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Effect of high saline alkaline conditions onto radionuclide transport in a CEM V/A hardened cement paste

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Introduction

In the French radioactive waste management context, some Intermediate-level long-lived (ILW-LL) waste contain high levels of soluble salts, mainly composed of $NaNO_3$ and Na_2SO_4. Under repository conditions and in contact with cementitious materials, the dissolution of these salts might induce changes in thermodynamic equilibria, mineralogical transformations and eventually, might have an effect on the migration (uptake and transport) properties of radionuclides (RN) or toxic elements (Tox). The current work is part of the CTEC laboratory group project managed by Andra, dedicated to the characterization of the behavior of RN or Tox in complex environments and particularly in high saline alkaline conditions.

This study is a cooperative work between CEA and Subatech, which main objective is the determination of transport parameters of RN/Tox, having different physicochemical properties such as tritiated water (HTO), Cs^+, Ni^{2+}, Cl^- and SeO_3^{2-}, for high saline (ionic strength from 0.2 to 4.3 $mol/kg_{solution}$) alkaline conditions ranging from an artificial cement pore-water (ACW) to ACW-salt mixtures with different salt compositions.

This work only focuses on HTO and Cs-137 results in ACW-salt mixtures with either $NaNO_3$ and/or Na_2SO_4.

Materials and methods

The experimental methodology is based on diffusion experiments using classical two-reservoir experimental set-ups. All hardened cement paste (HCP) samples were prepared at CEA from a CEM V/A (S-V) 42.5N CE PM-ES-CP1 NF "PMF3" (ROMBAS, Calcia) with a water/cement ratio of 0.4 and cured at least 6 months in ACW before starting diffusion experiments. ACW is a portlandite-based $(Ca(OH)_2)$ saturated solution in which Na^+ and K^+ were added at (79 ± 2) mmol/L and (291 ± 2) mmol/L respectively resulting to a pH value of (13.5 ± 0.1). Minor species such as Cl^- and SO_4^{2-} are also added at (0.57 ± 0.03) mmol/L and (0.96 ± 0.04) mmol/L, respectively. This solution was systematically filtered (Nylon, 0.45µm, Nalgene) before its use in diffusion experiments in order to remove the excess of portlandite. More details concerning the characterization of ACW are given in Savoye *et al.* (2018).

After the curing time, HCP samples were sliced into disks (*c.a.* 2 to 5 mm thick) and glued using an epoxy resin (Araldite, Hunstman Advanced materials) into a sample holder and placed in a diffusion cell between the two reservoirs. The upstream and downstream reservoirs were filled with *c.a.* 100 cm³ of ACW (reference experiment) and an appropriate amount of salt, either $NaNO_3$ or Na_2SO_4 as described in **Table 1**. The chemical equilibration step was achieved within at least 2 months before the addition of HTO ($\lambda = 1.784\ 10^{-9}\ s^{-1}$) and Cs-137 ($\lambda = 7.309\ 10^{-10}\ s^{-1}$) in the upstream reservoir.

HTO and Cs-137 diffusion experiments carried out at CEA

After 6 months of chemical equilibration, the upstream reservoir was replaced with a solution containing an appropriate ACW-salt mixture solution spiked with HTO. Then, a cesium-133 (non radioactive) solution was added to reach 1 mM of CsCl and spiked with Cs-137. All radioactive solutions came from diluted Orano-LEA stock solutions (see Table 1 for details). Regular samplings were performed and

measured by Liquid Scintillation Counting (LSC) technique in dual mode, especially developed for measuring H-3 and Cs-137 activities simultaneously. All 1-mL-samplings in the downstream reservoir were replaced by the same volume from a freshly prepared ACW with appropriate salt content and all 0.1-mL-samplings of the upstream compartment were replaced by the same volume of the initial prepared upstream solution (*i.e.* containing CsCl, HTO and Cs-137).

Concerning in-diffusion experiments, the Cs-137-profile was obtained using a classical multi-steps micro-abrasive procedure. Each HCP powder collected fraction was placed in a vial with an equivalent quantity of water and gelling agent to reach a fixed-geometry. Then, the Cs-137 activity is determined using a gamma-counter (Wizard, 1480, Perkin Elmer). Prior to the sample measurements, the counting efficiency was determined with well-known Cs-137 activity standards prepared in similar condition of geometry and using the same gelling agent.

