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Diffusion and Leaching of Selected Radionuclides (Iodine-129, Technetium-99, and Uranium) Through Category 3 Waste Encasement Concrete and Soil Fill Material

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Executive Summary

An assessment of long-term performance of Category 3 waste-enclosing cement grouts requires data about the leachability/diffusion of radionuclide species (iodine-129, technetium-99, and uranium) when the waste forms come in contact with groundwater. Leachability data were collected by conducting dynamic (ANS-16.1) and static leach tests on radionuclide-containing cement specimens. The diffusivity of radionuclides in soil and concrete media was collected by conducting soil-soil and concrete-soil half-cell experiments. We found that the effective diffusion coefficients for iodine-125 under dynamic leaching conditions (4×10^{-11} to 1×10^{-10} cm^2/s) were about an order of magnitude higher than values measured under static leaching conditions (3×10^{-12} to 7×10^{-11} cm^2/s). Effective diffusion coefficients for technetium-99 under dynamic leaching conditions (2×10^{-9} to 8×10^{-9} cm^2/s) were about an order of magnitude higher than diffusion coefficients obtained under static leaching conditions (2×10^{-10} to 6×10^{-9} cm^2/s). These data indicated that iodine-125 in these concrete formulations was about two orders of magnitude less leachable than technetium-99. Uranium in concrete specimens was in a nonleachable, recalcitrant solid form, and the cement matrix had a strong affinity to adsorb and immobilize additional uranium from contacting solution containing very low concentrations of uranium (6.7 ppb).

The results from the half-cell experiments showed that the diffusivity coefficients for iodide were 7.03×10^{-8} cm^2/s and 2.42×10^{-7} cm^2/s for soils at 4% and 7% moisture contents, respectively. The soil diffusivity coefficients for technetium-99 were $5.89 \pm 0.80 \times 10^{-8}$ cm^2/s (at ~4% moisture content) and $2.04 \pm 0.57 \times 10^{-7}$ cm^2/s (at ~7% moisture content), respectively. The soil diffusivity of iodine-125 and technetium-99 were similar in magnitude at both water contents (4% and 7% by mass), indicating that these ions have similar diffusion mechanisms in unsaturated coarse-textured Hanford soil.

The diffusivity of iodide in concrete ranged from 2.07×10^{-14} cm^2/s (~4% soil moisture content) to 1.31×10^{-12} cm^2/s (7% soil moisture content), indicating that under unsaturated soil moisture conditions, iodide diffusivity is highly sensitive to changing soil moisture conditions (~3% change in moisture content results in about two orders of magnitude increase in diffusivity). The diffusivity of technetium-99 in concrete for the initial (64-day) sampling period ranged from 6.22×10^{-12} cm^2/s (~4% soil moisture content) to 4.24×10^{-11} cm^2/s (7% soil moisture content), and for the 169-day sampling period ranged from 4.54×10^{-13} cm^2/s (~4% soil moisture content) to 8.02×10^{-12} cm^2/s (7% soil moisture content). These concrete diffusivity values indicated that 1) with increasing time (at a fixed soil moisture content), technetium-99 transport out of concrete will be significantly retarded (over an order of magnitude retardation in 105 days), and 2) technetium-99 will diffuse at a higher rate (about an order of magnitude) at a higher soil moisture content (~7%) than at a lower soil moisture content (~4%). Iodine-125 in concrete diffuses more slowly than technetium-99. Data showed that at a lower soil moisture content (~4%), iodide diffused about 20 times more slowly than technetium-99, and at a higher soil moisture content (~7%) iodide in concrete diffused about 6 times slower than technetium-99.

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1.0   Introduction

One of the methods being considered for safely disposing of Category 3 low-level radioactive wastes 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 with 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 a permanent closure cover is installed.

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 conduct an assessment of the performance of the concrete encasement structure and the surrounding soil's ability 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 radionuclides in category 3 waste that have been identified as long-term dose contributors are iodine-129, selenium-75, technetium-99, and uranium-238 (Wood et al. 1995, Mann et al. 1998). For solid waste encased in concrete, the radionuclides most likely to leach include iodine-129, selenium-75, and technetium-99 because of their anionic nature in aqueous solutions (Serne et al. 1989, 1992a,b; and 1995). These studies and others (Krupka and Serne 1996; Serne et al. 1996a,b) also indicate that uranium-238 encased in cement or concrete has limited solubility; therefore, its diffusion coefficient in these matrices is quite low. However, in groundwater environments, especially carbonate-rich waters typical of the Hanford Site, dissolved uranium is quite mobile because it forms anionic complexes with carbonate. Diffusion coefficient measurements for these four radionuclides would allow one to account for the containment factor in overall performance assessment calculations for solid waste disposal facilities.

We conducted an analysis of iodide diffusion data obtained from previous concrete/soil half-cell experiments (Crane et al. 1992). Based on the results of this analysis, a series of new experiments was designed to measure diffusion coefficients of radionuclides (iodine-129, technetium-99, and uranium-238) in half-cells consisting of concrete/soil and soil/soil.

An assessment of the long-term performance of waste grouts requires data about the leachability/ diffusion of radionuclide species when the waste forms come in contact with vadose zone porewater or groundwater. Such data can be obtained by subjecting waste concrete specimens to standardized leach tests. Therefore, we conducted dynamic (American Nuclear Society, ANS- 16.1) and static leach tests on concrete specimens containing the radionuclides of interest.

2.0   Concrete Composition and Fabrication of Test Specimens

The concrete mixture composition for the burial encasement was specified in *Specification for Concrete Encasement for Contact-Handled Category 3 Waste*.[a] This specification was used as the basis to prepare a concrete for fabrication of test specimens.

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 ±1.5 %. The nominal proportions and material specifications based on this initial design are listed in Table 2.1.

2.2   Materials and Laboratory-Scale Mixture Design

A laboratory-scale concrete mixture was prepared based on specifications shown in Table 2.1. Because of the required small dimensions of laboratory test specimens, the size of the coarse aggregate and the dimensions of the steel fiber specified in Table 2.1 had to be 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. Aggregate passing a 7-mesh sieve and retained on a 10-mesh sieve met this particle size specification. The scaled-down steel fibers used in

Table 2.1. Material Specifications and Composition

Material	Specifications	Specified Field Mix	Normalized Specification Design
Cement	Portland Type I or Type I/ II sulfate-resistant cement	381 kg/m^3 (642 lbs/yd^3)	0.27
Fly Ash	Class F fly ash; nominal 15% of cement volume	54 kg/m^3 (91 lbs/yd^3)	0.04
Coarse Aggregate	No. 676 or equivalent (3/4" nominal size)	55% by volume	0.04
Fine Aggregate	Sand	45% by volume	0.51
Water	Nominal water:cement ratio: 0.4	399 kg/m^3 (305 lbs/yd^3)	0.10
Steel Fiber	Deformed Type I, nominal length 2.5 - 3.8 cm (1 - 1.5 in,)	59 kg/m^3 (100 lbs/yd^3)	0.04
Air Content		6.0 ±1.5 %	

(a) Unpublished Report. Waste Management 1998.
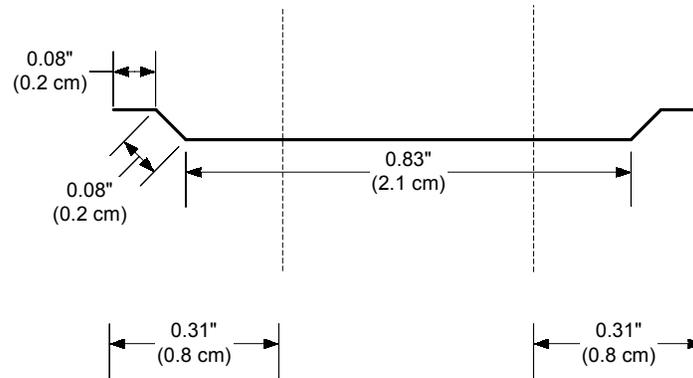
Figure 2.1. Steel Wire Fiber

the laboratory mix consisted of Bekaert Dramix brand deformed steel wire fibers that were cut, as shown in Figure 2.1, 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 material specification and composition for the laboratory-scale concrete mixture is given in Table 2.2. A laboratory sieve shaker was modified to serve as a vibrating table during the concrete membrane casting operation (Figure 2.2).

Table 2.2. Laboratory-Scale Material Specification and Composition

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 volume	0.04	Class F fly ash; 20% of cement volume
Coarse Aggregate	No. 676 or equivalent 2 mm (0.75 in.)	0.04	Sieve size +7 to −10 (2.83 - 2 mm size)
Fine Aggregate	Sand	0.48	Sand −10 sieve size (< 2 mm)
Water	Nominal water-to-cement ratio: 0.4	0.13	Water-to-cement ratio: 0.5
Steel Fiber	Deformed Type I, nominal length 2.5 - 3.8 cm (1 - 1.5 in.)	0.04	Deformed, nominal length 8 mm (0.32 in.)
Polyheed 997	--	0.00375	Water-entraining agent
Air Content	6.0 ±1.5 %	6.0 ±1.5 %	--

Figure 2.2. Vibrating Table for Concrete Membrane Molds

Before preparing the final mixture, concrete mixtures with varying proportions of an air-entraining agent (MB AE 90) were made to study the quality of resulting concrete and to assess whether the air contents of the laboratory specimens would meet the required specification for the field mix. The test batches of concrete were cast in to 30.5 cm x 30.5 cm x 2 cm (12 in. x 12 in. x 0.79 in.) thin membrane molds.

To assess the air content of the fresh concrete, a modified version of the ASTM C-138 method was used. This air content value was calculated as the percent error between the theoretical weight of the concrete materials in a specified volume compared to the actual weight of the fresh cement within a known volume. To determine the theoretical weight of the concrete materials in a specified volume, the specific gravities of the materials listed in Table 2.3 were used.

Table 2.3. Specific Gravities of Concrete Mix Components Used in Air-Content Calculations

Material	Specific Gravity	Source of Data
Cement	3.15	**ASTM C-150-99a**
Fly Ash	2.20	EPRI EA-3236
Coarse Aggregate	2.76	Calculated per ASTM C-127
Fine Aggregate	2.68	Calculated per ASTM C-128
Steel fibers	7.86	*Chemical Engineer's Handbook*, 5th Edition
Water	1.00	*Handbook of Chemistry and Physics*
Water entraining agent (Polyheed 997)	1.24	Calculated via density tests
Air entraining agent (MB AE 90)	1.01	Calculated via density tests

The concrete specimens were also examined visually to assess the degree of air entrainment. As an example, one of the examined concrete specimens with high air content showed visible air bubble entrainment on both 30 cm x 30 cm (~12 in. x ~12 in.) surfaces as well as excessive air pockets within the thickness of the membrane (Figure 2.3).

The bulk specific gravity for the coarse aggregate was determined using the ASTM C-127 method. The aggregate was first soaked in distilled water for 24 hours to saturate all the pores. The aggregate was weighed in the interstices-saturated but surface dry condition and then submerged in water and weighed again. The bulk specific gravity was calculated from these measured weights.

The bulk specific gravity for the fine aggregate was determined using the ASTM C-128 method. The fine aggregate was soaked in distilled water for 24 hours to saturate all the pores. Using a cone test, the fine aggregate was tested to confirm that it had reached the interstices-saturated but surface dry condition and then weighed. The aggregate was then placed in a water-filled pycnometer where both tare and gross weights were determined. The bulk specific gravity of the fine aggregate was calculated from these measured weights (Table 2.3).

2.3   Concrete Mix Design

A number of concrete batches were prepared to identify the optimal composition for the preparation of laboratory specimens. All concrete batches were mixed on a three-speed Hobart bench top mixer with a 4-L bowl. Most batches were made in either 1- or 2-L volumes using an estimated concrete density to determine the masses of the materials needed.

A batch of concrete (Batch #1) based on composition (Table 2.4) was prepared to evaluate the adequacy of mixing equipment, determine the concrete density, and assess the concrete shrinkage. Evaluation of shrinkage was necessary to determine if additional space needed to be incorporated into the membrane mold.

Figure 2.3. Surface of Batch 2, Mold III 30.5 cm x 30.5 cm Specimen, and
Cross Section of Batch 2, Mold VIII Specimen

Table 2.4. Concrete Mixture Composition #1

Material	Normalized Proportion
Cement	0.27
Fly Ash	0.04
Coarse Aggregate	0.04
Fine Aggregate	0.48
Steel	0.04
Water	0.13
Polyheed 997	0.00376
MB AE 90	0.00004
Total	1.01

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. A 1.08 kg batch was prepared and placed in practice molds or forms. The mixed concrete was filled into a 250-mL graduated cylinder and a plastic tray. The forms were stored in plastic bags with damp paper towels to provide moisture while the concrete set.

The density of the fresh concrete was calculated to be 2.22 g/mL. The concrete form in the graduated cylinder did not show appreciable shrinkage after a set time of 1 day, and the form surface was smooth with minimal air pockets. Because there were no problems associated with this mix design, we decided to prepare test specimens using the membrane molds designed previously.

A series of 2-L batches of concrete (designated Batch #2) based on mixture composition #1 (Table 2.4) was prepared with mix components added in the order: water, steel, coarse aggregate, fine aggregate, fly ash, cement, Polyheed 997, and MB AE 90. The concrete was mixed on medium speed for 30 to 45 sec. The molds were treated twice 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 mold.

All the molds were filled in the vertical position. After filling, the molds were tapped with a peek rod and rodded with a tamping rod. Molds I, II, III and VIII were filled. The forms were stored in plastic bags with damp paper towels to provide moisture while the concrete set.

When released from the molds, the top 31 cm x 2 cm side of the concrete membrane showed slight shrinkage. The concrete membranes did not release easily from the molds even after 3- to 4-day cure times. Residual concrete attached to the 31 cm x 31 cm faces of the mold created uneven concrete membrane surfaces. The surfaces of the concrete showed extensive trapping of air bubbles indicative of very porous concrete (Figure 2.4). The air content of these concrete membranes was calculated to be 12.4%, which was more than twice the desired air content of 6%.

