1 of 2

SOLID-WASTE LEACH CHARACTERISTICS AND
CONTAMINANT-SEDIMENT INTERACTIONS

VOLUME 1: Batch Leach and Adsorption
Tests and Sediment Characterization

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SUMMARY

The objectives of this report and subsequent volumes include describing progress on 1) development of conceptual-release models for Hanford Site defense solid-waste forms; 2) optimization of experimental methods to quantify the release of contaminants from solid wastes and their subsequent interactions with unsaturated sediments; and 3) creation of empirical data for use as provisional source term and retardation factors that become input parameters for performance assessment analyses for future Hanford disposal units and baseline risk assessments for inactive and existing disposal units.

Batch leach testing was performed for 12 weeks using actual Hanford groundwater as a surrogate for unsaturated sediment pore water from four simulated solid-waste forms: 1) paper, cardboard, and plywood; 2) plastic; 3) rubber, cotton, nylon, and canvas; and 4) all three mixed with hardened cement. Particular attention was directed to determining the types of organic compounds that leached into the groundwater. The tests show that wood, paper, cardboard, plastics, cloth, and rubber did not release significant amounts of inorganic constituents to Hanford groundwater. The materials did release measurable amounts of organic matter, especially the wood, paper, and cardboard. The leach test containing cement and a mixture of all the various wastes generated a leachate significantly different from the groundwater. The cement released significant amounts of hydroxide (pH rises to 12.1) and significant amounts of K^+ , Na^+ , Ca^{2+} , and Al . Again the wood and paper products present in the cement test also released significant amounts of organic matter.

From a contaminant-release perspective, the waste-form leaching tests suggest that the release of dissolved organic carbon may be the most potentially deleterious trend. Past studies of contaminant release from grout suggest that the high pH and high alkali metal concentrations do not increase release or mobility of most metallic, actinide, and fission product species. In fact, the high pH environment caused by cement dissolution aids sequestration of many metallic species because of lowered solubility.

Test methods that quantify contaminant retardation in sediments under partially saturated conditions were studied. Those methods include half-cell diffusion tests with unsaturated sediments, unsaturated flow column (Wierenga columns) tests, and column adsorption tests using an unsaturated flow ultra-centrifuge. The results of these tests will appear in Volume 2.

Empirical distribution coefficients, R_d values, were determined for nine contaminants [NO_3^- , NO_2^- , U(VI), Cr(VI), Se(VI), I^- , Tc(VII), Sr(II), and Cs(I)] spiked into actual Hanford groundwater, a simulated acidic-process waste water, and two simulated solid-waste leachates onto four representative Hanford sediments. Specific R_d values for the studied contaminants for leachates and groundwater contacting Trench-8 sediments are provided in Tables 21 and 30. These values should be used in any specific performance assessment analyses of the 200 Area W-5 burial ground. Conclusions from the adsorption studies are reported in Section 6.0.

Four Hanford sediments were collected and extensively characterized. These sediments are used in the laboratory tests to optimize experimental methodologies and to generate the site-specific database used in performance assessment calculations. Data from the physical and chemical characterization of the sediments are reported in Section 2.0.

Finally, several literature reviews to gather adsorption/desorption and solubility data for Ra, Sn, Nb, Be, Ni, and Sm, and for U, Np, and Pu, respectively, are described in Appendix A.

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1.0 INTRODUCTION

This report documents progress from FY90 through mid FY93 on waste-form release and contaminant/sediment adsorption properties germane to assessing performance/risk of future and past shallow-land burial of defense wastes in Hanford Site sediments. Originally, the work was funded by two distinct projects, Hanford Site Performance Assessment (HSPA) and Solid Waste Technology Support (SWTS), both funded through Westinghouse Hanford Company (WHC). The HSPA project support ended in FY91.

An overall objective of this work is to provide data and conceptual modeling support to performance/risk assessment in the areas of Hanford defense waste-form release and the subsequent interaction of leachate with Hanford sediments.

Waste-form release and leachate-sediment interactions (retardation) are generally quantified by a release rate and distribution coefficient, respectively. Release rates are either a constant concentration (solubility-controlled release), a constant distribution coefficient (desorption-controlled release), an effective diffusion coefficient (diffusion-controlled release), or a strictly empirical release rate (e.g., fixed percent by year). Retardation distribution coefficients or R_d values are generally derived from batch or column adsorption tests. Other, more sophisticated and technically defensible adsorption models exist but require additional measurements than generally are performed when collecting R_d values. However, as discussed in Serne and Wood (1990), such models are considered less practical or supportable in the context of current Hanford cleanup needs.

A specific objective of this work is to support a WHC solid-waste performance assessment activity to simulate the performance of a newly proposed solid low-level radioactive waste burial ground located in the currently operated W-5 Burial Ground in 200 West Area. In accordance with DOE Order 5820.2A, site-specific performance assessments must be performed. Key elements of the performance assessment include collection of site-specific geologic, hydrologic, and geochemical data, definition of natural processes and human-intrusion events, development of appropriate conceptual models, and conduct of computer simulations.

Within the SWTS project we are especially interested in optimizing experimental methodology and then collecting data that 1) quantify the release of radionuclides and other contaminants from solid-waste forms; and 2) quantify subsequent transport of radionuclides and regulated chemicals through the vadose zone to the unconfined aquifer. The emphasis is on measurement of radionuclide and regulated trace metal release from simulated solid-waste materials and waste forms as a function of moisture content, contaminant type and concentration, and waste material. Methods for measuring release under partially saturated conditions will be established to approximate a realistic environment for a shallow-land, low-level waste disposal facility in Hanford sediments. Results of the testing under unsaturated moisture conditions will be found in Volume 2. Data derived from this experimental work will be used as provisional source-term release input to the W-5 Burial Ground performance assessment analyses, which estimate radionuclide release and transport from the waste site. Once test methods are optimized and actual waste forms are identified, the thrust of this task will change to collection of technically defensible data. One key goal is to investigate whether leach rates and sediment adsorption reactions are fundamentally different in unsaturated sediments than those within saturated systems, the typical environment used in most laboratory tests.

In order to optimize experimental methodology and to provide a provisional database, a test matrix was developed in FY 1990 that incorporates four waste materials and six contaminants. Leach tests, sorption tests, diffusion tests, and transport tests (flow through column and centrifuge) are included as part of the matrix. After experimental methodology testing is completed, test procedures will be prepared that will control future data collection activities. These PNL Quality Assurance (QA) Impact Level 2 procedures will be submitted to WHC for approval prior to use in collecting technically defensible data. The W-5 Burial Ground test matrix to expedite data collection will consider "lessons learned" in FY 1990-1993 and other pertinent considerations. The matrix will be approved by the WHC cognizant scientist prior to the initiation of testing.

In FY 1990-1992 the six contaminants studied were Cs(I), Sr(II), Se(VI), U(VI), Tc(VII), and Cr(VI). The waste forms studied included 1) paper,

cardboard, and plywood; 2) plastic; 3) rubber, cotton, nylon, and canvas products; and 4) all three mixed with hardened cement. Presently, metallic materials, rocks, and soil will not be considered although they are commonly disposed in solid burial grounds. One Hanford sediment from the 200-W Area W-5 Burial Ground site (Trench-8 sediment) is being used in SWTS specific tests.

Test methodologies being evaluated include

1. static leach tests of nonradioactive waste forms in water saturated conditions
2. adsorption tests of simulated process wastes and groundwater onto four Hanford sediments
3. diffusion tests of spiked leachate through sediment under unsaturated conditions
4. batch adsorption tests of spiked waste-form leachates onto W-5 sediment
5. flow-through column tests of spiked groundwater through W-5 sediment under unsaturated conditions
6. unsaturated flow centrifuge tests of spiked groundwater through W-5 sediment.

Testing yet to be performed

1. diffusion tests of spiked grout placed in sediment under unsaturated conditions
2. flow-through column and/or centrifuge tests of spiked waste forms embedded in sediment and leached with simulated pore water under unsaturated conditions.

In addition to the W-5 sediment, three other Hanford sediments have been used to develop R_d adsorption values for the six contaminants listed above and NO_3^- , NO_2^- , and I^- . Solutions used in these batch adsorption tests were Hanford groundwater and a simulated acidic high-ionic-strength process waste water.

Appendix A summarizes literature reviews on adsorption of Ra, Sn, Nb, Be, Ni, and Sm onto sediments and solubility constraints on U, Np, and Pu in groundwater and cement pore waters. These data support performance assessment (PA) analyses being performed on the W-5 Burial Ground proposed expansion at the 200-W Area on the Hanford Site.

2.0 SEDIMENT COLLECTION AND CHARACTERIZATION

It was pointed out in Serne and Wood (1990) that past efforts at Hanford to measure contaminant migration potential often suffered from insufficient characterization of the sediments and waters used in laboratory tests. The efforts described herein are an example of the types of characterization deemed useful for generating adsorption data that can be used in technically defensible PA analyses.

In late December 1989 and early January 1990, Dr. Marc I. Wood and Mr. Steve P. Reidel, both of WHC, collected four types of sediments. The first three sediments were collected from the near surface using a shovel. The samples were placed in plastic-lined cardboard boxes (~0.037-m³ size). The fourth sample was collected from the side wall of the trench while standing on the bottom of the trench. The sample horizon was estimated to be about 20 feet below the natural surface grade. Samples were shoveled into plastic-lined pails and then dumped into plastic-lined cardboard boxes at the surface. Table 1 lists details and quantities collected. All samples are from Hanford formation sediments. The four sediment samples were given to PNL staff on January 25, 1990.

Detailed sediment characterization was performed to aid in interpreting geochemical processes between contaminants and Hanford sediments and as direct input to transport calculations (e.g., unsaturated hydraulic conductivities).

In early March 1990, the four sediment samples were removed from the plastic-lined boxes, air dried, and sieved through a 2-mm stainless steel screen to remove the gravel-sized particles. The weights of gravel and finer

TABLE 1. Sediment Descriptions

<u>Sample Designation</u>	<u>Sample Description</u>	<u>Sample Location</u>	<u>Volume Collected</u>
TBS-1	Touchet Bed Sand	Army Loop Road (S of 200-W)	73 L
MSG-1	Medium/Coarse Sand	Grout Vault (S of 200-E)	110 L
CSG-1	Coarse Gravel/Sand	Quarry (W of 200-E)	110 L
Trench-8	Medium/Coarse Sand	W-5 Burial Ground Side Wall	100 L

sediment were determined with a bathroom scale. The <2-mm portions of the sediments were coned and quartered on a plastic trap. One quarter of the homogenized soils were placed in a plastic bag for immediate use, and the other three quarters were stored in plastic-bag-lined garbage cans. The weights of gravel-sized material that were discarded and of the finer sediment retained for characterization are shown in Table 2. It is common practice in soil science to discard gravel-sized material because it is considered chemically inert in regard to contaminant interactions. Moisture contents (percent by weight) were determined on a small aliquot prior to air drying and screening the material to remove gravel. The moisture content values reported in Table 2 likely do not represent natural in situ moisture contents on the day of collection because of the several-month delay in preparing the samples.

The fine materials (<2 mm) were further characterized using procedures listed in Table 3. The results of the particle-size analysis of the fines are shown in Table 4 and Figures 1, 2, 3, and 4. Table 4 also shows the true in situ particle-size distribution that includes the gravel content. The break points for clay/silt, silt/sand, and sand/gravel are 2 μ m, 50 μ m, and 2 mm. Further, while preparing the size separates for semiquantitative crystalline mineral determinations, a second size-separation procedure yielded a slightly different percentage of clay for the first three sediments. These data are also shown in Table 4. This second particle-size distribution arbitrarily considers that the increased clay content is compensated by a slight drop in sand content. The first particle-size distribution was determined using standard methods (i.e., Gee and Bauder 1986) that disperse the sediment overnight in a sodium hexametaphosphate solution and use measurements of slurry specific gravity at designated times to calculate silt and clay contents.

TABLE 2. Results of Sieving

Sample	Total Weight (lb)	Wt. of Gravel (lb)	% Gravel	Wt. of Fines (lb)	% Fines	Moisture Content (% wt)
TBS-1	90	<1	<1.1	89	~99	1.91 $\pm$ 0.07
MSG-1	139	3	2.2	136	97.8	1.92 $\pm$ 0.10
CGS-1	183	151	82.5	32	17.5	0.73 $\pm$ 0.16
Trench-8	144	14	9.7	130	90.3	15.4 $\pm$ 4.0

TABLE 3. Sediment Characterization Procedures

Parameter	Method
Particle size by sieve method	Gee and Bauder (1986)
Particle size by hydrometer method	Gee and Bauder (1986)
Moisture content	ASTM (1980)
CaCO ₃ content	Nelson (1986)
TOC	Nelson and Sommers (1986)
CEC	Rhoades (1986)
Saturation extract	McLean (1986)
Mineralogy	Drever (1973), Rich and Barnhisel (1977), MacEwan and Wilson (1980)
Amorphous Fe, Mn, Al	Chou and Zhou (1983)
Hydraulic Conductivity (Saturated)	Klute and Dirksen (1986)
Hydraulic Conductivity (Unsaturated)	Calculated using methods found in Nielsen et al. (1986) and direct measurement (this report)
Diffusion Coefficient (Non-reactive Species vs. Moisture Content)	Conca and Wright (1990)

TABLE 4. Particle-Size Analysis (Percent by Weight)

Sediment	Fines				In Situ Sediments			
	Sand (%)	Silt (%)	Clay (%)	Particle Density g/cm ³	Gravel (%)	Sand (%)	Silt (%)	Clay (%)
<u>Gee and Bauder Technique</u>								
TBS-1	80	15	5	2.72	<1	79.2	14.8	5.0
MSG-1	98	<1	2	2.82	2.2	95.9	<1	2.0
CGS-1	89	7	4	2.73	82.5	15.6	1.2	0.7
Trench-8	87	7	6	2.70	9.7	78.6	6.3	5.4
<u>Clay-Slurry Draw-off Technique</u>								
TBS-1	79	15	6					
MSG-1	94	<1	6					
CGS-1	86	7	7

FIGURE 1. Particle-Size Analysis TBS-1

FIGURE 2. Particle-Size Analysis MSG-1

FIGURE 3. Particle-Size Analysis CGS-1

FIGURE 4. Particle-Size Analysis Trench-8

The second particle-size distribution was obtained by repeatedly drawing off the fine-grained particles suspended in the slurry after settling for a fixed time. The dispersant solution removed is saved, and replacement solution (deionized water for the second and ensuing separations) is added. The slurry is shaken vigorously and the settling procedure repeated. Each separated aliquot of slurry is mixed with the others. After 5 to 7 separations, the fine-grained materials drawn off are flocculated by addition of magnesium chloride. The flocculated clays are analyzed by X-ray diffraction in their existing wet state.

The slight increase in clay-sized particles observed arises either from incomplete particle dispersion when using the Gee and Bauder technique or from some silt-sized particles remaining in suspension during the repeated slurry draw-off procedure.

The particle densities of the fine particles are also shown in Table 4. The amorphous hydrous oxide content, calcium carbonate content, and organic carbon content of the sediments are shown in Table 5. Amorphous or poorly crystalline hydrous oxides (especially Al, Mn, and Fe) act as a prime adsorption substrate for cations under alkaline conditions and anions under acidic conditions. The Ca carbonate content indicates the capacity of the sediment to neutralize acidic solutions. Organic carbon in sediments can adsorb hydrophobic organic molecules dissolved in pore waters and gives an indication of the amount of biological activity present. Note that these data reflect only the material left after the gravel was discarded.

TABLE 5. Hydrous Oxide, Organic, and Carbonate Contents

<u>Sediment</u>	<u>Percent by Weight</u>					
	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>MnO₂</u>	<u>CaCO₃</u>	<u>Organic C</u>
TBS-1	0.38	0.25	0.28	0.03	1.87	0.021
MSG-1	0.36	0.24	0.41	0.04	0.83	0.023
CGS-1	0.36	0.24	0.41	0.04	0.96	0.067
Trench-8	0.03	0.30	0.30	0.47	2.00	0.190

The poorly crystalline hydrous oxide [determined by extraction with hydroxylamine-hydrochloride; see Chou and Zhou (1983)] and the organic carbon contents of the sediments are not very high, suggesting that neither will play a dominant role in contaminant adsorption studies. Trench-8 sediment does contain about 10 times more amorphous MnO_2 than the other three sediments and may exhibit slightly greater adsorption tendencies for trace metals that bind strongly to hydrous oxides.

