Radionuclide Transport through Cement Matrices

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Surface disposal is considered a suitable option for low and intermediate level (LIL) radioactive waste disposal containing mainly short lived radionuclides that decay up to insignificant radioactivity level in few decades or centuries. Cementitious materials are intensively used in disposal facility construction and also as waste immobilization matrix due to their ability to act as mechanical barriers and to prevent convective water flow. Also, these barriers will retard the transport (diffusion controlled) of dissolved radionuclides by a combination of mechanical constraints and chemical interaction with solid matrix. This paper presents the experimentally determined diffusion and distribution coefficients in Portland cement matrices for ^{3}H and ^{137}Cs, two of critical radionuclides from the LIL waste generated at Cernavoda Nuclear Power Plant.

Keywords: radioactive waste, disposal, diffusion, distribution, cesium, tritium

The low and intermediate level waste (L/ILW) generated from the Cernavoda Nuclear Power Plant operations and decommissioning will be disposed in a near surface facility on Saligny site. ^{137}Cs and tritium are two of the radionuclides present in high quantities in the L/ILW generated from Cernavoda NPP operation and decommissioning.

The matrix for waste conditioning will be cement, selected for its durability and long term retention of the radioactivity. Cementitious waste matrices exhibit diffusion controlled release for many radionuclides although, for some radionuclides, the release mechanism is solubility-limited. ^{137}Cs and tritium have high solubility limits and therefore their release from cement waste matrix will be diffusion controlled. Diffusion is an important mechanism for radionuclide transport but it is not a fast way for contaminant transfer into the porous media. While in the high permeability porous environments the dominant transport mechanism is advection and diffusion has a low contribution to the overall transport, for the low permeability media, where the advective transport component is negligible, diffusion is the dominant transport mechanism. Typical examples media where diffusion dominated transport occurs include low permeability clays and man-made structures such as concrete.

Experimental part

Experimental measurement of the tritium and cesium diffusion coefficients

Pore-water diffusion coefficient is required by the most of the computer codes used for simulations of the radionuclide migration to solve the transport equation. Experimentally, the apparent diffusion coefficient is determined and it is mathematically related to the pore-water diffusion coefficient by the means of retardation factor [1] that has also to be experimentally determined.

Tritium is predominantly present in the aqueous phase as dissolved gas or as tritiated water. In the dissolved gaseous form it will not sorb at all on cement, whereas tritium as tritiated water can undergo isotope exchange with bound protons, OH^- ions and water. The “sorption” resulting from isotope exchange will be dependent upon the ratio of “bound accessible” water to free water. Although a considerable quantity of water is “bound” during the cement hydration, only a small quantity of this water is accessible and usually, the sorption of tritium is neglected [2]. Consequently tritium pore-water diffusion coefficient is well approximated by the apparent diffusion coefficient experimentally determined.

Cesium is a sorbing cation which is released from the waste matrix as Cs^+ at any pH. To accurate estimate its pore-water diffusion coefficient both diffusion and sorption experiments have to be performed.

Diffusion cell experiments were performed in experimental diffusion cells consisting of two reservoirs of liquid separated by a cement wafer (fig. 1). The inlet reservoir was filled with a concentrated solution of tritiated

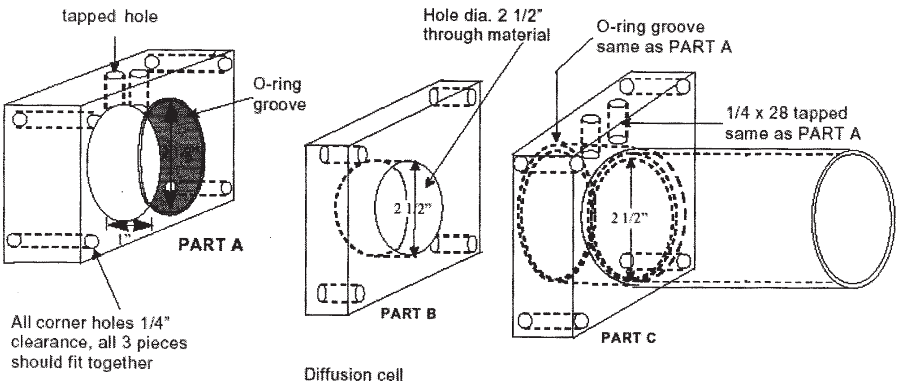

Fig. 1. Schematic of the diffusion cell assembly

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Table 1

CONCRETE SAMPLES COMPOSITION AND THEIR PHYSICAL CHARACTERISTICS

Sample ID	cement [%]	water [%]	Quart sand [%]	η [-]	ρ [kg/L]
S1	79.15	20.85	-	0.15	2.1
S2	42.55	14.89	42.55	0.21	1.8

