modifications are in turn at the origin of the portlandite and the aluminate phases (monosulfoaluminate and ettringite) dissolution and of the progressive decalcification of the Calcium Silicate Hydrates (C–S–H) present in concrete.

It has been shown that the hypothesis of local chemical equilibrium was valid for cement leaching and that the diffusive transport was the limiting phenomenon regarding the overall kinetics of leaching (Adenot and Buil 1992). Coupled chemo-transport models that combine local chemical equilibriums and transport equations for the most relevant leached chemical species of the system (K^+, Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, OH^-, $Al(OH)_4^-$) are thus appropriate to solve this problem (Adenot and Buil 1992, Maltais et al. 2004).

In order to perform 2D leaching calculations with variable boundary conditions, the generalized transport equation of calcium has been implemented in the code CAST3M as follows:

$$\frac{\partial(\Phi C_{\mathrm{ca}})}{\partial t} = \mathrm{div}[D_{\mathrm{Ca}}\mathrm{grad}(C_{\mathrm{ca}})] - \frac{\partial S_{\mathrm{ca}}}{\partial t} \tag{1}$$

In Eq. 1, C_{ca}, S_{ca}, Φ, D_{Ca} and t are the calcium concentration in the pore solution, the calcium concentration in the main solid phases (portlandite and C–S–H), the porosity, the effective diffusion coefficient of calcium and the time, respectively. As shown in many references (Berner 1988, Adenot 1992, Höglund 2001, Nonat et al. 2001, Harris et al. 2002, Albert 2002, Kamali 2003), the dissolution of the main solid phases constituting hydrated cements (portlandite, aluminate phases and C–S–H) can be computed simply as a function of the calcium concentration in the pore solution, C_{ca}: for decreasing calcium concentration in the pore solution (starting from chemical equilibrium), first the portlandite is dissolved, second, the aluminate phases and then the C–S–H are decalcified. This point will be detailed in Sect. 2.2. Moreover, as the calcium is mainly present in the portlandite and the C–S–H, a single curve linking the calcium concentration in the pore solution to these main solid phases can be used to describe the chemical aspect of cement leaching (Mainguy et al. 2000), i.e., $S_{\mathrm{Ca}}(C_{\mathrm{Ca}})$. As minerals progressively dissolve, the porosity increases inducing in turn a growth in the effective diffusion coefficient. In the model, the porosity and the effective diffusion coefficient vary therefore with the calcium concentration in the pore solution (i.e., $\Phi(C_{\mathrm{Ca}})$ and $D_{\mathrm{Ca}}(C_{\mathrm{Ca}})$) in order to account for the modifications of the physical properties of concrete due to leaching.

This simplified description of concrete leaching does not take into account the presence of dissolved alkalis (Na^+, K^+) in the pore solution of hydrated cements (the concentration of alkalis in the solid phases is equal to zero). Dissolved alkalis can contribute to increase the pH of the pore solution. The calcium concentration in the pore solution corresponding to a given chemical equilibrium with the solid phases can therefore diminish. In consequence, the calcium concentration gradient between the pore solution and the leachant is lowered and the leach rate of the main solid phases reduced. Using Eq. 1 to describe concrete leaching leads therefore to conservative estimates of calcium leach rates. The total amount of alkalis per unit volume of a standard concrete is in the range of 10–50 $\mathrm{mol\,m^{-3}}$ (Longuet et al. 1973, Taylor 1997), small compared to that of calcium which varies between 10^3 $\mathrm{mol\,m^{-3}}$ and 10^4 $\mathrm{mol\,m^{-3}}$ (see for example Mainguy et al. 2000 and Sect. 2.2). Moreover, the alkali concentration in the pore solution is not limited by the solubility of the solid phases. Consequently, the leaching of alkalis from the material is fast compared to that of calcium, as will be shown in more details in Sect. 4.

For an intermediate-level radioactive waste disposal containing a significant amount of concrete (containers, engineering barriers, ...), the source term for radionuclide migration in the host rock will be determined not only by diffusion in the cementitious materials but also by a combination of solubility and sorption constraints in these materials (Wieland and Van Loon 2003). In this paper, as illustrated in Fig. 1, the purpose is to estimate the RN release from a cracked concrete container submitted to leaching. RN is supposed to be embedded in a cementitious matrix cast within the concrete container. Because of the cement alkalinity, RN will precipitate in the matrix (Wieland and Van Loon 2003). The concentration of dissolved RN in the cementitous matrix pore water (typically 10^{-7}–10^{-5} $\mathrm{mol\,m^{-3}}$) will thus be limited by their solubility with respect to the solubility-limiting phases (Wieland and Van Loon 2003). Consequently, the boundary condition at the inner surface of the concrete container, i.e., the RN concentration in the concrete pore water, will be determined by solubility phenomena. It can thus be considered that RN retention in the concrete container will be limited to sorption (no precipitation) since the RN concentration in the concrete pore water will remain below the limit at which RN would precipitate. RN migration in the concrete container is thus described in terms of diffusion and sorption only, according to the following equation:

$$\frac{\partial\left[(\Phi+(1-\Phi)\rho_{\mathrm{s}}K_{\mathrm{d}})\,C_{\mathrm{RN}}\right]}{\partial t}=\mathrm{div}\left[D_{\mathrm{RN}}\mathrm{grad}(C_{\mathrm{RN}})\right]-\lambda\,(\Phi+(1-\Phi)\rho_{\mathrm{s}}K_{\mathrm{d}})\,C_{\mathrm{RN}} \tag{2}$$

in which C_{RN}, Φ, D_{RN}, ρ_{s}, K_{d}, λ and t are, respectively the RN concentration in the pore solution, the porosity, the effective diffusion coefficient of RN, the solid phase mass volume-density, the radionuclide distribution coefficient and decay constant, and the time.