The Ca carbonate contents are not particularly high compared to some Hanford sediments, but sediment TBS-1 and Trench-8 sediments should exhibit about twice as much acid-neutralizing capacity as the other two sediments.

The semiquantitative crystalline mineralogy of the bulk fine samples and of each size separate are shown in Tables 6 and 7, respectively. Randomly oriented <53- μm powdered specimens of the sand- and silt- size fractions were analyzed by X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation. Preferentially-oriented specimens of the clay size-fraction were prepared using the method of Drever (1973), after classical pretreatments to remove poorly crystallized components and to saturate the exchange sites with Mg^{+2} , K^+ , and/or glycerol (Jackson, 1979; unpublished method of J. E. Amonette of PNL). These specimens were equilibrated overnight at 30% relative humidity before XRD analysis.

TABLE 6. Semiquantitative Mineralogy of Bulk Samples (<2-mm Size)
(in Percent Weight)

<u>Mineral</u>	<u>CGS-1</u>	<u>MSG-1</u>	<u>TBS-1</u>	<u>Trench-8</u>
Plagioclase	35.4	41.5	20.5	26.1
Quartz	35.2	46.1	51.3	43.0
K-Feldspar	9.3	<0.1	3.6	5.1
Hornblende	1.0	1.8	1.8	1.7
Mica (Biotite)/Illite	8.6	3.1	11.7	9.1
Kaolinite/Serpentine	1.6	0.3	0.2	7.4
Chlorite	2.0	<0.1	2.6	0.8
Smectite	3.9	5.0	5.0	3.3
Vermiculite	1.0	0.2	0.3	0.3
Hydrous Oxides	1.0	1.0	0.9	1.1
CaCO_3	1.0	0.8	1.9	2.0

TABLE 7. Semiquantitative Mineralogy of Sediments
(Percent Weight of Each Size Fraction)

Mineral Group	CGS-1			MSG-1		
	Sand	Silt	Clay	Sand	Silt	Clay
Plagioclase	41	13	< ^(a)	45	80	<
Quartz	38	41	5	50	12	<
K-Feldspar	10	13	<	<	<	<
Hornblende	1	3	<	2	<	<
Kaolinite/Serpentine	1	7	4	<	<	6
Mica (Biotite)/Illite	7	21	19	3	8	5
Chlorite	2	3	2	<	<	1
Smectite	- ^(b)	-	57	-	-	85
Vermiculite	<	<	14	<	<	3

Mineral Group	TBS-1			Trench-8		
	Sand	Silt	Clay	Sand	Silt	Clay
Plagioclase	22	25	<	30	12	<
Quartz	56	57	1	48	35	3
K-Feldspar	4	4	<	5	13	<
Hornblende	2	2	<	2	<	<
Kaolinite/Serpentine	<	<	4	7	17	5
Mica (Biotite)/Illite	13	10	5	8	18	19
Chlorite	3	2	1	<	6	1
Smectite	-	-	84	<	<	57
Vermiculite	<	<	5	<	<	18

(a) < signifies that group abundance is below detection limit.

(b) Dash signifies that the group was not analyzed (smectites occur only in clay-sized fraction).

Table 6 was constructed by proportionating the semiquantitative values for the amorphous and crystalline minerals in Tables 5 and 7. The crystalline minerals in each size fraction in Table 7 were multiplied by the weight percent values of sand, silt, and clay shown in Table 4 for the "fines" quantified by the clay-slurry draw-off technique and summing the values for the three sizes. These values were then prorated for the amorphous materials content and calcium carbonate content in Table 5. That is, crystalline mineral results were all multiplied by the fraction $[1 - (\text{fractional hydrous oxide} + \text{CaCO}_3 + \text{organic content})]$.

Although the precision of XRD methods is generally very good (<5% relative error), the accuracy is less certain because of difficulties in ensuring that the mineral standards have compositions and structures similar to the minerals in the samples (this is particularly troublesome in the clay mineral analyses). Consequently, the mineralogical data in Tables 6 and 7 are reported as "semiquantitative" and should be treated accordingly.

The clay fractions of all four sediments are dominated by smectites, which exhibit large surface areas, moderate cation-exchange capacities and are generally present only in low-leaching environments (dry climates) and/or environments with pore waters rich in Si and Mg. The sediments also contain vermiculite (a high-cation-exchange-capacity mineral), two low-cation-exchange capacity minerals (chlorite and illite), and some kaolinite (a very low-cation-exchange-capacity clay). Although not quantified, XRD analysis also showed the presence of hydroxy-interlayered clay minerals (non-swelling weathering intermediates between chlorite and either vermiculite or smectite) in all four sediments. These intermediates were more prominent in MSG-1 and TBS-1 than in CGS-1 and Trench-8 sediments. The sand and silt fractions of all the sediments are predominantly quartz and plagioclase feldspars (Na or Ca rich aluminosilicates). The cation exchange capacities (CEC) determined by the method of Rhoades (1986) and exchangeable cation distributions for the sediments are shown in Table 8. The total cation exchange capacity reflects the capacity of the sediment to adsorb cations. The exchangeable cation distribution shows the cations associated with the sediment in its natural state.

Even though the mineralogical data shown in Table 6 suggest that the cation-exchange capacities should be comparable for the four sediments, the measured CEC for sediment CGS-1 is significantly lower, perhaps suggesting that the smectite clay content controls the actual exchange capacity of Hanford sediments. The exchange sites for all the sediments are predominantly filled with Ca and Mg cations, suggesting that pore waters are alkaline-earth rich.

TABLE 8. Cation-Exchange Capacity (CEC) and Exchangeable Cation Distribution

<u>Sediment</u>	<u>CEC (meq/100 g)</u>	<u>Percent Sites</u>			
		<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>
TBS-1	6.0 ± 2.0	90.6	9.1	0.0	0.3
MSG-1	7.8 ± 0.5	84.5	12.7	0.0	2.8
CGS-1	2.6 ± 0.6	89.2	9.6	0.0	1.2
Trench-8	5.2 ± 2.0	91.2	8.4	0.0	0.4

Table 9 contains data on the chemistry of water removed from the sediments after wetting to saturation with deionized water. This information provides an estimate of what the pore solution within the sediments would be after a wetting period. The data are reported in two ways: solution concentrations (mg/L) and amounts of material removed per gram of air-dry sediment ($\mu\text{g/g}$). The chemical composition of the Hanford groundwater used in the leaching and sorption tests is shown in Table 12 in the next section for comparison.

The saturation extract data suggest that all three surface sediments are contaminated with nitrate, especially TBS and CGS. The Trench-8 sediment taken at 20-foot depth from the wall of the trench, is not contaminated with nitrate. The CGS sediment also contains high amounts of evaporites (Ca or Mg chlorides). The nitrate contamination will have to be rinsed out before the sediments are used in half-cell diffusion tests, because nitrate is the usual tracer of choice to represent non-interacting constituents. The degree of rinsing (with CaCl_2 solution) is being determined.

The pore water composition of Trench-8 sediment is slightly more concentrated than the average Hanford groundwater composition shown in Table 12. The most notable differences are the pore water's increased chloride concentration (108 mg/L versus 27 mg/L in groundwater), the pore water's higher total organic carbon (13.9 mg/L versus 1 mg/L in groundwater), and the pore water's lower total alkalinity.

TABLE 9. Chemical Composition of Saturation Extract

Analysis Units	Solution Basis (mg/L)				Sediment Basis (µg/g)			
	MSG-1	TBS-1	CGS-1	Trench-8	MSG-1	TBS-1	CGS-1	Trench-8
pH	8.07	8.17	7.66	7.87				
Eh	377	374	384	383				
Al	<0.03	<0.03	<0.03	<0.03	<0.009	<0.006	<0.007	<0.006
B	0.01	0.01	0.01	0.01	0.003	0.002	0.002	0.002
Ba	0.02	0.05	0.06	0.04	0.006	0.009	0.015	0.008
Ca	17.80	35.10	129.00	58.5	5.28	31.7	6.62	11.35
Cd	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.0008
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.004
Cu	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.0008
Fe	0.06	<0.005	0.04	<0.005	0.018	<0.005	0.010	<0.001
K	4.80	2.30	9.30	6.8	1.42	0.43	2.28	1.32
Li	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.0008
Mg	4.40	9.60	20.70	15.0	1.31	1.81	5.08	2.91
Mn	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.0004
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.002
Na	25.00	45.20	45.90	34.8	7.42	8.53	11.3	6.75
P as PO ₄	1.07	0.95	1.26	1.2	0.32	0.18	0.31	0.224
Pb	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.012
Si	20.10	14.00	18.10	18.6	5.97	2.6	4.44	3.61
Sr	0.08	0.27	0.43	0.20	0.024	0.051	0.11	0.039
Zn	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.004
F ⁻	1.10	0.80	1.10	1.0	0.33	0.15	0.27	0.19
Cl ⁻	1.70	28.00	285.00	109	0.50	5.3	69.9	20.95
NO ₂ ⁻	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.058
NO ₃ ⁻	7.00	42.00	22.00	<0.5	2.08	7.92	5.4	<0.097
SO ₄ ²⁻	30.00	58.00	65.00	85.0	8.9	10.94	16.0	16.49
HCO ₃ ⁻	164.70	103.70	91.50	79.3	48.9	19.6	22.4	15.38
T-Alk ^(a)	81.00	51.00	45.00	39.	24.0	9.6	11.0	7.57
TOC	12.70	17.20	16.70	13.9	3.8	3.2	4.1	2.70

- - - - - (meq/L) - - - - -

Cations	2.46	4.57	10.38	5.9
Anions	3.54	4.42	11.32	6.2

(a) Reported as CO₃²⁻.

Table 10 contains the moisture retention data for the sediments, and Table 11 contains the saturated hydraulic conductivity data. Using these two data sets and empirical models described by Nielsen et al. (1986), it is possible to estimate the dependence of hydraulic conductivity on moisture content or matric potential (shown as suction pressure in Table 10).

For example, the moisture retention curve and saturated hydraulic conductivity value for Trench-8 sediment (of most interest to SWTS) were input to a computer code that calculates the hydraulic conductivity versus water content. The computer code uses two empirical relationships (Van Genuchten 1980 and Mualem 1976) to perform the calculations. Van Genuchten (1980) describes the volumetric water content (θ) as a function of water potential (metric potential or pressure head) as shown by the left-hand portion of Figure 5. Mualem (1976) describes hydraulic conductivity as a function of volumetric water content based on an expression that relies upon knowledge of the saturated hydraulic conductivity and an empirical constant derived from Van Genuchten's fit of the moisture retention data. The predicted hydraulic conductivity versus moisture content is shown in the right-hand portion of Figure 5. The conductivity units $\text{Kg}\cdot\text{s}/\text{m}^3$ are essentially the same as cm/s . At typical moisture contents found in Hanford sediments (4 to 7% by volume; see Gee and Heller 1985; Schalla et al. 1988) the Trench-8 sediment (with gravel removed) would likely transport water under a unit gradient at velocities of 10^{-8} to 10^{-7} cm/s or 0.3 to 3 cm/yr . These velocities are between 5×10^5 and 5×10^6 times slower than the velocities expected when the sediments are saturated.

Dr. Jim Conca (Appendix B) made actual measurements of hydraulic conductivity as a function of moisture content using a centrifugation method. After attaining steady-state flux conditions controlled by a constant flux pump and centrifugal force, small soil samples from Trench-8 (3-cm diameter x 5-cm length), packed to a bulk density of 1.59 to 1.60 g/cm^3 , were measured for moisture content. Using the bulk density and weight percent moisture content, volumetric moisture contents were calculated. From knowledge of the steady-state water flux and calculated moisture contents, the data (open triangles) can be plotted on the right-hand curve in Figure 5. The agreement

TABLE 10. Water Retention Data (Percent Weight Water Content)

Sediment	Suction Pressure (cm of H ₂ O)									
	5 cm	10 cm	25 cm	40 cm	55 cm	75 cm	102 cm	306 cm	1020 cm	3060 cm
CGS-1	0.216 ± 0.008	0.140 ± 0.004	0.104 ± 0.015	0.074 ± 0.009	0.070 ± 0.009	0.065 ± 0.007	0.052	0.042	0.033	0.027
MSG-1	0.281 ± 0.013	0.256 ± 0.007	0.136 ± 0.032	0.072 ± 0.009	0.062 ± 0.002	0.055 ± 0.000	0.052	0.027	0.026	0.026
TBS-1	0.309 ± 0.019	0.292 ± 0.011	0.284 ± 0.010	0.276 ± 0.007	0.270 ± 0.005	0.252 ± 0.005	0.281	0.046	0.026	0.025
Trench-8	0.248 ± 0.010	0.221 ± 0.009	0.187 ± 0.010	0.124 ± 0.002	0.103 ± 0.004	0.088 ± 0.006	0.099	0.040	0.032	0.028

TABLE 11. Saturated Hydraulic Conductivity

<u>Sediment</u>	<u>K (cm/s)</u>
CGS-1	$(1.01 \pm 0.07) \times 10^{-1}$
MSG-1	$(7.32 \pm 0.94) \times 10^{-2}$
TBS-1	$(6.56 \pm 0.75) \times 10^{-4}$
Trench-8	$(4.62 \pm 0.54) \times 10^{-2}$

between the measured hydraulic conductivities and calculated values (solid curve) is very good. Hydraulic conductivity data collected at wetter conditions (12.5 to 23% wt. moisture) by increasing water influx to values between 20 and 40 mL/h and decreasing centrifuge speed to 300 rpm show significant hysteresis as the sediment sample is taken from relatively wet conditions to drier conditions and then rewetted (see Figure 6).

We do acknowledge that running the centrifuge below 400 rpm is not recommended because the simplifying assumption that $d\Psi/dr \ll \rho\omega^2 r$ no longer holds (see Appendix B for the identity of the symbols and further discussion of this topic). When the above assumption does hold, Darcy's law reduces to $K(\Psi) = q/\rho\omega^2 r$, where q is the water flux density (cm/s), ω = centrifuge rotation speed (radians/s), r = centrifuge axis of rotation (cm), ρ = water density, and Ψ = metric potential (cm). Despite the fact that the centrifuge must be run at lower than ideal speeds to get very wet conditions in the coarse sands, we currently don't believe that the corrections needed to calculate K for lower speeds would be as large as the apparent hysteresis. Nielsen et al. (1986) discuss hysteresis in hydraulic conductivity. Their review shows that a small amount of hysteresis is often observed in the same direction but of lesser magnitude than shown in Figure 6.

Figure 7 shows that there is much less hysteresis at lower water content, in more agreement with Nielsen et al. (1986). All the centrifuge data are combined with the empirical curve fit in Figure 5. Recall that the uppermost datum (near 40% volumetric water content) is a separate experiment using the classical falling head technique and does not represent centrifuge-derived data. The data points on Figure 5 between 28 and 32% volumetric water content represent those points on Figure 6 collected in the drying mode (wet

FIGURE 5. Water Content in Soil Samples from Trench-8

S9308039.2

Volumetric Water Content (%)

FIGURE 6. Hysteresis in Hydraulic Conductivity (High Moisture)
(Sample bulk density was 1.6 g/cm^3 .)

Volumetric Water Content (%)

FIGURE 7. Hysteresis in Hydraulic Conductivity (Low Moisture)
(Sample bulk density was 1.6 g/cm³.)

to dry) and do not consider the hysteresis. For testing the relatively dry conditions normally found on the Hanford Site, the apparent larger-than-normal hysteresis at the wet conditions observed using the centrifuge should not present a problem. It is easy to obtain hydraulic conductivity data at wet moisture conditions using classical techniques. The value of the centrifuge technique is in obtaining data at dry conditions typically found in Hanford vadose zone sediments because classical techniques are time consuming and imprecise at low moisture.