The numerical tool I-Mode (Interpretation Model Of Diffusion Experiments), developed at CEA, is dedicated to data interpretation of one-dimensional diffusion experiments. This tool is based on a Laplace-transform analytic-element method used to solve the diffusion problem under the conditions of the diffusion cell experiments (Moridis (1999), Furman and Neuman (2003), Didierjean *et al.* (2004)). These include given fixed initial conditions, finite liquid volumes and temporally variable concentrations in the upstream and downstream reservoirs. Fully analytical solutions are obtained in the Laplace space, which are subsequently numerically inverted to provide the solution in time. These semi-analytical solutions have significant advantages over the more conventional approach based on the analytical solution of Crank (1975) because (a) they are not based on fixed boundary conditions (constant upstream and negligible downstream activities), and (b) can double the amount of data from which to extract the pertinent diffusion parameters (effective diffusion coefficient, D_e and material capacity factor, α). The diffusion model is based on Fick second law assuming equilibrium linear sorption, given in **Eq.1**:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} = \frac{D_e}{\alpha} \frac{\partial^2 C}{\partial x^2} = \frac{D_e}{\omega R} \frac{\partial^2 C}{\partial x^2} \qquad \textit{Eq. 1}$$

where C is the concentration or activity per volume unit in the solute phase (Bq.m^{-3}); t, the time (s); D_a, the apparent diffusion coefficient (m^2.s^{-1}); x, the distance in the porous material (m), D_e, the effective diffusion coefficient (m^2.s^{-1}); ω, the diffusion-accessible porosity (m^3.m^{-3}); α is the material capacity factor (-) and R the diffusion retardation factor.

Depending on the type of diffusion experiments (through- or in-diffusion), different boundary and initial conditions need to be considered. So either the semi-analytical I-Mode solution or the analytical one proposed by Crank (1975) can be applied. More details are available in Macé *et al.* (2018). Experimental results were analyzed by a least-square fitting of the model to the results of the normalized total activity in the downstream reservoir, the remaining activity in the upstream reservoirs and when necessary the diffusive profile in the solid.

Table 1: **Experimental conditions of current HTO and Cs-137 diffusion studies**

	Solution					HCP sample		
	NaNO$_3$ added to ACW [mol/kg$_{solution}$]	Na$_2$SO$_4$ added to ACW [mol/kg$_{solution}$]	Density at 21°C [g/cm^3]	A$_0$(HTO) [Bq/m^3]	A$_0$(^{137}Cs) [Bq/m^3]	S [m^2]	L [m]	Porosity [-]
CEA-ACW	-	-	1.015	4.9E+09	5.2E+09	2.0E-03	4.8E-03	0.33
SUB-ACW	-	-	1.004	1.6E+09	2.1E+09	1.8E-03	2.0E-03	0.34
CEA-MIX1	1.4		1.097	4.7E+09	5.4E+09	2.0E-03	5.2E-03	0.33
SUB-MIX1		0.3	1.055	1.9E+09	2.2E+09	1.8E-03	2.0E-03	0.35
CEA-MIX2	2.8		1.190	5.3E+09	3.1E+09	2.0E-03	4.8E-03	0.33
SUB-MIX2		1.0	1.147	1.5E+09	2.2E+09	1.8E-03	2.0E-03	0.37
CEA-MIX3	1.0	1.0	1.214	6.8+09	1.5E+09	2.0E-03	2.4E-03	0.33
SUB-MIX3	1.0	1.0	1.205	1.9E+09	-	1.8E-03	1.9E-03	0.34

HTO and Cs-137 diffusion experiments carried out at Subatech

A similar experimental protocol was applied to Subatech diffusion experiments for HTO and Cs-137 (with 1 mM CsCl) spikes in the upstream reservoir (A$_0$) and the measurement of samples by LSC technique. In order to maintain fixed boundary conditions (constant upstream reservoir activity and near-

zero downstream reservoir activity), i) the upstream reservoir solution was kept constant at A_0 by addition of activity once the remaining activity reaches 95% of A_0 and ii) the downstream reservoir solution was totally replaced once the cumulative activity reaches maximum 3% of A_0.