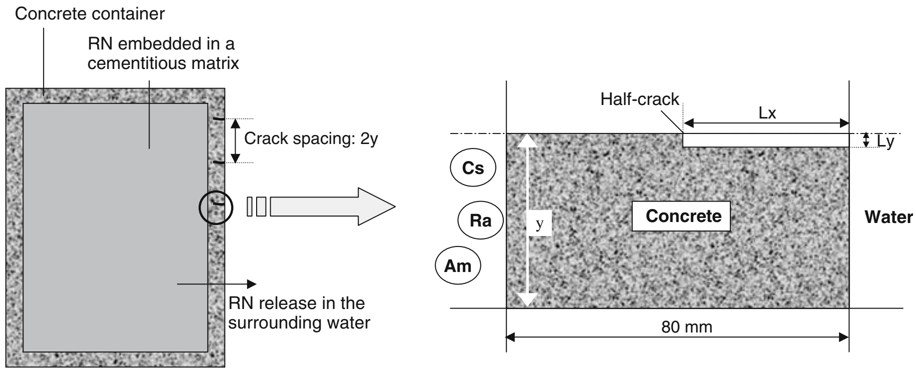

Fig. 1 Sketch of the studied configuration

In Eq. 2, sorption is described by making use of the distribution coefficient (K_d). It is recalled that the use of the K_d formulation in Eq. 2 is based on the assumption that RN sorption in the cement matrix is instantaneous, reversible and linear.

To account simultaneously for leaching of concrete and RN migration in concrete, Eqs. 1 and 2 are solved at each time step, successively, using the same mesh representing the concrete container. Changes of the physical properties of concrete (porosity and effective diffusion coefficient variations) are first taken into account when solving the leaching problem, i.e., $D_{Ca}(C_{Ca})$ and $\Phi(C_{Ca})$. An implicit numerical scheme is used to solve Eq. 1 where the material properties are estimated at the end of the time step (t_{n+1}). Non-linear terms are solved using a fixed point method. This leads to the calcium concentration, diffusion coefficients and porosity profiles at time t_{n+1}. These profiles are then used to solve the RN transport equation. Since it is the porosities and RN diffusion coefficients determined at the end of the time step, which are used in Eq. 2, a conservative estimation of the impact of leaching on RN release through the concrete container is obtained.

The mixed-hybrid finite element method available in the CAST3M code (Dabbene 1998) is used for solving the problem. The advantage of this method is that it ensures simultaneously the mass conservation and the fluxes continuity. This method is particularly well suited for the resolution of hydro-geological problems where flow properties such as permeability can vary over several orders of magnitude (Chavent and Roberts 1991). However, in the simulations presented in this paper where the diffusion coefficients vary by 3 orders of magnitude, a finite element method could have been used instead.

2.2 Material parameters

The concrete of interest in this study is cast with a French CEM V cement (Blast Furnace Slag—Pulverized Fly Ash cement). It has an 0.4 Water to Cement ratio (w/c) and 70% in volume of aggregates. CEM V based materials are often used in France for radioactive waste storage facilities and containers, because of their good resistance to external attacks (leaching, carbonation,. . .).

The chemical equilibrium curve of the studied CEM V concrete, i.e., $S_{Ca} = f(C_{Ca})$, is presented in Fig. 2. It gives the relation between the calcium concentration in the main solid phases of the concrete (C–S–H and portlandite), S_{ca}, and the calcium

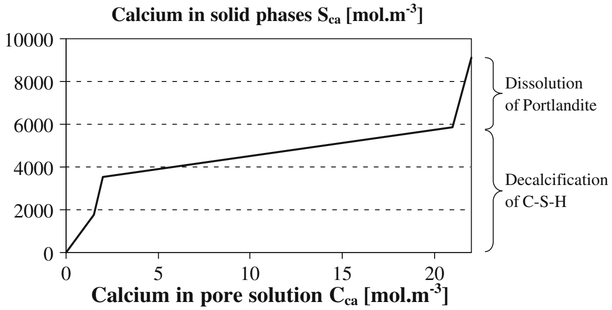

Fig. 2 Equilibrium curve between the calcium concentration in the main solid phases of the studied CEM V concrete and the calcium concentration in the pore solution

Table 1 Material parameters used in the simulations for the CEM V concrete

	Unleached CEM V concrete ($21 < C_{Ca} < 22\,\mathrm{mol\,m^{-3}}$)	Leached CEM V concrete ($C_{Ca} < 21\,\mathrm{mol\,m^{-3}}$)
D_{ca}, D_{RN} ($\mathrm{m^2\,s^{-1}}$)	9×10^{-14}	9×10^{-13}
Φ ($\mathrm{m^3\,m^{-3}}$)	0.078	0.12

concentration in the pore solution, C_{ca}. The curve is based on the experimentally well-established chemical equilibriums for cementitious materials (Berner 1988, Höglund 2001, Nonat et al. 2001, Harris et al. 2002, Chen et al. 2004): the portlandite is dissolved when C_{ca} decreases from 22 to 21 $\mathrm{mol\,m^{-3}}$ and the C–S–H are progressively decalcified when C_{ca} decreases from 21 to 0 $\mathrm{mol\,m^{-3}}$. In Fig. 2, the calcium concentrations in the main solid phases are determined from the mineralogical composition of the studied concrete.

As shown by experimental results on CEM I (ordinary Portland) cement pastes and concretes (Tognazzi 1998, Mainguy et al. 2000), the porosity and the effective diffusion coefficient of cementitious materials evolve continuously during leaching. Since very few experimental data are available for leached CEM V cement pastes or concretes, only the initial and final porosities and effective diffusion coefficients have been considered in the numerical simulations. The initial state refers to the state of the material before leaching. The final state corresponds to the state where there is no more portlandite in the material ($C_{Ca} < 21\,\mathrm{mol\,m^{-3}}$, see Fig. 2). Porosities and effective diffusion coefficients used in the simulations for the CEM V concrete are given in Table 1.