In the future we will extend the hydraulic conductivity tests to even lower moisture contents. To date we have limited centrifuge speeds to <2500 rpm. A second-generation centrifuge will be available in late 1993 to increase our capabilities to study extremely low moisture contents. Average moisture contents in Hanford subsurface sediments are 4 to 7% by volume. As shown in Figure 7, we are already getting results from 5.5% to wetter moistures at speeds from and below 2500 rpm. We should readily reach 4% or lower volumetric moisture contents for coarse sands with the second-generation centrifuge.

In general, the TBS-1 sediment exhibits the lowest hydraulic conductivity of the four sediments tested because of its fine-grained texture and high moisture-holding capacity. The coarsest sediment, CGS-1, exhibits the largest hydraulic conductivity. There are over three orders of magnitude difference in saturated hydraulic conductivities between TBS-1 and CGS-1 sediments. MSG-1 and Trench-8 exhibit intermediate hydraulic conductivities.

Conca (Appendix B) also measured the bulk diffusion coefficient of a non-reactive species, (K+), as a function of moisture content in Trench-8 soil. The technique is described in detail in Appendix B and briefly reviewed below.

A constant flux of 0.1 M KCl solution was percolated into the rotating sample cell filled with Trench-8 sediment packed to a uniform bulk density of 1.59 to 1.60 g/cm³. The choice of water flux into the cell and centrifuge rotation speed determines a uniform unsaturated moisture content within the sediment. After allowing several pore volumes of solution to drain through the cell to allow the 0.1 M KCl solution to acclimate with the sediment, the

conductivity of the moist sediment is measured. The K will react with sediments mainly through ion exchange until the entire soil column is in equilibrium. Other work, for example, Conca and Wright (1990), suggests that when the electrical conductivity of the effluent solution reaches a steady-state value equal to the conductivity of the original 0.1 M KCl solution, ion exchange and other chemical reactions are essentially complete. That is, influx of additional 0.1 M KCl solution does not cause further chemical reactions because the sediments are acclimated. At this point in time, when chemical reactions have ceased and hydraulic steady state is reached (influx = drainage within the cell), the centrifuge is stopped and the sediment cell quickly attached to a conductivity bridge. The sediment cell is fabricated with two ring electrodes around the inside surface such that the sample chamber becomes the conductivity cell.

The Nernst-Einstein equation relates the diffusion coefficient of the species in solution (K^+ , Cl^-) to the measured conductance, cell constant, temperature, and transference number, concentration, and charge of the ion of interest.

At each combination of centrifuge speed and constant influx, the conductance of the unsaturated sediment was measured once hydraulic steady state and chemical equilibrium were reached. The moisture content of the sediment was also determined such that plots of the calculated effective diffusion coefficient versus moisture content could be generated. Figure 8 shows the results. Figure 9 shows that there is no measurable hysteresis in measurements of the diffusion coefficient for K under relatively dry moisture contents.

Natural Hanford sediments below the near-surface zone affected by seasonal, diurnal, and plant evapotranspiration cycles generally are found to have a moisture content between 4 to 7% by volume or 2.6 to 5% by weight. Figure 8 suggests that the diffusion coefficient for a non-reacting tracer would be in the range $<5 \times 10^{-8}$ to 2.2×10^{-7} cm^2/s . Under steady-state

FIGURE 8. Diffusion Coefficient for Trench-8 Sediment

FIGURE 9. Effective Diffusion Coefficient (No Hysteresis)
(Sample bulk density was 1.6 g/cm^3 .)

conditions diffusive flux would allow soluble (non-reactive) species to travel a distance $L = \sqrt{Dt}$. In one year, using the above range in effective diffusion coefficients, a non-reactive species would travel between <1.2 and 2.6 cm. This range in travel is similar to the probable advective travel expected for water movement under unit gradient in unsaturated Hanford sediments (0.3 to 3 cm/y). Therefore, under natural moisture conditions around buried waste in the Hanford vadose sediments, diffusive flux will be of equal magnitude to advective flux.

Figure 8 can be used to compare centrifuge-derived effective diffusion coefficients with those measured with half cells to be discussed in Volume 2.

3.0 STATIC LEACH TESTS OF NONRADIOACTIVE WASTE FORMS

The objective of this leach test was to ascertain the types of soluble inorganic and organic constituents that might leach from representative materials found in solid waste buried at Hanford. Because it was not convenient to disturb wastes presently buried and the exact nature of future solid wastes to be buried in the W-5 Burial Ground expansion is not known, we elected to use uncontaminated materials in this scoping study. Representative samples of paper, cardboard, cloth, rubber, etc. were obtained from Hanford Stores. We separated the "waste" materials into four categories: 1) wood, cardboard, and paper; 2) plastic; 3) miscellaneous that contains rubber, nylon, cotton, cloth, canvas, and various tapes; and 4) all wastes commingled with cement.

Four large glass containers were used to perform static leach tests of the waste materials, one container per waste category. The leachant was actual Hanford groundwater (a simulant of sediment pore water) with a chemical composition shown in Table 12. For the first three waste-form categories, approximately 800 g of waste were cut into 10 cm³ pieces and immersed in 16.0 L of groundwater. For the cement commingled test, 800 g of waste and 1600 g of disaggregated cement were used. See Table 13 for details. The test containers were covered by thin black plastic bags commonly used as garbage can liners. The bags limit the amount of light reaching the tests to simulate subsurface burial.

After 1, 3, 6, and 12 weeks of contact at room temperature, approximately 1 L of supernatant solution was removed from each test for detailed organic analyses, for both volatile and semivolatile components, and detailed inorganic components analysis. This test matrix creates 4 x 4 = 16 samples for complete analyses. Appropriate reagent blanks, and the starting groundwater, were also analyzed. For the volatile components, the samples were analyzed according to U.S. Environmental Protection Agency (EPA) Method 8240 (EPA 1986), which involves the use of purge and trap/mass spectrometry. EPA Method 8240 (EPA 1986) is used to quantify most volatile organic compounds that have boiling points less than 200°C and that are insoluble or slightly soluble in water. Volatile but highly water-soluble compounds are only

TABLE 12. Chemical Composition (mg/L) of Groundwater From Well 6-S3-25

<u>Constituents</u>	<u>Sample Used (4/90)</u>	<u>Range in Composition (1985-1990)</u>
pH	8.14	7.82 - 8.47
Eh(mv)	309	283 - 385
Al	<0.03	<0.03 - 0.064
B	0.1	0.02 - 0.10
Ba	0.08	0.04 - 0.08
Ca	48.8	48.8 - 58.8
Cd	<0.004	<0.004
Cr	<0.020	<0.02 - 0.034
Cu	<0.004	<0.004
Fe	<0.005	<0.005 - 0.008
K	9.9	4.9 - 9.9
Li	<0.004	<0.004
Mg	14.6	13.2 - 14.6
Mn	<0.002	<0.002 - 0.13
Na	32.1	23.8 - 32.1
P	<0.1	<0.1
Pb	<0.06	<0.06
Si	16.4	14.6 - 16.4
Sr	0.25	0.23 - 0.25
Zn	<0.02	<0.02 - 0.08
F ⁻	0.5	<0.5 - 0.7
Cl ⁻	27	21 - 27
NO ₂ ⁻	<0.3	<0.3
NO ₃ ⁻	<0.5	<0.5
PO ₄ ³⁻	<0.4	<3
SO ₄ ²⁻	75	63 - 92
T-Alk (as CO ₃ ²⁻)	67.5	67.5 - 92.4
TOC	1	0.3 - 1.7
Cations (meq/L)	5.29	4.9 - 5.4
Anions (meq/L)	4.60	4.6 - 6.1

qualitatively recovered because of poor purging efficiency. Target compounds usually measurable with Method 8240 include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. Typical quantifiable limits for contaminated groundwaters are 5 µg/L for each organic compound. Internal standards (known concentrations of deuterated compounds) are added to the unknown samples to facilitate quantification of volatile compounds. An inert gas is bubbled through the sample solution at ambient temperature, and the volatile components purged into an adsorbent chromatography column. Once purging stops, the adsorbent

TABLE 13 Description and Weight of Solids

Test #1	SAMPLE CONTAINER 1: wood, cardboard, and paper	
	plywood	410.99 g
	rad box (cardboard)	273.81 g
	white paper towels	41.29 g
	brown paper towels	40.54 g
	paper wrapper surgeon gloves	10.27 g
	total	800.96 g
Test #2	SAMPLE CONTAINER 2: plastics	
	yellow plastic gloves	150.01 g
	yellow shoe covers	169.46 g
	clear plastic bags	198.26 g
	plastic head cover	37.83 g
	flame retardant sheet	40.03 g
	yellow plastic coverall	177.09 g
	5 ml plastic pipette tips	28.05 g
	total	800.61 g
Test #3	SAMPLE CONTAINER 3: miscellaneous (rubber, cotton, cloth, canvas & tape)	
	rubber shoe covers	116.09 g
	white cotton gloves	56.29 g
	silver duct tape	100.91 g
	white duct tape	100.06 g
	plastic rad rope	100.68 g
	orange canvas gloves	100.08 g
	rubber gloves	101.89 g
	cotton coveralls	55.74 g
	cotton skull cap	25.17 g
	silver flame retardant paper	50.62 g
	total	807.5 g

TABLE 13. Description and Weight of Solids (cont'd)

Test #4 SAMPLE CONTAINER 4: All waste types and cement

cement (Portland type I/II) 1600.00 g

Category 1

plywood	205.68 g
rad box (cardboard)	45.00 g
brown towels	15.22 g
white towels	15.06 g
glove wrapper	12.22 g
cardboard rad tag (glued back)	53.21 g

total category 1 346.39 g

Category 2

yellow plastic glove	42.82 g
yellow shoe cover	40.58 g
clear plastic bags	50.00 g
plastic head cover	13.61 g
flame retardant sheet	25.03 g
plastic coveralls	35.05 g
pipette tips	24.76 g

total category 2 231.85 g

Category 3

rubber shoe covers	50.65 g
white cotton gloves	20.44 g
silver duct tape	10.68 g
white duct tape	11.07 g
rad rope	25.34 g
orange canvas gloves	21.37 g
rubber gloves	30.00 g
cotton gloves	20.99 g
cotton skull cap	10.84 g
flame retardant paper	20.36 g

total category 3 221.74 g

total all waste types
and cement 2399.98 g

is heated and backflushed with inert gas and the carrier gas that contains the desorbed analytes is fed to the gas chromatograph/mass spectrometer.

Semivolatile organic compounds were analyzed using EPA Method 8270 (EPA 1986). A 200-mL subsample of leachate is acidified to pH = 2 with sulfuric acid and extracted three times with 100 mL aliquots of methylene chloride. The three methylene chloride extracts are combined and evaporated to a 1-mL concentrate. Internal standards are added to the concentrate and the sample injected into the gas chromatograph/mass spectrometer. Standard compounds added to reagent water were treated in a similar fashion to estimate extraction efficiencies. This method can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted from the gas chromatograph without derivatization. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, pesticides, phthalate esters, organophosphate esters, nitrosoamines, aromatic nitro compounds, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, and phenols. The practical quantitation limit for such compounds in contaminated groundwaters is 10 $\mu\text{g/L}$ for each compound.

For some components such as organic acids, derivatization is required prior to GC/MS analysis. Some components that are extracted are not amenable to GC/MS analysis. For those particular instances, liquid chromatography (LC) or liquid chromatography/mass spectrometry [(LC/MS) with both particle-beam and thermospray interfaces] should provide additional identification of extractable components. Such LC/MS was not performed on any of the samples generated by this project. A total dissolved organic carbon (DOC) value was determined for comparison with the mass of organic carbon species actually identified. The original goal was to determine organic species that are present at concentrations above 0.1 mg/L DOC.

Inorganic analyses included Eh, pH, DOC, alkalinity, major cations (Ca, Mg, K, Na), major anions (NO_3^- , NO_2^- , SO_4^{2-} , Cl^- , PO_4^{3-}), and trace species (Li, B, Al, Si, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ag, Cd, Ba, La, Pb, and U). Analyses performed included inductively coupled plasma-atomic emission (ICP),

spectroscopy, ion chromatography (IC), inductively coupled plasma-atomic emission-mass spectroscopy (ICP-MS), carbon analysis, and automatic titration.

The sampling procedure was to pressurize the large glass leaching bottles and remove several aliquots through a glass tube that was submerged into the leachate. The tip of the glass tube was covered with a small plastic bottle with numerous holes punched in the sides to minimize solids from entering the tube. A glass bottle (1-L capacity) was partially filled with leachate for dissolved organic analyses. Several small glass bottles (150 mL capacity) were filled to the three quarters mark to allow head space equilibration and extraction of semivolatiles. An additional sample was taken in a glass GC vial. The vial was filled to overflow and a septum equipped cap crimped into place. This sample was used to analyze for volatile components. A final sample of ~100 mL was taken for inorganic chemical analyses that included pH, Eh, alkalinity, ICP, and IC analyses. The leachate samples sent for ICP and IC analyses were prefiltered through 0.2- μ m membranes.

Leachates from test #1 (wood and paper products) and #4 (all wastes plus cement) rapidly developed color, brown and gray, respectively. Both these tests also developed a thin layer of mold on the leachate surface. The mold in the wood and paper test was green, while the mold in the cement/trash test was greenish white. By the end of the 12 week-leach test, all four test leachates developed distinctive odors. The wood and paper test smelled similar to a pulp mill.

Table 14 documents the leachate removed and volume remaining after each sampling period. All tests started with 16.0 L of Hanford groundwater as the leachant.

Tables 15 and 16 present the inorganic chemical composition of the groundwater and the resultant leachates after contact with the various wastes for 1, 3, 6, and 12 weeks. Table 15 contains the data for tests #1 and #2, while Table 16 contains the data for tests #3 and #4.

The leach test with wood and paper products generated acids that drop the pH from 8 to 5 within three weeks. The dissolved organic carbon steadily rises from 1 up to 561 mg/L after 12 weeks. The increase was likely continuing when the leach test ended. Other constituents also leached in small

TABLE 14. Leachate Removed and Volume Remaining

<u>Sample Id.</u>	<u>Leachate Removed</u>	<u>Volume Left</u>
1-1	1291.00 mls	14709.00 mls
1-2	864.51	13844.49
1-3	815.67	13028.82
1-4	835.80	12193.02
2-1	1283.62 mls	14716.38 mls
2-2	836.63	13879.75
2-3	810.94	13068.81
2-4	835.80	12233.01
3-1	1305.21 mls	14694.79 mls
3-2	894.91	13799.88
3-3	792.86	13007.02
3-4	802.35	12204.67
4-1	1298.32 mls	14701.68 mls
4-2	989.12	13712.56
4-3	794.28	12918.28
4-4	744.10	12174.18

quantities such that the dissolved solids content of the solution almost doubled from the groundwater starting solution. Inorganic constituents that increased include Al, B, Fe, Mn, Na, Pb, Zn, F⁻, and SO₄²⁻. After twelve weeks of leaching, Na increased from 32 to 125 ppm, fluoride from 0.5 to 30 ppm, sulfate from 75 to 90 ppm, and Pb from <0.06 to 0.13 ppm. The apparent increase in F may actually represent organic weak acids that elute from the ion chromatograph at the same times as fluoride.

The leach test with plastics (test #2) showed little change in pH or total dissolved solids, but did exhibit an increase in DOC from 0.5 to 40 to 60 ppm within one week. Minor increases in solution concentrations of Ba, Zn, F⁻, and NO₃⁻ were also observed. Again the apparent increase in fluoride could be an increase in dissolved weak organic acids.