Figure 2.4. Concrete Membrane Surface with Extensive Air Bubble Imprints
(Batch #2, Mold II Specimen)

Because the air content of concrete membranes prepared from the batch #2 mix exceeded the
specified air content of 6%, it was necessary to reduce the air content of the final mix. Therefore, the
concrete mixture composition #1 was revised to eliminate the air-entraining agent (MB AE 90) from the
mixture (designated as mixture composition #2, Table 2.5).

2.4 Half-Cell, Dynamic, and Static Leach Experiments

All specimens for leach tests and half-cell experiments were prepared using concrete mixture
composition #2. The nominal proportions in this mix design were identical in to the specified mix design
(Table 2.1) except the proportion of fine aggregate (sand) was decreased by 0.04, and water in the mix
was increased by about 0.03 to maintain workability and meet the specification for air content of the
concrete mixture.

2.4.1 Concrete Mold Design

The concrete molds for casting specimens were fabricated from Schedule 40 PVC piping material.
Gaskets were glued to the bottom of the molds and leak tested before use. For leach test specimens,
Teflon loops were set into the top surfaces so that the cured specimens could be suspended in leach
solutions. The mold dimensions and the number of molds used for specimen preparation is given in
Table 2.6.

Table 2.5. Concrete Mixture Composition #2

Material	Normalized
Cement	0.27
Fly Ash	0.04
Coarse Aggregate	0.04
Fine Aggregate	0.47
Steel	0.04
Water	0.13
Polyheed 997	0.00375
MB AE 90	0
Total	1.00

Table 2.6. Mold Dimensions for Half-Cell and Leach Test Specimens

Test	Diameter x Length (cm)	Number of Molds	Concrete Mixture
Dynamic Leach[a]	2.09 x 4.3	3	Mix #2 without steel fibers
Dynamic Leach[a]	2.09 x 4.3	3	Mix #2 with steel fibers
Static Leach	2.09 x 4.3	2	Mix #2 without steel fibers
Static Leach	2.09 x 4.3	2	Mix #2 with steel fibers
Concrete Half-Cell	3.81 x 4.3	4	Mix #2 with steel fibers
(a) ANS 16.1 Leach Test.			

2.4.2 Concrete Mix and Specimen Preparation

The specimens for leach tests and concrete half-cell tests (Table 2.6) were prepared using concrete mixture composition #2 (Table 2.5). The concrete prepared for specimens without steel fibers were formulated with water that contained glue from steel fibers. This formulation would allow the presence or absence of steel as the only variable between samples to be tested. The radionuclides and stable isotopes were first added to the water and then mixed into the dry ingredients. The calculated spike levels in the concrete mixture are listed in Table 2.7.

The concrete mixture was prepared by adding the ingredients into a 4-L mixing bowl in the order: water (with radionuclides and glue from steel fibers), Polyheed 997, coarse aggregate, fine aggregate, and fly ash. The mixture was stirred by hand to remove excess air, and the cement was added to complete the mixture. Next, using a three-speed Hobart bench top mixer, the concrete was mixed on low setting for 30 seconds, the mixture was scraped off the sides of the bowl with a spatula, and mixed again on low for 30 seconds. A portion of the resulting steel fiber-free mixture was used to fill the required five molds (Table 2.6). The required quantity of steel fibers were mixed into the wet concrete in the bowl, and the resulting mixture was used to prepare the rest of the specimens.

After filling, all sample molds were lightly tapped on the laboratory bench until a significant decrease in the release of air bubbles was observed. The concrete samples were cured in a plastic bag with damp paper towels and the exposed surfaces were periodically wetted.

Table 2.7. Radionuclide Spike Levels in Concrete

Spike	Calculated Activity or Conc. in Concrete
Iodine-125	~0.35 mCi/kg
Stable I	~460 mg/kg
Technetium-99	~0.03 mCi/kg
U	~10.3 mg/kg

3.0   Radionuclide Leaching Tests

Two types of tests (dynamic and static) were conducted to assess the leachability of iodine and technetium from the concrete specimens. The dynamic test was conducted according to a standard method (ANS-16.1). According to this procedure, the test solution is replaced with fresh groundwater at specified intervals. This dynamic test maintains an aggressive leaching environment in that a high difference in contaminant chemical potential is maintained between the concrete specimen and the leach solution. The static test, in comparison, is much less aggressive in that only a small portion of the leaching solution is renewed periodically to monitor the radionuclide activities in solution. Therefore, in the static test the chemical potential difference of a contaminant decreases as a function of time. In each test, the ratio of leachant volume to the surface area of test specimens was held constant at ~10 cm (350 cm^3/35 cm^2).

3.1   Dynamic Leach Test

The dynamic leach test is a ANS-16.1 standard test that is designed to examine the rate of leaching of contaminants in concrete and grout specimens to determine the cumulative fractions leached and effective diffusion coefficients. These tests were conducted according to protocol specified by ANS (1986). The ANS leach tests were conducted on specimens of intact concrete cylinders ~2 cm in diameter and 4 cm length. The characteristics of the specimens used are listed in Table 3.1. The test protocol was slightly modified in that actual groundwater from the Hanford Site was used as the leachant instead of the demineralized water specified in ANS-16.1. The composition of Hanford Site groundwater is listed in Table 3.2.

In leachates, the concentration of uranium was measured using inductively coupled plasma mass spectrometry (ICP-MS), and the activities of iodine-125 and technetium-99 were measured with liquid scintillation counting. Additionally, the concentrations of technetium-99 in leachates of selected leach experiments were also measured using ICP-MS so that a comparison could be made about the accuracy of this method . From the data, the cumulative leached fraction, the effective diffusion coefficient, and the leachability index for each contaminant were calculated.

Table 3.1. Characteristics of Cement Specimens Used in ANS and Static Leach Tests

Specimen No.	Length (cm)	Diameter (cm)	Surface Area (cm^2)	Volume (cm^3)
1	4.20	2.10	34.64	14.55
2	4.10	2.10	33.98	14.20
3	4.10	2.10	33.98	14.20
5	4.30	2.10	35.30	14.89
6	4.50	2.10	36.62	15.59
7	4.20	2.10	34.64	14.55
8	4.30	2.10	35.30	14.89
9	4.20	2.10	34.64	14.55

Table 3.2. Composition of Hanford Groundwater Used in the Leaching Tests

Constituent	Concentration (mg/L)	Constituent	Concentration (mg/L)
Al	0.14	Si	16.2
B	0.05	Sr	0.28
Ba	0.069	U	0.0067
Ca	67.5	Cl	22.0
Fe	3.0	NO_3	1.7
K	3.0	SO_4	108.0
Mg	16.4	Tot Alk (as CO_3)	67.5
Mn	0.046	TOC	0.73
Na	27.6	pH	8.46 (SU)

3.2   Static Leach Test

The static leach test was designed to determine the diffusion coefficient under conditions of decreasing chemical potential between solid and solution phases. As discussed previously, the static leach test differs from the dynamic leach test (ANS-16.1), wherein the chemical potentials of leaching constituents between the solid and the solution phases is maintained nearly at a constant level by periodically renewing the solution phase. The static leach tests were conducted on specimens of intact concrete cylinders ~2 cm in diameter and ~4 cm in length. The leachant consisted of Hanford Site groundwater. At prescribed times, 50 mL of leachate was removed for analysis, and 50 mL of fresh groundwater was added to the containers to maintain the total volume of the leach solution at ~350 mL.

The 50-mL aliquots were filtered through a 0.45-μm membrane and analyzed for activities of iodine-125 and technetium-99 using liquid scintillation. Additionally, the concentrations of technetium-99 and uranium in leachates of selected leach experiments were also measured using ICP-MS. From the data, the cumulative leached fraction, the effective diffusion coefficient, and the leaching index for each contaminant were calculated.

3.3   Effective Diffusivity Calculations

Based on a number of leach studies, Serne et al. (1992a, 1995) concluded that leaching from a semi-infinite solid source would be the most appropriate model to describe the release of trace contaminants from grout and cement specimens. Seven critical assumptions in their model were:

1. The concentration of leaching contaminant species at the surface of the specimen is always zero; i.e., the contaminant is instantaneously removed by the liquid as soon as the species diffusing from the solid reaches the solid-liquid interface.

2. The composition of the liquid in contact with the solid being leached is constant. This implies that the leaching contaminant will not significantly change the liquid composition.

3. 3.   The solid waste form does not alter physically or chemically during the leaching process. A critical part of this assumption is that the mass of constituents leached is insignificant when compared to the total mass of these constituents in the solid, thus fulfilling the semi-infinite solid requirement.

4. 4.   The surface area of the solid is constant and does not change by armoring (i.e., formation of a protective layer during leaching).

5. 5.   Any chemical reaction is rapid enough so that chemical equilibrium always exists between leaching species in the solid and the liquid.

6. 6.   Each contaminant exists as a single chemical species such as all free, cationic, anionic, or neutral) or in a complexed form (either a single cationic, anionic, or neutral species).

7. 7.   Bulk diffusion is the rate-limiting process for contaminant leaching.

Leaching of semi-infinite solids has been described mathematically using either incremental leach rates or cumulative leach rates (Serne et al. 1992a, b; 1995). Using incremental leach rates, the effective diffusion coefficient for each leach interval (D_{ei}) for a species of interest is expressed as:

$$D_{ei} = \pi \left[(a_n/A_0)/\Delta t_n\right]^2 [V/S]^2 [T] \tag{3.1}$$

Using cumulative leaching rates, the effective diffusion coefficient (D_{ec}) is expressed as:

$$D_{ec} = \pi/4 \left[(\Sigma a_n/A_0)\right]^2 [V/S]^2 [1/t] \tag{3.2}$$

where
D_{ei} = effective diffusivity coefficient (cm^2/s) for the leaching interval, $t_n - t_{n-1}$
D_{ec} = effective diffusivity coefficient (cm^2/s) for the cumulative leach interval, $t_n - t_0$
a_n = activity of radionuclide leached during the leaching interval, $t_n - t_{n-1}$
Σa_n = total activity of radionuclide cumulatively leached during the interval, $t_n - t_0$
A_0 = total initial activity of radionuclide in the specimen
a_n/A_0 = fraction of radionuclide leached during interval $t_n - t_{n-1}$
$\Sigma a_n/A_0$ = cumulative fraction of radionuclide leached during the interval $t_n - t_0$
Δt_n = duration of the nth leaching interval $t_n - t_{n-1}$ in s
V = volume of the specimen, cm^3
S = geometric surface area of the specimen, cm^2
T = mean leaching time = $[1/2(\sqrt{t_n} + \sqrt{t_{n-1}})]^2$
t = total elapsed time from leaching initiation in s.

According to Serne et al (1992a, b; 1995), if the leach experiments satisfy all the seven conditions listed above for semi-infinite solids, both equations (3.1 and 3.2) would provide the same effective diffusion coefficient for all times. However, in actual leaching experiments, many of the conditions cannot be met; therefore, the calculated average D_{ei} and D_{ec} are different. For instance, Serne et al. (1992a, b; 1995)

observed that armoring is a common phenomena in leach studies of cement specimens, which would affect the leach rates depending on the rate of formation, thickness, and the chemical nature of surface armoring. Additionally, certain species may leach out in sufficient quantities, which would invalidate the third assumption of insignificant leach fraction. Also, a number of chemical speciation studies have indicated that in cement specimens, each leaching species does not exist as a single chemical species. Therefore, the assumption of single diffusing chemical species may not be valid.

In leaching experiments where the leaching fraction of a species is significant (>20% the amount contained initially in a specimen), the ANSI protocol recommends a specimen shape-specific solution of the mass transport equation. The effective diffusion coefficient in this case for a cylindrical specimen is calculated by using the equation

$$D_{ec} = Gd^2/t \tag{3.3}$$

where G = a dimensionless time factor for the cylinder
         d = the diameter of the cylinder in cm
         t = total elapsed time from leaching initiation in s

The average effective diffusion coefficients were calculated from the values calculated for each leaching interval (D_{ei}) and each cumulative leach time (D_{ec}).

The leachability index for each radionuclide was calculated from the average effective diffusion coefficient values as:

$$L = \log (\beta/D_e) \tag{3.4}$$

where L = leachability index
         β = a constant = 1 cm^2/s
         D_e = average effective diffusion coefficient.

3.4   Results and Discussion

The leaching data from both dynamic and static tests are plotted as cumulative leach fractions (iodine-125, and technetium-99) or the cumulative uranium adsorbed (ng/cm^2) as a function of leaching time (Figures 3.1 through 3.6 and Appendix). The calculated effective diffusion coefficients are listed in Tables 3.3 and 3.4.

3.4.1   Leaching Characteristics

The results showed that in the dynamic leach test, iodine-125 leaches rapidly during the first 5 days. Iodine continues to leach at an attenuated rate for the remainder of the experiment. All four specimens showed differing leaching rates, and specimens 1 and 2, prepared without steel fibers in the concrete mixture, indicated on average slightly higher leach rates than specimens 6 and 7 containing steel fibers.

