

Diffusion of Radionuclides in Concrete and Soil

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1. Introduction

One of the methods being considered for safely disposing of low-level radioactive wastes (LLW) is to encase the waste in concrete. Such concrete encasement would contain and isolate the waste packages from the hydrologic environment and would act as an intrusion barrier. The current plan for waste isolation consists of stacking low-level waste packages on a trench floor, surrounding the stacks with reinforced steel, and encasing these packages in concrete. These concrete-encased waste stacks are expected to vary in size with maximum dimensions of 6.4 m long, 2.7 m wide, and 4 m high. The waste stacks are expected to have a surrounding minimum thickness of 15 cm of concrete encasement. These concrete-encased waste packages are expected to withstand environmental exposure (solar radiation, temperature variations, and precipitation) until an interim soil cover or permanent closure cover is installed, and to remain largely intact thereafter.

Any failure of concrete encasement may result in water intrusion and consequent mobilization of radionuclides from the waste packages. The mobilized radionuclides may escape from the encased concrete by mass flow and/or diffusion and move into the surrounding subsurface environment. Therefore, it is necessary to assess the performance of the concrete encasement structure and the ability of the surrounding soil to retard radionuclide migration. The retardation factors for radionuclides contained in the waste packages can be determined from measurements of diffusion coefficients for these contaminants through concrete and fill material. Some of the mobilization scenarios include 1) potential leaching of waste form before permanent closure cover is installed; 2) after the cover installation, long-term diffusion of radionuclides from concrete waste form into surrounding fill material; 3) diffusion of radionuclides from contaminated soils into adjoining concrete encasement and clean fill material. Additionally, the rate of diffusion of radionuclides may be affected by the formation of structural cracks in concrete, the carbonation of the buried waste form, and any potential effect of metallic iron (in the form of rebar) on the mobility of radionuclides.

The radionuclides iodine-129 (^{129}I), technetium-99 (^{99}Tc), and uranium-238 (^{238}U) are identified as long-term dose contributors in LLW (Mann et al. 2001; Wood et al. 1995). Because of their anionic nature in aqueous solutions, ^{129}I , ^{99}Tc , and carbonate-complexed

^{238}U may readily leach into the subsurface environment (Serne et al. 1989, 1992a, b, 1993, and 1995). The leachability and/or diffusion of radionuclide species must be measured to assess the long-term performance of waste grouts when contacted with vadose-zone pore water or groundwater.

Although significant research has been conducted on the design and performance of cementitious waste forms, the current protocol conducted to assess radionuclide stability within these waste forms has been limited to the Toxicity Characteristic Leaching Procedure, Method 1311 Federal Registry (Environmental Protection Agency [EPA] 1992) and ANSI/ANS-16.1 leach test (American National Standards Institute [ANSI] 1986). These tests evaluate the performance under water-saturated conditions and do not evaluate the performance of cementitious waste forms within the context of waste repositories which are located within water-deficient vadose zones. Moreover, these tests assess only the diffusion of radionuclides from concrete waste forms and neglect evaluating the mechanisms of retention, stability of the waste form, and formation of secondary phases during weathering, which may serve as long-term secondary hosts for immobilization of radionuclides.

The results of recent investigations conducted under arid and semi-arid conditions (Al-Khayat et al. 2002; Garrabrants et al. 2002, 2003, and 2004; Gervais et al. 2004; Sanchez et al. 2002, 2003) provide valuable information suggesting structural and chemical changes to concrete waste forms which may affect contaminant containment and waste form performance. However, continued research is necessitated by the need to understand the mechanism of contaminant release; the significance of contaminant release pathways; how waste form performance is affected by the full range of environmental conditions within the disposal facility; the process of waste form aging under conditions that are representative of processes occurring in response to changing environmental conditions within the disposal facility; the effect of waste form aging on chemical, physical, and radiological properties, and the associated impact on contaminant release. Recent reviews conducted by the National Academies of Science recognized the efficacy of cementitious materials for waste isolation, but further noted the significant shortcomings in our current understanding and testing protocol for evaluating the performance of various formulations. The objective of our study was to measure the diffusivity of Re, Tc and I in concrete containment and the surrounding vadose zone soil. Effects of carbonation, presence of metallic iron, and fracturing of concrete and the varying moisture contents in soil on the diffusivities of Tc and I were evaluated.

2. Concrete composition and fabrication of test specimens

The concrete composition for the burial encasement was indicated in Specification for Concrete Encasement for Contact-Handled LLW. This specification was used as the basis to prepare concrete for fabrication of test specimens. Details of concrete composition and test specimen fabrication has been described in a technical report (Wellman et al. 2006).

2.1 Specified concrete composition for encasement

The specified composition includes sulfate-resistant Portland Type I or Type II cement, a pozzolanic material (Class F fly ash), fine and coarse aggregates, and steel fiber. Additional specifications include a water-to-cement ratio of 0.4 and an air content $6.0 \pm 1.5\%$. The

nominal proportions and material specifications based on this initial design are listed in the material specifications for field mix column in Table 1.

A laboratory-scale concrete mixture (Table 1) was prepared based on specifications for Portland Type I and Type II cement. Because of the required small dimensions of laboratory test specimens, the size of the coarse aggregate and the dimensions of the steel fiber were proportionately reduced. This was accomplished by decreasing the 2-cm (~0.75 in.) coarse aggregate size in the original specification to a particle size ranging from 2.83 mm to 2 mm in the laboratory mix. The aggregate mixture passing a 7-mesh sieve and retained on a 10-mesh sieve met this particle size specification. The scaled-down steel fibers used in the laboratory mix consisted of Bekaert Dramix brand deformed steel wire fibers that were cut to a nominal length of 8 mm (0.31 in). The deformed end portions were retained for use in the concrete mixture and the straight middle section of the fiber was discarded. Based on these modifications, a concrete mix was prepared that consisted of Portland Cement (Type I & II, ASTM C-150 compliant), Class F fly ash, scaled-down coarse aggregate, fine aggregate, scaled-down deformed steel fiber, and a water-entraining agent (PolyHeed® 997). The water-entraining agent was included in the mix to facilitate the workability of the concrete. The volumes of the PolyHeed® 997 and the air-entraining agent, MB-AE™ 90, were not included in the normalization calculations because of their negligible contribution to the overall mix volume. The material specification and composition for the laboratory-scale concrete mixture is given in Table 1.

Material	Material Specifications for Field Mix	Normalized Laboratory Design	Material Specifications Used in Revised Laboratory Mix Comparison
Cement	Portland Type I or Type I/II sulfate-resistant cement	0.27	Portland Type I & II
Fly Ash	Class F fly ash; nominal 15% of cement by volume	0.04	Class F fly ash; nominal 20% of cement by volume
Coarse Aggregate	No. 676 or equivalent (3/4" nominal size)	0.04	Sieve size +7 to -10 (2.83 – 2 mm size)
Fine Aggregate	Sand	0.51	Sand -10 sieve size (< 2 mm)
Water	Nominal water-to-cement ratio: 0.4	0.10	Water-to-cement ratio: 0.5
Steel Fiber	Deformed Type I, nominal length 2.5 – 3.8 cm (1 – 1.5")	0.04	Deformed, nominal length 8 mm (0.32 in)
PolyHeed® 997	N/A	0.00375	Water-entraining agent
Air Content	6.0±1.5%	6.0±1.5%	N/A

Table 1. Laboratory-Scale Material Specification and Composition

2.1.1 Concrete mold design

The concrete molds for casting specimens were fabricated from Schedule 40 polyvinyl chloride (PVC) piping material. Gaskets were glued to the bottom of the molds and leak tested before use. The PVC forms were pre-treated with form release, a liquid that allows the concrete specimen to release easily from the mold. The first treatment was applied 3 days prior, and the second treatment was applied a few hours before wet concrete was added to the molds.