The leach test with miscellaneous cotton cloth, nylon, tapes, etc. (test #3) caused the pH of the leachate solution to drop slightly from 8 to 7.4, while total dissolved solids increased about 50%. The most striking increases in dissolved species included total organic carbon (TOC), which

TABLE 15. Solid-Waste Performance Leach Study (Tests #1 and #2)

		HGW	Test #1 Wood, Cardboard, Paper				Test #2 Plastics			
			1-1	1-2	1-3	1-4	2-1	2-2	2-3	2-4
			1 week	3 weeks	6 weeks	12 weeks	1 week	3 weeks	6 weeks	12 weeks
pH		8.14	6.4	5.09	5.02	5.04	8.00	7.70	8.05	7.52
Eh		309	354	377	394	403	351	335	300	406
Al	mg/l	<0.03	1.35	2.5	2.4	1.5	0.07	0.07	0.06	<0.01
B	mg/L	0.1	1.66	1.7	1.62	1.7	0.08	0.1	0.1	0.11
Ba	mg/L	0.08	0.1	0.13	0.14	0.16	0.23	0.26	0.25	0.26
Ca	mg/L	48.8	48.2	50.7	48	49.9	51	51	48	49.3
Cd	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	0.08	<0.004	0.05	<0.004
Cr	mg/L	<0.020	<0.020	0.03	0.04	<0.020	<0.020	<0.020	<0.020	<0.020
Cu	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Fe	mg/L	<0.005	0.21	0.4	0.4	0.4	<0.005	<0.005	<0.005	<0.005
K	mg/L	9.9	10	12	13	11	7	8	7	6
Li	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Mg	mg/L	14.6	11.7	12.7	14.6	13.4	14.4	14.6	13.8	14
Mn	mg/L	<0.002	0.19	0.29	0.32	0.37	<0.002	<0.002	<0.002	<0.002
Na	mg/L	32.1	103	122	127	125	29	30.2	29.8	30
P	mg/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.4	<0.10
Pb	mg/L	<0.060	<0.060	<0.060	0.09	0.13	<0.060	<0.060	<0.060	<0.060
Si	mg/L	16.4	13.7	14.4	14.1	15	13.7	14	13.3	13.9
Sr	mg/L	0.25	0.2	0.22	0.22	0.26	0.24	0.25	0.23	0.25
Zn	mg/L	<0.020	0.04	0.14	0.05	0.19	0.36	0.52	0.43	0.64
F ⁻	mg/L	0.5	32.5	21.2	30	29	0.5	0.5	4	4
Cl ⁻	mg/L	27	30.9	30.9	25	40	21.2	21.3	26	24
NO ₂ ⁻	mg/L	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300
NO ₃ ⁻	mg/L	<0.500	2.2	<0.500	0.3	0.3	1.1	1.5	0.9	0.6
PO ₄ ⁻	mg/L	<0.400	0.1	<0.400	<0.400	<0.400	<0.400	<0.400	<0.400	<0.400
SO ₄ ⁻	mg/L	75	68.9	66.4	91	92	57.3	58.5	76	77
T-ALK	mg/L	67.5	123	171	157.5	157.5	69	82.5	82.5	82.5
TOC	mg/L	1	407	440	480	561	39	40	40	59
IC	mg/L	28	15	7	3	17	33	30	30	31
CATIONS	meq/L	5.29	8.11	9.19	9.46	9.31	5.18	5.27	5.01	5.08
ANIONS	meq/L	4.60	8.16	9.08	9.45	9.84	4.14	4.62	5.29	5.25

TABLE 16. Solid-Waste Performance Leach Study (Tests #3 and #4)

	HGW	Test #3 Miscellaneous				Test # 4 All Waste Types and Cement			
		3-1	3-2	3-3	3-4	4-1	4-2	4-3	4-4
		1 week	3 weeks	6 weeks	12 weeks	1 week	3 weeks	6 weeks	12 weeks
pH		8.14	7.75	7.16	7.39	7.37	11.77	12.04	12.12
Eh		309	329	315	328	342	266	95	149
Al	mg/L	<0.03	0.11	0.2	0.16	0.2	17	55.5	57.3
B	mg/L	0.1	0.1	0.1	0.1	0.12	0.1	0.05	0.24
Ba	mg/L	0.08	0.03	0.04	0.04	<0.002	0.37	1.18	1.7
Ca	mg/L	48.8	51	55.7	54	53.8	177	311	360
Cd	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Cr	mg/L	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020
Cu	mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Fe	mg/L	<0.005	<0.005	0.04	<0.005	<0.005	<0.005	<0.005	<0.005
K	mg/L	9.9	23	23	22	20	94	146	186
Li	mg/L	<0.004	<0.004	<0.004	<0.004	0.02	0.07	0.09	<0.004
Mg	mg/L	14.6	19.5	25.5	27.3	27.6	<0.06	<0.06	<0.06
Mn	mg/L	<0.002	0.03	0.05	<0.002	0.05	<0.002	<0.002	<0.002
Na	mg/L	32.1	35	36.2	37.1	37	58	75.6	88
P	mg/L	<0.10	1	<0.10	1.2	1	<0.10	<0.10	<0.10
Pb	mg/L	<0.060	<0.060	<0.060	<0.060	<0.060	<0.060	<0.060	<0.060
Si	mg/L	16.4	13.5	13.4	13.3	13.3	3.2	1.5	1.1
Sr	mg/L	0.25	0.22	0.24	0.23	0.24	0.66	1.29	1.6
Zn	mg/L	<0.020	1.4	5.77	11.8	20.8	<0.020	<0.020	<0.020
F-	mg/L	0.5	1.3	1.6	12	6.5	6.8	8.4	15
Cl-	mg/L	27	27.3	30.8	40	38	16.7	12.9	15
NO ₂ -	mg/L	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300	<0.300
NO ₃ -	mg/L	<0.500	0.7	1	0.9	0.5	0.6	0.6	1.7
PO ₄ -	mg/L	<0.400	<0.400	3.6	<0.400	2	<0.400	<0.400	<0.400
SO ₄ -	mg/L	75	57.5	57	80	84	35.1	13.2	1.1
T-ALK	mg/L	67.5	63	105	135	142.5	225	645	727.5
TOC	mg/L	1	75	30	70	64	90	110	148
IC	mg/L	28	46	60	40	61	5	3	2
CATIONS	meq/L	5.29	6.26	7.05	7.12	7.08	13.77	22.57	26.58
ANIONS	meq/L	4.60	4.15	5.66	7.94	7.93	9.07	22.59	25.51

increased to 70 ppm, and Zn, which continually increased to 20 ppm. Smaller increases in Cl, F, Mg, K, Al, and Na solution concentrations were observed.

The test that contained portions of all the waste types and cement (test #4) showed the largest changes in inorganic chemistry. The leachate pH values rapidly rose to 12.1 and the total dissolved solids increased 5 to 6 times over the original groundwater. It appears that several constituents were steadily dissolving and equilibrium was not reached even after 12 weeks. Concentrations of B, K, Na, Sr, F, and TOC in solution steadily rose throughout the 12 weeks. Concentrations of Al and Ca in solution also increased. Concentrations of Mg, Si, Cl and SO_4 in solution dropped to values near <0.06, 1, 15, and 1 ppm, respectively, suggesting that some precipitation reactions were also occurring. Past work with grout waste forms suggest compounds such as brucite [$\text{Mg}(\text{OH})_2$], calcium/magnesium carbonates, Ca-Al-sulfates (mono-sulfate, ettringite), and trace-metal hydroxides form during cement reactions with Hanford groundwater (Serne et al. 1987).

In all four tests the dissolved organic carbon content was significantly increased. The wood and paper leach test generated much more dissolved organic material than the other tests. Wood and paper within the cement leach test may also be the source of the high TOC in test #4's leachate. A summary of the results of the GC-MS analyses of the leachates from the four tests at each sampling time (1, 3, 6, and 12 weeks) is shown in Tables 17 and 18 for semivolatile and volatile organic analytes, respectively. The most frequently observed types of semivolatile organic compounds identified include phenols, alcohols, aromatic S and N containing species, aromatic acids, ketones, and aromatic hydrocarbons. The largest masses identified were alcohols and carboxylic acids.

The most common volatile compounds were chlorinated hydrocarbons, ketones, and aromatic hydrocarbons, but ketones accounted for most of the mass identified. Table 19 shows that less than 5% of the total dissolved organic carbon has been identified to date. Therefore, it is premature to make conclusions about major contributors. We had planned to use LC (liquid chromatography) and LC-MS to further study the leachates, but other project priorities have caused us to postpone further work. In addition, batch adsorption work to be discussed in the next section lead us to conclude that organics

TABLE 17. Summary of Semivolatile Organic Compound Types and Amounts Found in Leachates

	Leachate 1 (Test #1)								Leachate 2 (Test #2)								Leachate 3 (Test #3)								Leachate 4 (Test #4)							
Sampling Times (1, 3, 6, and 12 weeks)	1-1	1-2	1-3	1-4	2-1	2-2	2-3	2-4	3-1	3-2	3-3	3-4	4-1	4-2	4-3	4-4																
	# (a)	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm
Chain hydrocarbons																																
Ring hydrocarbons																																
Aromatic hydrocarbons	1	0.11	1	0.21				1	0.27									1	0.12	1	0.13											
Carboxylic acids								1	1.3	1	1.3	1	0.51																			
Aromatic Acids													1	0.20	2	3.0	1	0.05					2	0.06								
Alcohols	2	0.05	3	17.4	4	3.5	4	7.0																		2	0.07					
Aromatic Alcohols (includes phenol)	1	0.02			3	0.09	2	0.04			1	0.1	1	0.73											2	1.2	3	2.9	3	0.98	5	2.23
Ketones	1	0.18	1	0.13																					1	0.01	1	0.06	1	0.03	1	0.06
Phosphate Esters								1	0.1	1	0.04	1	0.03																			
Aromatic Esters (includes phthalates)	1	0.18			2	0.11	1	0.38	1	0.4																						
Aromatic S. N Compounds																																
Tri Butyl Phosphate	1	0.04																1	0.04	2	0.05	3	0.47	3	0.25							
TOTALS	7	0.6	5	17.8	9	3.7	8	7.7	3	1.8	3	1.4	3	1.3	1	0.20	5	3.2	5	0.3	3	0.5	5	0.3	3	1.2	9	3.1	4	1.0	9	3.0

(a) # = number of different compounds in this class that were identified

TABLE 18. Summary of Volatile Organic Compound Types and Amounts Found in Leachates

Sampling Times (1, 3, 6, and 12 weeks)	Leachate 1 (Test #1)								Leachate 2 (Test #2)								Leachate 3 (Test #3)								Leachate 4 (Test #4)							
	1-1		1-2		1-3		1-4		2-1		2-2		2-3		2-4		3-1		3-2		3-3		3-4		4-1		4-2		4-3		4-4	
	#(a)	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm	#	ppm
Chlorinated hydrocarbons	2	0.1	3	0.003	2	0.12	1	0.04	3	0.05	2	0.001	2	0.12	1	0.10	3	0.08	1	0.001	2	0.12	1	0.08	3	0.006			2	0.11	2	0.31
Ketones	2	0.02	2	0.36	2	0.15	2	0.21	2	0.09	2	0.13	2	0.20	2	0.09	2	0.07	2	0.22	1	0.08	1	0.01	3	0.260	2	0.68	2	0.70	1	0.33
Aromatic hydrocarbons	1	0.01	2	0.002	2	0.08	2	0.03					2	0.10	2	0.08			2	0.001	2	0.05	1	0.08					2	0.07	2	0.056
Organic Sulfides	1	0.001	1	0.02	1	0.04	1	0.016	1	0.001	1	0.001					1	0.04	1	0.001	1	0.23	1	0.16	1	0.001						
TOTALS	6	0.12	8	0.38	7	0.39	6	0.30	6	0.14	5	0.13	6	0.42	5	0.27	6	0.19	6	0.22	6	0.48	4	0.33	7	0.27	2	0.68	6	0.88	5	0.70

(a) # = number of different compounds in this class that were identified

TABLE 19. Comparison of Mass of Identified Organics Versus TOC Values

	Leachate 1 (Text #1)				Leachate 2 (Text #2)				Leachate 3 (Text #3)				Leachate 4 (Text #4)			
	1-1	1-2	1-3	1-4	2-1	2-2	2-3	2-4	3-1	3-2	3-3	3-4	4-1	4-2	4-3	4-4
Volatiles (ppm)	0.12	0.38	0.39	0.30	0.14	0.13	0.42	0.27	0.19	0.22	0.48	0.33	0.27	0.68	0.88	0.70
Semivolatiles (ppm)	0.60	17.8	3.7	7.7	1.8	1.4	1.3	0.20	3.2	0.3	0.5	0.3	1.2	3.1	1.0	3.0
Total (ppm)	0.72	18.2	4.1	8.0	1.9	1.5	1.7	0.5	3.4	0.5	1.0	0.6	1.5	3.8	1.9	3.7
TOC (ppm OC)	407	440	480	561* 520*	39	40	40	59	75	30	70	64	90	110	148	245* 230*
% OC Identified	<0.2	<4	<0.9	<1.4	<5	<4	<4	<0.8	<5	<2	<1	<1	<2	<3	<1	<2

* Independent duplicate analyses

present in the leachate have only moderate effects on the adsorption tendencies of a few nuclides and little or no influence on many nuclides. Thus, we elected to concentrate FY92 and FY93 funds in other areas.

The mold present in the test solution #1 (wood, cardboard, and paper) was sent to Washington State University where microbiologists determined that there were at least nine different species of filamentous fungi present. Two of the species were readily identifiable as *Aspergillus* (5×10^5 propagules/mL) and *Penicillium* (6.6×10^4 propagules/mL). The remaining seven species were difficult to identify. The total fungi content of the slurry was 4.2×10^7 propagules/mL. A propagule is one viable organism, spore, or piece of an organism.

4.0 BATCH DISTRIBUTION COEFFICIENT RESULTS USING SOLID-WASTE LEACHATES

The objective of this test was to investigate whether the high dissolved organic carbon (DOC) in solid-waste leachates and the mold present in some of the leachates affect radionuclide adsorption onto Hanford Trench-8 sediments.

The leach tests described in Section 3.0 created a leachate that we assume represents solutions that will migrate away from the burial grounds carrying dissolved and suspended particles bearing potentially hazardous chemicals. Leachates percolating away from the buried waste will interact with the unsaturated sediments and likely lose some of the contaminants via precipitation and adsorption reactions.

The chemical composition of the four solid-waste leachates discussed in Section 3.0 showed two unique attributes. First, the solutions in tests contacting paper, cardboard, and wood (test #1 and test #4) contained relatively high DOC content and visible organic biomass (molds). Second, test solution 4 (from test #4) in contact with cement reached pH values of 12 and relatively high dissolved salt content (5 times groundwater). The other two solutions, from tests #2 and #3, contacting plastics and miscellaneous wastes were less different from the original groundwater.

We decided to perform standard batch adsorption tests using solutions 1 and 4 from the solid-waste leach tests to investigate whether the high DOC, and in the case of solution 4, high pH, significantly affect contaminant adsorption. We ran two sets of tests with solution 1; one set with a known amount of the mold and one set without mold.

The sediment used in all the tests is the Trench-8 sediment described in Section 2.0. The batch tests were performed at a solution to solids ratio of 30 mL/g. Triplicate tests with and without sediment were performed. The sample containers were continuously agitated slowly to facilitate sediment/solution reaction. At 5 and 44 days, the samples were centrifuged and small aliquots of solution withdrawn, filtered through 0.22- μ m membranes, and measured for contaminant concentrations remaining in solution. For these tests the Trench-8 sediments were not pre-washed/acclimated with unspiked solution as is typically performed in batch adsorption testing. At the end of the

44-day contact period, the chemical composition of the contacting solutions was determined. Additional details on our batch adsorption protocol can be found in Relyea, Serne, and Rai (1980).

The batch adsorption test matrix consisted of eighteen solutions shown in Table 20. The batch R_d tests that contained mold were prepared by adding about 0.037 mL of mold slurry to each mL of leachate. Thus, the total propagule concentration in the solutions used to measure contaminant adsorption in the presence of mold was 1.6×10^6 propagules/mL. R_d values were determined for TcO_4^- , I^- , UO_2^{2+} , CrO_4^{2-} , SeO_4^{2-} , Sr^{2+} , Cs^+ , Co^{2+} , Ni^{2+} , and NpO_2^+ . Results (triplicate measurements) are shown in Table 21. Table 22 presents the chemical composition of the leachates before spiking with contaminants and contact with the sediments and composition after the 44 days of contact with the sediments.