One explanation for these small differences in leaching may be due to the type of iodine redox species that exist in these specimens. For instance, the steel fibers in specimens 6 and 7 through oxidation may
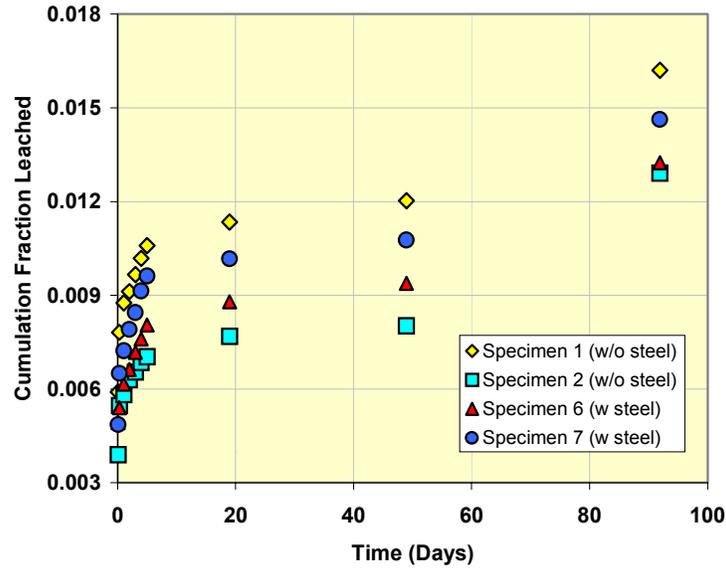
Figure 3.1. Dynamic Leach Test: Cumulative Leaching Fraction as a Function of Time for Iodine-125
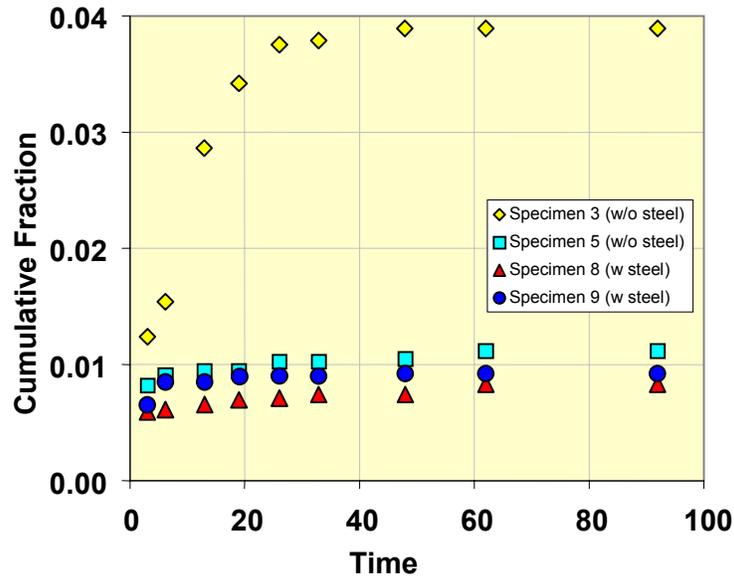
Figure 3.2. Static Leach Test: Cumulative Leaching Fraction as a Function of Time for Iodine-125
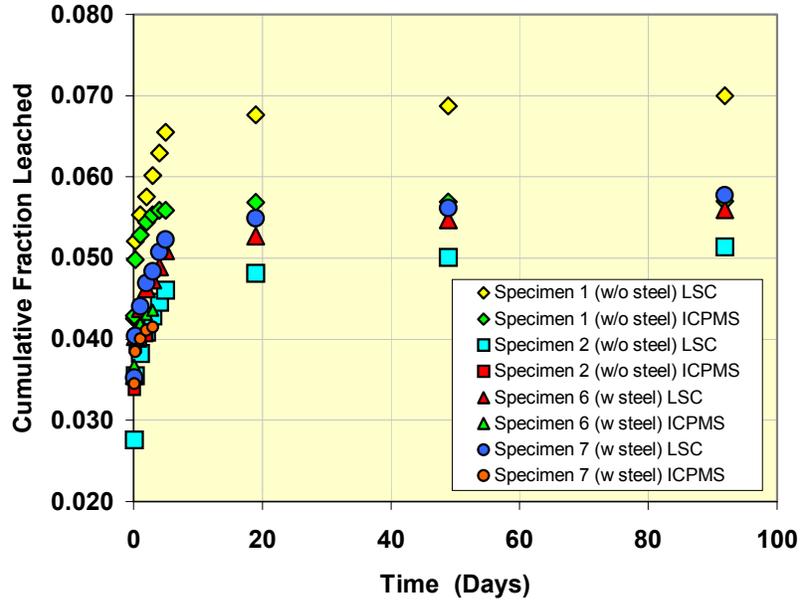
Figure 3.3. Dynamic Leach Test: Cumulative Leaching Fraction as a Function of Time for Technetium-99
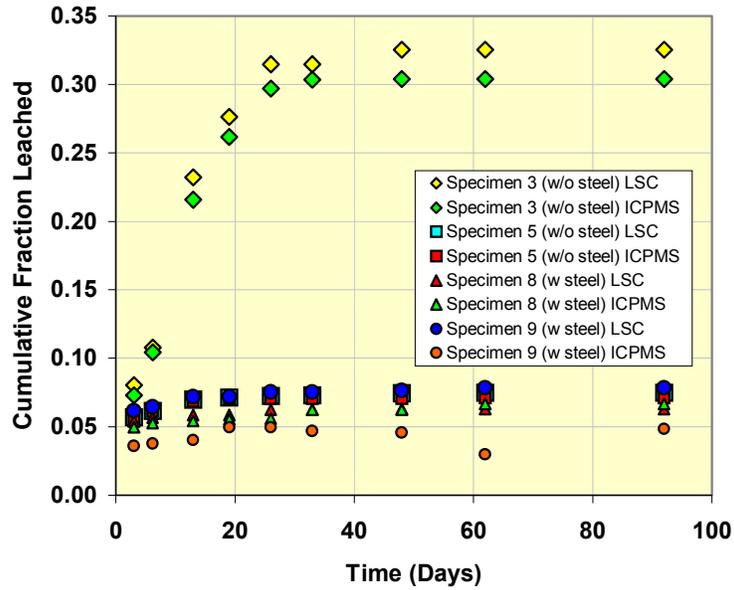
Figure 3.4. Static Leach Test: Cumulative Leaching Fraction as a Function of Time for Technetium-99
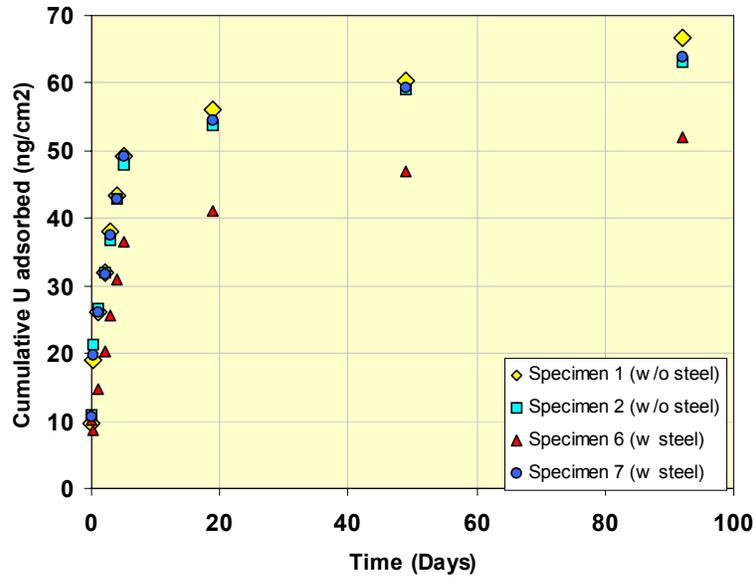
Figure 3.5. Dynamic Leach Test: Cumulative Uranium Adsorbed as a Function of Time
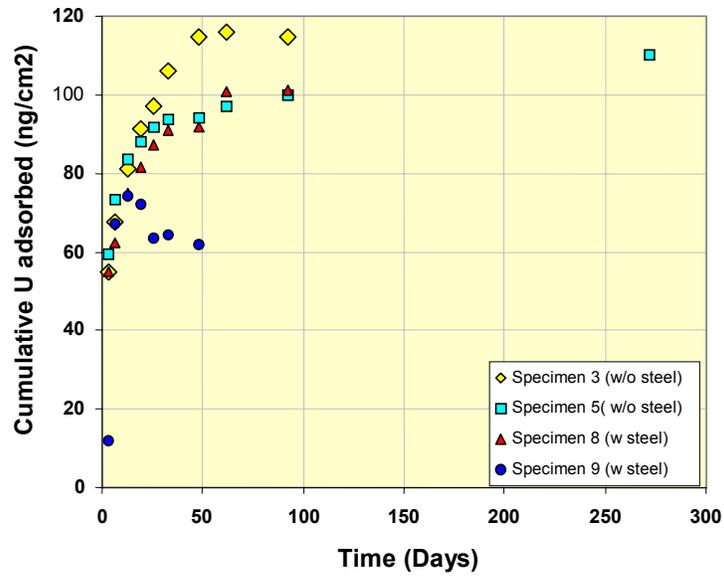
Figure 3.6. Static Leach Test: Cumulative Uranium Adsorbed as a Function of Time

Table 3.3. Calculated Effective Diffusion Coefficients and Leaching Indices of Iodine-125 and Technetium-99 from Dynamic and Static Leach Tests

Dynamic Leach Test												
Specimen Number	Iodine-125		Technetium-99[a]		Technetium-99[b]		Iodine-125		Technetium-99[a]		Technetium-99[b]	
	Effective Diffusion Coefficient (cm^2/s)						Leachability Index					
	D_{ei}	D_{ec}	D_{ei}	D_{ec}	D_{ei}	D_{ec}	L_i	L_c	L_i	L_c	L_i	L_c
1[c]	7.77×10^{-11}	1.32×10^{-10}	3.69×10^{-9}	7.68×10^{-9}	3.58×10^{-9}	7.36×10^{-9}	10.1	9.9	8.4	8.1	8.4	8.1
2[c]	3.59×10^{-11}	7.36×10^{-11}	1.61×10^{-9}	3.39×10^{-9}			10.4	10.1	8.8	8.5		
6[d]	4.94×10^{-11}	1.00×10^{-10}	3.15×10^{-9}	5.18×10^{-9}			10.3	10.0	8.5	8.3		
7[d]	5.44×10^{-11}	9.17×10^{-11}	2.42×10^{-9}	4.03×10^{-9}			10.3	10.0	8.6	8.4		
Static Leach Test												
3[d]	6.40×10^{-11}	6.79×10^{-11}	5.81×10^{-9}	4.25×10^{-9}	5.81×10^{-9}	3.77×10^{-9}	10.2	10.2	8.2	8.4	8.2	8.4
5[d]	6.64×10^{-12}	1.08×10^{-11}	2.40×10^{-10}	5.36×10^{-10}	2.25×10^{-10}	5.02×10^{-10}	11.2	11.0	9.6	9.3	9.6	9.3
8[d]	3.06×10^{-12}	5.42×10^{-12}	3.20×10^{-10}	4.30×10^{-10}	2.21×10^{-10}	3.78×10^{-10}	11.5	11.3	9.5	9.4	9.7	9.4
9[d]	6.76×10^{-12}	8.02×10^{-12}	3.56×10^{-10}	5.85×10^{-10}	1.88×10^{-10}	2.07×10^{-10}	11.2	11.1	9.4	9.2	9.7	9.7

(a) Technetium-99 activity measured by using LSC.
(b) Technetium-99 concentration measured by using ICP-MS.
(c) Specimen without steel fibers.
(d) Specimen with steel fibers.

Table 3.4. Range of Effective Diffusion Coefficients and Leachability Indices
for the Selected Mix Design and Contaminant Loading

Leaching Condition	Iodine-125 Effective Diffusion Coefficient (cm^2/s)	Iodine-125 Leachability Index	Technetium-99 Effective Diffusion Coefficient (cm^2/s)	Technetium-99 Leachability Index
Dynamic	$4 \times 10^{-11} - 1 \times 10^{-10}$	$10.4 - 10.0$	$2 \times 10^{-9} - 8 \times 10^{-9}$	$8.7 - 8.1$
Static	$3 \times 10^{-12} - 7 \times 10^{-11}$	$11.5 - 10.2$	$2 \times 10^{-10} - 6 \times 10^{-9}$	$9.7 - 8.2$

reduce iodine species, and this reduced species may have a lower rate of diffusion than the oxidized species. For example, if the original iodine spike was in the form of iodate ions (IO_3^-), the reduction of this species coupled by oxidation of metallic iron would result in the formation of iodide ions (I^-). This redox reaction may be represented by:

$$IO_3^- + 3Fe^0 + 3H_2O = I^- + 3Fe^{2+} + 6OH \tag{3.5}$$

Therefore, if the original spike is in the form of iodate, the differing diffusion behavior of iodate and iodide species may be reflected in the observed differences in the leach rates. However, there are no data at present to confirm either the initial redox state of the iodine spike or the chemical species of iodine in the leachate.

The results from the static leach test (Figure 3.2) indicated that, in general, the leaching tendency of iodine was similar (except for specimen 3) to what was observed in dynamic leach tests; however, the overall cumulative leach fractions on average were lower than that of dynamic leach tests. Also, one of the specimens (specimen 3) cumulatively leached about four times more iodine than other three specimens. Because all the specimens were prepared at the same time, the anomalous leaching of iodine from specimen 3 may be due to the more porous nature and/or microcracks in this specimen. Also, when compared to the results of the dynamic leach test, there was no difference in iodine leachability between specimens with and without steel fibers.

The cumulative leaching data for technetium-99 is shown in Figures 3.3 and 3.4, and the Appendix. As a check, the leach fractions were calculated using both liquid scintillation counting (LSC) activity data and the mass measured by using ICP-MS. The cumulative leach fractions calculated by both these methods agreed well in all cases except for specimen 1. For this specimen, the LSC data consistently indicated about 20% higher leaching than the data obtained from the ICP-MS measurements. The dynamic leach test indicated that technetium-99 in these specimens had a greater leaching tendency than iodine-125. In these tests, technetium-99 appeared to leach rapidly during the first 5 days and leached at a significantly reduced rate for the remaining period. The leaching behavior of technetium-99 is similar to the leaching pattern of iodine-125 observed from the same cement specimens. There were no significant differences in cumulative leach fractions of technetium-99 between specimens with or without the addition of steel fibers, indicating that steel fibers did not cause any significant changes in the species of technetium as indicated by the redox reaction:

$$2TcO_4^- + 3Fe^0 + 4H^+ = 3Fe^{2+} + 2TcO_2 + 4OH^- \tag{3.6}$$

3.9
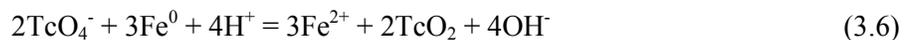
If reduction had occurred, the leaching would be lower because the very low solubility of TcO_2. The leaching data from the static tests also indicated that technetium-99 leaches to a greater degree than iodine-125 from the same set of specimens. As compared to all other specimens, specimen 3, which leached anomalously high fractions of iodine-125, also leached significantly higher fractions (about 5 times) of technetium-99. Such leaching behavior suggested that specimen 3, for some unknown reason, had distinctly different physical characteristics than the other specimens, most likely a more porous nature and/or microcracks that promoted a significantly higher rate of leaching for these two radionuclides.