Effective diffusion coefficient (D_e) and material capacity factor (α) are determined by modeling the normalized total diffused activity results in the downstream reservoir with a least-square fitting based on Crank's analytical solution (Eq.2).

$$Q(t) = \frac{q(t)}{L * S * A_0} = D_e \frac{t}{L^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{\left(-\frac{D_e n^2 \pi^2 t}{\alpha L^2}\right)} \qquad Eq. \; 2$$

where Q(t) is the normalized total diffused activity, q(t) is the total activity in the downstream reservoir (Bq), A_0 the initial activity per volume unit in the upstream reservoir (Bq.m^{-3}); t, the time (s); D_e, the effective diffusion coefficient (m^2.s^{-1}) and α the material capacity factor (-).

Results and discussion

A benchmarking exercise between CEA and Subatech was performed on HTO diffusion experiments in the reference ACW system. By choosing a specific representation, Q(t)×L^2 *vs.* time, D_e values are easily determined from the slope of the linear part of the curve (**Eq.2**). For each set of experimental data, Subatech and CEA's diffusion models were applied in order to determine HTO diffusion parameters (D_e(HTO) and α) and by comparing data, to validate the consistency of both modeling approach. Results are shown in **Figure 1**.
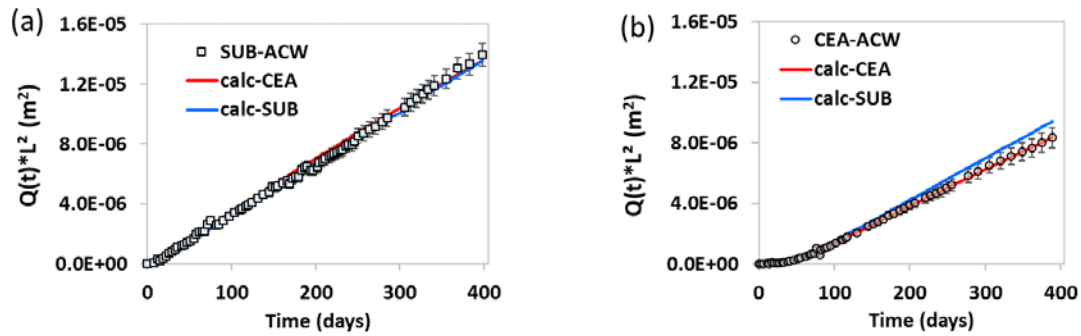
Figure 1: Comparison of HTO normalized total activity experimental data and modeling as a function of time (up to 400 days) in ACW. Experimental data from Subatech and CEA are plotted in Fig 1 (a and b) respectively. Solid lines represent Subatech (blue) and CEA (red) best fit modeling curves.

The benchmark exercise shows on one hand, that both modeling approaches describe Subatech experimental data with a good accuracy (**Fig. 1a**). The best-fit curves are well centered in the experimental uncertainty bar ranges and can be superimposed. Thus, HTO diffusion parameters values are very similar whatever the modeling approach used (**Table 2**).

On the other hand, for CEA experimental data (**Fig. 1b**), while both models give a good overall description, CEA approach using I-Mode is more accurate than just applying the analytical solution (Subatech approach). This result is not a surprise. In fact, as Crank's analytical solution is elaborated for constant boundary conditions and as only data from the downstream reservoir are used, this approach is not able to accurately take into account a significant decrease (> 10%) of the activity in the upstream reservoir. Diffusion parameters values (all systems) are reported in **Table 2**. Whatever the system, D_e(HTO) values ranges from 2 to 4 10^{-13} m^2.s^{-1} meaning that the effect of salt (and composition) is of little (if any) importance on HTO transport in HCP. Moreover, α factor values are similar to water porosity (**Table 1**), reflecting the absence of any significant retardation effect (R close to 1).