water (1.3×10^9 Bq/m^3) and ^{137}Cs (2.5×10^8 Bq/m^3) in 10 mM NaCl. The outlet reservoir was filled with tracer-free solution of 10 mM NaCl and more solution was continuously flushed through the outlet reservoir at very slow flow rate. Usually, deionized water is used to dissolve the radionuclides but given that the cement based materials in contact with water increase its *p*H at around 13 to avoid the risk of cesium precipitation NaCl 10 mM was used to dissolve ^{137}Cs and the same solution was used to fill the outlet reservoir (C). The pressures between the two chambers were kept equal to minimize advective flow and ensuring that main mechanism for the contaminants movement from the inlet reservoir through the cement pellet into the outlet reservoir is diffusion only.

The concentration of contaminant is measured in the flow of tracer-free solution leaving the outlet reservoir and the change of concentration over time is used to estimate the tracer apparent diffusion coefficient in cement. ^{137}Cs concentration was measured using a CANBERRA gamma multi-channel spectrometer with a Ge(Li) detector while the tritium concentrations were measured using a 2100 Tri-Carb Packard model liquid scintillation analyzer.

Diffusion experiments were run on two types of concrete samples, one with quart sand as aggregate and the other one with no aggregate. The concrete samples composition and physical characteristics are presented in table 1. The concrete wafers were used in the experiments after 30 days from their preparation to allow developing its resistance structure. Experiments were run in saturated conditions.

Experimental determination of the distribution coefficients

The phenomena involved in radionuclide sorption are complex and hard to be separated. These processes include absorption, chemisorption, absorption, and ion exchange. From a practical view the important aspect is the removal of the tracer from solution, irrespective of the process and the term sorption is used to indicate the overall result of the various processes that lead to the partitioning of the contaminant between solid and liquid phase [3].

To calculate the retardation factor based on the distribution coefficient of the radionuclide on the solid and the structural properties of the solid (bulk density and porosity) [3], additional sorption/desorption experiments were performed on the two cement matrices (S1 and S2). In batch method is commonly used in many laboratories to assess the sorption properties of a contaminant on a solid matrix and it consists in contacting a certain volume of contaminant solution with a known mass of crushed material. In our experiments, a volume of 25 mL NaCl solution (10 mM) containing ^{137}Cs radionuclide was added to one gram of crushed cement in a 50-mL polycarbonate centrifuge tube, and the mixture was intermittently shaken for 24h at room temperature (21±3°C). After the sorption equilibrium was reached (24 h) the tubes were centrifuged at 4.000 rpm for 30 min and the supernatant was separated and measured for ^{137}Cs concentration. All the samples were run in duplicate and one control sample with only the Cs solution (cesium dissolved in 10 mM NaCl solution) was run in the same conditions in order to check the possible sorption on the surfaces of the test tubes. Also, a blank sample was run for each cement matrices to determine the ^{137}Cs background [4].

Desorption experiments were performed to determine if cesium is reversibly or irreversibly sorbed on cement matrices. Desorption is defined as ratio between the percentage of the contaminant which is desorbed to the quantity of contaminant previously adsorbed. Desorption experiments were performed after sorption experiments were finished and liquid was removed from the test tubes by centrifugation and decantation and liquid removed was replaced by NaCl solution [4]. Test tubes were intermittently shaken until desorption equilibrium was reached (48 h, twice the time needed to reach the sorption equilibrium). After desorption equilibration test tubes were centrifuged at 4,000 rpm for 30 min and a 10 mL aliquot of the supernatant was removed for cesium analysis.