Measured concentrations in both the dynamic and static leach tests indicated none of the specimens leached uranium (Figures 3.5 and 3.6). In fact, the concrete specimens adsorbed uranium from Hanford Site groundwater used in these experiments, which initially contained approximately 6.7 ppb (Table 3.2). Even though the total mass of uranium in each specimen exceeded the mass of uranium in contacting groundwater by more than two orders of magnitude, no uranium leaching was observed from any of the specimens. Therefore, these data indicated that the spiked uranium in the specimens was in a nonleachable, recalcitrant solid form and that the cement matrix had a strong affinity to adsorb and immobilize additional uranium from solution. Such uranium adsorption from groundwater by cement specimens has been observed previously by Serne et al. (1989). Overall, the cement specimens in static tests on average adsorbed 50% more uranium than specimens in the ANS tests. The higher adsorption observed in static tests can be explained on the basis of continual long contact of leach solutions (with fractional solution exchange) with the specimens. Comparatively, in dynamic leach tests the leach solutions are renewed frequently; therefore, the specimens are in contact with the leach solution for shorter times. The leach test pH also would likely affect the amount of uranium adsorbed. Uranium adsorption increases with pH and in static leach tests the amount of uranium adsorbed is higher because the pH conditions are higher than in dynamic tests.

3.4.2 Effective Diffusion Coefficients

The calculated average effective diffusion coefficients and the corresponding leachability indices are listed in Table 3.3. The results of the dynamic leach tests (ANS-16.1) indicated that the average D_{ei} for iodine-125 ranged from 3.59×10^{-11} to 7.77×10^{-11} cm^2/s, and the average D_{ec} ranged from 7.36×10^{-11} to 1.32×10^{-10} cm^2/s. Although the cumulative leach fractions from specimens with and without the steel fibers showed slight differences, there were no significant differences in the calculated average diffusion coefficients. In all cases, the calculated D_{ec} values were about twice as high the D_{ei} values. As discussed in Section 3.3, these differences can be attributed to the lack of conformity with the conditions imposed by the semi-infinite solid leaching formulation.

The static leach test data yielded average D_{ei} values for iodine-125 that ranged from 3.06×10^{-12} to 6.4×10^{-11} cm^2/s, and average D_{ec} values that ranged from 5.42×10^{-12} to 6.79×10^{-11} cm^2/s. Excluding the data from specimen 3, which exhibited anomalous leaching behavior, there were no significant differences in diffusion coefficient values calculated from the leaching of specimens with or without steel fibers. The data from the static tests yielded D_{ec} values that were about 50% higher the average D_{ei} values.

The effective diffusion coefficients for iodine-125 derived from the dynamic leach tests (ANS-16.1) are, on average, about an order of magnitude higher than the values calculated from the static leach tests. These differences can be attributed to the differences in the leaching regime between these tests. In dynamic leach tests, all contact solution is renewed at each sampling time, whereas in static tests, only about 15% of the contact solution is replaced. The dynamic leach tests subject the specimens to more aggressive leaching conditions; therefore, these tests yield higher effective diffusion coefficients (and higher leachability indices) than the values generated under the moderate leaching conditions encountered in the static tests.

The data from the dynamic leach tests on technetium-99 indicated that the average D_{ei} ranged from 1.61×10^{-9} to 3.69×10^{-9} cm^2/s, and the average D_{ec} ranged from 3.39×10^{-9} to 7.68×10^{-9} cm^2/s. No significant differences were found in average diffusion coefficients between specimens with or without steel fibers, indicating that if the redox reaction occurred, it did not cause measurable leaching differences between the specimens. The D_{ec} values for technetium-99 were about twice as high as the D_{ei} values, indicating that leaching of concrete specimens in this test did not meet all the requirements inherent in the semi-infinite solid leaching model.

The static test data for technetium, measured by LSC, resulted in average D_{ei} values that ranged from 2.4×10^{-10} to 5.81×10^{-9} cm^2/s, and average D_{ec} values that ranged from 4.3×10^{-10} to 4.25×10^{-9} cm^2/s. There were no significant differences between the diffusion coefficient values calculated from either the activity or mass measurements. Excluding the data from specimen 3, which exhibited anomalous leaching behavior, there were no significant differences in diffusion coefficient values calculated from the leaching of specimens with or without steel fibers. As in the case of iodine-125, the data from the static tests (except for specimen 3) resulted in calculated D_{ec} values that were about 50% higher the average D_{ei} values. Also, the more aggressive leaching regime used in the dynamic leach tests resulted in effective diffusion coefficients that were, on average, about an order of magnitude higher than the values calculated from the static leach tests.

These tests showed that iodine-125 in these concrete formulations was about two orders of magnitude less leachable than technetium-99. Iodine-125 in these cement specimens also appears to be significantly less leachable (three to four orders of magnitude) than iodine in some of the Hanford Site grout formulations studied by Serne et al. (1992a, b). These differences in iodine leachability can be attributed to a different concrete formulation used in these studies as compared to the Hanford Site grouts (which contained several waste types, higher waste loadings, and different grout formulations). Previous studies have shown that leaching of technetium-99 varies as a function of waste type, waste loading (mix ratio), grout fluid density, and amount of blast furnace slag in the blend (Serne et al. 1992a, b; Tallent et al. 1988). These factors can cause technetium-99 leachability to range over four to five orders of magnitude (leachability index ranging from ~7 to 12). The leachability index for technetium-99 in this study ranged from about 8.1 to 9.6, which is within the range of 7 to 12 observed for various types of grouts.

Based on the data obtained in these studies, a selected range of effective diffusion coefficients and corresponding leachability indices for iodine-125 and technetium-99 were chosen for use in performance assessment calculations (Table 3.4).

4.0   Soil-Soil and Concrete-Soil Half-Cell Diffusion Tests

Based on the analysis of previous data on the diffusion of iodide in a Hanford sediment (Mattigod et al. 1998),[a] test specimens were designed to measure diffusion coefficients of key contaminants (iodide, technetium-99, and uranium) in concrete and in representative soil under unsaturated conditions. The specimen dimensions, radionuclide spiking levels, and the sampling intervals to be used in these experiments were based on the analysis of diffusion data obtained by Crane et al. (1992) on concrete-soil half-cell systems. The half-cell diffusion experiments are described in the following sections.

4.1   Soil-Soil Diffusion Test

This experiment consisted of half cells (~4-cm diameter and ~39-cm long) of Trench 8 soil with the hot side (~18 to 21 cm long) sediment spiked with stable iodide, technetium-99, and uranium. The cold side (~20 to 22 cm long) contained the same soil unspiked. The Trench 8 soil is a medium coarse sand that was obtained from the sidewall of the W-5 burial ground located in the Hanford Site. The physical, chemical, and mineralogical properties of this soil has been previously characterized by Serne et al. (1993). Quantities of soil with appropriate moisture contents (~4% and ~7% by weight) were packed into plastic cylinders (~4.13-cm diameter) to form these half cells (Figure 4.1). The characteristics of these half cells including the dimensions, bulk densities, and moisture contents are listed in Table 4.1. The radionuclide spike concentrations in the hot side of the soil half cells are listed in Table 4.2. Before sampling, these plastic cylinders containing the soil-soil half cells were frozen with dry ice to facilitate the extrusion and slicing of low moisture soil cores. Sampling was conducted at 64- and 170-day
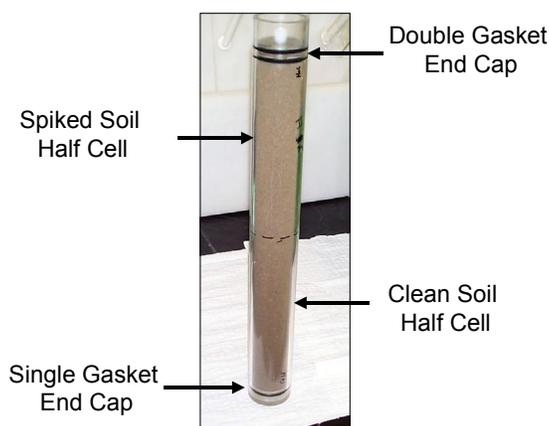
Figure 4.1. View of a Soil-Soil Diffusion Half Cell

(a) Mattigod, S.V., G. A. Whyatt, K. E. Schwab, P. F. A. Martin, and R. J. Serne. 1998. *"Diffusion and Leaching of Selected Radionuclides (Iodine-129, technetium-99, and uranium) through category 3 Waste Encasement Concrete and Soil Fill Material: Progress Report for FY 98"*, Letter Report Pacific Northwest National Laboratory, Richland, Washington.

Table 4.1. Characteristics of the Concrete-Soil and Soil-Soil Half Cells

Cell ID	Length of Concrete Half Cell (cm)	Length of Hot Soil Half Cell (cm)	Length of cold Soil Half Cell (cm)	Density of Concrete Half Cell (g/cm3)	Hot Side Soil Bulk Density (g/cm3)	Cold side Soil Bulk Density (g/cm3)	Soil Moisture Content (%)	Test Duration (days)
SS-I-7%		18.2	19.7		1.41	1.53	7.17	64
SS-II-7%		17.5	20.5		1.45	1.62	7.17	170
SS-III-4%		21.1	22.0		1.32	1.40	4.10	64
SS-IV-4%		18.0	20.7		1.50	1.53	4.10	170
CS-I-4%	4.3		19.6	2.23		1.41	4.10	64
CS-II-4%	4.2		19.5	2.21		1.42	4.10	169
CS-III-7%	4.2		20.9	2.25		1.42	7.17	64
CS-IV-7%	4.2		21.5	2.21		1.37	7.17	169
The diameter of all half-cells was 4.13 cm.								

Table 4.2. Spike Concentrations in the Hot Side of the Soil-Soil Half Cell

Spike	Half Cell With 4% Moisture Content	Half Cell With 7% Moisture Content
Stable I	574 µg/g	640 µg/g
^{99}Tc	10.6 nCi/g	14.8 nCi/g
U	0.56 ng/g	0.57 ng/g

intervals by freezing the cells in dry ice and 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 remainder of the half cell (Figures 4.2 and 4.3). The soil samples were weighed and extracted with either nitric acid or deionized distilled water, and the extracts were analyzed for iodide, technetium-99, and uranium using ICP-MS.
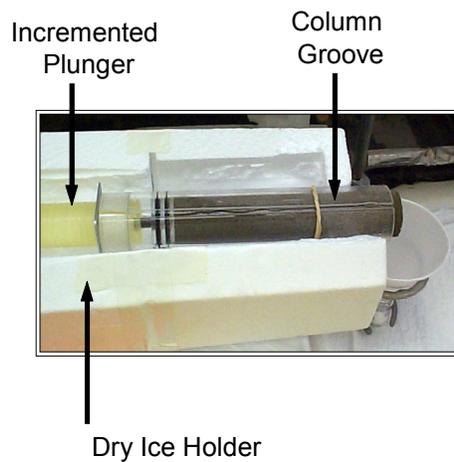
Figure 4.2. Mechanism Used for Sampling a Soil-Soil Diffusion Half Cell
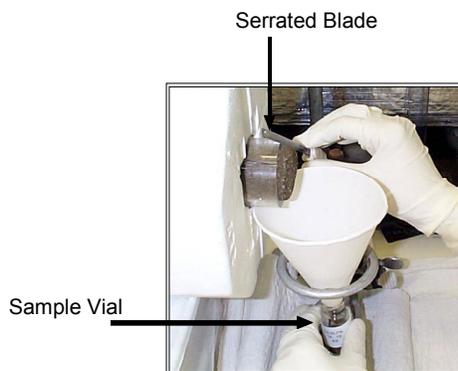
Figure 4.3. Sampling Soil from a Diffusion Half Cell

4.2   Concrete-Soil Diffusion Test

The objective of this test was to examine the rate of diffusion of key, long-lived, mobile contaminants in unsaturated Hanford sediment (~4% and ~7% moisture content by weight) in contact with a spiked concrete monolith. This experiment was conducted using a half cell of Trench 8 soil (~4-cm diameter and ~20-cm long) in contact with a concrete monolith (~4-cm diameter and ~4-cm long) spiked with iodine-125, stable iodine, technetium-99, and uranium (Table 2.7). The characteristics of these half cells including the dimensions, bulk densities, and moisture contents are listed in Table 4.1. The concrete monolith was prepared using concrete mixture composition #2 (Table 2.5). The radionuclides were first added to the water and then mixed into the dry ingredients. Sampling was conducted at 64- and 169-day intervals by freezing the cells in dry ice and 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 remainder of the half cell. The soil samples were weighed and extracted with either nitric acid or deionized distilled water, and the extracts were analyzed for stable iodide, technetium-99, and uranium using ICP-MS.

4.3   Diffusion Coefficient Calculations

The diffusivities in the soil were reduced 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/C_0), as a function of diffusion distance produced in a half-cell diffusion experiment to a linear plot. The slope (b) of this plot is then used to calculate the diffusivity (D) as $D = 1/(2b^2 t)$, where t is the sampling time. This approach has been used previously to determine diffusivity in half-cell diffusion experiments such as those by Brown et al. (1964) and by Lamar (1989).

In a diffusion test where one boundary can be represented by a constant concentration, the concentration profile that develops is one-half of the normal sigmoid curve produced in the half-cell diffusion experiment. Thus, to apply the probit transformation, the concentrations are normalized by

dividing by $2*C_i$, where C_i is the concentration at the constant concentration interface. This approach has been used to model diffusion from a non-depleting reservoir into asphalt (Martin et al. 1994).[a]

The configuration of concrete-soil experiments had the soil in a half-cell arrangement with a dissimilar material (hardened concrete) containing the radionuclide spike. In the case of diffusion occurring between two dissimilar media, one of which is spiked and both of which are semi-infinite in dimension from the interface, the concentration at the interface will quickly reach and remain at a constant concentration as the diffusion proceeds. For an explanation of why this occurs, refer to Crank (1975). Because of this result, the problem is mathematically the same as the case where a boundary is held at a constant concentration and the data can be normalized by dividing by $2*C_i$, where C_i is the concentration at the interface. However, because the concentration C_i at the interface of the two dissimilar materials is not known, the concentration in the soil slice nearest the interface is used to approximate this value. This approximation introduces some bias in the calculated diffusivity because the concentration profile averaged over the first soil slice is systematically lower than the concentration at the interface of the first soil slice with the spiked mortar. The extent of the error is estimated to be about 12% from one of Crane et al.'s (1992) concentration profiles. We assumed that the relative errors for the other tests were similar. This error magnitude is considered acceptable relative to the variance in the diffusivity values for all the tests.