TABLE 20. Batch Adsorption Test Matrix

1. Test 1 leachate with mold + 100 $\mu\text{Ci/L}$ $^{99}\text{TcO}_4^-$
2. Test 1 leachate with mold + 200 $\mu\text{Ci/L}$ $^{125}\text{I}^-$
3. Test 1 leachate with mold + 0.05 mg U/L as UO_2^{2+} , 0.10 mg Cr/L as CrO_4^{2-} , 0.10 mg Se/L as SeO_4^{2-} and 10 mg/L NO_3^-
4. Test 1 leachate with mold + 100 $\mu\text{Ci/L}$ ^{86}Sr as Sr^{2+} , 100 $\mu\text{Ci/L}$ ^{137}Cs as Cs^+ and 100 $\mu\text{Ci/L}$ ^{60}Co as Co^{2+}
5. Test 1 leachate without mold same spike as 1
6. Test 1 leachate without mold same spike as 2
7. Test 1 leachate without mold same spike as 3
8. Test 1 leachate without mold same spike as 4
9. Test 4 leachate without mold same spike as 1
10. Test 4 leachate without mold same spike as 2
11. Test 4 leachate without mold same spike as 3
12. Test 4 leachate without mold same spike as 4
13. Test 1 leachate without mold + 100 $\mu\text{Ci/L}$ ^{63}Ni as Ni^{2+}
14. Test 1 leachate without mold + 100 $\mu\text{Ci/L}$ ^{60}Co as Co^{2+}
15. Test 1 leachate without mold + 100 $\mu\text{Ci/L}$ ^{237}Np as NpO_2^+
16. Test 4 leachate without mold same spike as 13
17. Test 4 leachate without mold same spike as 14
18. Test 4 leachate without mold same spike as 15

TABLE 21. Distribution Coefficient Values (mL/g)

Solution Type		5-Day Contact	44-Day Contact
TcO₄			
#1 (Wood/paper/mol'd)	-0.6 ± 0.1	0.02 ± 0.3	
#2 (Wood/paper)	-0.2 ± 0.4	-0.2 ± 0.3	
#3 (Wastes/cement)	-0.4 ± 0.2	0.02 ± 0.3	
I⁻			
#1 (Wood/paper/mol'd)	0.6 ± 0.3	0.6 ± 0.6	
#2 (Wood/paper)	0.6 ± 0.1	-0.1 ± 0.3	
#3 (Wastes/cement)	-0.5 ± 0.2	-0.4 ± 0.2	
Cs⁺			
#1 (Wood/paper/mol'd)	390 ± 40	610 ± 120	
#2 (Wood/paper)	420 ± 50	410 ± 40	
#3 (Wastes/cement)	45 ± 10	50 ± 2	
Sr²⁺			
#1 (Wood/paper/mol'd)	17.2 ± 1.9	6.1 ± 4.2	
#2 (Wood/paper)	13.2 ± 4.4	12.8 ± 1.2	
#3 (Wastes/cement)	3.5 ± 2.1	4.4 ± 2.5	
UO₂²⁺			
#1 (Wood/paper/mol'd)	-6.2 ± 0.8	-7.4 ± 3.1	
#2 (Wood/paper)	0.3 ± 0.8	-0.2 ± 0.9	
#3 (Wastes/cement)	2850 ± 960	320 ± 140	
CrO₄²⁻			
#1 (Wood/paper/mol'd)	1.9 ± 6.0	6.7 ± 2.9	
#2 (Wood/paper)	-1.1 ± 6.6	0.7 ± 3.0	
#3 (Wastes/cement)	4.4 ± 2.7	0.9 ± 0.2	
SeO₄²⁻			
#1 (Wood/paper/mol'd)	-2.6 ± 10.9	0.3 ± 1.1	
#2 (Wood/paper)	0.1 ± 4.2	-2.2 ± 2.8	
#3 (Wastes/cement)	-0.9 ± 0.9	2.1 ± 1.6	
Co²⁺			
#1 (Wood/paper/mol'd)	60 ± 40	80 ± 45	
#2 (Wood/paper)	60 ± 10	50 ± 15	
#3 (Wastes/cement)	15 ± 5	17 ± 1	
Ni²⁺			
#1 (Wood/paper/mol'd)	14 ± 1	28 ± 6	
#2 (Wood/paper)	3 ± 0.5	6 ± 1	
#3 (Wastes/cement)			
NpO₂⁺			
#1 (Wood/paper/mol'd)	6 ± 2	20 ± 7	
#2 (Wood/paper)	200 ± 70	>3000	
#3 (Wastes/cement)			

TABLE 22. Chemical Composition of Solutions

	Solutions 1 and 2			Solution 3	
	Start of Test	44 Days	44 Days	Start of Test	44 Days
		Contact with Sediments	Contact with Blank		Contact with Sediments
pH	5.04	7.1	7.5	12.12	12.26
Eh	403	-- (a)	--	149	--
Al	mg/L 1.5	0.4	0.8	43.5	4.8
B	mg/L 1.7	1.61	1.64	2.18	<0.01
Ba	mg/L 0.16	0.07	0.15	<0.002	1.55
Ca	mg/L 49.9	97	50	296	377
Cd	mg/L <0.004	<0.004	<0.004	<0.004	<0.01
Cr	mg/L <0.020	0.09	0.11	<0.020	0.10
Cu	mg/L <0.004	<0.004	<0.004	<0.004	0.016
Fe	mg/L 0.4	0.44	0.2	<0.005	0.015
K	mg/L 11	11	12	235	256
Li	mg/L <0.004	<0.004	<0.004	0.17	0.15
Mg	mg/L 13.4	15.1	13	<0.06	<0.06
Mn	mg/L 0.37	2.05	0.34	<0.002	<0.01
Na	mg/L 125	125	124	96	110
P	mg/L <0.10	--	--	<0.10	--
Pb	mg/L 0.13	<0.1	<0.1	<0.060	<0.10
Si	mg/L 15	16.5	14.8	0.7	2.3
Sr	mg/L 0.26	0.3	0.24	1.96	2.4
Zn	mg/L 0.19	<0.05	0.18	<0.020	<0.05
F-	mg/L 29	13.4	8	20	20
Cl-	mg/L 40	31.5	31.6	14	9.2
NO ₂ -	mg/L <0.300	<0.3	<0.3	<0.300	<0.3
NO ₃ -	mg/L 0.3	<0.5	<0.5	3	25
PO ₄ -	mg/L <0.400	<0.4	<0.4	3	<0.3
SO ₄ -	mg/L 92	84.6	91.2	1.5	1.4
T-ALK	mg/L 157.5	--	--	1050	--
TOC	mg/L 561	398	426	245	460
IC	mg/L 17	79	24	14	0
Cations meq/L	9.31	9.38	9.27	25.00	30.18
Anions meq/L	9.84	9.94	--	36.53	--

Note: Solutions 1 and 2 are leachates formed when groundwater contacts wood and paper wastes for greater than 12 weeks. Solution 1 also contains suspended mold.

Solution 3 is the leachate formed when groundwater contacts all types of waste and crushed cement for greater than 12 weeks.

(a) -- not measured

Trace quantities of ^{99}Tc , ^{125}I , ^{137}Cs , ^{85}Sr , ^{60}Co , ^{63}Ni , and ^{237}Np ; 100 $\mu\text{g/L}$ of Se and Cr; and 50 $\mu\text{g/L}$ U were used as the spikes. Gamma and liquid scintillation counting were used to determine radioisotope contents. ICP-MS was used to measure Cr, Se, and U contents. ICP, IC, and a total carbon analyzer were used to measure the chemical composition of the solutions presented in Table 22.

The adsorption results will be discussed by contaminant. As suspected, the ^{99}Tc as pertechnetate anion did not show any adsorption tendencies from the leachates studied. The high organic carbon content, presence of mold and variable pH values (cement leachate $\text{pH} > 12$) did not influence adsorption. All blanks (solutions spiked with ^{99}Tc) remained stable over the 44-day test period.

The iodide adsorption data show more scatter but appear to reflect no significant adsorption onto Hanford sediments from any of the waste leachates. Iodide is known to associate with solid organic matter in sediments but apparently does not react with mold that flocculates with the sediments during adsorption testing.

The Cs adsorption data suggest that the mold and DOC do not influence adsorption. The $R_d(\text{Cs})$ remains high $\sim 500 \text{ mL/g}$ for leachates containing almost 500 mg/L dissolved organic C. The adsorption of Cs is significantly diminished in the test with waste/cement leachate. As shown in Table 22, this solution contains about 250 mg/L K (from cement dissolution) that readily competes with Cs for adsorption sites. Thus the $R_d(\text{Cs})$ is only about 10% as large as in test solutions containing $\sim 15 \text{ mg/L}$ K.

The Sr adsorption data suggest that solutions with high dissolved organic carbon do decrease adsorption somewhat (40% reduction over adsorption in groundwater). It is difficult to differentiate whether the effect is caused by organic C or the increased Ca concentrations also found in these solutions. The tests with leachate exposed to cement contain almost 400 mg/L Ca and exhibit the lowest adsorption.

The adsorption of UO_2^{2+} onto Hanford sediments from the waste leachates suggests that under near-neutral pH (7 ± 1) high concentrations of dissolved organics lower UO_2^{2+} adsorption to zero. In other adsorption work (see

Section 5.0) UO_2^{2+} adsorption from a slightly acidic to neutral process water without dissolved organic carbon yielded R_d values ranging from 100 to 1000 mL/g. The data presented in Table 21 show essentially no adsorption for UO_2^{2+} in the presence of organics dissolved from wood and paper.

The apparent high UO_2^{2+} adsorption from the solutions containing cement leachate can be explained by two complementary reactions. First at high pH values ($\text{pH} > 12$), much of the 50- $\mu\text{g/L}$ U spike precipitated in the blank tests with solution but no sediment. Secondly, the cement removes all carbonate species from the solution through precipitation of CaCO_3 . The resultant solution (see Table 22) contains mainly OH^- anions. In such a solution the dominant species of U(VI) are UO_2^{2+} and its hydrolysis species $\text{UO}_2(\text{OH})^+$, and $\text{UO}_2(\text{OH})_2^0$, which adsorb readily onto geologic materials (Hsi and Langmuir 1985). Thus the combination of precipitation and lack of carbonate complexation allow strong adsorption of UO_2^{2+} in the system where sediments contact leachate dominated by cement leaching.

The CrO_4^{2-} and SeO_4^{2-} anions do not show any appreciable adsorption onto Hanford sediments from the leachates studied. In past adsorption studies (see Section 5.0) there was no adsorption onto fine- or coarse-grained Hanford sediments from groundwater. There did appear to be minor adsorption of SeO_4^{2-} ($R_d < 5 \text{ mL/g}$) and some adsorption of CrO_4^{2-} ($R_d \sim 10 \text{ mL/g}$) onto the fine-grained sediment from a process waste solution at pH values < 4.5 (see Section 5.0). In the present tests pH values ranged from 7 to 12.2 and no appreciable adsorption was observed.

The Co adsorption data for leachate 1 with mold are quite variable, caused by interferences in counting ^{60}Co in the presence of higher levels of ^{85}Sr and ^{137}Cs . The other two data sets came from test matrices 14 and 17 (see Table 20) where no Sr and Cs were present. The added Co tracer remained in solution in the blank specimen tubes suggesting no precipitation or wall adsorption problems. Cobalt is one contaminant that has been found to become mobile in subsurface environments when associated with organics (e.g., Fruchter et al. 1984, 1985; Jones et al. 1988; Killey et al. 1984; Means et al. 1976, 1978). The adsorption data collected to date do suggest lower adsorption of ^{60}Co in the presence of leachates with high organics versus sorption from Hanford groundwater. The lowered adsorption is especially

noticeable for the high pH tests where cement leachate is present. Typically one would expect that dissolved inorganic Co would be less soluble at high pH and contribute to higher retardation or distribution ratios. The observed data where Co distribution ratios are small for the high pH environment could reflect that organic acid (carboxylic), organic alcohols, organic amines, etc. all tend to deprotonate (lose H^+) at high pH values. The organic molecule thus obtains a more negative charge and can readily attract soluble cationic species such as Co^{2+} . The organo-metal complexes often retain negative charges and in general are much larger species in solution. Both attributes, net negative charge and large size, lower the adsorption potential onto inherently negatively charged geologic materials. Despite the dissolved organic carbon lowering of Co sorption, the R_d values are still large enough to cause significant retardation of Co in Hanford sediments. The Ni-63 adsorption data follow the same trends as the Co^{2+} but the R_d values show less adsorption by a factor of 2 to 5. The reduced adsorption is not expected from simple ion-exchange principles because both Co and Ni form divalent cations with similar sizes and properties. The lowered adsorption tendencies for Ni may reflect preferential adsorption of Co onto hydrous oxides of Fe, Mn, and Al. Nickel is known to adsorb less preferentially than Pb, Cu, and Zn on such compounds (McKenzie 1980; Murray 1975).

The NpO_2^+ cation is moderately adsorbed from the organic-rich leachate formed by leaching wood, cardboard, and paper products. For leachates containing cement dissolution products (high pH ~12) Np precipitates readily in blank tubes and adsorbs/precipitates onto sediments. It appears that in an actual burial ground containing cement, dissolved Np emanating from wastes would be kept at very low concentrations. Alternatively, if a solution laden with Np encountered cement, there would be a significant loss of Np from solution.

The effects of organics on Np sorption cannot be determined from these preliminary tests. Although the least adsorption is observed for the leachate with the highest DOC, this solution also has the lowest pH. Adsorption of NpO_2^+ is very sensitive to pH (sorption increases as pH increases). The tests using cement leachate corroborate the importance of pH. In the Hanford environment NpO_2^+ appears to be moderately mobile but not as mobile as UO_2^{2+} ,

which forms strong and soluble complexes with dissolved carbonates. In cement-influenced environments, both UO_2^{2+} and NpO_2^+ are considerably less mobile than in normal groundwater environments (see Section 5).

To date the tests suggest that the presence of mold in the tests does not significantly change adsorption tendencies for I^- , TcO_4^- , UO_2^{2+} , CrO_4^{2-} , and SeO_4^{2-} , Cs^+ , Sr^{2+} , or Co^{2+} . The presence of high concentrations of DOC from dissolution of wastes (i.e. wood, cardboard, plastic, nylon, rubber, etc.) may be significantly influencing the adsorption properties of Co and to much smaller extents Sr and U. Known cation competition effects (K vs. Cs) and (Ca vs. Sr) influence the observed R_d values for Cs and Sr. The presence or absence of carbonate species (also related to system pH) is also influencing the adsorption of UO_2^{2+} . In these tests none of the variables discussed seems to be changing the adsorption tendencies of TcO_4^- , I^- , CrO_4^{2-} , or SeO_4^{2-} . In each instance these anionic species show no tendency to adsorb.

The chemical composition of the leachates prior to starting and at the end of the adsorption tests are shown in Table 22. The paper, wood, and cardboard leachates (solutions 1 and 2) remain fairly stable during the 44 day adsorption testing. The Ca concentration in solution about doubles (50 to 97 mg/L), and Mn in solution increases when sediment is present. The apparent drop in F solution concentration is most likely a drop in DOC that appears on the ion chromatogram in the same region as F and is often mistaken as high concentrations of fluoride. The cement leachate (solution 3) shows a small drop in Al and B upon contacting the sediments and small increases in Ca and Ba. The elevated nitrate values in the leachates after contact with Trench-8 sediment come from spiking nitrate and nitrate-based tracers such as $\text{UO}_2(\text{NO}_3)_2$ into the solution prior to contact with the sediments.

5.0 BATCH ADSORPTION TESTS USING SIMULATED PROCESS WASTE WATER AND GROUNDWATER

These batch adsorption tests were performed to begin a database of R_d values for key radionuclides and regulated chemicals that appear to be the more problematical constituents in Hanford defense wastes. The constituents of concern have been chosen based on past PA activities and judgements based on defense waste inventories and hydrogeochemical characteristics of Hanford sediments, groundwater, and individual contaminants (see Serne and Wood 1990). To develop a database rapidly, while improving on past work that often did not characterize the sediments and waters used, we elected to use the simple batch adsorption technique. We applied this technique to three of the well-characterized sediments discussed in Section 2.0; a well-characterized Hanford groundwater; and a simulated acidic, high-ionic-strength process waste water. The two fluids represent bounds of expected geochemical conditions found in Hanford near-surface unsaturated sediments during past disposal practices. Although these tests were not performed under the unsaturated moisture conditions expected in shallow Hanford sediments, a key technical issue that we hope to address in the SWTS project, the tests were performed to initiate efforts to generate a technically defensible adsorption database on constituents of concern at the Hanford Site. Nine constituents were studied: NO_3^- , NO_2^- , U(VI) , Cr(VI) , Se(VI) , Tc(VII) , I^- , Sr(II) , and Cs(I) . For sorption tests using Trench-8 sediment and Hanford groundwater, Co(II) , Ni(II) , and Np(V) were also used.