Results and discussions

Sorption experiments

To evaluate the effects of contaminant concentration on the distribution coefficients (K_d), contaminant concentration is varied while other parameters are held as constant as possible resulting so called sorption isotherms. Four cesium concentrations were used (1.5E+05, 8E+04, 4E+04 and 1.7E+04 Bq/L) to estimate the cesium sorption isotherm at the room temperature (21±3°C). The soil/ solution ratio was kept constant for all experiments (1/10) and the contact time was 24 h. The contact time was chosen based on the kinetic experiments previously performed showing no significant changes in K_d values were between contact times of 12, 24 h, 7 days and 100 days [5].

The contaminant concentrations in solution, at equilibrium, were plotted versus the amount of contaminant sorbed on the solid and these data were fitted to different sorption models [3]. For both concrete samples, the best fits were obtained using linear sorption isotherms model indicating that equilibrium was attained and the cesium concentrations were low enough not to saturate all sorption sites presented in the cement samples.

The sorption isotherms obtained for the two concrete samples are presented in figure 2, while the distribution coefficients estimated from the slope of the sorption linear isotherms and retardation factor calculated using equation 1 are presented in table 2.

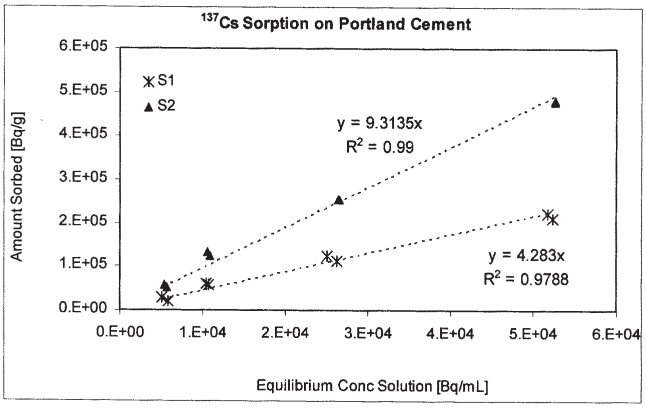

Fig. 2. Cesium sorption isotherm on S1 and S2 concrete matrices

Table 2

DISTRIBUTION COEFFICIENTS AND RETARDATION FACTORS FOR ^{137}CS AND PORE-WATER DIFFUSION COEFFICIENTS OBTAINED FOR TRITIUM AND CESIUM

Sample ID	K_d [L/kg]	R	D_p [m^2/s]	
			^{3}H	^{137}Cs
S1	4.8	60.92	$2.2\cdot10^{-11}$	-
S2	9.6	80.80	$4.2\cdot10^{-11}$	$1.8\cdot10^{-12}$

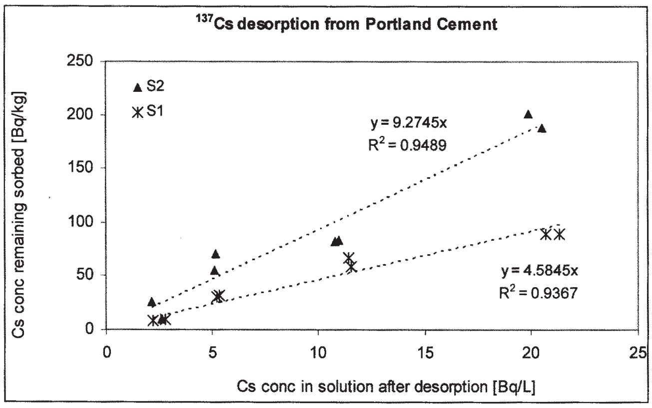

Fig. 3. Cesium desorption isotherm on S1 and S2 concrete matrices

$$R = 1 + \frac{K_d \cdot \rho}{\eta} \qquad (1)$$

where:

R is the retardate factor;

ρ - bulk density, [kg/m^3];

η - porosity, [m^3/m^3];

K_d - distribution coefficient, [m^3/kg].