For purposes of data reduction, the radionuclide diffusivity is defined by the equation:

$$J = - D_w \, dC_w/dx \tag{4.1}$$

where   J = flux of radionuclide at a given point
$\quad\quad$ D_w = the diffusivity of water-based radionuclide concentration
$\quad\quad$ C_w = the radionuclide concentration in the porewater.

Using this definition, and acknowledging that in the case of a two-phase system (water and soil) there will be insignificant amounts of radionuclides within the air phase of the unsaturated sediment, a mass balance can be performed over a small volume leading to the equation

$$dC_w/dt = D_w/\theta * (d^2C_w/dx^2) \tag{4.2}$$

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,

$$dC/dt = D * (d^2C/dx^2) \tag{4.3}$$

The diffusion coefficient, D_w, was calculated from D obtained from the probit plot based on concentrations in the porewater that must then be multiplied by θ.

(a) Martin, P. F., R. J. Serne, V. L Legore, C. W. Lindenmeier. 1994. *" Status Report on Ionic Diffusion Through Asphalt"*. Letter Report to Westinghouse Hanford Company. HGTP-93-0602-01. Pacific Northwest Laboratory, Richland, Washington.

From concrete-soil experiments, the diffusivity coefficients in concrete were calculated using soil diffusivity coefficients derived from probit plots. Also, a second set of concrete diffusivity coefficients was calculated by using soil diffusivity coefficients determined from probit plots of soil-soil half-cell experiments and the interfacial concentrations from the soil half cells of concrete-soil half-cell experiments.

Due to the difficulty involved in sampling the first 0.5-cm soil slice at the interface, the accuracy of concentration measurements in this soil slice is less reliable than the measurements made on other slices of the soil half cell. Because the calculated concrete diffusivity values are sensitive to the measured concentrations of the diffusing radionuclide in the soil at the soil-concrete interface, a second approach was used to calculate the diffusivity values. This profile-matching approach consisted of using calculated soil diffusivities for a radionuclide from the soil-soil half-cell experiment to calculate diffusion profiles for a range of assumed interface concentrations in the concrete-soil half-cell experiments. Based on the best qualitative matching of the actual concentration profile with the calculated diffusion profiles, the concentration of the radionuclide at the interface was estimated. This estimated interface concentration and soil diffusivity was then used to estimate a concrete diffusivity value required to maintain the esti-mated interface concentration in concrete.

4.4   Results and Discussion

The normalized concentration profiles for iodide, technetium-99, and the concentration profiles for uranium from soil-soil diffusion experiment are shown in Figures 4.4 through 4.8. The corresponding probit plots for iodide and technetium-99 are shown in Figures 4.9 – 4.14, and the results are summarized in Table 4.3.

The normalized concentration profiles for iodide and technetium-99 from the concrete-soil diffusion experiment are shown in Figures 4.15 through 4.17. The probit plots for iodide and technetium-99 are shown in Figures 4.18 – 4.22, and the results are summarized in Table 4.4. For most cases, the probit plots provided a very good data fit except in a few cases where there were too few data points (64-day technetium-99 data for ~4% of the half cell). The diffusivity coefficients in concrete calculated from the probit plots are listed in Table 4.4.
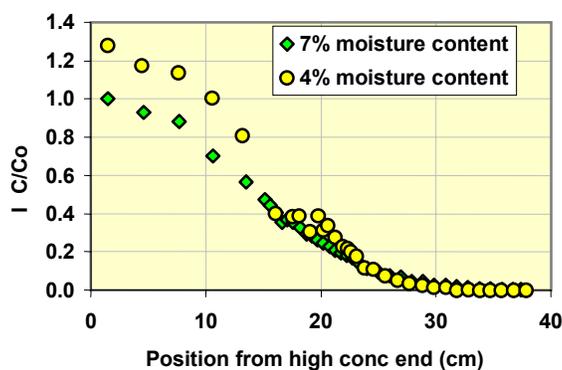
Figure 4.4. Normalized Concentration Profiles for Iodide in SS-IV-4% and SS-II-7%

4.5

Soil-Soil Half Cells (170-day sampling period)
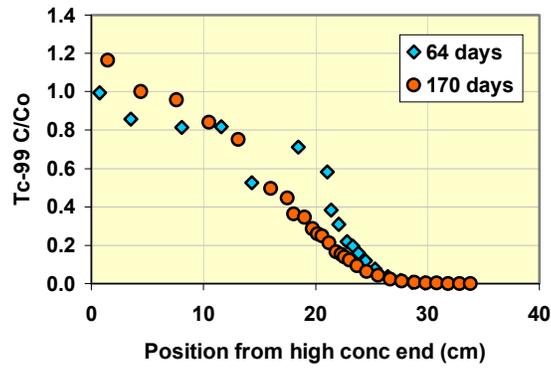
Figure 4.5. Normalized Concentration Profiles for Technetium-99 in SS-III-4% and SS-IV-4% Soil-Soil Half Cells (~4% moisture content)
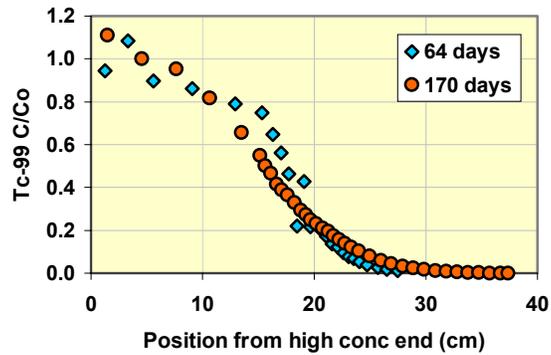
Figure 4.6. Normalized Concentration Profiles for Technetium-99 in SS-I-7% and SS-II-7% Soil-Soil Half Cells (~7% moisture content)
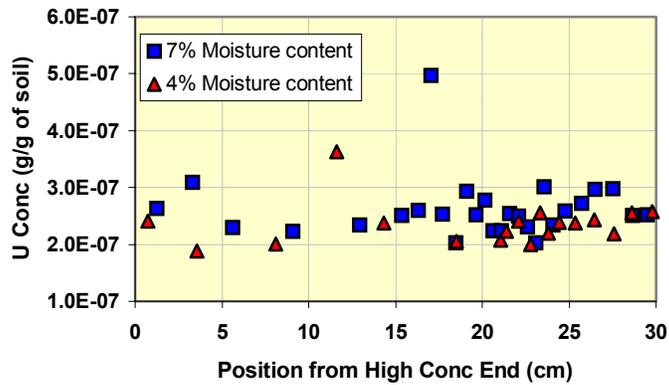
Figure 4.7. Uranium Concentrations in Soil Slices from SS-I-7% and SS-III-4% Soil-Soil Half Cells at the End of 64 Days
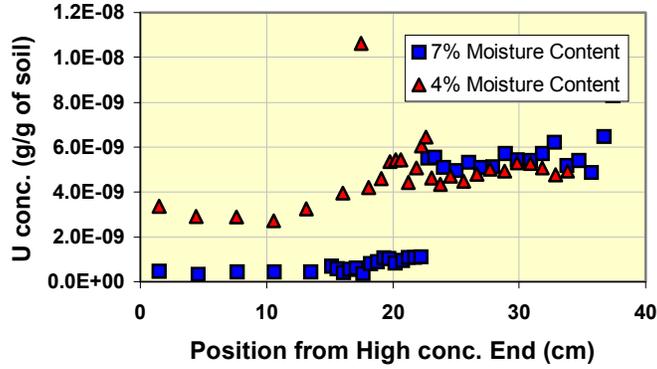
Figure 4.8. Uranium Concentrations in Soil Slices from SS-II-7% and SS-IV-4% Soil-Soil Half Cells at the End of 170 Days
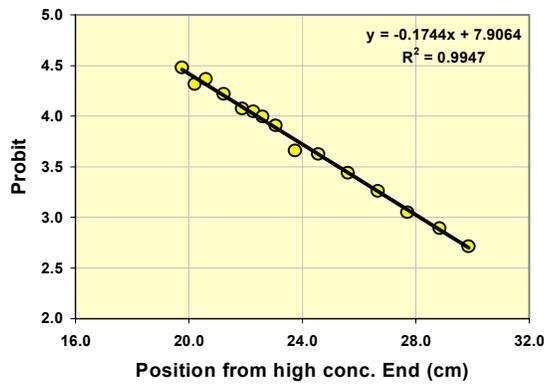
Figure 4.9. Probit Plot for Iodide Diffusion in SS-IV-4% Half Cell (~4% moisture content, 170-day sampling period)
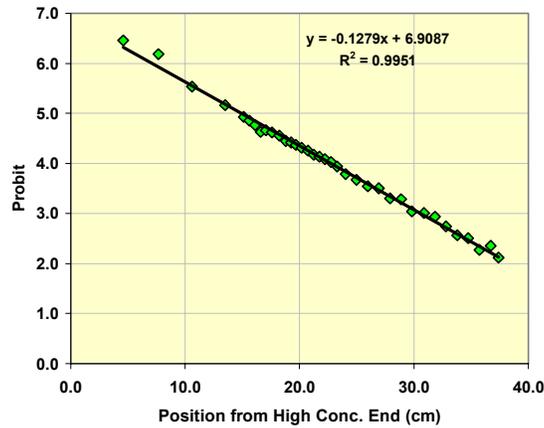
Figure 4.10. Probit Plot for Iodide Diffusion in SS-II-7% Half Cell (~7% moisture content, 170- day sampling period)

4.7
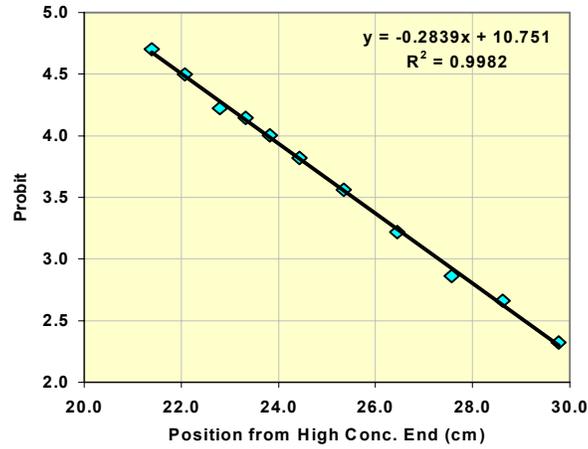
Figure 4.11. Probit Plot for Technetium-99 Diffusion in SS-III-4% Half Cell (~4% moisture content, 64-day sampling period)
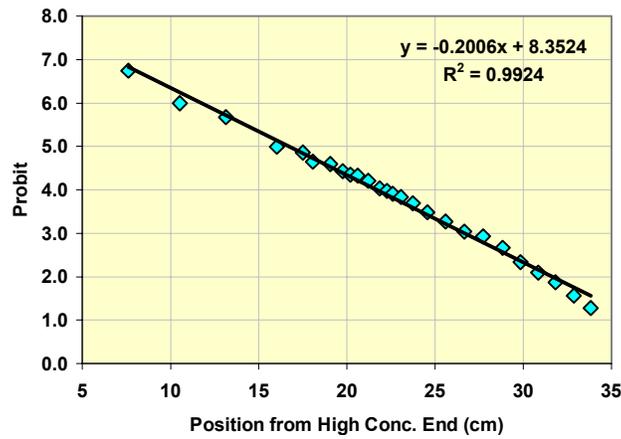
Figure 4.12. Probit Plot for Technetium-99 Diffusion in SS-IV-4% Half Cell (~4% moisture content, 170-day sampling period)
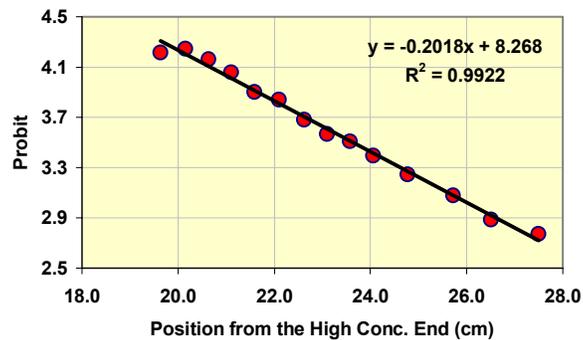
Figure 4.13. Probit Plot for Technetium-99 Diffusion in SS-I-7% Half Cell (~7% moisture content, 64-day sampling period)

4.8
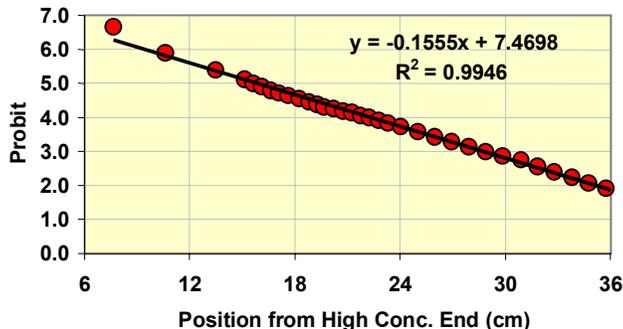
Figure 4.14. Probit Plot for Technetium-99 Diffusion in SS-II-7% Half Cell
(~7% moisture content, 170-day sampling period)

4.4.1   Soil-Soil Diffusion Test

The 64-day concentration profile for iodide could not be obtained because during the nitric acid extraction of the samples the iodide ions were oxidized to iodine, which was lost through volatilization. The 170-day normalized concentration profiles for iodide obtained from using deionized distilled water extraction showed well developed sigmoidal distributions in the soil-soil half cells at both moisture contents (Figure 4.4). Similarly, the 64- and 170-day normalized concentrations in the soil-soil half cells for technetium-99 also exhibited typical sigmoidal profiles (Figures 4.5 and 4.6). In contrast, the distribution of uranium concentrations showed that there was no measurable diffusion of uranium in these soil-soil half cells (Figure 4.7 and 4.8). The reason for this anomaly is that the Trench-8 soil contains about 2.5×10^{-7} g/g of nitric acid- extractable, and about 5×10^{-9} g/g of water-extractable, native uranium. Because the spike levels of uranium in the hot side were less than the native uranium concentrations (Table 4.2), diffusion of uranium did not occur in these soil-soil half cells.