Porosities have been determined analytically from the mineralogical composition of the CEM V concrete, before and after being leached. As proposed by Adenot (1992) and Mainguy et al. (2000), the progressive dissolution of ettringite and monosulphoaluminate occurring during the decalcification of C–S–H has been taken into account to determine the porosity of the leached material. The step-like evolution of the porosity Φ with the calcium concentration in the pore solution C_{Ca} is illustrated in the left graph of Fig. 3.

The concrete diffusion coefficients used in the simulations (D_{Ca} or D_{RN}) are based on HTO diffusion measurements performed on a non-leached CEM V cement paste with an 0.4 w/c ratio (Lovera 1999) and on an 0.4 w/c CEM V concrete leached by a

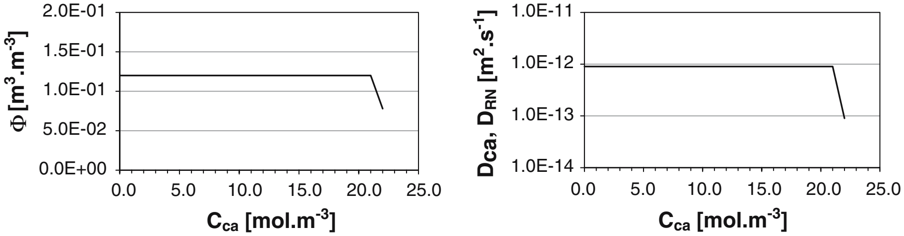

Fig. 3 Evolution in the model of the porosity (left) and of the Ca and RN effective diffusion coefficient (right) of the CEMV concrete in function of the calcium concentration in the pore solution

solution of ammonium nitrate until there is no more portlandite in the material, i.e., $C_{\mathrm{Ca}} < 21\,\mathrm{mol\,m^{-3}}$ (Lamotte and Le Cocguen 2002). Leaching of cementitious materials by ammonium nitrate solutions is widely used because the chemical degradation is faster than with pure water (Carde et al. 1997, Tognazzi 1998, Heukamp et al. 2003). For example, readers can refer to Galle et al. (2004) to obtain a detailed description of the experimental procedure applied to perform accelerated leaching tests on cement pastes using ammonium nitrate solutions.

The HTO diffusion experiments have been performed on fine discs of sound (non-leached) and leached materials by using diffusion cells, according to the widely used through diffusion technique (Tits et al. 2003a, Richet 1992, Tognazzi 1998). The apparatus used for these measurements is described in details in the following references (Richet 1992, Tognazzi 1998). The diffusion coefficient measured on the non-leached CEM V cement paste has been transposed to the CEM V concrete by applying a simple dilution law assuming that the aggregates (70% in volume) do not contribute to transport in concrete. As mentioned before, since only the initial and final (no portlandite remains, i.e., $C_{\mathrm{Ca}} < 21\,\mathrm{mol\,m^{-3}}$) states of the material are considered in the numerical simulations, the evolution of the diffusion coefficient (of calcium or of the RN) with the calcium concentration in the pore solution C_{Ca} can be represented by the step-like curve of Fig. 3 (right). Note that the diffusion coefficient for leached concrete has been obtained on a specimen in which some solid phases remain (since only the portlandite is completely leached, $0 < C_{\mathrm{Ca}} < 21\,\mathrm{mol\,m^{-3}}$ and $0 < S_{\mathrm{Ca}} < 6{,}000\,\mathrm{mol\,m^{-3}}$, see Fig. 2). The specimen is therefore not completely leached (i.e., $C_{\mathrm{Ca}} \neq 0$, $S_{\mathrm{Ca}} \neq 0$). Complete leaching can hardly be reached in practise. It is possible that further leaching of the specimen would have generated additional variations of porosity and hence would have lead to a higher diffusion coefficient.

Obviously, it was decided in this study not to use distinct diffusion coefficients for calcium and RN. To the author's knowledge, the effective diffusion coefficients of calcium and of the studied RN have never been measured in sound and/or leached CEM V cement pastes or concretes. To model CEM I cement paste leaching and hence calcium diffusion, Mainguy et al. (2000) used an effective diffusion coefficient—porosity evolution law obtained from experimental measurements of tritium (HTO) diffusivity performed on sound cement pastes with porosities varying between 0.2 and 0.6. Leaching rates were correctly described by this approach. For all these reasons, it was therefore chosen here, in a first approximation, to attribute HTO effective diffusion coefficients to both calcium and RN (i.e., $D_{\mathrm{Ca}} = D_{\mathrm{RN}} = D_{\mathrm{HTO}}$ given in Table 1).

In the next section, release calculations are presented for four RN: ^{137}Cs, ^{241}Am, ^{226}Ra and ^{243}Am. The distribution coefficients for these elements have been determined from measurements performed on a CEM V cement paste (w/c = 0.38) leached up to different states (Landesman et al. 2001).

In these experiments, samples made of 10 g of cement paste powder have been leached to different levels by carrying out repeated washings in calcium hydroxide solutions with a calcium concentration varying between 2 and 22 mol m^{-3}. After each washing, the cement powder has been separated from the solution by centrifugation (at 15,000 revolutions per minute) and the CaO/SiO$_2$ ratio of the sample measured by chemical analyses. 12–13 successive washings were necessary to reach the expected chemical equilibrium (corresponding to a stabilization of the CaO/SiO$_2$ ratio).