The test matrix is shown in Table 23. Two solutions, three soils, and contaminants at one set concentration in each solution were used. The R_d measurements were made at three contact times (4, 14, and 35 days). The solid-to-solution ratio was fixed at 1 g:30 mL. The sediment samples were pre-washed three times with unspiked solution to acclimate the sediments with the major constituents in the solution.

The slurries were centrifuged and clarified and supernatant solution was filtered through 0.22- μm membranes prior to analyses. Blank tests (with no sediment present) were included. All tests were performed in triplicate. Details on procedure and calculation of R_d values are given in Relyea et al. (1980).

TABLE 23. Batch Test Experimental Matrix

- (a) Spikes 5, 6, 7 were only used in combination with sediment #3
(b) Trench-8 sediment was not contacted with acidic process waste because it is within a solid-waste burial ground that will not contact liquid wastes.

The three sediments were TBS-1, CGS-1, and Trench-8 as described in Section 2.0. The TBS-1 is rather fine grained, whereas the CGS-1 sample is very coarse grained. The adsorption properties of these two sediments should provide the bounds of values for most Hanford sediments. Trench-8 sediment is of particular interest to the SWTS project and was included to give site-specific data for the ongoing PA. Solution 1 is an uncontaminated groundwater obtained from Hanford well 6-S3-25 in the southeast quadrant of the Hanford Site (see Table 12 for composition). Solution 2 is a synthetic process waste water similar to PUREX process condensates and chemical sewer-ion exchange

regenerate wastes. The composition chosen is shown in Table 24. The solution was prepared using reagent-grade chemicals and aged in air for several days. Prior to use, the solution was filtered through a 0.2- μ m membrane filter.

The spikes that were added to the solutions are shown in Table 25. The spiked solutions were equilibrated for at least three days and filtered through 0.2- μ m filters prior to contact with the sediments.

After the sediments and spiked solutions were mixed, the slurries were gently rocked in a linear shaker to facilitate reaction. At set times (4, 14, and 35 days) the slurries were centrifuged. Then a small portion (~3.0 mL) of the supernatant liquid was removed, filtered through a 0.2- μ m membrane, and prepared for analyses. The following preservation steps and solution volumes were used.

SPIKE #1 effluents

- 0.5 mL no preservation; NO_2^- , NO_3^- run on ion chromatograph
- 0.5 mL dilute with nitric acid (pH=2); U run on laser fluorescence spectrophotometer
- 2.0 mL dilute with nitric acid (pH=2); Se, Cr run on graphite furnace-atomic absorption spectroscopy (GFAA)

SPIKE #2

- 3.0 mL no preservation; ^{99}Tc analyzed by liquid scintillation

SPIKE #3

- 3.0 mL no preservation; ^{125}I analyzed by liquid scintillation

SPIKE #4

- 3.0 mL dilute with nitric acid (pH=2); ^{85}Sr and ^{137}Cs analyzed by NaI detector

SPIKE #5

- 2.0 mL dilute with nitric acid (pH=2); ^{60}Co measured by NaI detector

SPIKE #6

- 2.0 mL dilute with nitric acid (pH=2); ^{63}Ni analyzed by liquid scintillation

SPIKE #7

- 2.0 mL dilute with nitric acid (pH=2); ^{237}Np analyzed by liquid scintillation.

TABLE 24. Simulated Process Waste Composition (Solution #2)

<u>Constituent</u>	<u>Molarity</u>	<u>Total Composition</u>	<u>mg/L</u>
Mg(NO ₃) ₂	0.41 x 10 ⁻³ M ± 1%	Mg	10
Ca(NO ₃) ₂	1.50 x 10 ⁻³ M ± 1%	Ca	60
Na ₂ SO ₄	3.12 x 10 ⁻³ M ± 1%	Na	170
		SO ₄	300
NaNO ₂	1.09 x 10 ⁻³ M ± 1%	NO ₂	50
HNO ₃	to pH 4.5	NO ₃	~260

TABLE 25. Contaminant Spike Compositions

Solution #1 - Spike #1, added to the Hanford groundwater:

10 mg/L NO₃ as NaNO₃
 10 mg/L NO₂ as NaNO₂^(a)
 0.05 mg/L U as UO₂(NO₃)₂
 0.10 mg/L Cr as Na₂CrO₄
 0.10 mg/L Se as Na₂SeO₄

Solution #2 - Spike #1, added to the synthetic process waste:

0.05 mg/L U as UO₂(NO₃)₂
 0.10 mg/L Cr as Na₂CrO₄
 0.10 mg/L Se as Na₂SeO₄

Solutions #1 and #2 - Spike #2, added to both solutions:

100 µCi/L ⁹⁹Tc as TcO₄⁻

Solutions #1 and #2 - Spike #3, added to both solutions:

200 µCi/L ¹²⁵I as I⁻

Solutions #1 and #2 - Spike #4, added to both solutions:

100 µCi/L ⁸⁵Sr as Sr²⁺
 100 µCi/L ¹³⁷Cs as Cs⁺

Solution #1 - Spike #5, #6, #7, added to separate groundwater aliquots:

100 µCi/L ⁶⁰Co as Co²⁺
 100 µCi/L ⁶³Ni as Ni²⁺
 100 µCi/L ²³⁷Np as NpO₂⁺

(a) Nitrite was not added to the groundwater that contacted Trench-8 sediment because NO₂ was found to be unstable in the tests on the other two soils.

The pH of most supernatant solutions was measured with a combination pH electrode/meter prior to restarting the batch adsorption tests for the longer contact periods. No additions of replacement influent were made but the solution-to-solid ratio was corrected at each period to calculate the R_d values.

At the end of the 35-day contact period, supernatant solution from each of the 23 test combinations (2 sediments x 2 solutions x 4 spikes and 1 sediment x 1 solution x 7 spikes) was completely analyzed for pH, Eh, cations by ICP, anions by IC, and alkalinity by titration. Only one sample of each set of three replicates was characterized from each test to conserve costs. The sample was randomly chosen.

The contaminants' R_d values were calculated for two to three periods in all tests. The blank tests were used to generate the adjusted influent concentration for each spike solution at each period. That is, blank tests allowed us to compensate for any container wall adsorption and precipitation that could occur regardless of sediment adsorption. The adjusted influent concentration value is needed to calculate the R_d value.

During the pre-equilibration steps with the simulated acidic waste solution, we determined that both sediments, but especially the TBS-1 sediment, neutralized the pH from 4.5 up to about 7. To counteract the buffering capacity of the sediments, small amounts of 1 M nitric acid were added to the process waste water to exhaust the sediment's alkalinity. By the end of the third cold wash, the TBS-1 samples required 0.85 mL and the CGS-1 samples 0.25 mL of 1 M HNO_3 to force the sediment slurries to pH values around 4.5. The early washes actually created pH regimes as low as 2.7 for the TBS-1 samples and 3.2 for the CGS-1 samples. We expect that much of the amorphous Fe oxides and all of the Ca carbonate present in the sediment aliquots dissolved during the pre-equilibration tests. In the actual in situ case, carbonates would be removed by continual contact with waste water at pH ~4.5, and hydrous oxides would likely remain. If the pH is more acidic than pH ~4 in areas adjacent to acid waste disposal units, hydrous oxides would likely dissolve, be transported in solution to more alkaline pH environments, and then reprecipitate as surface coatings. At the end of the three cold washes with acidic process waste to precondition the two sediments, the pH values were

4.1 to 5.0 for CGS-1 and ~2.7 for TBS-1. At the three sample times (4, 14, and 35 days) during the batch R_d test, the pH of the slurries continued to drift upwards, as shown in Table 26. The goal was to create a slurry environment that remained near pH = 4.5. Without frequent pH adjustments, however, it is difficult to maintain Hanford sediments at an acidic pH value. By contact with extremely acidic wash solution (pH <2.9), we managed to keep the TBS-1 systems near pH = 4.2 during the tracer adsorption portion of the tests. The less extreme washing of the CGS-1 systems allowed the pH to drift well above the desired acidic pH value during the adsorption periods. At pH values between 6.0 and 7.5, hydrous oxides of Fe, Al, and Mn do not readily adsorb anions. As mentioned previously, we suspect most of the hydrous oxides were removed during the washing step.

The pH of the sediment slurries in contact with groundwater during the preconditioning wash with cold groundwater and during the batch R_d 35-day contact tests remained between 8.0 and 8.5. The pH of the original groundwater was 8.1 to 8.2.

The chemical composition of the two spiked solutions (groundwater and simulated acidic process water) remained fairly constant over the 35-day contact period with the sediments, suggesting that the preconditioning washes had brought the sediment and solutions to a steady-state (perhaps equilibrium) condition excepting the pH for the acidic solution. The composition of the groundwater and simulated acidic process water before and after contact with the sediments is shown in Table 27.

TABLE 26. pH Values of Slurries During Batch Distribution Coefficient Tests Using Simulated Process Waste Water

<u>Sediment</u>	<u>pH at 4 days</u>	<u>pH at 14 days</u>	<u>pH at 35 days</u>
CGS-1	5.2 to 6.9	5.5 to 7.3	5.9 to 7.6
TBS-1	3.9 to 4.1	4.0 to 4.2	4.1 to 4.3

TABLE 27. Chemical Composition of Solutions Used in Batch Distribution Coefficient Tests

Constituent Units	Groundwater				Acid Process Waste		
	Before Contact	After 35 Days Contact		Trench-8 ^(a)	Before Contact	After 35 Days Contact	
		CGS-1	TBS-1			CGS-1	TBS-1
pH Units	8.14	7.9 - 8.4	8.0 - 8.4	8.22	3.5	5.9 - 7.5	4.13 - 4.30
Al mg/L	<0.03	<0.03	<0.03	NA ^(b)	<0.03	<0.03	0.58 - 0.67
B mg/L	0.1	0.22	0.20 - 0.23	0.10	<0.01	<0.01 - 0.09	<0.01 - 0.08
Ba mg/L	0.09	0.10 - 0.17	0.10 - 0.15	0.09	0.06	0.06 - 0.13	0.09 - 0.15
Ca mg/L	60.4	58 - 60	57.9 - 60.9	53	64.7	67.6 - 74.0	68.4 - 77.4
Cd mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Cr mg/L	<0.02	<0.01 - 0.1	<0.01 - 0.12	<0.004	<0.02	<0.02	<0.02
Cu mg/L	<0.004	<0.004	<0.004	0.10	<0.08	<0.004	<0.004
Fe mg/L	<0.005	<0.005	<0.005 - 0.075	<0.004	<0.005	<0.005	<0.005
K mg/L	10.2	8.7 - 9.1	8.4 - 9.6	7.0	4.1	2.7 - 3.6	3.9 - 4.4
Li mg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Mg mg/L	14.4	14.9 - 15.3	14.9 - 15.3	15	9.8	9.9 - 10.4	11.9 - 12.7
Mn mg/L	<0.002	<0.002	<0.002	<0.002	<0.002	0.10 - 0.24	<0.02 - 0.71
Mo mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na mg/L	34.9	42.1 - 43.1	42.0 - 43.7	33	192	198 - 206	193 - 198
P mg/L	0.36	<0.2 - 0.24	<0.2 - 0.24	NA	0.2	<0.2 - 0.21	<0.2 - 0.31
Pb mg/L	<0.06	<0.06	<0.06	<0.10	<0.06	<0.06	<0.06
Si mg/L	16.7	17.3 - 17.7	16.8 - 17.5	14.7	0.17	6.1 - 8.2	12.7 - 14.1
Sr mg/L	0.25	0.22 - 0.27	0.27 - 0.28	0.22	<0.02	<0.02 - 0.04	<0.02 - 0.06
Zn mg/L	<0.02	<0.02	<0.02 - 0.13	<0.05	0.12	<0.02 - 0.14	0.14 - 0.17
F ⁻ mg/L	0.5	0.8 - 1.6	0.6 - 1.1	<0.5	<0.5	0.7 - 0.9	0.6 - 1.0
Cl ⁻ mg/L	30.	26.9 - 31.3	26.3 - 27.3	29.2	0.8	3.4 - 4.0	4.5 - 6.4
NO ₂ ⁻ mg/L	<0.3	<0.3	<0.3	<0.3	12.9	8.1 - 9.9	<0.3
NO ₃ ⁻ mg/L	7.8	14.9 - 16.7	21.8 - 58.1	29.2	340	362 - 428	433 - 489
PO ₄ ³⁻ mg/L	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
SO ₄ ²⁻ mg/L	70	58.8 - 64.0	56.0 - 62.8	80.0	310	246 - 289	279 - 298
Tot. Alk ^(c)	67.5	137.5 - 150.0	137.5	NA	0	0 - 37.5	0
TOC mg/L	1.0	NA	NA	NA	NA	NA	NA
IC mg/L	30.2	NA	NA	NA	NA	NA	NA
Cations (meq/L)	5.99	6.3	6.2 - 6.4	5.50	12.50	13.3	13.2
Anions (meq/L)	4.68	6.9 - 7.5	7.0 - 7.5	NA	12.25	13.2	13.3 - 14.2

(a) Trench-8 sediment contact time was 44 days, not 35 days.

(b) NA = not analyzed.

(c) Reported as CO₃²⁻.

The data in Table 27 show very little change in the chemical composition of either water after contact with the Hanford sediments. Therefore, the adsorption data (see Tables 28-30) can be considered representative of near-equilibrium conditions, excepting pH for the acidic process water.

For the process water contacting the Hanford sediments, there were very minor increases in B, Ba, Ca, Mg, Na, and a slight decrease in K and SO_4 . The tests with process water show increases in solution concentrations of Al when the pH remains acid (TBS-1 sediment), as well as increases in Mn, Si, Cl, and NO_3 . Aluminum is soluble under acidic conditions; the silicon comes from the sediment, and the excess nitrate results from the addition of 1 M HNO_3 to generate the acidic conditions. Aside from the large variations in pH that occur between the CGS-1 and TBS-1 sediments in contact with the process waste water, the few observed changes in chemical composition should have little influence on the adsorption properties of the selected contaminants.

Nitrite added to the two solutions appears to be unstable, especially in the groundwater. In some instances, nitrite was measurable but in most groundwater tests (either blanks or sediments), after 14 to 35 days no nitrite was found. Nitrite likely oxidized to nitrate during these tests.

The R_d values for contaminants in Hanford groundwater contacting the three sediments will be discussed first. (Recall that the sediments used in all tests have had gravel-sized particles removed.) Geochemical and soil science principles suggest that sediment TBS-1 by virtue of its finer texture and higher cation exchange capacity should adsorb cationic contaminants to a greater extent than sediment CGS-1. Trench-8 sediment would be expected to adsorb cations similar to TBS-1. Tables 28 through 30 show that TBS-1 does indeed adsorb more ^{137}Cs (especially from the groundwater) than sediment CGS-1. It is not clear why Trench-8 sediment adsorbs significantly less Cs than the other two sediments. For PA needs it is sufficient to note that all these sediments adsorb Cs readily from either type of solution studied. TBS-1 and Trench-8 sediments adsorb more ^{85}Sr than the CGS-1 soil, but the difference is small. TBS-1 adsorbs more U when present in groundwater than CGS-1 or Trench-8 sediments, but the variance in $R_d(\text{U})$ is quite large and the available data cannot be guaranteed to be statistically different.

TABLE 28. Values for the Distribution Coefficient for Contaminants on Hanford Sediment CGS-1. The pH of the groundwater was 8.3 and the pH for the process waste stream was 4.5.