For most cases, the probit plots provided a very good fit to the data for both sides of the half cells (Figures 4.9 through 4.14). However, in a few cases, the probit plots yielded noticeably different slopes on the spike side when compared to the slopes on the initially cold side. In such cases, the probit plots of the cold side data containing more closely spaced concentration measurements were used to calculate the diffusivity coefficients.

The calculated diffusivity coefficients for iodide were 7.03×10^{-8} cm^2/s and 2.42×10^{-7} cm^2/s for soils at 4% and 7% moisture contents, respectively (see Table 4.3). These values are similar in magnitude to the soil diffusivity values of $2.51 \pm 1.60 \times 10^{-8}$ cm^2/s (~4% moisture content) and $1.23 \pm 0.73 \times 10^{-7}$ cm^2/s (~7% moisture content) calculated from a previous set of data (Mattigod et al. 1998)[1]. Both these data sets indicated that iodide diffusivity is a function of soil moisture content and is about an order of magnitude slower at lower moisture content (~4% by weight). The diffusivity coefficients calculated for technetium-99 (see Table 4.3) were $5.89 \pm 0.80 \times 10^{-8}$ cm^2/s (~4% moisture content) and $2.04 \pm 0.57 \times 10^{-7}$ cm^2/s (~7% moisture content), respectively. These values indicated that soil moisture content has a significant impact on technetium-99 diffusivity because at lower moisture content (~4%) the ion diffusion was about an order of magnitude lower than values obtained at higher moisture content (~7%). The diffusivity

Table 4.3. Calculated Soil Diffusion Parameters for Iodide and Technetium-99 from Soil-Soil Half-Cell Experiments

Cell No	Diffusing Component	Sampling Time (Days)	Sampling Time (s)	Gravimetric Moisture Content (g/g of dry soil)	Initial Bulk Density (g/cm^3)	Volumetric Moisture Content (cm^3/ cm^3 of soil)	Probit Plot Slope	Homogeneous Media-Based Diffusivity Estimates (cm^2/s)	Diffusivity for flux across a boundary (cm^2/s)
SS-IV-4%	I	170	1.47 x 10^7	0.0410	1.53	0.0629	0.1744	1.12 x 10^{-6}	7.03 x 10^{-8} [a]
SS-II-7%	I	170	1.47 x 10^7	0.0717	1.62	0.1164	0.1279	2.08 x 10^{-6}	2.42 x 10^{-7} [a]
SS-III-4%	Tc-99	64	5.53 x 10^6	0.0410	1.40	0.0575	0.2839	1.12 x 10^{-6}	6.45 x 10^{-8} [b]
SS-IV-4%	Tc-99	170	1.47 x 10^7	0.0410	1.53	0.0629	0.2006	8.46 x 10^{-7}	5.32 x 10^{-8} [b]
SS-I-7%	Tc-99	64	5.53 x 10^6	0.0717	1.53	0.1099	0.2018	2.22 x 10^{-6}	2.44 x 10^{-7} [b]
SS-II-7%	Tc-99	170	1.47 x 10^7	0.0717	1.62	0.1164	0.1555	1.41 x 10^{-6}	1.64 x 10^{-7} [a]

~~(a)~~(a) Calculated from fitting cold-side diffusion profile.
(b) Calculated from both hot- and cold-side diffusion profiles.
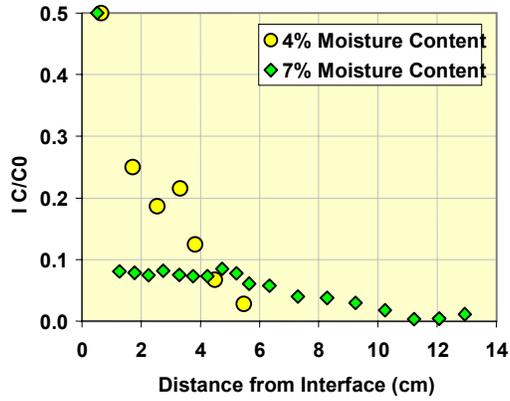
Figure 4.15. Normalized Concentration Profiles for Iodide in CS-II-4% and CS-IV-7% Concrete-Soil Half Cells (169-day sampling period)
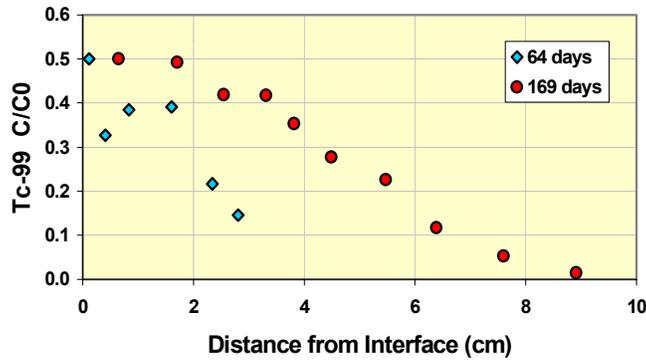
Figure 4.16. Normalized Concentration Profiles for Technetium-99 in CS-I-4% and CS-II-4% Concrete-Soil Half Cells (~4% moisture content)
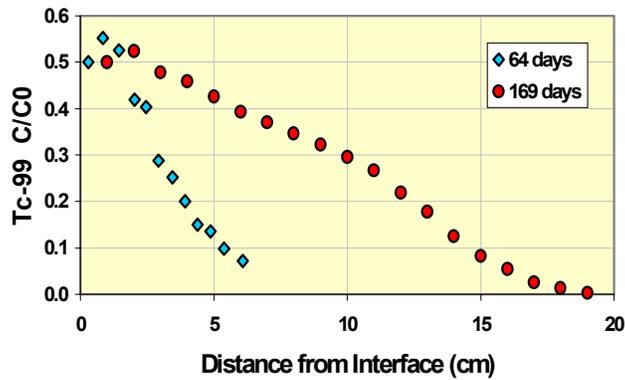
Figure 4.17. Normalized Concentration Profiles for Technetium-99 in CS-III-7% and CS-IV-7% Concrete-Soil Half Cells (~7% moisture content)
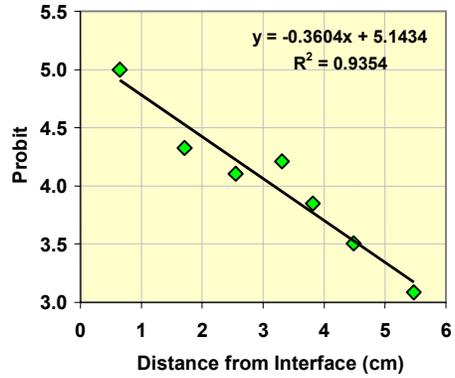
Figure 4.18. Probit Plot for Iodide Diffusion in CS-II-4% Concrete-Soil Half Cell
(~4% moisture content, 169-day sampling period)
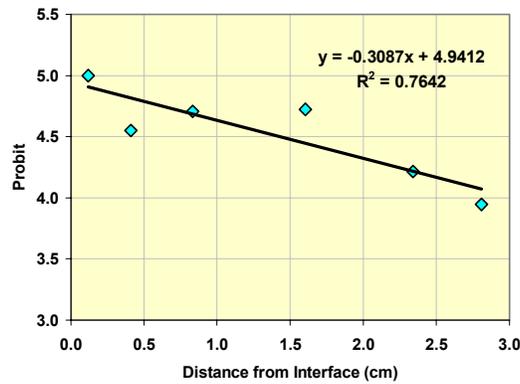
Figure 4.19. Probit Plot for Technetium-99 Diffusion in CS-I-4% Concrete-Soil Half Cell
(~4% moisture content, 64-day sampling period)
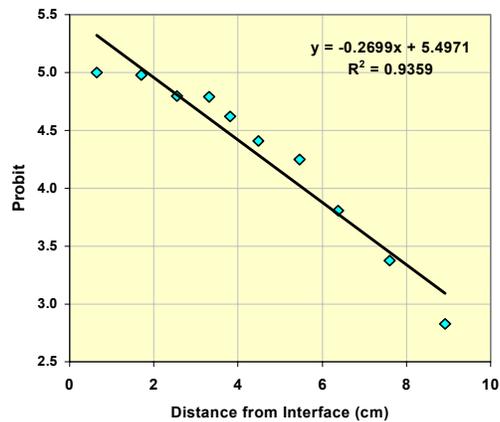
Figure 4.20. Probit Plot for Technetium-99 Diffusion in CS-II-4% Concrete-Soil Half Cell
(~4% moisture content, 169-day sampling period)

4.12
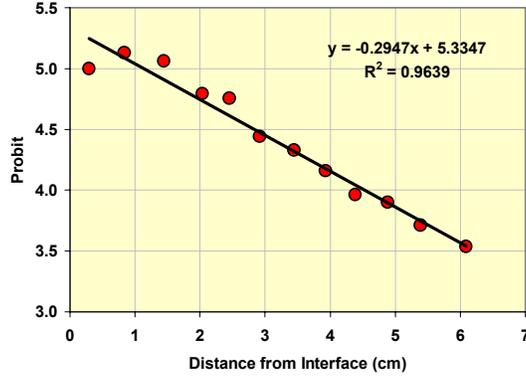
Figure 4.21. Probit Plot for Technetium-99 Diffusion in CS-III-7% Concrete-Soil Half Cell (~7% moisture content, 64-day sampling period)
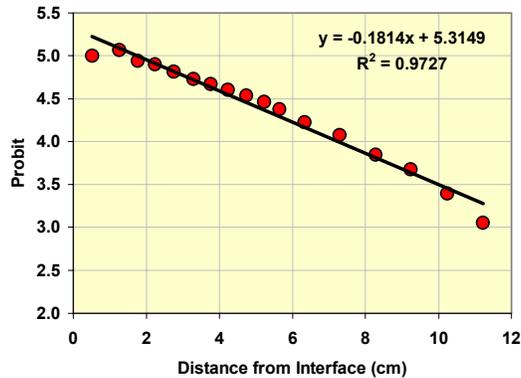
Figure 4.22. Probit Plot for Technetium-99 Diffusion in CS-IV-7% Concrete-Soil Half Cell (~7% moisture content, 169-day sampling period)

values obtained from these experiments for iodide and technetium-99 are similar in magnitude at each water content, indicating that these ions have similar diffusion mechanisms in unsaturated coarse textured soils.

4.4.2 Concrete-Soil Diffusion Test

The normalized concentration profiles for iodide and technetium-99 are shown in Figures 4.15 through 4.17. As indicated earlier, the iodide concentrations for the 64-day sampling period could not be determined due to oxidation of iodide to iodine during nitric acid extraction and the loss of iodine through volatilization. For some unknown reason, the 169-day normalized profile for iodide in the soil half cell (at 7% moisture content) exhibited anomalous concentrations in the first 4 cm of the interfacial region (Figure 4.15). In contrast, the 64- and 169-day data for technetium-99 showed predictable diffusion profiles that indicated relatively constant interfacial concentrations that were independent of sampling times. As discussed previously, in the case of soil-soil half cells, the distribution of uranium concentrations

Table 4.4. Calculated Concrete Diffusion Parameters for Iodide and Technetium-99 from Concrete-Soil Half-Cell Experiments

Cell No	Diffusing Component	Sampling Time (Days)	Sampling Time (s)	Probit Plot Slope	Soil Diffusivity Estimates From Concrete-Soil Experiments (cm²/s)	Soil Diffusivity Values From Soil-Soil Experiments (cm²/ s)	Initial Concentrations in Concrete (g/cm³)	Soil Interface Concentrations (g/cm³)	Ratio Volume Moisture Content (Concrete/Soil)	Concrete Diffusivity From Concrete-Soil Half-Cell Data (cm²/ s)	Concrete Diffusivity Calculations From Soil-Soil Half-Cell Data (cm²/ s)
CS-II-4%	I	169	1.46×10^7	0.3604	2.64×10^{-7}	1.12×10^{-6}	1.01×10^{-3}	1.74×10^{-7}	0.3963	7.90×10^{-15}	3.35×10^{-14}
CS-IV-7%	I	169	1.46×10^7	(a)	--	2.08×10^{-6}	1.01×10^{-3}	--	--	(a)	--
CS-I-4%	Tc-99	64	5.53×10^6	0.3087	9.49×10^{-7}	1.12×10^{-6}	2.99×10^{-6}	7.27×10^{-9}	0.3900	5.70×10^{-12}	6.74×10^{-12}
CS-II-4%	Tc-99	169	1.46×10^7	0.2699	4.70×10^{-7}	8.46×10^{-7}	2.96×10^{-6}	1.80×10^{-9}	0.3963	1.75×10^{-13}	3.14×10^{-13}
CS-III-7%	Tc-99	64	5.53×10^6	0.2947	1.04×10^{-6}	2.22×10^{-6}	3.01×10^{-6}	1.32×10^{-8}	0.6808	2.04×10^{-11}	4.34×10^{-11}
CS-IV-7%	Tc-99	169	1.46×10^7	0.1814	1.04×10^{-6}	1.41×10^{-6}	2.96×10^{-6}	6.63×10^{-9}	0.6687	5.26×10^{-12}	7.11×10^{-12}
(a) Not calculated due to poor data fit.											

showed that there was no measurable diffusion of uranium due to the inherent extractable uranium in Trench 8 soil (about 2.5 x 10^{-7} g/g of nitric acid-extractable, and about 5 x 10^{-9} g/g of water- extractable native uranium).