The samples were then placed in solutions with appropriate RN concentrations, ranging from 10^{-6} to 6×10^{-5} mol m^{-3}. For each RN, the concentration used in the tests was always lower than its solubility in cementitious materials, as proposed by Wieland and Van Loon (2003). For each sample, the quantity of retained RN has been deduced from measurements of the solution activity before and after its immersion. The estimation of the distribution coefficient for each leach state is based on measures performed with a single RN concentration in the solution. The distribution coefficients are furthermore calculated on the approximation that RN sorption in cement paste is linear and reversible, as it was shown for example for uranium in CEM I cement paste (Pointeau et al. 2004). It must however be said that the linearity and reversibility of cesium, radium and americium sorption in CEM V paste are not established. Very few data are available for radium. Concerning americium, a study showed that europium (a trivalent RN as americium) sorption onto C–S–H (the main phase up-taking trivalent RN in cementitious materials) is linear (Tits et al. 2003b). However, solid analyses suggest that these species are incorporated within the CSH structure, rather than on their surface. This means that there is a low probability concerning the reversibility of americium sorption. To the authors knowledge, sorption linearity for cesium has never been demonstrated. Moreover, its sorption in CEM I pastes seems to be only partially reversible (Rudin et al. 2005).

RN distribution coefficients are presented in Table 2 in function of the leaching level of the CEM V cement paste (i.e., the CaO/SiO$_2$ ratio or the C_{Ca} concentration). No uncertainties are given for the radium distribution coefficients since the duration of immersion for this sample (about 4 days) was smaller than the duration needed to establish a constant activity ratio between the radium and its decay products (about 17 days). The activity of the solution measured after the immersion of the sample was thus modified by the presence of soluble decay products of radium. These components do probably not have the same distribution coefficients as radium because of their different chemical states and oxidation degrees. Consequently, the values mentioned for radium in Table 2 correspond to orders of magnitude and not to precise values.

It can be seen from Table 2 that the distribution coefficients usually increase with the degradation state of the samples (i.e., with lower CaO/SiO$_2$ ratios or C_{Ca} concentrations). In the model, the RN distribution coefficient (K_{d}) does not evolve with the calcium concentration in the pore solution (C_{Ca}). To perform conservative calculations, the smallest value of Table 2 minored from the uncertainty (when available) has been chosen for each RN. Moreover, K_{d} values have been decreased by 20% to conservatively account for the possible differences in composition and density between the CEM V cement paste used in the sorption experiments (w/c = 0.38) and that entering in the mix-design of the concrete considered in the simulations (w/c = 0.40). The

Table 2 Distribution coefficients of the studied RN for a 0.38 w/c CEMV cement paste leached to various levels

C_{ca} (mol m^{-3})	Ca/Si ratio of the sample	Cs	K_d (m^3 kg^{-1}) Ra	Am
22.5	1.7	$3.9 \pm 0.3 \times 10^{-3}$	1.66×10^{-1}	7.0 ± 1.0
19.6	1.6	$6.0 \pm 0.3 \times 10^{-3}$	1.38×10^{-1}	6.8 ± 0.7
16.6	1.5	$14.9 \pm 0.3 \times 10^{-3}$	2.02×10^{-1}	5.5 ± 0.6
13.7	1.4	$7.4 \pm 0.3 \times 10^{-3}$	3.11×10^{-1}	9.0 ± 1.0
7.9	1.2	$9.2 \pm 0.3 \times 10^{-3}$	3.95×10^{-1}	13 ± 2.0
4.9	1.1	$8.5 \pm 0.3 \times 10^{-3}$	5.24×10^{-1}	10 ± 2.0

Table 3 Characteristics of the studied radionuclides and sorption capacity of the CEM V concrete

Radionuclide	Period (year)	λ (s^{-1})	K_d (m^3 kg^{-1})
^{137}Cs	30	7.32×10^{-10}	7.9×10^{-4}
^{241}Am	432	5.08×10^{-11}	1.1
^{226}Ra	1600	1.37×10^{-11}	3.0×10^{-2}
^{243}Am	7400	2.97×10^{-12}	1.1

RN half-life and decay constants, and distribution coefficients used in the simulations of RN transport in the CEM V concrete are given in Table 3. The distribution coefficients of Table 3 have been extrapolated from that of cement paste (see Table 2) assuming that, in concrete, aggregates do not contribute to the overall porosity and to the retention properties of the material. More precisely, the transposition takes into account the aggregate volume fraction of the concrete and the differences in porosities and solid phases mass volume-densities between the two materials. As it can be seen from Table 3, the RN selected for calculations allowed us to study the impact of large variations of RN half-life and level of retention on the RN release.

3 Studied configurations

The purpose of this work is to estimate the release of RN from a cracked concrete container submitted to leaching. The reference configuration used in this study is presented in Fig. 1. The thickness of the container is equal to 80 mm. The depth of the crack and its half-opening are equal to L_x and L_y, respectively. As the studied system is symmetric, only half of the distance between two cracks (2y) is considered to generate the CAST3M mesh. The impact of crack density on RN release is studied hereafter by varying these parameters. An example of the mesh used for release calculations is given in Fig. 6, detailed latter in Sect. 5.

Boundary conditions are applied as follows (see Fig. 4): zero calcium and RN concentrations on the external surface of the concrete element (including the crack outlet), decreasing RN concentration due to radioactive decay and zero calcium flux on the internal surface of the concrete element. Note that the calcium concentration in the crack (lips and tip) is not set to zero during calculations. Diffusion of calcium and RN in the crack is assumed to be similar to that of HTO in water, i.e., with $D_{ca} = D_{RN} = 2.2 \times 10^{-9}$ m^2 s^{-1} (Richet 1992). The initial conditions consist of a zero