2.1.2 Concrete mix and specimen preparation

Concrete monoliths were prepared with mix components added in this order: water, steel (if applicable), coarse aggregate, fine aggregate, fly ash, cement, PolyHeed® 997, and MB-AE™ 90. The concrete was mixed on medium speed using a Hobart 3-speed bench top mixer in a 4 L steel bowl. The PVC molds were filled in the vertical positions. After filling, the molds were lightly tapped on the laboratory bench until a significant decrease in the release of air bubbles was observed. The forms were stored in plastic bags with damp paper towels to provide moisture while the concrete set.

2.2 Concrete-soil diffusion tests

The objective of half-cell tests was to examine the rate of diffusion of key, long-lived, mobile contaminants in unsaturated Hanford Site vadose zone sediment in contact with concrete monolith. These experiments were conducted using half cells of Trench 8 soil (~4-cm diameter and ~10-cm long) in contact with concrete monolith (~4-cm diameter and ~4-cm long). The soil was oven dried, then brought up to 4, 7, or 15% soil moisture content with 18 MΩ cm distilled de-ionized water. Moisture content analysis was performed and the nominal moisture content for 4% cores was 1%, 7% cores were found to be 4%, and 15% were found to be 11%.

For spiked concrete tests, iodine, technetium or rhenium (as Tc surrogate) were first added to water and then mixed into the dry ingredients. For soil spiked tests, the contaminants were first added to water and then added oven-dried soil. Sampling of soil half-cells was conducted at appropriate time intervals by extruding and taking transverse sections of the sediment at about 0.5-cm intervals for the first 4 to 6 cm from the interface and at 1-cm intervals for the remaining part of the half cell. The soil samples were weighed and extracted with either deionized distilled water, and the extracts were analyzed for stable iodide, rhenium and technetium-99 using ICP-MS. The diffusion profile in concrete half-cells were determined by dry-slicing the cells with a circular diamond saw. The resulting thin slices were then crushed and extracted with deionized distilled water and the solutions were analyzed for concentrations of the contaminant of interest.

3. Diffusion coefficient calculations

The radionuclide diffusivity is defined by Fick's equation as

$$J = - D_w \frac{dC_w}{dx} \quad (1)$$

where, J = flux of radionuclide at a given point, D_w = the diffusivity of water-based radionuclide concentration, and C_w = the radionuclide concentration in the pore water.

Ignoring the possibility that radionuclides might be present in the air within the unsaturated sediment, and recognizing that in the case of a two-phase system (water and soil), Equation 1 can be used in performing a mass balance over a small volume leading to the equation (Crank 1975)

$$\frac{dC_w}{dt} = D_w/\theta * \left(\frac{d^2C_w}{dx^2} \right) \quad (2)$$

where θ = the volume fraction water in the soil's pore space. However, the slope on the probit plot provides the diffusivity that solves the equation for diffusion in a homogeneous single phase medium,

$$\frac{dC}{dt} = D * \left(\frac{d^2C}{dx^2} \right) \quad (3)$$

The solution for this diffusion equation is provided by

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{x}{\sqrt{4Dt}} \right) \quad (4)$$

Where, C/C_0 is the normalized concentration, and erfc is the error function (Crank 1975). The diffusivities in the soil were calculated using a probit analysis approach. The details of the probit analysis are provided in Finney (1971). This technique allows the transformation of a sigmoid curve of concentrations, normalized with respect to the initial concentration (C_0) as a function of diffusion distance (x) produced in a half-cell diffusion experiment to a linear plot. The transformed equation is,

$$\text{Probit}(p) = \Phi^{-1}(p) = a - \frac{x}{\sqrt{2Dt}} \quad (5)$$

When probit transform of C/C_0 is plotted against x , the resulting slope $b = 1/\sqrt{2Dt}$ can be used to calculate the diffusivity (D) as $D = 1/(2b^2t)$, where t is the sampling time. This approach has been used previously to determine diffusivity in half-cell diffusion experiments (Brown et al. 1964. Lamar 1989). The diffusion coefficient D_w that was calculated from the D obtained from the probit plot based on concentrations in the pore water must then be multiplied by θ . Detailed statistical analysis (Abdel Rahman and Zaki 2011) was not conducted to assess the uncertainties associated with slopes from the linear regression and the calculated diffusion coefficient values.

4. Effects of carbonation and metallic iron on the diffusion of technetium and iodine in soils and concrete

Diffusion experiments were conducted using carbonated (by immersion in sodium carbonate solution) concrete-soil half cells. Soil half-cell specimens were spiked with I and Tc to achieve a measurable diffusion profile in the concrete part of the half-cell. The goal of this test was to examine the effect of carbonation and metallic iron addition on diffusion of I and Tc into concrete.

Typical diffusion profiles for Tc and I in concrete and the corresponding Probit plots are shown in figures 1 and 2.

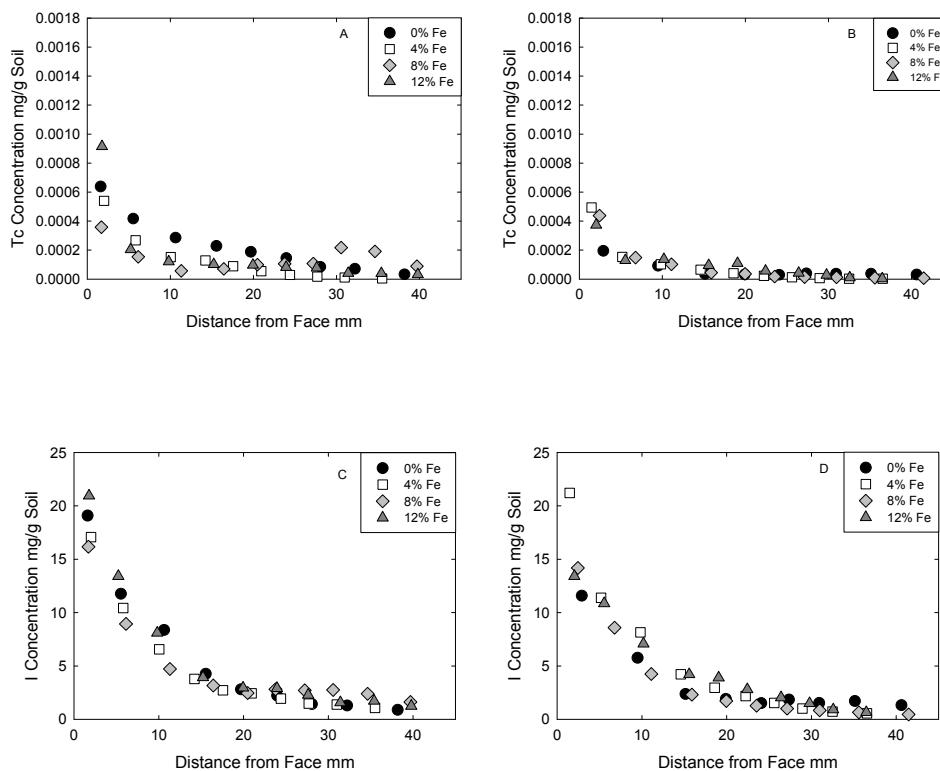


Fig. 1. Concrete half-cell concentration profiles as a function of iron content:
 Top left: Tc concentration for non-carbonated concrete at 4% soil moisture;
 Top right: Tc concentration for carbonated concrete at 4% soil moisture;
 Bottom left: I concentration for non-carbonated concrete at 4% soil moisture;
 Bottom right: I concentration for carbonated concrete at 4% soil moisture.