Compared with distribution coefficients obtained for cesium on geologic formations characteristic to Saligny site [6], its distribution coefficients on cement matrices were low. This was expected since cation exchange is the main sorption mechanism for the monovalent cations in the most systems [7] and the cement has a low exchange capacity [8]. Potassium and sodium presented in the concrete pore water have a competitive effect on cesium sorption and consequently cesium sorption in this *p*H region is weak. For the sample with quartz sand as aggregate the k-$_d$ value is higher than for the concrete with no aggregate due to the additional exchange positions brought in the system by the aggregate. The values determined for cesium distribution ratio on concrete agree with values find in the literature [2].

Desorption experiments showed that almost 85% from the cesium previously sorbed on S1 matrix and around 80% for the S2 matrix was desorbed in 24 h showing that cesium sorption on the two cement matrices is reversible. The study of laser desorption mass spectrometry on cesium-doped Portland cement showed that cesium resides in the adsorbed water in the cement pores (the pore-water) and it was easily leached [9].

The apparent desorption coefficients estimated from desorption isotherms were very close to the distribution coefficients determined from the sorption isotherms indicating that cesium sorption on the Portland cement matrix is accurately described by the linear sorption model (at least for the cesium concentration range used in these experiments) and equilibrium was indeed attained.

Diffusion experiments

To estimate diffusion coefficients, it was assumed that the tracers moved according to one-dimensional diffusive transport through the concrete wafers:

$$\frac{\partial c}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2} = \frac{D_p}{R}\frac{\partial^2 c}{\partial x^2} \qquad (2)$$

where:

c is the tracer concentration, [Bq/m^3];

D_a - apparent diffusion coefficient, [m^2/s];

D_p - pore-water diffusion coefficient, [m^2/s];

R - retardation factor (1 for non-sorbing solutes);

x - distance, [m];

t - time, [s].

Although analytical solutions to this partial differential equation exist for simple boundary conditions [10], the time-dependent concentration boundary conditions at the inlet and outlet reservoirs in the diffusion cell experiments demand a numerical solution. Thus, equation (2) was solved using an implicit finite-difference technique. The equations describing the tracer concentrations in the inlet and the outlet reservoirs (the first and last finite difference nodes), respectively, are [11]:

$$\frac{\partial c_i}{\partial t} = \frac{\eta \pi r^2 D_p}{V_i}\left.\frac{\partial c}{\partial x}\right|_{x=0} \qquad (3)$$

$$\frac{\partial c_o}{\partial t} = -\frac{\eta \pi r^2 D_p}{V_o}\left.\frac{\partial c}{\partial x}\right|_{x=L} - \frac{Q}{V_o}c_o \qquad (4)$$

where:

c_i is the tracer concentration in the inlet reservoir, [Bq/m^3];

c_o - tracer concentration in the outlet reservoir, [Bq/m^3];

V_i - inlet reservoir volume, [m^3];

V_o - the outlet reservoir volume, [m^3];

Q - flush rate of the outlet reservoir, [m^3/s];

η - cement matrix porosity;

r -concrete wafer radius, [m];

L - concrete wafer thickness, [m].

The numerical solution of equations (2), (3), and (4) was obtained using DiffCell Software developed by Los Alamos National Laboratory [12].

For S1 sample only tritium was detected in the outlet reservoir and therefore the pore water diffusion coefficient was estimated only for this radionuclide. Figure 4 presents the experimental results and the fitted breakthrough curve used for tritium pore-water diffusion coefficient estimation. The fitted breakthrough curve was obtained using the DiffCell software by manually adjusting the diffusion coefficient till it matched the experimental curve.

The S2 sample has a more porous structure (with a porosity of around 21%) compared with S1 (with a porosity of 15%) and both radionuclides were measured in the liquid collected from the outlet reservoir of the diffusion cell containing S2 concrete wafer.

The experimental results and the fitted breakthrough curve used for cesium pore-water diffusion coefficient estimation on S2 concrete sample are presented in figure 5.