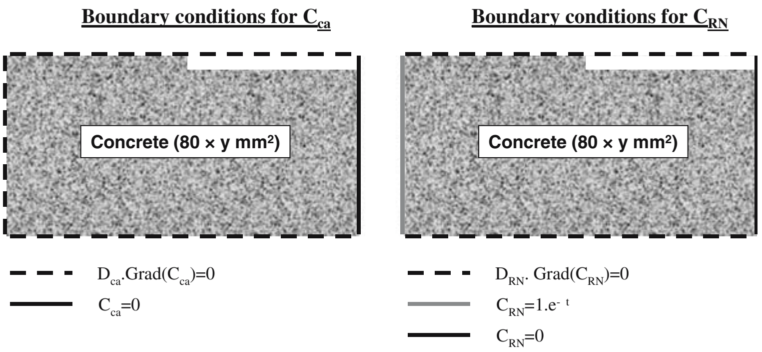

Fig. 4 Boundary conditions used in the calculations of C_{ca} (left) and C_{RN} (right)

Table 4 Studied configurations for the radionuclide release calculations

Configuration	Retention	Leaching	Cracking
1	No	No	No
2	Yes	No	No
3	Yes	Yes	No
4	Yes	No	Yes
5	Yes	Yes	Yes

RN concentration in concrete and in the crack, a 22 mol m^{-3} calcium concentration in the pore solution of the concrete and a zero calcium concentration in the crack.

For the calculations of RN transport, an arbitrary unit value is attributed to the initial RN concentration on the internal surface of the concrete element. This choice was made to compare more easily the release of different RN. In the next sections, the quantities of RN released from the CEM V concrete (moles of released RN per m^2 of concrete) are normalized with respect to the initial RN concentration on the internal surface of the concrete element (moles of RN per m^3 of solution). Since the linearity of the K_{d} approach used to account for sorption, these normalized quantities can in theory be extrapolated to any initial RN concentration by a simple rule of three. Quantitative estimates of the RN fluxes based on realistic RN concentrations (10^{-6}–10^{-5} mol m^{-3}, see Sect. 2.1) can therefore be easily obtained from the normalized released quantities given in the next sections. Transport calculations for each RN are performed on a period of time equal to 10 times the radioactive half-life of the RN.

To study the impact of the different phenomena (retention, leaching and cracking) on the RN release, the different configurations listed in Table 4 are studied. In the first three configurations (1, 2 and 3), no cracks are considered in the CAST3M mesh. The complexity of the RN diffusion problem is progressively increased: configuration 1 refers to pure RN diffusion with no retention in non-leached concrete, configuration 2 to RN diffusion with retention in non-leached concrete, configuration 3 to RN diffusion with retention in leached concrete. In the last two configurations (4 and 5), the impact of cracking is studied. In these two configurations, retention is always considered in the simulations while leaching is only taken into account in configuration 5.

4 Impact of retention and leaching on radionuclide release

In this part, the impact of retention and leaching of concrete on the RN release is first studied. No cracks are considered in the concrete element ($L_x = L_y = 0$). To check the implementation of the RN transport equation in the CAST3M code, the calculations were first compared to analytical solutions of standard diffusion problems (Crank 1975).

Before studying RN release, it is shown hereafter, as stated in part 2.1., that the impact of alkalis on calcium leaching can be neglected, in a first approximation. The calculations presented in this section gives an estimated time of about 5,000 years to obtain a portlandite-free concrete thickness of 80 mm. In comparison, the time scale of alkalis leaching from a similar concrete element can be estimated at 115 years (calculation performed with initial and final pore concentrations in alkalis, respectively equal to 500 mol m^{-3} and 1 mol m^{-3} and with the diffusion coefficient of unleached CEM V concrete, see Table 1). Chemical speciation calculations performed with the CHESS code (Van der Lee and De Windt 2000) showed that an alkali concentration of 1 mol m^{-3} had no more impact on the chemical equilibrium between the calcium in solution and that in the solid phases of concrete. The leaching of alkalis is fast compared to that of calcium and, thus, alkali leaching will have a negligible impact on calcium leaching.

Figure 5 presents the evolution versus time of the normalized quantities of ^{137}Cs, ^{226}Ra and ^{243}Am released in the configurations 1 (reference case), 2 (retention) and 3 (retention and leaching). In the case of ^{241}Am (not represented in Fig. 5), the high level of retention and the medium life-time of the RN induce that no release ($< 10^{-30}$ m) is observed during the 4,320 years of the calculation, whatever the configuration (with or without leaching and retention).

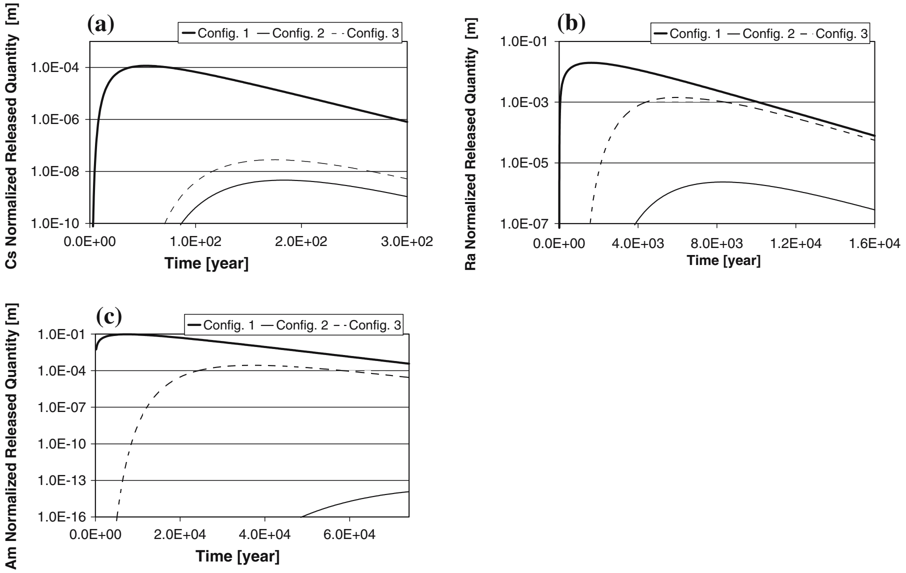

Fig. 5 Impact of radionuclide retention and concrete leaching on the normalized released quantities of the following radionuclides: (**a**) ^{137}Cs, (**b**) ^{226}Ra and (**c**) ^{243}Am. Config 1: RN diffusion; Config 2: RN diffusion and retention; Config 3: RN diffusion and retention, concrete leaching

As shown in Fig. 5a, the normalized released quantity of ^{137}Cs decreases considerably when retention is taken into account (compare, for example, the curves "config 1" and "config 2"), even if the retention capacity of the cement paste for this RN is small compared to the others. Leaching has a small impact, leading a normalized released quantity increased only by a factor 6 (compare the curves "config 2" and "config 3").