The results indicated diffusivities ranging from 1×10^{-10} to $1.9 \times 10^{-9} \text{ cm}^2/\text{s}$ for Tc, and 1.3×10^{-10} to $2.3 \times 10^{-9} \text{ cm}^2/\text{s}$ for I (Table 2). The highest Tc and I diffusivities were observed in all uncarbonated, Fe-free concrete cores contacting spiked soils at all three moisture contents (4%, 7%, and 15%). However, the diffusivities of both Tc and I (except in one case) were significantly attenuated in all carbonated concrete cores. The reduction of Tc diffusivities ranged from 55% to 72%. Meanwhile, I diffusivities were reduced by 61% at soil moisture content of 4% and by 58% at soil moisture content of 15%. However, I diffusivity showed an anomalous increase of ~38% in an uncarbonated, Fe-free concrete core in contact with a soil core with 7% moisture content.

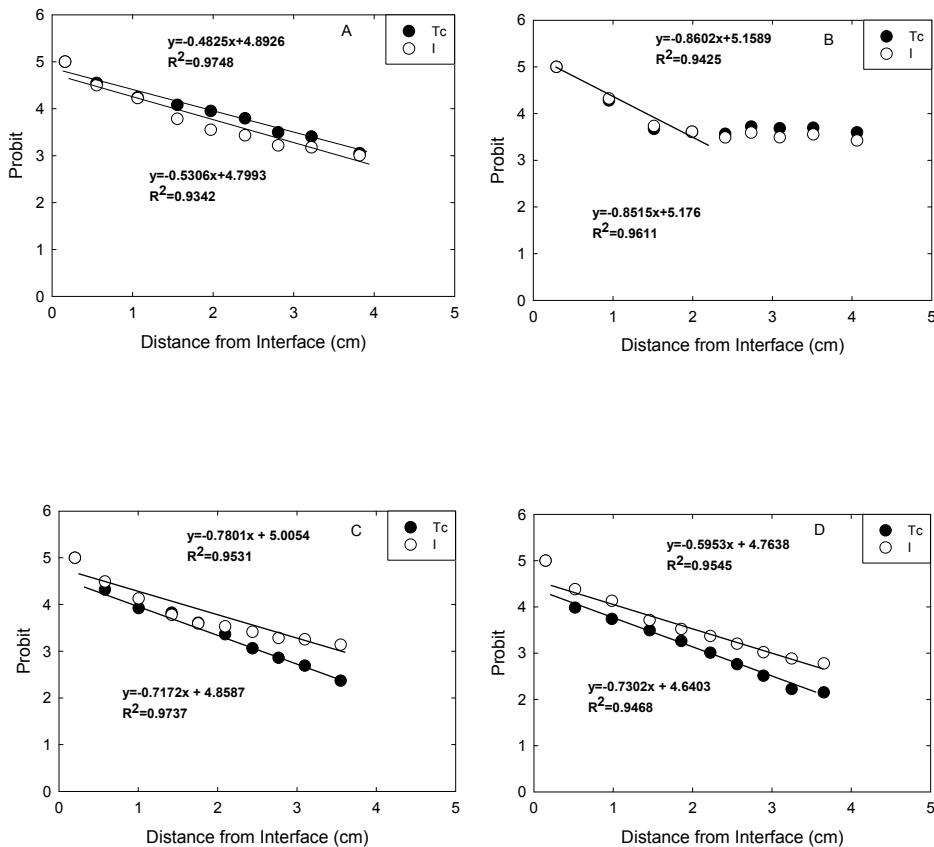


Fig. 2. Probit plots for concrete cores. Top left: 4% moisture content, no Fe, no carbonation; Top right: 4% moisture content, no Fe, carbonated; Bottom left: 4% moisture content, 4% Fe, no carbonation; Bottom right: 4% moisture content, 4% Fe, carbonated.

Similar attenuation in Tc and I diffusivities were also observed in carbonated concrete half cells containing various quantities of Fe. The diffusivities of Tc showed reduction typically ranging from 25 to 81%, except enhanced diffusivities (~40 - 30%) were observed in two concrete cores containing 4% Fe and in contact with soil with 4 and 15% moisture contents. In these same cores, similar increases in I diffusivities were also observed (10% - 6%). However all other Fe-containing carbonated concrete cores exhibited reduction in I diffusivities that ranged from 9% to 76%.

Core ID	Initial Moisture Content (Wt %)	Carbonation	Fe (wt %)	Tc Diffusivity (cm ² /s)	I Diffusivity (cm ² /s)
Tc-C-08-3-0-325	4	N	0	1.7E-09	1.4E-09
Tc-C-08-3-0-329	7	N	0	1.9E-09	4.0E-10
Tc-C-08-3-0-330	15	N	0	1.3E-09	1.2E-09
Tc-C-08-3-0-332	4	Y	0	5.3E-10	5.4E-10
Tc-C-08-3-0-333	7	Y	0	5.4E-10	5.5E-10
Tc-C-08-3-0-334	15	Y	0	5.9E-10	5.1E-10
Tc-C-08-3-4-350	4	N	4	7.7E-10	6.5E-10
Tc-C-08-3-4-351	7	N	4	6.9E-10	2.3E-09
Tc-C-08-3-4-353	15	N	4	3.6E-10	7.9E-10
Tc-C-08-3-4-357	4	Y	4	7.4E-10	1.1E-09
Tc-C-08-3-4-359	7	Y	4	2.6E-10	4.2E-10
Tc-C-08-3-4-360	15	Y	4	7.8E-10	5.4E-10
Tc-C-08-3-8-401	4	N	8	1.9E-10	7.1E-10
Tc-C-08-3-8-402	7	N	8	(a)	5.6E-10
Tc-C-08-3-8-403	15	N	8	(a)	6.0E-10
Tc-C-08-3-8-407	4	Y	8	5.1E-10	4.9E-10
Tc-C-08-3-8-409	7	Y	8	2.2E-10	3.4E-10
Tc-C-08-3-8-410	15	Y	8	3.6E-10	3.4E-10
Tc-C-08-3-12-425	4	N	12	(a)	4.3E-10
Tc-C-08-3-12-426	7	N	12	2.3E-10	4.0E-10
Tc-C-08-3-12-427	15	N	12	4.7E-10	7.7E-10
Tc-C-08-3-12-432	4	Y	12	1.1E-10	1.3E-10
Tc-C-08-3-12-433	7	Y	12	1.0E-10	3.3E-10
Tc-C-08-3-12-435	15	Y	12	4.4E-10	3.1E-10

(a) Probit analysis could not be performed due to poorly defined diffusion profile

Table 2. Diffusivity of Tc and I in concrete half cells

5. Diffusion of iodine, rhenium, and technetium from soil into fractured concrete

A set of diffusion experiments were conducted to examine the effect of fracturing of spiked encasement concrete on the diffusion of radionuclides into soil. Spiked and cured concrete monoliths were encased in shrink wrap and struck with a hammer to prevent the formation of rubble. Each fractured core possessed a single fracture extending the length of the core, perpendicular to the concrete-sediment interface.