The probit plots for iodide and technetium-99 are shown in Figures 4.18 through 4.22, and the results are summarized in Table 4.4. For most cases, the probit plots provided a very good data fit except in a few cases where there were too few data points (64-day technetium-99 data for ~4% of the half cell). The diffusivity coefficients in concrete calculated from the probit plots are listed in Table 4.4. Additionally, the table also lists a second set of concrete diffusivity values calculated from soil diffusivity coefficients determined from soil-soil half-cell experiments and the interfacial concentrations from the soil half cells of concrete-soil half-cell experiments. The data showed that the concentrations in the first slice near the interface were consistently lower than in the second slice. Such anomalous concentrations at the interface were due to either the interface sampling problems and/or the lower moisture content of the soil near the interface.

The results of the profile-matching approach are shown in Figures 4.23 through 4.28, and the calculated diffusivities are listed in Table 4.5. Some of the data for iodide (Figure 4.23) and technetium-99 (Figure 4.25) showed a poor fit with calculated concentration profiles due to large scatter among a limited number of data points. Other concentration data that showed a relatively fair to good fit with calculated concentration profiles were used to estimate the interfacial concentrations and concrete diffusivity values. The concrete diffusivity values calculated using both the approaches are summarized in Table 4.6.

The concrete diffusivity values for iodide ranged from 2.07 x 10^{-14} cm^2/s (~4% soil moisture content) to 1.31 x 10^{-12} cm^2/s (7% soil moisture content), indicating that under unsaturated soil conditions, a small change (~3% change) in moisture content results in about a two orders of magnitude increase in diffusivity. The concrete diffusivity of technetium-99 calculated for the 64- day sampling period ranged from 6.22 x 10^{-12} cm^2/s (~4% soil moisture content) to 4.24 x 10^{-11} cm^2/s (7% soil moisture content), and
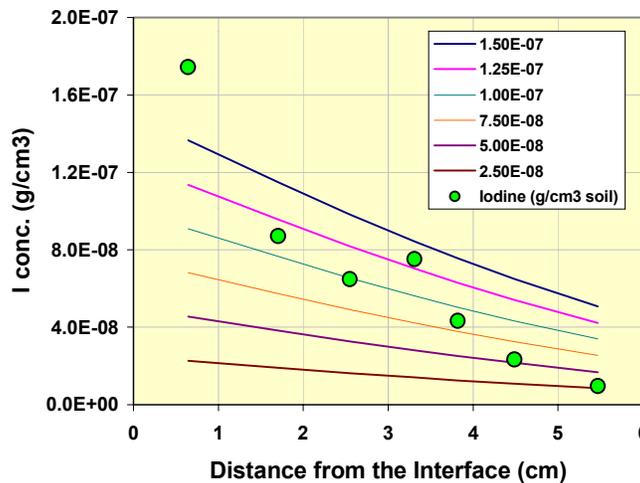
Figure 4.23. Calculated and Measured Concentration Profiles for Iodide in CS-II-4% Concrete-Soil Half Cells (~4% moisture content, 169-day sampling period)

4.15
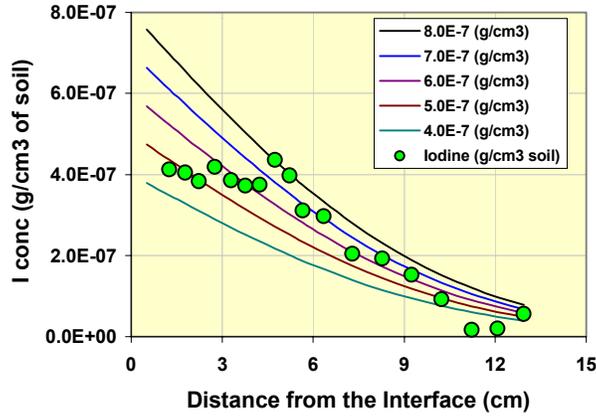
Figure 4.24. Calculated and Measured Concentration Profiles for Iodide in CS-IV-7% Concrete-Soil Half Cells (~7% moisture content, 169-day sampling period)
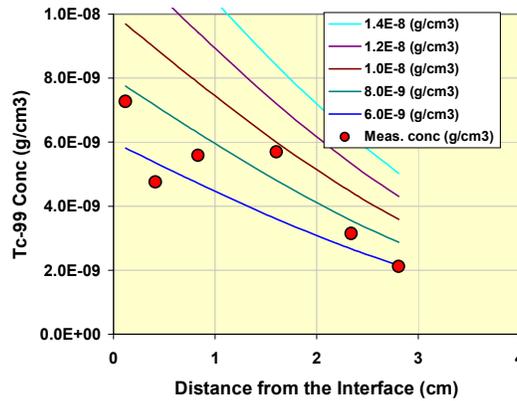
Figure 4.25. Calculated and Measured Concentration Profiles for Technetium-99 in CS-I-4% Concrete-Soil Half Cells (~4% moisture content, 64-day sampling period)
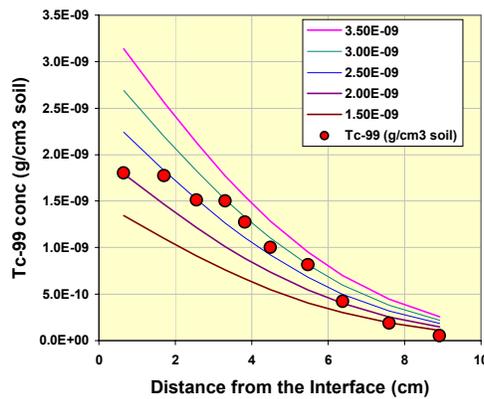

Figure 4.26. Calculated and Measured Concentration Profiles for Technetium-99 in CS-II-4% Concrete-Soil Half Cells (~4% moisture content, 169-day sampling period)

4.16
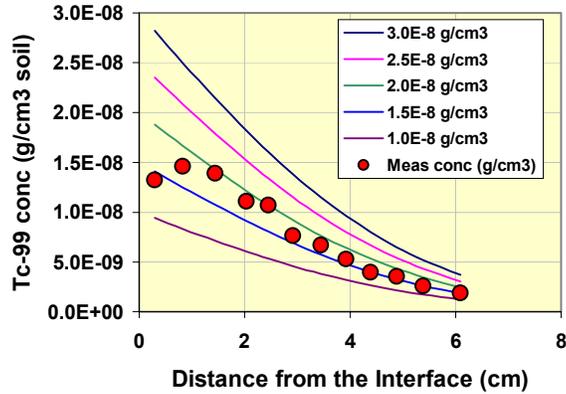
Figure 4.27. Calculated and Measured Concentration Profiles for Technetium-99 in CS-III-7% Concrete-Soil Half Cells (~7% moisture content, 64-day sampling period)
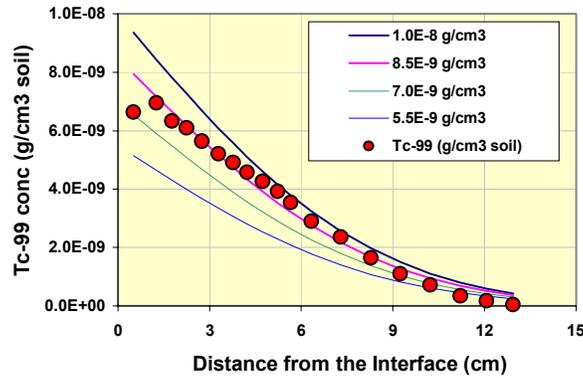
Figure 4.28. Calculated and Measured Concentration Profiles for Technetium-99 in CS-IV-7% Concrete-Soil Half Cells (~7% moisture content, 169 day-sampling period)

for the 169-day sampling period ranged from 4.54 x 10^{-13} cm^2/s (~4% soil moisture content) to 8.02 x 10^{-12} cm^2/s (7% soil moisture content). These ranges of values indicated that

1) 1. At a fixed moisture content, technetium-99 transport out of concrete slowed by more than an order of magnitude between the two sampling periods (105 days)

2) 2. For each sampling period, the diffusivity of technetium-99 at higher moisture content (~7%) was about an order of magnitude higher than diffusivity at lower moisture content (~4%).

3) 3. For the same diffusion period (169 days), at both soil moisture contents, iodide seemed to diffuse more slowly than technetium-99.

4. At lower moisture content (~4%), iodide diffused about 20 times more slowly than technetium-99, whereas at higher moisture content (~7%), iodide diffused only about 6 times slower than technetium-99.

Table 4.5. Concrete Diffusion Parameters for Iodide and Technetium-99 Calculated from the Concentration Profile Matching Technique (Concrete-Soil Half-Cell Experiments)

Cell No	Diffusing Component	Sampling Time (Days)	Sampling Time (s)	Volume Moisture Content of Soil (cm³/ cm³)	Volume Moisture Content of Concrete (cm³/ cm³)	Ratio Volume Moisture Content (concrete/soil)	Initial Concentrations in Concrete (g/cm³)	Estimated Soil Interface concentrations (g/cm³)	170-Day Soil Diffusivity From Soil-Soil Half-Cell Data (cm²/ s)	Concrete Diffusivity (cm²/ s)
CS-II-4%	I	169	1.46×10^7	0.0583	0.1472	0.3961	1.01×10^{-3}	(a)	1.12×10^{-6}	--
CS-IV-7%	I	169	1.46×10^7	0.0984	0.1472	0.6685	1.01×10^{-3}	8.00×10^{-7}	2.08×10^{-6}	1.31×10^{-12}
CS-I-4%	Tc-99	64	5.53×10^6	0.0579	0.1785	0.3901	2.99×10^{-6}	(a)	8.46×10^{-7}	--
CS-II-4%	Tc-99	169	1.46×10^7	0.0583	0.1472	0.3961	2.96×10^{-6}	3.00×10^{-9}	8.46×10^{-7}	8.73×10^{-13}
CS-III-7%	Tc-99	64	5.53×10^6	0.1020	0.1499	0.6805	3.01×10^{-6}	2.00×10^{-8}	1.41×10^{-6}	6.35×10^{-11}
CS-IV-7%	Tc-99	169	1.46×10^7	0.0984	0.1473	0.6685	2.96×10^{-6}	8.50×10^{-9}	1.41×10^{-6}	1.17×10^{-11}
(a) Not estimated due to poor data fit.										

Table 4.6. Concrete Diffusivity Coefficients for Iodide and Technetium-99

Diffusing Component	~Moisture Content (%)	Sampling Time (Days)	Diffusivity in Concrete (cm^2/s)			
			Probit Method[a] (Concrete-Soil Half-Cell Data)	Probit Method [b] (Soil-Soil Half-Cell Data)	Profile Matching[c]	Average
I	4	169	7.90×10^{-15}	3.35×10^{-14}	--	$2.07 \pm 1.81 \times 10^{-14}$
I	7	169	--	--	1.31×10^{-12}	1.31×10^{-12}
Tc-99	4	64	5.70×10^{-12}	6.74×10^{-12}	--	$6.22 \pm 0.74 \times 10^{-12}$
Tc-99	4	169	1.75×10^{-13}	3.14×10^{-13}	8.73×10^{-13}	$4.54 \pm 3.69 \times 10^{-13}$
Tc-99	7	64	2.04×10^{-11}	4.34×10^{-11}	6.35×10^{-11}	$4.24 \pm 2.16 \times 10^{-11}$
Tc-99	7	169	5.26×10^{-12}	7.11×10^{-12}	1.17×10^{-11}	$8.02 \pm 3.32 \times 10^{-12}$

(a)(a)   Calculated from the soil diffusivity values from probit plots of concrete-soil half-cell experiments and measured interface concentrations.

(b)(b)   Calculated from soil diffusivity values from probit plots of soil-soil half-cell experiments and measured interface concentrations from concrete-soil half-cell experiments.

(c)   Calculated from interfacial concentrations derived from matching concentration profiles from concrete-soil half-cell experiments with calculated concentration profiles from 170-day soil diffusivities calculated from soil-soil half-cell experiments.

Using these data, a range of concrete diffusivity values for iodide and technetium-99 can be selected for use in performance assessment calculations (Table 4.7)

Table 4.7. Range of Diffusivity Coefficients for Concrete in Contact with Unsaturated Hanford Soil

Diffusing Component	Moisture Content of Soil in Contact With concrete (%)	Diffusivity in Concrete (cm^2/s)
Iodide	4	8×10^{-15} - 3×10^{-14}
Iodide	7	1×10^{-12}
Technetium-99	4	$2 \times 10^{-13} – 7 \times 10^{-12}$
Technetium-99	7	$5 \times 10^{-12} – 6 \times 10^{-11}$

5.0   Conclusions

An assessment of long-term performance of Category 3 waste-enclosing cement grouts requires data about the leachability/diffusion of radionuclide species (iodine-129, technetium-99, and uranium) when the waste forms come in contact with groundwater. Leachability data were collected by conducting dynamic (ANS-16.1) and static leach tests on radionuclide-containing cement specimens. The diffusivity of radionuclides in soil and concrete media was collected by conducting soil-soil and concrete-soil half-cell experiments. These data indicated that

- Under dynamic leaching conditions, iodine-125 leached rapidly during the first 5 days. Under static leaching conditions, the leaching behavior of iodine-125 was similar to what was observed in dynamic tests except that the overall cumulative leach fractions were, on average, lower than that of the dynamic leach (ANS) tests. The addition of steel fibers to concrete (4% by mass) did not significantly influence the leachability of iodine.

- Effective diffusion coefficients for iodine-125 under dynamic leaching conditions (4×10^{-11} to 1×10^{-10} cm^2/s) were about an order of magnitude higher than values measured under static leaching conditions (3×10^{-12} to 7×10^{-11} cm^2/s).

- The leaching behavior of technetium-99 is similar to the leaching pattern of iodine-125 observed from the same cement specimens. There were no differences in leachability between specimens with and without steel fibers, which indicated that steel fibers did not cause any significant changes in the redox state of technetium-99.

- Effective diffusion coefficients for technetium-99 under dynamic leaching conditions (2×10^{-9} to 8×10^{-9} cm^2/s) were about an order of magnitude higher than diffusion coefficients obtained under static leaching conditions (2×10^{-10} to 6×10^{-9} cm^2/s).

- Iodine-125 in these concrete formulations was about two orders of magnitude less leachable than technetium-99.