Comparing Fig. 5b and a indicates that the release of ^{226}Ra from unleached concrete (curve "config 2") is more important than that of ^{137}Cs, in spite of the higher ^{226}Ra retention capacity of the concrete (see Table 3). This result can be explained by the time scales considered for the two calculations: 300 years for ^{137}Cs and 16,000 years for ^{226}Ra. The potential reduction in ^{226}Ra release due to sorption is compensated by the important RN half-life. Leaching multiplies the normalized released quantity of ^{226}Ra by approximately a factor 600. For this RN, the impact of leaching is important. This can be explained by the fact that the duration of the simulations (16,000 years, i.e. 10 times the RN half-life) is greater than the duration needed to leach completely the 80 mm thick concrete element (4,867 years) (i.e., till there is no more portlandite in the material, $C_{ca} < 21\,\mathrm{mol\,m^{-3}}$). This significant increase in the normalized released quantity of ^{226}Ra is thus due to the increase of the RN effective diffusion coefficient associated to leaching.

For configuration 2, the maximum normalized released quantity of ^{243}Am is close to 10^{-14} m showing the important impact of retention (see Fig. 5c). For this RN, the impact of leaching is also predominant since it induces an increase in the normalized released quantity of approximately 10 orders of magnitude (compare the curves "config 3" and "config 2"). In comparison with ^{226}Ra, the results obtained for ^{243}Am indicate that the importance of leaching increases with the release duration and hence with the RN half-time, particularly when it is much greater than the time necessary to leach completely the 80 mm thick concrete element.

Note that non-conservative estimates of the normalized released quantities of ^{226}Ra and ^{243}Am may have been obtained from the simulations in which leaching and retention were taken into account (configuration 3). In fact, the simulations of leaching-RN transport performed for ^{226}Ra (16,000 years) and ^{243}Am (74,000 years) indicate that the final calcium concentrations in the pore solution of the concrete element (at the end of the calculations) are less than $2.1\,\mathrm{mol\,m^{-3}}$ and $0.7\,\mathrm{mol\,m^{-3}}$, respectively. In Sect. 2.2, it has been specified that the effective diffusion coefficient of leached concrete (see Table 1) has been estimated from diffusion tests performed on a specimen that was not completely leached, i.e., in which some solid phases remained, with the exception of portlandite ($0 < C_{Ca} < 21\,\mathrm{mol\,m^{-3}}$). In consequence, the diffusion coefficient used in the calculations might be too small for a concrete material leached to important levels such as those prevailing in the simulations performed for ^{226}Ra and ^{243}Am. This may therefore have led to an underestimation of the leached zone diffusivity and hence of the normalized released quantities. Further experimental acquisitions are necessary to confirm this point. One must keep this point in mind when interpreting the simulations performed for ^{226}Ra and ^{243}Am.

5 Impact of leaching and cracking on radionuclide release

Due to time consuming calculations, the simulations have been performed only for ^{137}Cs and ^{226}Ra. However, the results are sufficient to draw general conclusions on the

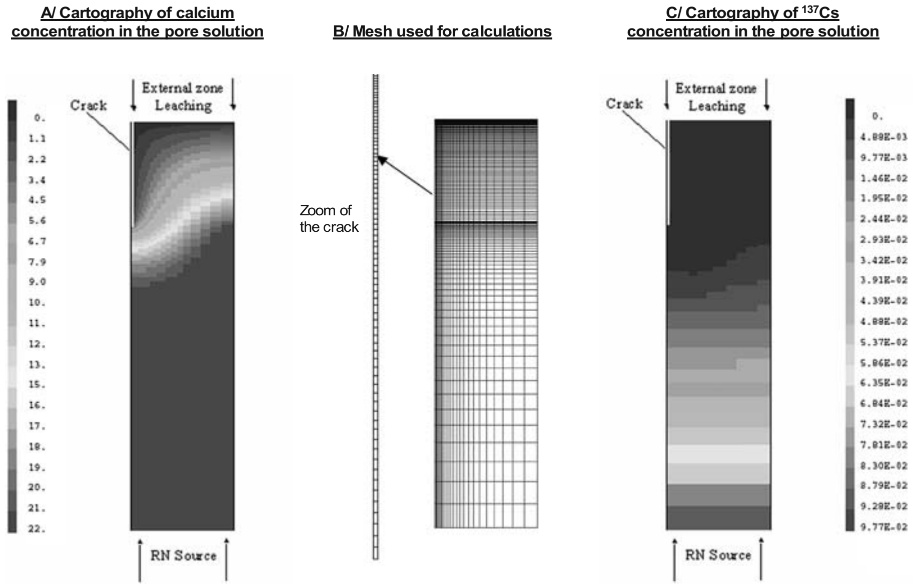

Fig. 6 Isovalues of the calcium concentration (mol m^{-3}) (**A**) and of the normalized ^{137}Cs concentration (**C**) in the pore solution after 300 years (configuration 5-40-20-350: leaching, crack spacing 40 mm, crack depth 20 mm and crack opening 350 μm) together with the mesh used in the simulations (**B**) (the crack is meshed using 80 elements of constant thickness (175 μm) and increasing lengths, from 100 μm at the top of the mesh to 480 μm at the bottom)

impact of leaching and cracking with respect to the release of RN from the concrete element.