In one set of experiments, soil half-cell specimens were spiked with I and Re to achieve a measurable diffusion in the fractured concrete part of the half-cell. The diffusion tests were

conducted under unsaturated conditions at 4%, 7%, and 15% (moisture content by weight) with or without Fe addition (4 wt %) and carbonation. In a second set of experiments, Tc-spiked soil half cells at a fixed moisture content were contacted with fractured concrete half cells.

Typical probit plots are shown in Figure 3 and the data is listed in Table 3. Overall, the calculated diffusivities for Re ranged from 3.8×10^{-12} to $2 \times 10^{-9} \text{ cm}^2/\text{s}$ and for I ranged from 1.3×10^{-10} to $2.3 \times 10^{-9} \text{ cm}^2/\text{s}$ in fractured concrete. The highest Re and I diffusivities were observed in fractured concrete cores that were in contact with spiked soils with 15% moisture content. Effects of carbonation in enhancing diffusion are noticeable at higher moisture contents (7 and 15%) of the contacting soil. Additions of 4% by weight Fe did not noticeably affect the diffusivities of Re and I in fractured concrete.

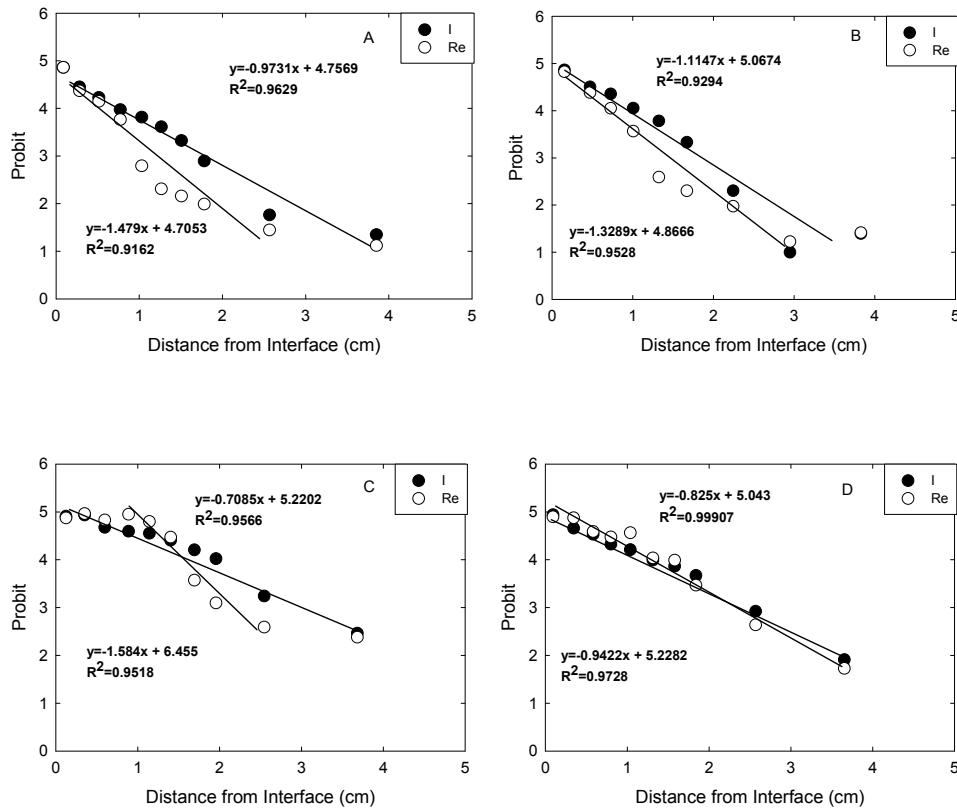


Fig. 3. Probit plots for concrete cores. Top left: 4% moisture content, no Fe, no carbonation; Top right: 4% moisture content, 4% Fe, no carbonation; Bottom left: 4% moisture content, no Fe, carbonated; Bottom right: 4% moisture content, 4% Fe, carbonated half cells.

Core ID	Moisture Content wt%	Carbonation	Fe (wt %)	Re Diffusivity (cm ² /s)	I Diffusivity (cm ² /s)
C-5-0-2	4	N	0	1.36E-10	3.13E-10
C-5-4-26	4	N	4	1.68E-10	2.39E-10
C-5-0-1	4	Y	0	1.18E-10	5.90E-10
C-5-4-21	4	Y	4	3.34E-10	4.35E-10
C-5-0-7	7	N	0	3.75E-12	1.25E-10
C-5-4-27	7	N	4	8.88E-11	1.93E-10
C-5-0-5	7	Y	0	2.60E-10	2.77E-10
C-5-4-23	7	Y	4	1.69E-10	4.00E-10
C-5-0-10	15	N	0	2.03E-09	2.33E-09
C-5-4-30	15	N	4	4.02E-10	1.76E-09
C-5-0-6	15	Y	0	6.90E-10	5.10E-10
C-5-4-24	15	Y	4	6.72E-10	1.21E-09

Table 3. Diffusivity data for Re-I in fractured concrete half cells

In a second set of experiments, Tc-spiked soil half cells at a fixed moisture content were contacted with fractured concrete half cells. The resulting probit analysis for Tc diffusivity in concrete cores is listed in Table 4. These values ranged from 3.1×10^{-11} cm²/s to 3.6×10^{-10} cm²/s. The data indicated that carbonation in all cases enhanced Tc diffusivity in concrete cores. Significant increases in Tc diffusivities were noted when cores with higher concentrations of Fe (8% and 12%) were carbonated. These data indicate that carbonation of Fe containing concrete cores may enhance micro-cracking of concrete resulting in an increase in Tc diffusivity. Similar phenomena have been noted in previous studies in which Fe containing carbonated concrete cores was in contact with Tc-spiked soil cores with 4% moisture content. Also, the beneficial effect of Fe on reducing Tc diffusivity in non-carbonated specimens is not observable until the Fe content is at least 8% by mass. These data indicated that diffusivity in concrete is controlled by carbonation and Fe content and the presence of a single fracture had no measurable effect.