Contaminant	Solution	Distribution Coefficient (mL/g)			Overall Average
		4 days	14 days	35 days	
CrO ₄ ²⁻	Groundwater	0.5 ± 0.6	-0.5 ± 0.6	0.3 ± 1.3	0.09 ± 0.92
	Proc. Waste	7.5 ± 2.3	13.3 ± 4.4	16.3 ± 10.3	12.4 ± 6.9
SeO ₄ ²⁻	Groundwater	0.9 ± 1.1	3.1 ± 0.8	-1.6 ± 0.03	0.78 ± 2.17
	Proc. Waste	-1.7 ± 1.9	-2.6 ± 1.4	0.4 ± 1.7	-1.32 ± 1.96
NO ₃ ⁻	Groundwater	-1.1 ± 3.8	5.9 ± 8.7	-1.3 ± 1.1	0.54 ± 6.06
	Proc. Waste	-0.5 ± 0.8	-1.9 ± 2.2	-1.9 ± 0.6	-1.45 ± 1.38
UO ₂ ²⁺	Groundwater	1.6 ± 3.4	-1.5 ± 4.5	5.2 ± 1.8	1.7 ± 4.2
	Proc. Waste	147 ± 39	486 ± 25	1000 ± 53	544 ± 373
Tc	Groundwater	-0.1 ± 0.8	0.4 ± 1.1	0.1 ± 0.2	0.1 ± 0.7
	Proc. Waste	0.8 ± 0.8	-0.4 ± 0.3	-0.3 ± 0.1	0.02 ± 0.7
I	Groundwater	0.2 ± 0.3	0.9 ± 0.4	1.2 ± 0.4	0.7 ± 0.5
	Proc. Waste	0.5 ± 1.2	4.4 ± 0.7	15.9 ± 1.6	6.9 ± 6.6
Cs	Groundwater	1270 ± 36	2190 ± 414	3120 ± 630	2190 ± 870
	Proc. Waste	1630 ± 310	3120 ± 520	3580 ± 904	2780 ± 1040
Sr	Groundwater	17.9 ± 1.3	18.8 ± 2.9	20.7 ± 3.2	19.1 ± 2.8
	Proc. Waste	7.4 ± 1.2	11.7 ± 0.8	13.0 ± 0.7	10.7 ± 2.6

The very high R_d values observed for Cs relative to Sr suggest the presence of specific sites (minerals) that are highly selective to adsorption of Cs. The interlayer regions of vermiculites and micas are well-known for preferentially adsorbing K⁺, Cs⁺, Rb⁺ and NH₄⁺ (Tamura and Jacobs 1960; Sawhney 1964). Similar behavior has been observed for hydroxy-interlayer weathering products (Barnhisel and Bertsch 1989). Mica, vermiculite, and hydroxyl-interlayer minerals are present in Hanford sediments.

Past work on Cs adsorption onto Hanford sediments includes works by Rhodes and Nelson (1957), where Cs adsorption was observed to remain above R_d values of 200 mL/g at pH values between 3 and 10. Routson et al. (1981) found Cs R_d values to be >1200 mL/g in dilute waters (Na <23 mg/L and Ca <80 mg/L) similar to Hanford groundwater. Both data sets produced in our current studies show similar strong adsorption tendencies for Cs.

TABLE 29. Values for the Distribution Coefficient for Contaminants on Hanford Sediment TBS-1. The pH of the groundwater was 8.3 and the pH for the process-waste stream was 4.5.

Contaminant	Solution	Distribution Coefficient (mL/g)			Overall Average
		4 days	14 days	35 days	
CrO_4^{2-}	Groundwater	1.02 ± 0.79	-0.34 ± 0.52	-0.88 ± 0.19	-0.07 ± 0.98
	Proc. Waste	2.49 ± 1.98	13.5 ± 8.5	22.1 ± 6.0	12.7 ± 10.0
SeO_4^{2-}	Groundwater	-3.07 ± 0.78	-2.78 ± 0.51	-4.48 ± 2.05	-3.44 ± 1.37
	Proc. Waste	4.23 ± 0.54	4.69 ± 1.03	4.87 ± 0.53	4.60 ± 0.70
NO_3^-	Groundwater	-27.2 ± 0.53	-27.0 ± 0.75	-26.6 ± 0.5	-26.9 ± 0.6
	Proc. Waste	3.4 ± 0.7	0.6 ± 2.4	-4.8 ± 1.8	-0.3 ± 4.0
UO_2^{2+}	Groundwater	104 ± 28	74 ± 18	60.5 ± 6.1	79.3 ± 25.6
	Proc. Waste	109 ± 66	223 ± 57	579 ± 330	377 ± 312
Tc	Groundwater	0.2 ± 0.8	0.1 ± 0.2	0.1 ± 0.8	0.1 ± 0.5
	Proc. Waste	0.2 ± 0.8	-0.2 ± 0.5	0.3 ± 1.2	0.1 ± 0.8
I	Groundwater	0.4 ± 0.6	1.2 ± 0.9	2.6 ± 0.4	1.4 ± 1.1
	Proc. Waste	4.7 ± 0.2	5.5 ± 0.2	5.8 ± 0.6	5.3 ± 0.6
Cs	Groundwater	3720 ± 760	5110 ± 690	14000 ± 1630	7610 ± 4690
	Proc. Waste	2330 ± 420	3380 ± 270	3180 ± 130	2960 ± 540
Sr	Groundwater	35.4 ± 14.7	18.2 ± 2.1	16.1 ± 6.8	23.2 ± 12.8
	Proc. Waste	8.1 ± 6.0	9.2 ± 2.2	7.8 ± 1.0	8.4 ± 3.8

TABLE 30. Values for the Distribution Coefficient for Contaminants on Hanford Sediment Trench-8. The pH of the groundwater was 8.3.

Contaminant	Solution	Distribution Coefficient (mL/g)			Overall Average
		5 days	44 days		
CrO_4^{2-}	Groundwater	-1.3 ± 1.3	-3.4 ± 6.6		-1.8 ± 4.6
SeO_4^{2-}	Groundwater	-0.6 ± 1.9	-4.1 ± 6.1		-2.4 ± 4.5
UO_2^{2+}	Groundwater	1.9 ± 1.4	2.4 ± 0.6		2.3 ± 1.2
TcO_4^-	Groundwater	-0.1 ± 0.2	0.2 ± 0.7		0.1 ± 0.5
I ⁻	Groundwater	0.9 ± 0.2	1.5 ± 2.4		1.3 ± 1.4
Cs ⁺	Groundwater	540 ± 30	690 ± 80		620 ± 100
Sr^{2+}	Groundwater	23.4 ± 4.1	18.1 ± 4.0		21.5 ± 4.0
Co^{2+}	Groundwater	$1.25 \pm 0.06 \times 10^4$	$1.16 \pm 0.06 \times 10^4$		$1.21 \pm 0.07 \times 10^4$
Ni^{2+}	Groundwater	440 ± 30	$2.35 \pm 0.68 \times 10^3$		$1.4 \pm 1.1 \times 10^3$
NbO_2^+	Groundwater	13.5 ± 3	29.1 ± 3.6		21.7 ± 8.6

The geochemical environment present in the sediment-groundwater slurries is such that adsorption of anions is not likely. The R_d data for CrO_4^{2-} , SeO_4^{2-} , NO_3^- , and TcO_4^- support such a conclusion. Adsorption of these anions essentially does not occur. The iodide data suggest slight adsorption but we have no definitive explanation. Similar slight adsorption tendencies were observed for another Hanford sediment several years ago (Gee and Campbell 1980; Gee et al. 1981). Several authors have discussed strong iodide adsorption on soil organic matter and/or iodide incorporation into sediments by microbiologic activity (Whitehead 1973, 1974 a,b,; Koch et al. 1988; Koch and Kay 1987). None of the three sediments used in this study contains much organic matter, and the possibility of microbiologic activity was not studied.

Past work on adsorption of radionuclides onto Hanford sediments emphasized studies of Sr, Cs, Pu, and Co (see Serne and Wood 1990). Using an uncharacterized or unspecified Hanford sediment, Rhodes (1956, 1957) studied Sr adsorption from distilled water and Ca salt (40 mg/L Ca) solutions. At pH values of 6 and 8, Rhodes found the R_d value of Sr to be 5 and 30 mL/g when present in distilled water. When 40 mg/L Ca was present at near-neutral pH, the Sr R_d value was 10 mL/g. These values are quite similar to the values reported in Tables 28, 29, and 30 where the Sr R_d value is 20-25 mL/g when present in pH 8 groundwater and 8-10 mL/g when present in pH 4.3 to 7 process waters containing 70 mg/L Ca and 200 mg/L Na competing ions. Routson et al. (1981) showed Sr adsorption to be more sensitive to Ca solution concentrations than Na concentrations. When the competing Ca concentration is 200 mg/L at neutral pH, the Sr R_d value was 10 mg/L. When Ca was not present but Na was present at 350 mg/L, the Sr R_d value was 40 mL/g. McHenry (1958) varied the solution salt concentration, and measured Sr adsorption onto a Hanford Site sand. The Sr R_d value ranged from 20 to 80 mg/L. The current data agree well with past studies and corroborate known Sr adsorption tendencies. As pH drops from a value near 8, Sr adsorption decreases. As Ca and to a lesser extent Na solution concentrations increase, Sr adsorption also decreases.

Routson et al. (1976) measured TcO_4^- adsorption from dilute salt solutions at neutral pH onto a Hanford sediment more similar to TBS-1 than CGS-1. In all tests the R_d value for Tc was 0 to <1 mL/g. All our results suggest Tc exhibits little tendency to adsorb, in complete agreement with Routson et al. (1976).

Cobalt and Ni spiked into groundwater as divalent cations readily adsorb onto Trench-8 sediments. R_d values greater than 1000 mL/g are measured. For dilute water similar to Hanford groundwater, Routson et al. (1981) found Co R_d values above 3000 mL/g for various Hanford 200 Area sediments. Our value of 12,000 mL/g is in the same range. Routson et al. (1981) also found Co adsorption did not follow pure ion exchange trends when solution competing ions were varied. As mentioned in Section 4, Co sorption onto hydrous oxides may be the cause of the large R_d values.

Neptunium adsorption on Trench-8 sediment was moderate ($R_d \sim 20$ mL/g). This value is larger than a previous Hanford specific data point for a Hanford Formation sand (Burbank Sand) contacting slightly higher ionic strength solutions. Values of R_d for Np varied from 0.4 to 4 mL/g in Routson et al.'s (1976) work.

In summary, the Hanford sediments show a similar trend for adsorbing contaminants from groundwater: $\text{Co} \gg \text{Ni}$, $\text{Cs} \gg \text{Sr}$, $\text{NpO}_2^+ \gg \text{U} > \text{SeO}_4^{2-}$, CrO_4^{2-} , I^- , TcO_4^- , and NO_3^- . Sediment TBS-1 adsorbs considerably more Cs and UO_2^{2+} than the other two sediments and may adsorb slightly more Sr and I than sediment CGS-1.

Results for adsorption onto Hanford sediments from acidic process wastes show less adsorption of the cations Cs and Sr than when contact is with groundwater. The lesser adsorption is explained by higher Na and hydrogen (in the case of TBS-1 tests) concentrations competing for exchange sites. Uranium adsorption is dramatically greater in the process waste slurries than groundwater/sediment slurries. One explanation for higher U adsorption from process waste waters is that the slurries have pH values between 3.9 and 7.5, where uranyl carbonate complexes are nonexistent or weak compared to the calculated speciation in Hanford groundwater (pH >8) where anionic carbonate

complexes predominate. Thus, in the process waste stream systems, cationic forms of U are more prevalent and higher adsorption would be expected (see Hsi and Langmuir 1985).

The adsorption of CrO_4^{2-} , SeO_4^{2-} , and I^- also increases to R_d values about 5 to 10 mL/g when the Hanford sediments are maintained at weakly acidic conditions (pH ~4). Typically, anion adsorption onto sediments at this pH is attributed to adsorption onto variable-charged edge sites on certain clays and to adsorption onto hydrous oxides, especially Fe, Al, Mn, and Ti oxides. As shown in Table 7 and mentioned earlier, the original hydrous oxide content of the Hanford sediments is quite low and was likely dissolved during the pre-conditioning acidification steps. It is not clear what solid phases are controlling the adsorption of the anions CrO_4^{2-} , SeO_4^{2-} , and I^- present in the acidic process waste water. Despite also being anionic, neither TcO_4^- or NO_3^- appear to adsorb onto the two Hanford sediments when they contact acidic waste waters.

In summary, when Hanford sediments acclimate with a weakly acidic Na nitrate-dominated solution, adsorption tendencies follow the sequence $\text{Cs} \gg \text{UO}_2^{2+} \gg \text{Sr}$, $\text{CrO}_4^{2-} > \text{I}^- > \text{SeO}_4^{2-} > \text{TcO}_4^-$, NO_3^- . In batch tests it is difficult to control and maintain Hanford sediment slurries at acidic pH values. Furthermore, for weakly adsorbing contaminants (those with $R_d < 5$ mL/g), the batch method is not very precise. Better R_d values would be obtained using flow-through column tests.

As shown in Table 2, the in situ sediments contain gravel that was discarded prior to performing the batch adsorption tests. For performance assessment calculations, it is common practice to assume that the gravel portion of sediments has minimal adsorption capacity and can be ignored. However, to predict contaminant transport, one must consider the volume of the porous media that exists as inert gravel. The appropriate method for converting the laboratory-derived R_d values shown in Tables 28 through 30 is to multiply them by the fraction (1 - fractional gravel content). Thus the R_d values for the coarse sediment CGS-1 shown in Table 28 should be multiplied by 0.175, those (see Table 29) for the finer-grained sediment TBS-1 should be multiplied by 0.99, and those (see Table 30) for Trench-8 should be multiplied

by 0.90. The corrected values would then be used in PA calculations along with in situ bulk densities and volumetric water contents to calculate retardation factors and contaminant migration.

The results of this sorption work (Section 4 and 5) suggest that the contaminants when present in groundwater can be broken into two categories (good adsorbers and non-absorbers). We were hoping to find a contaminant that exhibited a small amount of adsorption from groundwater that could be used in the Solid Waste Performance Assessment Support Project in half-cell diffusion and flow-through column tests to study the effects of partial saturation on adsorption. Half-cell diffusion and partially saturated flow-through column tests of adsorbing species are optimally performed on weak to moderate adsorbers. Species with very large adsorption coefficients require inordinately long time periods to diffuse large enough distances to allow quantifiable profiles (concentration versus distance) to develop or to break through in column tests. From practical considerations we were searching for moderately adsorbing species with R_d values between 2 and 5 mL/g. As mentioned, sorption work to date showed many species did not adsorb (anions), and five cations (Sr, Np, Ni, Co and Cs) adsorbed strongly (R_d values 20 to 10^4 mL/g). Uranium as U(VI) did exhibit weak adsorption but the R_d values were quite variable.

To investigate whether adsorption processes for Hanford relevant contaminants, solutions, and sediments are dependent on the amount of moisture present, we performed some standard batch R_d tests under saturated moisture conditions to find an appropriate solution composition to use for tests under varying partially saturated moisture conditions. We chose ^{85}Sr as the preferred tracer, and from past work discussed in Serne and Wood (1990), chose three salt solutions containing Ca, Na, Cl, and NO_3 in various proportions to determine an appropriate solution that controls the Sr R_d to a value within the range of 1-5 mL/g. To reiterate, the goal of this activity was to find an appropriate solution in which ^{85}Sr tracer exhibits moderate adsorption upon contacting Trench-8 sediment. The solution-sediment-tracer would then be used in partially saturated tests to investigate whether moisture content changes affect calculated R_d values.

Results of the adsorption tests to lower the Sr adsorption properties of Trench-8 sediment are shown in Table 31. The data suggest that either solution B or D could be successfully used in partially saturated moisture tests to force Sr to only adsorb slightly.

The test details for this activity are shown in Table 31. Batch R_d tests were run in triplicate and blank containers (no Trench-8 sediment present) were run to correct for any container adsorption or tracer instabilities.