In the simulations, RN retention, leaching and a skin microcracking of concrete are taken into account. Skin microcracking of concrete structures is due to thermal gradients originating from the exothermicity of cement hydration or moisture gradients, which occur during the service life of the structures. This type of cracking is characterized by small crack densities. According to Acker (1992), the maximum depth of skin microcracks and the distance between two skin microcracks (crack spacing) are, respectively equal to the quarter and to the half of the wall thickness. It results here in a crack spacing 2y equal to 40 mm and a crack depth L_x equal to 20 mm. For standard low level radioactive waste containers, a maximum crack opening $2L_y$ of 350 μm is allowed (Tognazzi 1998). To distinguish the different calculations performed on cracked containers, the following notation will be used: "configuration 5-40-20-350" means that the calculation includes retention, leaching and cracking (configuration 5, see Table 4) and that the crack parameters are, respectively equal to 40 mm (crack spacing), 20 mm (crack depth) and 350 μm (crack opening). Figure 6 presents isovalues of the calcium and of the ^{137}Cs concentrations in the pore solution obtained for this configuration after 300 years. The mesh used in the simulation is also given in Fig. 6. Due to its small opening (350 μm), the crack can hardly be seen in Fig. 6. Note however the refinement of the mesh in the neighbourhood of the crack. The impact of the crack on diffusion is better seen on the isovalues of calcium and ^{137}Cs concentrations.

A careful analysis of Fig. 6 shows that the progression of leaching within the material is smaller at the tip of the crack than from the external surface of the concrete element. This result is due to the fact that the Dirichlet boundary condition (zero calcium concentration) is only applied to the crack outlet in contact with the surrounding water. In consequence, the calcium concentration at the tip and at the lips of the crack is not equal to zero. The calcium release from the crack is therefore limited by the calcium diffusion rate in the crack. The calcium concentration gradient between the pore solution of concrete and the solution contained in the crack is furthermore small, leading smaller leaching rates. It was shown by Mainguy and Ulm (2001) that for small crack openings, the leach rates at the lips and the tip of the crack are reduced and evolve proportionally to the quadratic root of time, instead of the standard square root of time observed for leaching in the bulk of the concrete element.

The impact of the crack density on the RN release has been studied. Calculations have been performed with increasing cracking densities. Thus, in the studied configurations (configuration 4 accounts for RN retention and cracking, configuration 5 for RN retention, cracking and leaching) and in order to cover a large range of crack densities (consistent with normal and accidental conditions), crack parameters have been modified as follows:

- crack spacing between 4 mm and 40 mm,
- crack depth between 20 mm and 75 mm,
- crack opening between 350 μm and 1 mm.

Results are presented hereafter for the reference cracked scenario (crack spacing 40 mm, crack depth 20 mm and crack opening 350 μm) and for a critical scenario (crack spacing 4 mm, crack depth 75 mm and crack opening $1,000\,\mu$m), with (configuration 5) or without (configuration 4) accounting for leaching.

Figure 7 presents the ^{137}Cs release curves for these four calculations together with the previous results of configurations 2 (retention, no leaching and no crack) and 3 (retention and leaching, no crack). The smallest crack density without leaching leads to an increase of the normalized quantity of released ^{137}Cs by one order of magnitude (compare the curves “config 2” and “config 4-40-20-350” in Fig. 7), which is comparable to the impact of leaching alone (compare “config 3” and “config 2” in Fig. 7). Accounting simultaneously for the smallest crack density and leaching induces an increase by two orders of magnitude (compare the curves “config 5-40-20-350” and “config 2” in Fig. 7). When the crack density increases, the normalized quantity of released ^{137}Cs increases very significantly, leaching being taken into account or not (compare, for example, the curves “config 4-40-20-350” and “config 4-4-75-1000” of Fig. 7). The increase of the normalized quantity of released ^{137}Cs between the non-cracked configurations (“config 2” and “config 3” in Fig. 7, respectively) and the configurations with the greatest crack density (“config 4-4-75-1000” or “config 5-4-75-1000”) is of approximately six orders of magnitude. The impact of cracking is definitely more important than that of leaching alone. However, the effect of leaching cannot be neglected.

To determine which of the crack parameter has the greatest influence on the release of ^{137}Cs, a parameter study has been undertaken in which parameters have been changed one by one. This approach is possible because additional calculations have shown that there is no correlation between the three crack parameters when considering their impact on the ^{137}Cs release. The crack depth was clearly found to be the most important parameter with respect to the release of ^{137}Cs. Similar results were

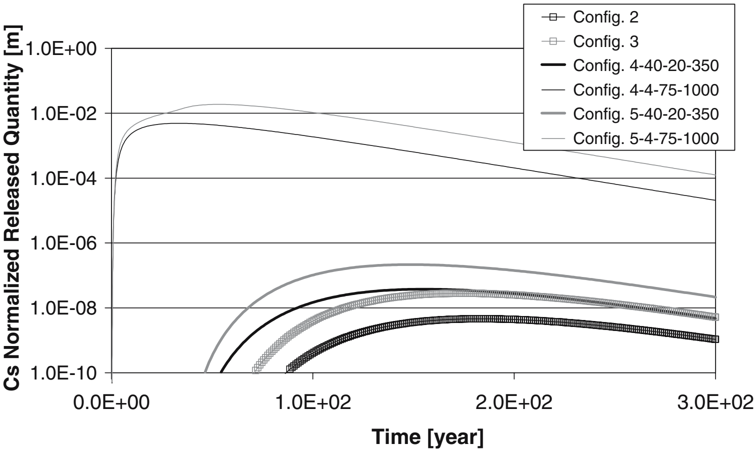

Fig. 7 Impact of concrete cracking and leaching on the normalized released quantities of ^{137}Cs