Core ID	Carbonation	Fe (wt %)	Tc Diffusivity (cm ² /s)
Tc-C-10-5-0-101	N	0	1.1E-10
Tc-C-10-5-0-102	Y	0	1.4E-10 ⁰
Tc-C-10-5-4-105	N	4	2.1E-10
Tc-C-10-5-4-106	Y	4	3.6E-10
Tc-C-10-5-8-107	N	8	3.1E-11
Tc-C-10-5-8-108	Y	8	1.9E-10
Tc-C-10-5-12-110	N	12	8.4E-11
Tc-C-10-5-12-111	Y	12	2.1E-10

Table 4. Diffusivity of Tc in fractured concrete cores

6. Diffusion of iodine and rhenium from fractured concrete into soil

Two sets of diffusion experiments were initiated using fractured concrete-soil half cells. The objective was to examine the diffusion from spiked and fractured concrete cores into soil half cells. In one set, Re and I spiked concrete specimens were prepared with and without carbonation and additions of 0, 4, 8, and 12% Fe. After curing, these concrete specimens were fractured and half cells were prepared by placing these specimens in contact with soil at 4, 7, and 15% initial moisture content. Typical probit plots are shown in Figure 4 and the results of probit analysis for these sets of diffusion data are shown in Table 5.

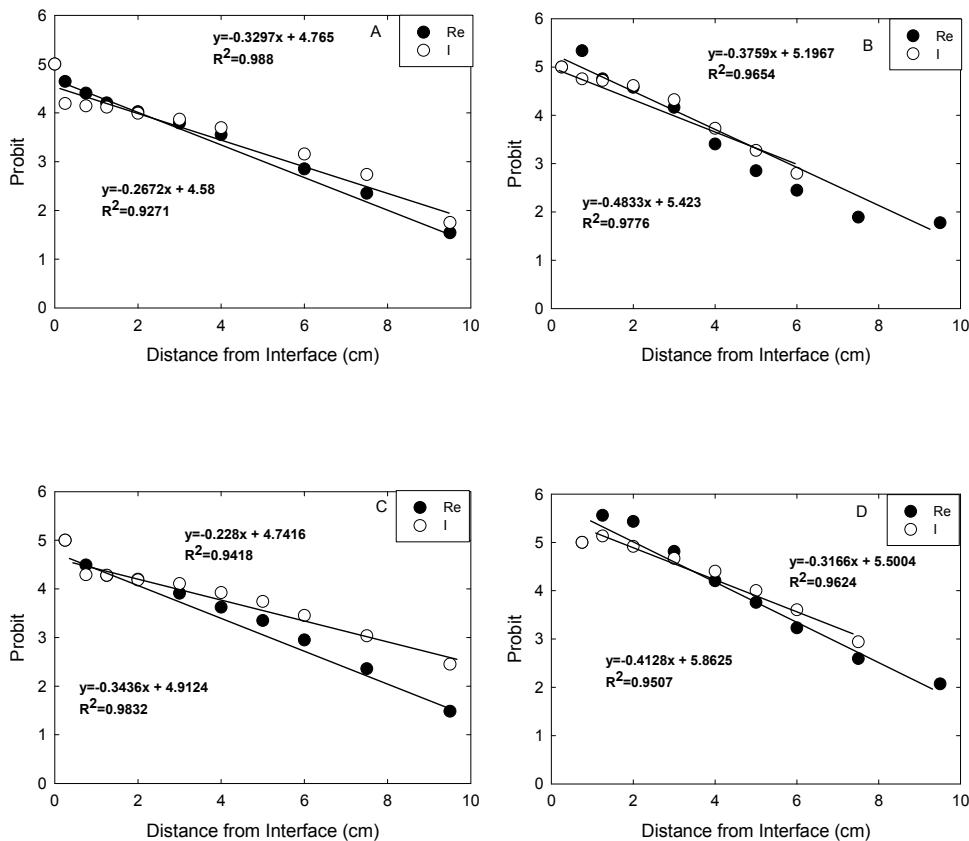


Fig. 4. Probit analysis for Re and I in soil cores. Top left: 4% moisture content, no Fe, no carbonation; Top right: 4% moisture content, no Fe, carbonated; Bottom left: 4% moisture content, 4% Fe, no carbonation; Bottom right: 4% moisture content, 4% Fe, carbonated.

The calculations showed that at 4 % moisture content, with no iron present, carbonation reduced the diffusivities of both Re and I in soils, roughly by half. The addition of 4% by mass Fe into un-carbonated concrete did not significantly affect Re and I diffusivities in soil. In carbonated specimens, adding 4% Fe seemed to increase only I diffusivity without significantly affecting Re diffusivity. When the concentrations of Fe in concrete cores were increased to 8%, significantly enhanced diffusivities in soils were observed. For instance, in soils in contact with un-carbonated concrete cores, the presence of 8% Fe in the concrete increased Re and I diffusivities by ~17 and 36%, respectively. With carbonation, however, the diffusivities of both Re and I more than doubled as compared to carbonated specimens with no Fe. Similarly, increasing the Fe content to 12% by mass in both un-carbonated and carbonated concrete increased Re diffusivities soils by about a third as compared to soils contacting cores with no added Fe. In soils contacting similarly treated concrete cores, the I diffusivities did not change significantly (carbonation) or decreased by ~20% (no carbonation).

In soil cores with higher moisture content (7%) and in contact with carbonated concrete cores containing no iron, the diffusivity of Re was ~20% lower than in soils in contact with un-carbonated concrete cores. The addition of 4% Fe by mass to carbonated concrete cores increased Re and I soil diffusivities by ~1.5 and ~3 times as compared to diffusivities in soil cores contacting concrete half cells with no Fe content. Rhenium diffusivity in soil cores in contact with noncarbonated concrete half cells with 12% Fe was about an order of magnitude lower than in soil cores in contact with similar concrete half cells containing no Fe.

Core ID	MC (Wt %)	Carbonation	Fe (wt %)	Re Diffusivity (cm ² /s)	I Diffusivity (cm ² /s)
C-08-5-0-501	4	N	0	2.2E-09	3.3E-09
C-08-5-0-502	7	N	0	2.1E-07	NA ^a
C-08-5-0-504	4	Y	0	1.0E-09	1.7E-09
C-08-5-0-505	7	Y	0	1.7E-07	1.2E-07
C-08-5-4-526	4	N	4	2.0E-09	4.5E-09
C-08-5-4-530	4	Y	4	1.4E-09	2.3E-09
C-08-5-4-531	7	Y	4	2.6E-07	3.6E-07
C-08-5-8-552	4	N	8	2.5E-08	4.4E-08
C-08-5-8-555	4	Y	8	2.4E-09	3.8E-09
C-08-5-12-576	4	N	12	1.5E-09	2.6E-08
C-08-5-12-580	4	Y	12	1.4E-09	1.7E-09

^a Probit analysis could not be performed due to poorly defined diffusion profile

Table 5. Diffusivity analysis Re and I in soil half cells

In soil cores (7% moisture content) contacting Fe-free concrete with and without carbonation, the Re and I diffusivities were more than an order of magnitude higher than in soils containing 4% moisture content.

At the end of the experiment lasting over a year, Re and I diffusion in soil cores with 15% moisture content had proceeded to the degree that no distinct concentration gradients were present; therefore, diffusivity values could not be ascertained. These data suggest that diffusivities in soil are affected mainly by its moisture content. State of carbonation, Fe content and the presence of fracture in source-concrete do not significantly affect soil diffusivities except mass transfer of contaminants.