As an illustration of Cs-137 diffusion in ACW salt-mixture systems, **Figure 2** shows Cs-137 diffusive flux in Na$_2$SO$_4$ SUB-MIX1 system and its diffusion profile in HCP sample in NaNO$_3$ CEA-MIX1 system. Both interpretations for different diffusion time, lead to comparable diffusion parameters:

Table 2: **HTO diffusion parameters**

	$NaNO_3$ [mol/kg$_{solution}$]	Na_2SO_4 [mol/kg$_{solution}$]	Total diffusion time (days)	Model	Alpha [-]	D_e [m^2/s]
CEA-ACW	-	-	778	CEA	0.33	$3.00\ 10^{-13}$
				SUB	0.34	$3.19\ 10^{-13}$
SUB-ACW	-	-	530	CEA	0.35	$4.40\ 10^{-13}$
				SUB	0.33	$4.08\ 10^{-13}$
CEA-MIX1	1.4		673	CEA	0.43	$2.40\ 10^{-13}$
SUB-MIX1		0.3	530	SUB	0.35	$3.66\ 10^{-13}$
CEA-MIX2	2.8		688	CEA	0.45	$2.50\ 10^{-13}$
SUB-MIX2		1.0	530	SUB	0.37	$2.97\ 10^{-13}$
CEA-MIX-3	1.0	1.0	502	CEA	0.40	$1.80\ 10^{-13}$
SUB-MIX3	1.0	1.0	450	SUB	0.34	$2.99\ 10^{-13}$

{D_e(Cs-137) = $1.2\ 10^{-14}$ m^2/s; $\alpha = 0.55$} and {D_e(Cs-137) = $1.8\ 10^{-14}$ m^2/s; $\alpha = 0.35$} for CEA and Subatech best fit modeling, respectively. These data are very similar to that obtained in ACW, *i.e.* {D_e(Cs-137) = $1.9\ 10^{-14}$ m^2/s; $\alpha = 0.5$}, (Subatech data).

(a)

(b)
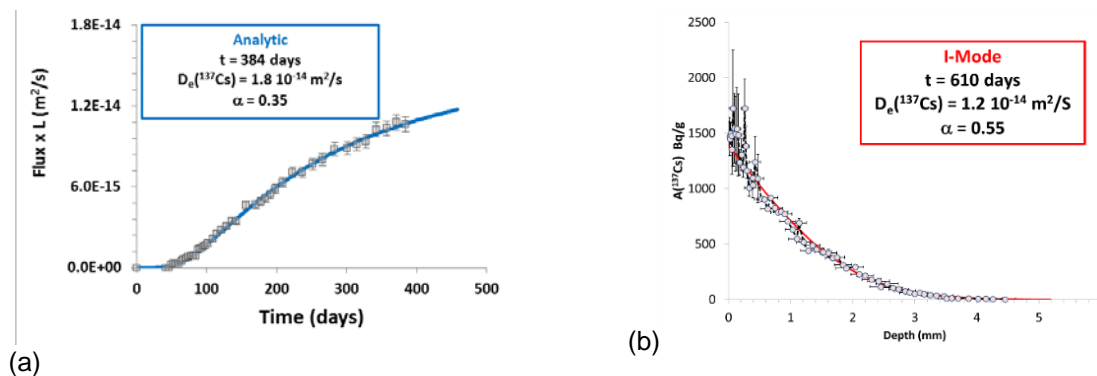
Figure 2: Cs-137 diffusive flux (*L) in the Na_2SO_4 SUB-MIX1 system (a) and Cs-137 diffusive profile in the $NaNO_3$ CEA-MIX1 system (b). **Solid lines represent Subatech (blue) and CEA (red) best fit modeling curves.**

Conclusion

For all of the experiments, HTO steady-state diffusive flux is reached after around 200 days. Considering measurements uncertainties, whatever the salt mixture and the modeling approach, the mean value of D_a(HTO) is $(8.6 \pm 2.7).10^{-13}$ m^2/s. Cs experiments are still on-going due to a very low diffusivity compared to that obtained for HTO. All experiments confirm that Cs migrates more slowly than HTO, then considered as conservative for cesium transfer. Finally, no significant effect of salt could have been evidenced on HTO and Cs diffusion parameters.

Acknowledgment

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