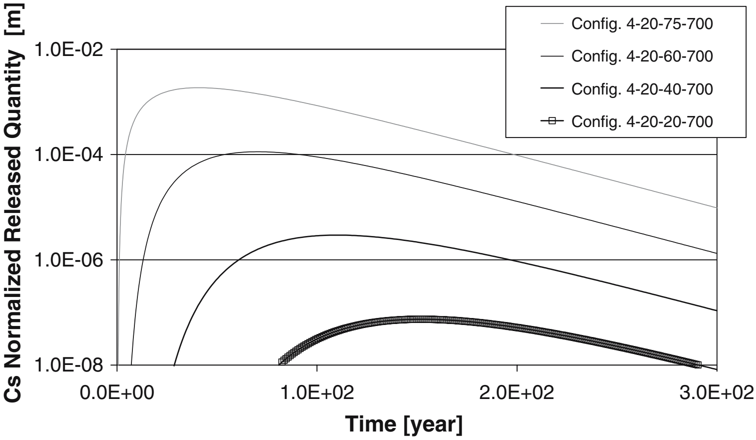

Fig. 8 Impact of the crack depth on the normalized quantities of ^{137}Cs released from the CEM V concrete. Crack spacing and opening are constant, equal to 20 mm and 700 μm, respectively. Crack depth is increased from 20 mm to 75 mm

obtained when accounting for leaching in the calculations. Other simulations have shown that the other crack parameters have only a small impact, even when leaching is considered. The impact of the crack depth on the quantity of ^{137}Cs released from the non-leached CEM V concrete element is illustrated in Fig. 8.

Figure 9 presents the ^{226}Ra release curves for increasing crack densities, with and without accounting for concrete leaching (configurations 4 and 5, respectively). Previous results obtained for configurations 2 and 3 are also included in Fig. 9. The normalized quantity of released ^{226}Ra increases very significantly when the crack density increases, even when concrete leaching is not considered in the calculations (compare the curves “config 4-40-20-350” and “config 4-4-75-100” for example). The effect of leaching alone on the RN release is more important in the case of ^{226}Ra (Fig. 9) than in the case of ^{137}Cs (Fig. 7). As explained before, this is due to the fact

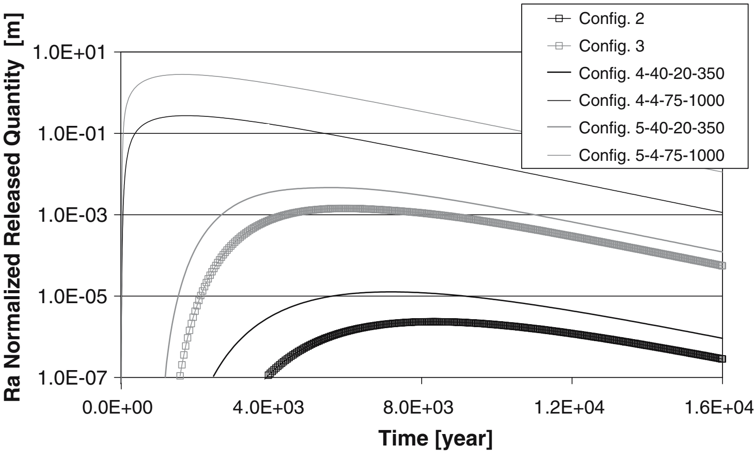

Fig. 9 Impact of concrete cracking and leaching on the normalized released quantities of ^{226}Ra

that the duration of ^{226}Ra release accounted in the simulations (related to its half-life) is greater than the one needed to leach completely the concrete thickness. Additional simulations showed that the impact of cracking on the normalized quantity of ^{226}Ra released is roughly similar to that of leaching alone (curve "config 3" in Fig. 9) for a crack depth of 40 mm (as stated before, the other parameters related to crack densities have a small influence on the RN release). Both lead to an increase by two orders of magnitude compared to the configuration accounting for retention only (curve "config 2" in Fig. 9). For higher crack densities, the impact of cracking becomes predominant when compared to that of leaching alone. However, the effect of leaching remains significant. It is reminded that ^{226}Ra release may be underestimated in the simulations because of a possible underestimation of the ^{226}Ra diffusion coefficient in the leached zone (see Sect. 4). As for ^{137}Cs, additional calculations have shown that the most important crack parameter for the ^{226}Ra release is the crack depth, even when leaching is taken into account in the calculations.

6 Conclusion

In this study, a model has been implemented to perform radionuclide (RN) release calculations at the scale of a cracked concrete container submitted to leaching by pure water. The release rates of four RN (^{137}Cs, ^{241}Am, ^{226}Ra and ^{243}Am) with very different distribution coefficients have been studied through numerous simulations. The calculations carried out have shown that the RN normalized released quantities are impacted by the RN retention in the concrete and its half-life. As expected, the normalized released quantities decrease with the RN retention augmentation and with decreasing duration of release accounted in the simulations in relation with the RN half-life. For a given RN, the couple (distribution coefficient K_d/radioactive decay constant λ) is thus predominant with regards to the normalized released quantity through the concrete container. Concrete leaching increases significantly the normalized quantity of RN released, particularly when the duration of RN release (related to its half-life) is large compared to the duration necessary to leach completely the concrete thickness. In this case, the increase of the effective diffusion coefficient of the concrete due to leaching is at the origin of the more important RN release. Calculations also highlighted the important impact of concrete cracking on the RN release when the crack density increases, even when leaching is not considered in the calculations. The most sensitive parameter concerning the impact of cracking on RN release is the crack depth.

Further work will consist in integrating other concrete-related degradation phenomena in the model, such as carbonation and sulphate attack (Bary and Le Bescop 2004, Bary and Sellier 2004), in order to perform RN release calculations in more realistic conditions. Carbonation of concrete may for example considerably decrease the RN release due to its impact on concrete porosity. In the future, advection and elevated temperature (up to 80°C) should also be taken into account.

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