7. Modeling the diffusion of iodine and technetium from a reservoir through a concrete enclosure and into surrounding soil

To model the diffusion of iodine and technetium through 6 inches of concrete into the surrounding soil, pairs of high- and low-diffusivity values were selected from the experimental data. The values selected are listed in Table 6.

Diffusing Component	Material	Low Diffusivity, cm ² /s	High Diffusivity, cm ² /s
Iodine	Concrete	1.30E-10	2.30E-09
	Soil	1.70E-09	2.50E-08
Tc	Concrete	3.10E-11	3.60E-10
	Soil	1.30E-08	5.80E-08

Table 6. Diffusivity values for concrete and soil used in the simulations

7.1 Modeling approach

The computational fluid dynamics (CFD) code, STAR-CD¹ was used for the calculations. STAR-CD is a commercial CFD code that solves the finite volume formulations for conservation of mass, momentum, and energy for general-purpose thermal-fluids simulations. STAR-CD was used to simulate the iodine and technetium species diffusion through the concrete encasement box and into the soil using the analogy of thermal conduction,

$$\frac{dT}{dt} = \frac{k}{\rho C_p} \frac{d^2T}{dx^2} \quad (6)$$

and mass diffusion:

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad (7)$$

¹STAR-CD, Version 4.14 Methodology 2010: Computational Dynamics Ltd.

In the heat conduction equation (6) T is the absolute temperature in Kelvin, ρ is the density, and C_p is the specific heat of the material. In the mass diffusion equation (7) C is the species concentration and D is the species diffusivity. In STAR-CD we can simulate the species diffusion through the porous concrete and soil by setting the coefficients of (6) and (7) as equal and solving the thermal conduction problem through the two materials.

The following assumptions were made for performing the simulations:

- Constant species concentration reservoir exists adjacent to inside wall of concrete encasement box.
- 1-dimensional diffusion through encasement box wall and into the surrounding soil.
- No additional resistance between concrete and soil to decrease the species diffusion.

A one-dimensional (1-D) finite volume model was constructed to represent the species transport through the concrete encasement wall and into the soil. A 1-D rectangular mesh was used for transport through the encasement wall. As the species exit the concrete and enter the surrounding soil, the environment is more cylindrical in nature as the species are free to diffuse radially into the soil. Thus the mesh for the concrete wall was mated to a cylindrical mesh extending out into the surrounding soil as shown schematically in Figure 5. The model domain is shown outlined with a dashed line in the figure. In the model, the concrete wall is assumed to be in contact with a constant species reservoir (at location 1 in the figure). The contact between concrete and soil (at location 2 in the figure) is assumed to be perfect with no additional resistance there for species diffusion. The outer radius of the model was established far away from the reservoir such that species concentration remained zero for the times examined (1000, 3000, 10000, and 30000 years). Simulations were performed for diffusion of Iodine and Tc under low-diffusivity and high-diffusivity conditions (Table 6).

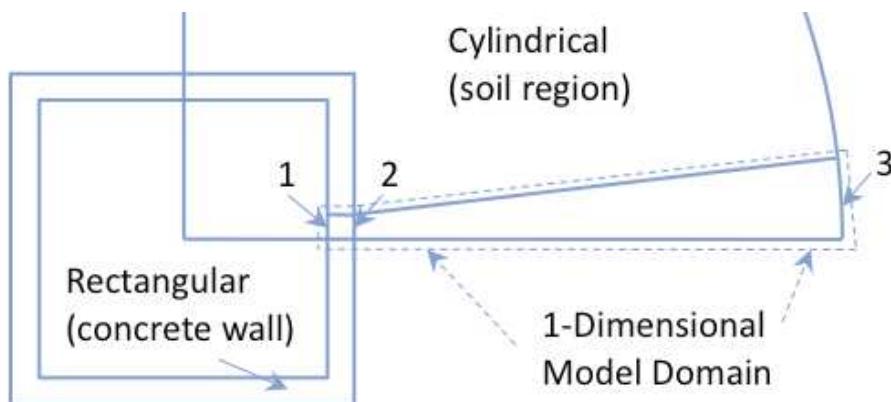


Fig. 5. Plan-view schematic of the model domain (dashed outline) where the rectangular concrete encasement wall is in contact with the surrounding soil region into which the species diffuse radially. 1. Concrete wall in contact with species reservoir. 2. Concrete in contact with soil. 3. Outer radius is established far enough away from the reservoir that species concentration is zero at long times (i.e., 30,000 years).

7.2 Results

The results of the simulations are listed in 7 and 8 and the diffusion profiles are shown in Figures 6 through 9.

The normalized concentrations (C/C_0) at the concrete (~15 cm thick) soil interface as a function of time are listed in Table 7. The data indicates that under low diffusivity conditions, the C/C_0 for both I and Tc at all simulated times are very low (0 - 0.07). Under high diffusivity conditions, the C/C_0 values for Tc ranged from 0 - 0.03, whereas, iodine had C/C_0 values ranging from 0.05 - 0.22 indicating deeper penetration into concrete.

Diffusivity	Time (Y)			
	1,000	3,000	10,000	30,000
				C/C_0
I Low	0.00	0.00	0.02	0.07
I high	0.05	0.10	0.17	0.22
Tc Low	0.00	0.00	0.00	0.00
Tc High	0.00	0.01	0.02	0.03

Table 7. Normalized concentration values for I and Tc at the concrete-soil interface

The depths of penetration, defined as C/C_0 of ~0.005 for various simulated time periods, are listed in Table 8. Under low diffusivity conditions, iodine at the end of 30,000 years is predicted to penetrate about 69 cm into soil (Table 8 and Figure 6), whereas Tc appears to be confined within the encasing of ~15-cm thick concrete (Table 8 and Figure 8). Under higher diffusivity conditions, the simulations indicated higher depths of penetration of I and Tc into soil. For instance, iodine is predicted to penetrate from ~ 39 – 398 cm into the soil for the time period ranging from 1,000 – 30,000 years (Table 8, Figure 7). Technetium under high diffusivity conditions is predicted to penetrate ~112 – 286 cm into the soil at the end of 10,000 and 30,000 years respectively (Table 8, Figure 9).

Diffusivity	Time (Y)			
	1,000	3,000	10,000	30,000
				Depth of Soil Penetration (cm) at $C/C_0 = \sim 0.005$
I Low	0	0	18	69
I high	39	99	215	398
Tc Low	0	0	0	0
Tc High	0	0	112	286

Table 8. Depth of penetration of I and Tc into soil as a function of time

The experimental data indicates that low diffusivity for I is engendered when carbonated encasing concrete is surrounded by soil with very low moisture contents. For Tc, low diffusivity is observed when carbonated and Fe-containing concrete is in contact with very low moisture content sediments. Comparatively, higher diffusivities of I and Tc are typically observed when higher moisture content soil is in contact with uncarbonated, Fe-free encasing concrete.