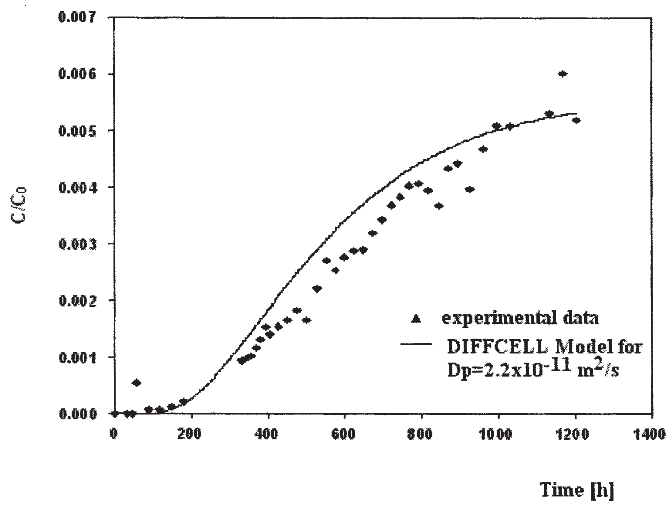

Fig. 4. Tritium experimental and fitted breakthrough curves in S1 concrete wafer

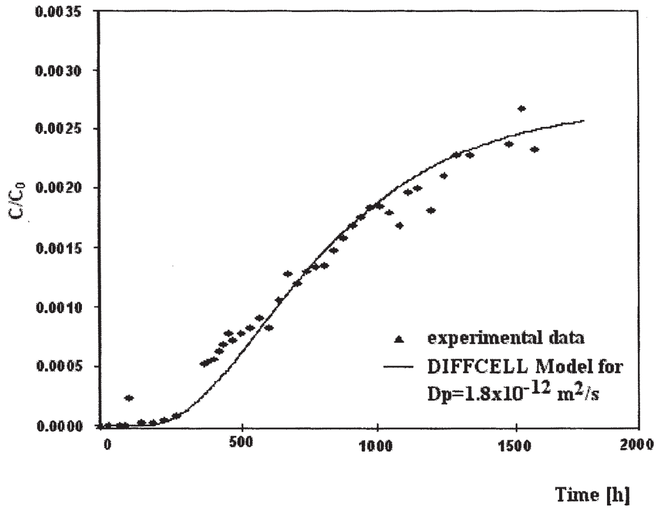

Fig. 5. Cesium experimental and fitted breakthrough curves in S2 concrete wafer

The values for pore-water diffusion coefficients obtained for tritium and cesium on the two concrete samples are presented in table 2.

Conclusions

The values determined for tritium diffusion coefficients through the two concrete slab samples (S1 and S2) were 2.2x10^{-11} m^2/s (for concrete sample with no aggregate) and 4.2x10^{-11} m^2/s (for concrete sample with quart sand as aggregate). The diffusion coefficients are usually well correlated with the matrix porosity, the lowest porosity sample exhibiting the lowest diffusion coefficients. Since tritium is a non-sorbing radionuclide, the small difference between pore-water diffusion coefficients experimentally obtained on two concrete wafers is explained by the higher porosity of the S2 sample.

The cement based materials provide low retention for ^{137}Cs, distribution coefficient obtained for the S2 cement matrix (with sand as aggregate) was a little bit higher than that obtained on the S1 cement matrix due to the additional exchange positions brought in the system by the aggregate.

Desorption experiments showed that cesium sorption on concrete matrices is reversible, usually sorption is considered reversible when desorption equilibrium is attained even within twice the time of the sorption equilibrium, and the total desorption is more than 75% of the amount sorbed [4].

Cesium pore-water diffusion coefficient obtained for S2 concrete sample (with quart sand as aggregate) was 1.8x10^{-12} m^2/s. It was expected that ^{137}Cs has smaller diffusion coefficients in concrete than tritium due to the larger size of the cesium cation and to the presence of the retardation component, as determined from the sorption experiments. Cesium apparent diffusion coefficient on S2 sample is 2.16x10^{-14} m^2/s.

Experimental values obtained for tritium and cesium pore-water diffusion coefficients on concrete agree with values fond in the literature. Values for pore-water diffusion coefficients identified in other studies [1] are 1.0x10^{-11} and 1.9x10^{-12} m^2/s for tritium and cesium pore-water diffusion coefficient, respectively.

The low values of the diffusion coefficients on concrete matrices indicate that the radionuclide release from the repository is extremely low in the first years when the concrete is intact.

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