- Uranium in concrete specimens was in a nonleachable, recalcitrant solid form, and the cement matrix had a strong affinity to adsorb and immobilize additional uranium from contacting solution containing very low concentrations of uranium (6.7 ppb).

- The soil diffusivity coefficients for iodine-125 were 7.03×10^{-8} cm^2/s and 2.42×10^{-7} cm^2/s for soils at 4% and 7% moisture contents, respectively. Iodine-125 diffusivity in soil is a function of moisture content and is about an order of magnitude slower at a lower moisture content.

- The soil diffusivity coefficients for technetium-99 were $5.89\pm0.80 \times 10^{-8}$ cm^2/s (at ~4% moisture content) and $2.04\pm0.57 \times 10^{-7}$ cm^2/s (at ~7% moisture content), respectively. The diffusivity of technetium-99 at a lower moisture content (~4%) is about an order of magnitude lower than values at a higher moisture content (~7%).

- The soil diffusivity of iodide and technetium-99 were similar in magnitude at both water contents (4% and 7% by mass), indicating that these ions have similar diffusion mechanisms in unsaturated coarse-textured Hanford soil.

- The diffusivity of iodide in concrete ranged from 2.07×10^{-14} cm^2/s (~4% soil moisture content) to 1.31×10^{-12} cm^2/s (7% soil moisture content), indicating that under unsaturated soil moisture conditions, iodide diffusivity is highly sensitive to changing soil moisture conditions (~3% change in moisture content results in about two orders of magnitude increase in diffusivity).

- The diffusivity of technetium-99 in concrete for the initial (64-day) sampling period ranged from 6.22×10^{-12} cm^2/s (~4% soil moisture content) to 4.24×10^{-11} cm^2/s (7% soil moisture content), and for the 169-day sampling period ranged from 4.54×10^{-13} cm^2/s (~4% soil moisture content) to 8.02×10^{-12} cm^2/s (7% soil moisture content). These concrete diffusivity values indicated that 1) with increasing time (at a fixed soil moisture content), technetium-99 transport out of concrete will be significantly retarded (over an order of magnitude retardation in 105 days), and 2) technetium-99 will diffuse at a higher rate (about an order of magnitude) at a higher soil moisture content (~7%) than at a lower soil moisture content (~4%).

- Iodine-125 in concrete diffuses more slowly than technetium-99. At a lower soil moisture content (~4%), iodide diffused about 20 times more slowly than technetium-99, and at a higher soil moisture content (~7%) iodide in concrete diffused about 6 times slower than technetium-99.

6.0   References

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Appendix

Leaching and Adsorption Data

Appendix

Leaching and Adsorption Data

Table A.1. ANS Leach Test: ^{125}I Leaching Data for Specimen 1 (Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	5.91E-03	5.91E-03	6.55E-10	6.55E-10
2	0.21	0.29	1.91E-03	7.81E-03	9.48E-11	3.36E-10
3	0.77	1.06	9.48E-04	8.76E-03	5.96E-12	1.16E-10
4	0.94	2.00	3.61E-04	9.12E-03	1.43E-12	6.67E-11
5	1.00	3.00	5.40E-04	9.66E-03	4.63E-12	4.99E-11
6	1.00	4.00	5.16E-04	1.02E-02	5.95E-12	4.15E-11
7	1.00	5.00	4.13E-04	1.06E-02	4.91E-12	3.60E-11
8	13.99	18.99	7.54E-04	1.13E-02	2.03E-13	1.09E-11
9	29.94	48.93	6.73E-04	1.20E-02	1.04E-13	4.73E-12
10	42.99	91.92	4.18E-03	1.62E-02	4.17E-12	4.58E-12

Table A.2. ANS Leach Test: ^{99}Tc Leaching Data (LCS Data) for Specimen 1 (Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	4.25E-02	4.98E-01	3.39E-08	3.39E-08
2	0.21	0.29	9.54E-03	4.62E-02	2.38E-09	1.49E-08
3	0.77	1.06	3.28E-03	4.24E-03	7.13E-11	4.61E-09
4	0.94	2.00	2.19E-03	2.34E-03	5.24E-11	2.65E-09
5	1.00	3.00	2.64E-03	2.64E-03	1.11E-10	1.94E-09
6	1.00	4.00	2.77E-03	2.77E-03	1.71E-10	1.59E-09
7	1.00	5.00	2.55E-03	2.55E-03	1.86E-10	1.38E-09
8	13.99	18.99	2.15E-03	1.54E-04	1.65E-12	3.86E-10
9	29.94	48.93	1.13E-03	3.78E-05	2.95E-13	1.55E-10
10	42.99	91.92	1.22E-03	2.85E-05	3.58E-13	8.55E-11

Table A.3. ANS Leach Test: ^{99}Tc Leaching Data (ICP-MS Data) for Specimen 1 Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	4.28E-02	5.02E-01	3.45E-08	3.45E-08
2	0.21	0.29	6.96E-03	3.37E-02	1.26E-09	1.36E-08
3	0.77	1.06	3.05E-03	3.95E-03	6.18E-11	4.21E-09
4	0.94	2.00	1.56E-03	1.67E-03	2.66E-11	2.37E-09
5	1.00	3.00	9.25E-04	9.25E-04	1.36E-11	1.64E-09
6	1.00	4.00	5.48E-04	5.48E-04	6.70E-12	1.25E-09
8	13.99	18.99	9.89E-04	7.07E-05	3.48E-13	1.00E-09
9	29.94	48.93	6.40E-05	2.14E-06	9.45E-16	2.73E-10
10	42.99	91.92	4.27E-05	9.93E-07	4.34E-16	1.06E-10

Table A.4. ANS Leach Test: U Adsorption Data (ICP-MS Data) for Specimen 1 (Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Adsorbed (ng)	Cum Adsorbed (ng)
1	0.09	0.09	338.1	338.1
2	0.21	0.29	323.5	662
3	0.77	1.06	239.8	901
4	0.94	2.00	208.6	1110
5	1.00	3.00	205.6	1316
6	1.00	4.00	185.3	1501
7	1.00	5.00	204.5	1705
8	13.99	18.99	231.9	1937
9	29.94	48.93	153.7	2091
10	42.99	91.92	221.4	2312

Table A.5. ANS Leach Test: ^{125}I Leaching Data for Specimen 2 (Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	3.90E-03	4.56E-02	2.8E-10	2.8E-10
2	0.21	0.29	1.57E-03	7.61E-03	6.4E-11	1.6E-10
3	0.77	1.06	3.56E-04	4.61E-04	8.3E-13	5.1E-11
4	0.94	2.00	4.75E-04	5.07E-04	2.4E-12	3.1E-11
5	1.00	3.00	2.43E-04	2.43E-04	9.3E-13	2.3E-11
6	1.00	4.00	3.13E-04	3.13E-04	2.2E-12	1.9E-11
7	1.00	5.00	1.83E-04	1.83E-04	9.5E-13	1.6E-11
8	13.99	18.99	6.53E-04	4.67E-05	1.5E-13	4.9E-12
9	29.94	48.93	3.28E-04	1.10E-05	2.5E-14	2.1E-12
10	42.99	91.92	4.90E-03	1.14E-04	5.7E-12	2.9E-12

Table A.6. ANS Leach Test: ^{99}Tc Leaching Data (LCS Data) for Specimen 2 (Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	2.76E-02	3.23E-01	1.41E-08	1.41E-08
2	0.21	0.29	7.93E-03	3.85E-02	1.63E-09	6.87E-09
3	0.77	1.06	2.76E-03	3.58E-03	5.02E-11	2.19E-09
4	0.94	2.00	2.57E-03	2.75E-03	7.19E-11	1.32E-09
5	1.00	3.00	2.01E-03	2.01E-03	6.37E-11	9.72E-10
6	1.00	4.00	1.64E-03	1.64E-03	5.98E-11	7.86E-10
7	1.00	5.00	1.53E-03	1.53E-03	6.65E-11	6.73E-10
8	13.99	18.99	2.07E-03	1.48E-04	1.51E-12	1.94E-10
9	29.94	48.93	1.97E-03	6.59E-05	8.88E-13	8.14E-11
10	42.99	91.92	1.28E-03	2.97E-05	3.86E-13	4.56E-11

Table A.7. ANS Leach Test: U Adsorption Data (ICP-MS Data) for Specimen 2 (Without Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Adsorbed (ng)	Cum Adsorbed (ng)
1	0.09	0.09	370.1	370
2	0.21	0.29	351.8	722
3	0.77	1.06	182.1	904
4	0.94	2.00	181.5	1085
5	1.00	3.00	166.9	1252
6	1.00	4.00	204.6	1457
7	1.00	5.00	171.9	1629
8	13.99	18.99	195.8	1825
9	29.94	48.93	180.1	2005
10	42.99	91.92	143.7	2149

Table A.8. ANS Leach Test: ^{125}I Leaching Data for Specimen 6 (With Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	4.92E-03	5.71E-02	4.63E-10	4.63E-10
2	0.21	0.29	4.89E-04	2.37E-03	6.43E-12	1.65E-10
3	0.77	1.07	7.48E-04	9.67E-04	3.81E-12	5.85E-11
4	0.94	2.00	4.75E-04	5.07E-04	2.54E-12	3.62E-11
5	1.00	3.00	5.39E-04	5.39E-04	4.74E-12	2.82E-11
6	1.00	4.00	4.38E-04	4.38E-04	4.40E-12	2.38E-11
7	1.00	5.00	4.38E-04	4.38E-04	5.68E-12	2.13E-11
8	13.99	18.99	7.48E-04	5.35E-05	2.05E-13	6.71E-12
9	29.94	48.93	5.83E-04	1.95E-05	8.04E-14	2.96E-12
10	42.99	91.92	3.87E-03	9.01E-05	3.68E-12	3.14E-12

Table A.9. ANS Leach Test: ^{99}Tc Leaching Data (LCS Data) for Specimen 6 (With Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	3.56E-02	4.13E-01	2.42E-08	2.42E-08
2	0.21	0.29	4.77E-03	2.31E-02	6.13E-10	9.17E-09
3	0.77	1.07	3.46E-03	4.48E-03	8.18E-11	2.97E-09
4	0.94	2.00	2.39E-03	2.56E-03	6.46E-11	1.76E-09
5	1.00	3.00	1.09E-03	1.09E-03	1.93E-11	1.23E-09
6	1.00	4.00	1.64E-03	1.64E-03	6.17E-11	9.86E-10
7	1.00	5.00	1.99E-03	1.99E-03	1.17E-10	8.54E-10
8	13.99	18.99	1.77E-03	1.26E-04	1.14E-12	2.41E-10
9	29.94	48.93	1.99E-03	6.64E-05	9.37E-13	1.01E-10
10	42.99	91.92	1.30E-03	3.03E-05	4.16E-13	5.61E-11

Table A.10. ANS Leach Test: U Adsorption Data (ICP-MS Data) for Specimen 6 (With Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Adsorbed (ng)	Cum Adsorbed (ng)
1	0.09	0.09	417.8	370
2	0.21	0.29	-52.8	317
3	0.77	1.07	220.4	538
4	0.94	2.00	202.8	741
5	1.00	3.00	201.9	942
6	1.00	4.00	188.6	1131
7	1.00	5.00	206.6	1338
8	13.99	18.99	168.8	1506
9	29.94	48.93	213.1	1719
10	42.99	91.92	180.6	1900

Table A.11. ANS Leach Test: ^{125}I Leaching Data for Specimen 7 (With Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	4.86E-03	5.64E-02	4.40E-10	4.40E-10
2	0.21	0.29	1.64E-03	7.94E-03	7.03E-11	2.31E-10
3	0.77	1.07	7.25E-04	9.38E-04	3.49E-12	7.85E-11
4	0.94	2.00	6.80E-04	7.27E-04	5.07E-12	5.00E-11
5	1.00	3.00	5.39E-04	5.39E-04	4.61E-12	3.81E-11
6	1.00	4.00	6.93E-04	6.93E-04	1.07E-11	3.34E-11
7	1.00	5.00	4.77E-04	4.77E-04	6.54E-12	2.96E-11
8	13.99	18.99	5.57E-04	3.98E-05	1.10E-13	8.73E-12
9	29.94	48.93	5.92E-04	1.98E-05	8.07E-14	3.79E-12
10	42.99	91.92	3.87E-03	9.00E-05	3.57E-12	3.73E-12

Table A.12. ANS Leach Test: ^{99}Tc Leaching Data (LCS Data) for Specimen 7 (With Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Leach Fraction	Cum Leach Fraction	D_{ei} (cm^2/s)	D_{ci} (cm^2/s)
1	0.09	0.09	3.52E-02	4.09E-01	2.31E-08	2.31E-08
2	0.21	0.29	5.11E-03	2.48E-02	6.86E-10	8.93E-09
3	0.77	1.07	3.70E-03	4.79E-03	9.09E-11	2.92E-09
4	0.94	2.00	2.86E-03	3.06E-03	8.99E-11	1.76E-09
5	1.00	3.00	1.42E-03	1.42E-03	3.18E-11	1.25E-09
6	1.00	4.00	2.45E-03	2.45E-03	1.35E-10	1.03E-09
7	1.00	5.00	1.49E-03	1.49E-03	6.37E-11	8.77E-10
8	13.99	18.99	2.61E-03	1.87E-04	2.43E-12	2.54E-10
9	29.94	48.93	1.28E-03	4.28E-05	3.79E-13	1.03E-10
10	42.99	91.92	1.55E-03	3.61E-05	5.76E-13	5.81E-11

Table A.13. ANS Leach Test: U Adsorption Data (ICP-MS Data) for Specimen 7 (With Steel Fibers)

Interval	Incremental Time (day)	Cumulative Time (day)	Incremental Adsorbed (ng)	Cum Adsorbed (ng)
1	0.09	0.09	398.4	370.1
2	0.21	0.29	310.9	681.0
3	0.77	1.07	225.9	906.9
4	0.94	2.00	192.2	1099.1
5	1.00	3.00	201.7	1300.8
6	1.00	4.00	187.8	1488.6
7	1.00	5.00	220.1	1708.8
8	13.99	18.99	178.5	1887.3
9	29.94	48.93	171.7	2059.0
10	42.99	91.92	154.1	2213.1

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