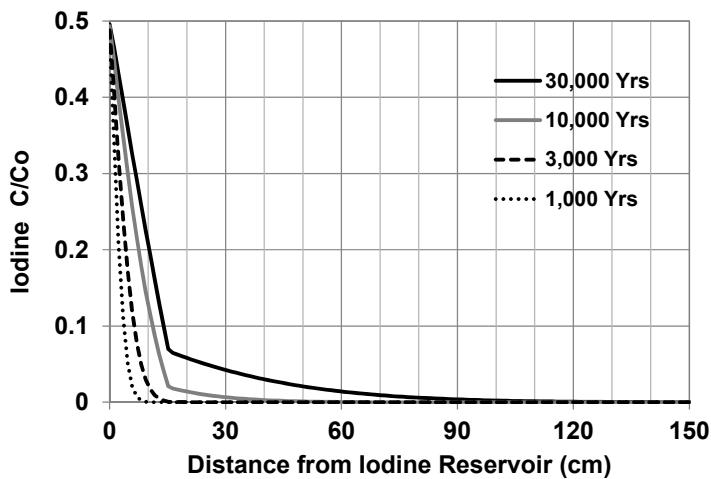


Fig. 6. Iodine concentration profiles for the low diffusivity case. Zero to 15 cm represents concentrations within the concrete encasement wall. Fifteen cm beyond are concentrations in the surrounding soil. $C/C_0 = 0.005$ was about 69 cm into the soil at 30,000 years.

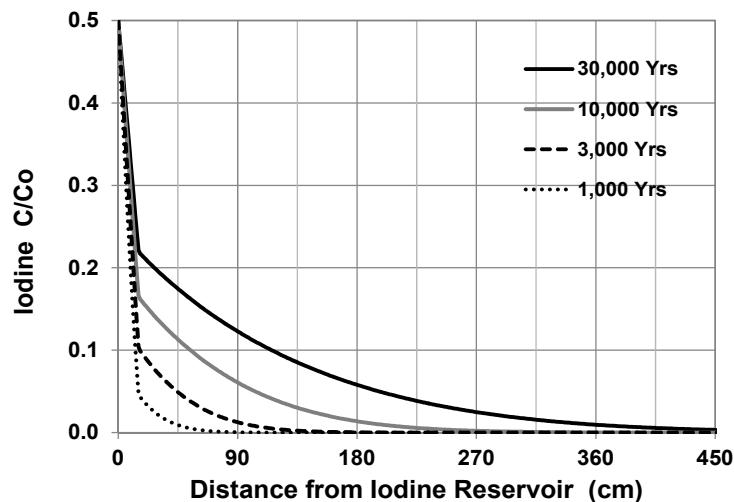


Fig. 7. Iodine concentration profiles for the high diffusivity case. Zero to 15 cm represents concentrations within the concrete encasement wall. Fifteen cm and beyond are concentrations in the surrounding soil. $C/C_0 = 0.005$ was about 398 cm into the soil depth at 30,000 years.

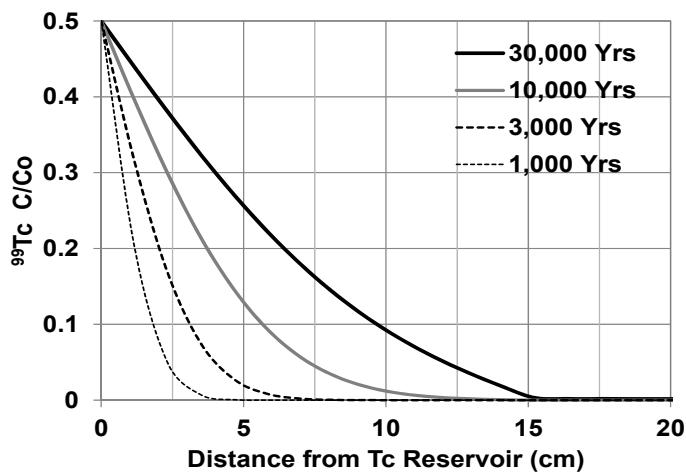


Fig. 8. Technetium concentration profiles for the low diffusivity case. Zero to 15 cm represents concentrations within the concrete encasement wall. Fifteen cm and beyond are concentrations in the surrounding soil. $C/C_0 = 0.005$ was about to the outer edge of the concrete encasement (15 cm total penetration depth) at 30,000 years.

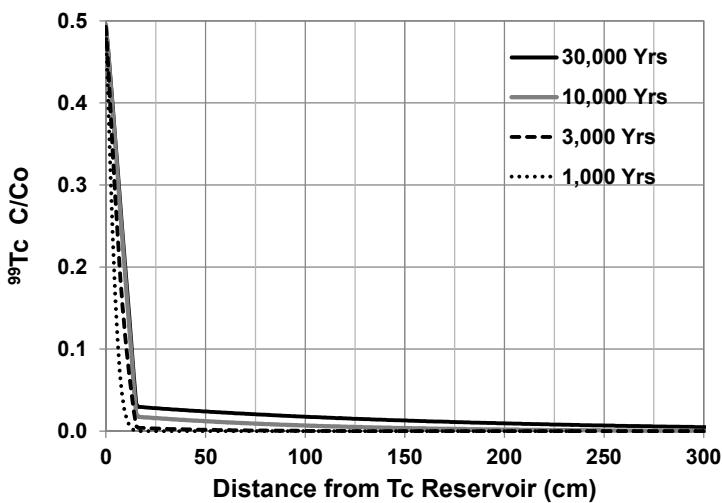


Fig. 9. Technetium concentration profiles for the high diffusivity case. Zero to 15 cm represents concentrations within the concrete encasement wall. Fifteen cm and beyond are concentrations in the surrounding soil. $C/C_0 = 0.005$ was about 286 cm into the soil at 30,000 years.

8. Conclusions

Tests were conducted to measure the diffusion of Tc, Re (as a surrogate for Tc), and I in unsaturated sediments and in concrete that encases low-level radioactive wastes. In these tests, effects of varying sediment moisture content, carbonation, metallic iron addition, and fracturing of concrete on diffusivity of these nuclides were also evaluated. The conclusions from these tests are as follows.

1. Regardless of the variables introduced in the analysis (e.g., water content of the sediment, level of iron additives and carbonation of concrete), diffusion coefficients for both Tc and I varied over a range of about 2 orders of magnitude with Tc being slightly more retarded than I.
2. Degradation of concrete through fracturing and carbonation will not strongly influence diffusion rates primarily because of expected low moisture contents in the waste environment (vadose zone sediments).
3. Within the range of measurements, increasing moisture content of the sediment routinely increased diffusion rates.
4. The addition of metallic iron appeared to have competing effects on diffusion. In some cases, limited reduction of Tc may have occurred. On the other hand, metallic iron appears to have facilitated microcracking during carbonation.
5. In the context of a 1,000 year compliance period, concrete encasement of waste provides a significant delay in radionuclide release into the subsurface.

9. Acknowledgment

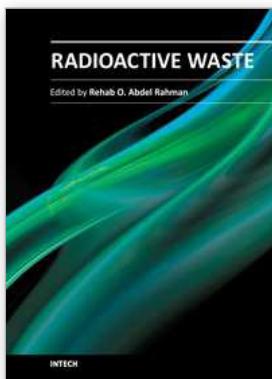
This work was conducted at Pacific Northwest National Laboratory, operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830. Funding for this project was provided by CH2M Hill Plateau Remediation Company and the Department of Energy Environmental Management Office of Technology Innovation and Development. We would like to thank Steven Baum, Kenton Rod, Sara Rither, John Nelson, and Danielle Saunders for assisting in the sectioning of the concrete soil half-cells. We also thank the anonymous reviewer for helpful comments.

10. References

- Abdel Rahman RO, and AA Zaki. 2011. "Comparative study of leaching conceptual models: Cs leaching from different ILW cement based matrices". *Chemical Engineering Journal*. doi:10.1016/j.cej.2011.08.038.
- Al-Khayat H, MN Haque, and NI Fattuhi. 2002. "Concrete Carbonation in Arid Climate." *Materials and Structures* 35(7):421-426.
- ANSI. 1986. *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure*, ANSI/ANS-16.1, American Nuclear Society, Chicago.
- Brown DA, BE Fulton and RE Phillips. 1964. "Ion Exchange Diffusion: I. A Quick-Freeze Method for the Measurement of Ion Diffusion in Soil and Clay Systems." *Soil Sci. Soc. Am. Proc.* 28:628-632.
- Crank J. 1975. *The Mathematics of Diffusion*. Second Edition. Oxford University Press, New York.

- EPA—U.S. Environmental Protection Agency. 1999. *Toxicity Characteristics Leaching Procedure. Test Methods for Evaluating Solid Wastes – Physical and Chemical Methods* SW-846. Method 1311.
- Finney DJ. 1971. *Probit Analysis; A Statistical Treatment of the Sigmoid Response Curve*. Third edition, Cambridge University Press, New York.
- Garrabrants AC, and DS Kosson. 2003. "Modeling Moisture Transport from a Portland Cement-Based Material During Storage in Reactive and Inert Atmospheres." *Drying Technology* 21(5):775-805.
- Garrabrants AC, F Sanchez, C Gervais, P Moszkowicz, and DS Kosson. 2002. "The Effect of Storage in an Inert Atmosphere on the Release of Inorganic Constituents during Intermittent Wetting of a Cement-Based Material." *Journal of Hazardous Materials* 91(1-3):159-185.
- Garrabrants AC, F Sanchez, and DS Kosson. 2004. "Changes in Constituent Equilibrium Leaching and Pore Water Characteristics of a Portland Cement Mortar as a Result of Carbonation." *Waste Management* 24(1):19-36.
- Gervais C, AC Garrabrants, F Sanchez, R Barna, P Moszkowicz, and DS Kosson. 2004. "The Effects of Carbonation and Drying During Intermittent Leaching on the Release of Inorganic Constituents from a Cement-Based Matrix." *Cement and Concrete Research* 34(1):119-131.
- Lamar DA. 1989. *Measurement of Nitrate Diffusivity in Hanford Sediments via the Half-Cell Method*. Letter Report to Westinghouse Hanford Company, Pacific Northwest National Laboratory, Richland, Washington.
- Mann FM, RJ Puigh II, SH Finfrock, EJ Freeman, R Khaleel, DH Bacon, MP Bergeron, PB McGrail, and SK Wurstner. 2001. *Hanford Immobilized Low-Activity Waste Performance Assessment: 2001 Version*, DOE/ORP-2000-24, Rev. B. Pacific Northwest National Laboratory, Richland, WA.
- Sanchez F, C Gervais, AC Garrabrants, R Barna, and DS Kosson. 2002. "Leaching of Inorganic Contaminants from Cement-Based Waste Materials as a Result of Carbonation during Intermittent Wetting." *Waste Management* 22(2):249-260.
- Sanchez F, AC Garrabrants and DS Kosson. 2003. "Effects of Intermittent Wetting on Concentration Profiles and Release from a Cement-Based Waste Matrix." *Environmental Engineering Science* 20(2):135-153.
- Serne RJ, WJ Martin, VL LeGore, CW Lindenmeier, SB McLaurine, PFC Martin, and RO Lokken. 1989. *Leach Tests on Grouts Made with Actual and Trace Metal-Spiked Synthetic Phosphate/Sulfate Waste*. PNL-7121, Pacific Northwest Laboratory, Richland, WA.
- Serne RJ, RO Lokken, and LJ Criscenti. 1992a. "Characterization of Grouted LLW to Support Performance Assessment." *Waste Management* 12(2-3):271-287.
- Serne, RJ, LL Ames, PF Martin, VL LeGore, CW Lindenmeier, and SJ Phillips. 1992b. *Leach Testing of in Situ Stabilization Grouts Containing Additives to Sequester Contaminants*. PNL-8492, Pacific Northwest Laboratory, Richland, Washington.
- Serne RJ, JL Conca, VL LeGore, KJ Cantrell, CW Lindenmeier, JA Campbell, JE Amonette, and MI Wood. 1993. *Solid-Waste Leach Characterization and Contaminant-Sediment Interactions. Volume 1, Patch Leach and Adsorption Tests and Sediment Characterization*. PNL-8889, Pacific Northwest Laboratory, Richland, WA.
- Serne RJ, WJ Martin, and VL LeGore. 1995. *Leach Test of Cladding Removal Waste Grout Using Hanford Groundwater*. PNL-10745, Pacific Northwest Laboratory, Richland, WA.

- Wellman DM, SV Mattigod, GA Whyatt, L Powers, KE Parker, and MI Wood. 2006. *Diffusion of Iodine and Rhenium in Category 3 Waste Encasement Concrete and Soil Fill Material.* PNNL-16268, Pacific Northwest National Laboratory, Richland, WA.
- Wood, MI, R Khaleel, PD Rittman, AH Lu, SH Finfrock, TH DeLorenzo, RJ Serne, and KJ Cantrell. 1995. *Performance Assessment for the Disposal of Low-Level Waste in the 200 West Area Burial Ground.* WHC-EP-0645, Westinghouse Hanford Company, Richland, Washington



Radioactive Waste

Edited by Dr. Rehab Abdel Rahman

ISBN 978-953-51-0551-0

Hard cover, 502 pages

Publisher InTech

Published online 25, April, 2012

Published in print edition April, 2012

The safe management of nuclear and radioactive wastes is a subject that has recently received considerable recognition due to the huge volume of accumulative wastes and the increased public awareness of the hazards of these wastes. This book aims to cover the practice and research efforts that are currently conducted to deal with the technical difficulties in different radioactive waste management activities and to introduce to the non-technical factors that can affect the management practice. The collective contribution of esteemed international experts has covered the science and technology of different management activities. The authors have introduced to the management system, illustrate how old management practices and radioactive accident can affect the environment and summarize the knowledge gained from current management practice and results of research efforts for using some innovative technologies in both pre-disposal and disposal activities.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Shas V. Mattigod, Dawn M. Wellman, Chase C. Bovaird, Kent E. Parker, Kurtis P. Recknagle, Libby Clayton and Marc I. Wood (2012). Diffusion of Radionuclides in Concrete and Soil, Radioactive Waste, Dr. Rehab Abdel Rahman (Ed.), ISBN: 978-953-51-0551-0, InTech, Available from:
<http://www.intechopen.com/books/radioactive-waste/diffusion-of-radionuclides-in-concrete-and-soil>

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