All batch adsorption tests were performed at room temperature, in the presence of air, at a solution-to-solids ratio of 30 mL/1 g and with a contact time of 7 days. The Trench-8 sediment was pre-washed with Hanford groundwater for 1 day prior to contacting the spiked solutions. Carrier-free ^{85}Sr as SrCl_2 dissolved in dilute HCl was used as a tracer. The Hanford groundwater (see Table 12) was obtained from an uncontaminated region in the southwest quadrant of the Hanford Site near Horn Rapids (Well 6-53-25).

TABLE 31. Distribution Coefficient Test Matrix and Results for Artificially Lowering Sr Sorption

Solutions	Results
A. Groundwater + 0.8 $\mu\text{Ci/L}$ ^{85}Sr as Sr^{2+}	22.97 ± 2.69
B. 0.038M CaCl_2 + 0.8 $\mu\text{Ci/L}$ ^{85}Sr as Sr^{2+}	1.02 ± 0.64
C. 0.7 M NaNO_3 + 0.038 CaCl_2 + 0.7 $\mu\text{Ci/L}$ ^{85}Sr as Sr^{2+}	0.07 ± 0.13
D. 0.7 M NaNO_3 + 1 mg/L Sr^{2+} + 0.9 $\mu\text{Ci/L}$ ^{85}Sr as Sr^{2+}	4.45 ± 0.12

6.0 CONCLUSIONS

The physical and chemical characterization of the four Hanford sediments yielded the following data. The Hanford sediment particle size distributions are generally coarse with 80 to 98% gravel and sand and only 2 to 20% silt and clay, by weight. The sediments contain 1.0 to 2.0% by weight Ca carbonate and negligible organic C (0.02 to 0.19%). The mineralogic composition of the sediments after discarding the gravel is predominately quartz and plagioclase with some K feldspar, mica, and kaolin/serpentine. The clay fraction is predominately smectite with some vermiculite/chlorite and illite and a trace of kaolinite. The total cation-exchange capacity varies from 2.6 to 7.8 meq/100g. The exchange sites are naturally filled with Ca and Mg. The saturation extract pH varies from 7.7 to 8.2 with Ca, Mg and Na being the predominant cations. Chloride, sulfate and bicarbonate constitute the anions that dissolve into the saturation extract. The salt composition that constitutes the saturation extract is similar to Hanford groundwater but exhibits a slightly larger total ionic strength.

The four sediment's hydrologic properties are similar to other Hanford sands. The coarse sediments (excluding TBS-1) rapidly drain when pressure is applied. At about 40 cm of water (0.04 bars), the sediments are only 25 to 50% saturated. At about 300 cm of water (0.3 bars), the sediments are about 10 to 20% saturated. At 1 bar pressure, the sediments contain about 10 to 15% saturation. The hydraulic conductivity of the coarser sediments varies from 1×10^{-2} to 7×10^{-2} cm/s at saturation down to $<10^{-8}$ cm/s at moisture contents near 5% by volume (12% saturated). Typical moisture contents of Hanford sediments are 4 to 7% by volume (9 to 16% saturation). At these moisture contents under a unit hydrologic gradient (typical for vadose zone sediments) pore water velocities would be 0.3 to 3 cm/y. This rate for advection would be about the same as diffusive fluxes for unreactive contaminants. Therefore, under typical Hanford conditions in the vadose sediments, unreactive tracers (e.g., NO_3^- , TcO_4^- , SeO_4^{2-} , AsO_4^{2-} , and I^-) could diffuse fractions to a few centimeters per year even if there were no advective flux. An insignificant advection could occur if a barrier were placed over the burial ground to prevent

any infiltration. Thus, some contaminants would migrate slowly whether advection occurs or not. Reactive contaminants (Cs, Sr) would diffuse one to three orders of magnitude more slowly.

The waste-form leach tests show that wood, paper, cardboard, plastics, cloth, rubber, etc. do not release significant amounts of inorganic constituents to Hanford groundwater. The materials do release measurable amounts of organic matter, especially the wood, paper, and cardboard. The wood, paper, cardboard test also drops the solution pH from 8 to 5, which is probably caused by dissolved organic acids. Currently the speciation of the dissolved organics in the leachates has not been identified using GC-MS techniques. The organics are likely polar, relatively large molecular weight, nonvolatile species not amenable to identification using standard GC-MS methods.

The leach test containing cement and a mixture of all the various wastes did generate a leachate significantly different from the groundwater. The cement releases significant amounts of hydroxide (pH rises to 12.1) and significant amounts of K^+ , Na^+ , Ca^{2+} , and Al. Again the wood and paper products present in the cement test also release significant amounts of organic matter.

From a contaminant-release perspective, the waste-form leaching tests suggest that the release of dissolved organic carbon may be the most potentially deleterious trend. Past studies of contaminant release from grout suggest that the high pH and high alkali metal concentrations do not increase release or mobility of most metallic, actinide, and fission product species. In fact, the high pH environment caused by cement dissolution aids sequestration of many metallic species because of lowered solubility.

Because the waste forms used in the tests were not contaminated, we can not address actual release rates for contaminants or state unequivocally that actual wastes will not change the leachate chemical composition in ways that enhance contaminant release. For example, actual wastes may contain higher concentrations of salts, acids, bases, organic chelators, and solvents that change the chemical nature of leachates further.

The adsorption studies using spiked groundwater and spiked waste-form leachates allow the following conclusions. The presence of viable and dead mold cells did not significantly alter adsorption properties of any of the

contaminants studied. The presence of the high concentrations of dissolved organic carbon from wood and paper may be significantly lowering the adsorption properties of Co and slightly lowering the adsorption properties of Sr and UO_2^{2+} . In leachates with elevated K^+ and Ca^{2+} concentrations (from cement dissolution), the adsorption tendencies of Cs and Sr are diminished. In the case of Sr however, the cement environment generally would also lower release tendencies out of the buried wastes. None of the variables (higher organic C, increased alkali metal concentrations, altered leachate pH values) changes the adsorption tendencies of I^- , TcO_4^- , CrO_4^{2-} , SeO_4^{2-} , or NO_3^- . These five anionic contaminants do not adsorb on Trench-8 or the other Hanford sediments when present in groundwater or waste-form leachates. Specific R_d values for the studied contaminants for leachates and groundwater contacting Trench-8 sediments are provided in Tables 21 and 30. These values should be used in any specific performance assessment analyses of the 200 Area W-5 Burial Ground after correction for removing the gravel-sized particles prior to lab testing.

Sorption of contaminants from acidic, high-ionic-strength process waste waters is higher than from groundwater for anions such as CrO_4^{2-} and perhaps SeO_4^{2-} and I^- , and the UO_2^{2+} cation species. For cationic contaminants that adsorb by ion exchange processes (Sr, Cs), sorption onto Hanford sediments from process waste waters is lower than from groundwater. Chemical explanations for these trends include anion adsorption by variably charged edge sites and hydrous oxides under low pH conditions, the instability of uranyl carbonate complexes at low pH and high adsorption potential for UO_2^{2+} cations and their hydrolysis products, and cation competition from the process waste waters inhibiting Sr and Cs adsorption.

Nitrate and TcO_4^- do not appear to adsorb onto Hanford sediments under any of the conditions studied.

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APPENDIX A

LITERATURE SEARCH: ADSORPTION AND SOLUBILITY
PROPERTIES IN HANFORD SITE SOIL AND GROUT

APPENDIX A

LITERATURE SEARCH: ADSORPTION AND SOLUBILITY PROPERTIES IN HANFORD SITE SOIL AND GROUT

At the request of Marc I. Wood (WHC), a literature search was completed to determine the solubility and adsorption properties of Be, Ni, Sn, Nb, and Sm in Hanford soil and grout porewaters and onto Hanford soil, respectively. In addition, the solubility of U, Pu, Np, and Ra in Hanford soil and cement-leachate solutions was estimated.

Comparing the data from Tables 9 and 12 in the body of this report indicates that distilled water saturation extracts of Hanford soil have nearly the same composition as Hanford groundwater. Solubility calculations for soil solutions in Hanford vadose zone were, therefore, determined using the composition of Hanford groundwater, which is listed in Table A.1. The chemical composition of the cement leachate used is listed in Table A.2. These data were taken from Table 16 from the body of this report. The cement-leachate concentrations obtained after 12 weeks of equilibration were used for the solubility calculations. The solubility calculations were generated with the MINTEQA2 geochemical code (Allison et al. 1991), using the solution compositions discussed above and the thermodynamic data reviewed below. Estimated solubility concentrations in both Hanford groundwater and cement leachate, which were determined by this review, are provided in Table A.3. A qualitative assessment of the expected reliability of this data is also provided in the text. The thermodynamic data that were used in these calculations, but were not part of the original MINTEQA2 (version 3.0) database, are tabulated in Table A.4.

Of the five elements (Be, Ni, Sn, Nb, and Sm) for which adsorption data were to be reviewed, data specific to Hanford were available only for Ni.

BERYLIUM SOLUBILITY

Beryllium solubility was determined using thermodynamic data available in Baes and Mesmer (1976) for the solubility of $\text{Be}(\text{OH})_2(\alpha)$. These data were

entered into the MINTEQ computer code database. MINTEQ was then used to calculate the equilibrium solubility and speciation scheme. In natural Hanford groundwater the solubility of Be^{2+} was determined to be 2.5×10^{-7} M. In cement leachate the solubility of Be^{2+} is estimated to be 3.7×10^{-5} M.

TABLE A.1. Chemical Composition (mg/L) of Groundwater (Hanford Well 6-S3-25).

<u>Constituents</u>	<u>Sample Used (4/90)</u>	<u>Range in Composition (1985-1990)</u>
pH	8.14	7.82 - 8.47
Eh(mv)	309	283 - 385
Al	<0.03	<0.03 - 0.064
B	0.1	0.02 - 0.10
Ba	0.08	0.04 - 0.08
Ca	48.8	48.8 - 58.8
Cd	<0.004	<0.004
Cr	<0.020	<0.02 - 0.034
Cu	<0.004	<0.004
Fe	<0.005	<0.005 - 0.008
K	9.9	4.9 - 9.9
i	<0.004	<0.004
Mg	14.6	13.2 - 14.6
Mn	<0.002	<0.002 - 0.13
Na	32.1	23.8 - 32.1
P	<0.1	<0.1
Pb	<0.06	<0.06
Si	16.4	14.6 - 16.4
Sr	0.25	0.23 - 0.25
Zn	<0.02	<0.02 - 0.08
F ⁻	0.5	<0.5 - 0.7
Cl ⁻	27	21 - 27
NO ₂ ⁻	<0.3	<0.3
NO ₃ ⁻	<0.5	<0.5
PO ₄ ³⁻	<0.4	<3
SO ₄ ²⁻	75	63 - 92
T-Alk (as CO ₃ ²⁻)	67.5	67.5 - 92.4
TOC	1	0.3 - 1.7
Cations (meq/L)	5.29	4.9 - 5.4
Anions (meq/L)	4.60	4.6 - 6.1

TABLE A.2. Solid-Waste Performance Leach Study

		<u># 4 All Waste Types and Cement</u>			
		4-1	4-2	4-3	4-4
		1 week	3 weeks	6 weeks	12 weeks
pH		11.77	12.04	12.03	12.12
Eh		266	95	117	149
Al	mg/L	17	55.5	57.3	43.5
B	mg/L	0.1	0.05	0.24	2.18
Ba	mg/L	0.37	1.18	1.7	<0.002
Ca	mg/L	177	311	360	296
Cd	mg/L	<0.004	<0.004	<0.004	<0.004
Cr	mg/L	<0.020	<0.020	<0.020	<0.020
Cu	mg/L	<0.004	<0.004	<0.004	<0.004
Fe	mg/L	<0.005	<0.005	<0.005	<0.005
K	mg/L	94	146	186	235
Li	mg/L	0.07	0.09	<0.004	0.17
Mg	mg/L	<0.06	<0.06	<0.06	<0.06
Mn	mg/L	<0.002	<0.002	<0.002	<0.002
Na	mg/L	58	75.6	88	96
P	mg/L	<0.10	<0.10	<0.10	<0.10
Pb	mg/L	<0.060	<0.060	<0.060	<0.060
Si	mg/L	3.2	1.5	1.1	0.7
Sr	mg/L	0.66	1.29	1.6	1.96
Zn	mg/L	<0.020	<0.020	<0.020	<0.020
F ⁻	mg/L	6.8	8.4	15	20
Cl ⁻	mg/L	16.7	12.9	15	14
NO ₂ ⁻	mg/L	<0.300	<0.300	<0.300	<0.300
NO ₃ ⁻	mg/L	0.6	0.6	1.7	3
PO ₄ ³⁻	mg/L	<0.400	<0.400	<0.400	3
SO ₄ ²⁻	mg/L	35.1	13.2	1.1	1.5
T-ALK	mg/L	225	645	727.5	1050
TOC	mg/L	90	110	148	245
IC	mg/L	5	3	2	14
Cations	meq/L	13.77	22.57	26.58	25.00
Anions	meq/L	9.07	22.59	25.51	36.53

TABLE A.3. Estimated Solubility Concentrations (M) of Be, Ni, Sn, Nb, Sm, U, Pu, Np, and Ra (oxidation state of the dissolved species is also indicated)

<u>Species</u>	<u>Hanford Groundwater Solubility</u>	<u>Cement-Leachate Solubility</u>
Be(II)	2.5×10^{-7}	3.7×10^{-5}
Ni(II)	2.8×10^{-4}	9.9×10^{-8}
Sn(IV)	5.5×10^{-10}	5.5×10^{-10}
Nb(V)	4.9×10^{-5}	0.32
Sm(III)	4.9×10^{-9}	3.3×10^{-8}
U(VI)	2.7×10^{-4}	1.8×10^{-8}
Pu(IV) or Pu(V)	$< 2 \times 10^{-8}$	$< 2 \times 10^{-8}$
Np(V)	3.2×10^{-5}	1.1×10^{-4}
Ra(II)	1.6×10^{-7}	1.0×10^{-5}

Although the solubility data for $\text{Be}(\text{OH})_2(\alpha)$ appear to be reliable, the effects of carbonate on the solubility of Be^{2+} are unknown. It is known that a BeCO_3 phase does form, but its solubility is unknown, and the importance of carbonate complexation with Be^{2+} to form soluble species is also unknown.

BERYLIUM ADSORPTION

No data were found concerning the adsorption of Be onto Hanford soils. Very little data are available for other soils as well. Data reviewed by Rai and Zachara (1984) indicate that Be adsorption onto 11 soils from seven prominent soil orders was stronger than for Zn, Cd, Ni, and Hg. It was also indicated that calcareous soils containing high concentrations of layer silicates were most effective at adsorbing Be. For a sandy top soil in equilibrium with a 0.0035 M solution of $\text{CaCl}_2 + \text{NaCl} + \text{KCl}$ in a 3:2:2 ratio, R_d values determined by Gerritse et al. (1982) at trace Be concentrations range from 50 to 700 mL/g; for a sandy loam top soil, R_d values ranged from 8000 to 12,000 mL/g in equilibrium with the same solution.

TABLE A.4. Thermodynamic Data That Were Used but are not in the MINTEQA2 Database (data appropriate to zero ionic strength)

Reaction	Log K
$\text{Be}^{2+} + 2\text{H}_2\text{O} = \text{Be}(\text{OH})_2(\alpha) + 2\text{H}^+$	-6.69
$\text{Be}^{2+} + \text{H}_2\text{O} = \text{BeOH}^+ + \text{H}^+$	-5.40
$\text{Be}^{2+} + 2\text{H}_2\text{O} = \text{Be}(\text{OH})_2^{\circ}(\text{aq}) + 2\text{H}^+$	-13.65
$\text{Be}^{2+} + 3\text{H}_2\text{O} = \text{Be}(\text{OH})_3^- + 3\text{H}^+$	-37.41
$\text{Be}^{2+} + 4\text{H}_2\text{O} = \text{Be}(\text{OH})_4^{2-} + 4\text{H}^+$	-23.25
$\text{Sn}^{4+} + 2\text{H}_2\text{O} = \text{SnO}_2(\text{c}) + 4\text{H}^+$	8.40
$\text{Sn}^{4+} + \text{H}_2\text{O} = \text{SnOH}^{3+} + \text{H}^+$	0.57
$\text{Sn}^{4+} + 2\text{H}_2\text{O} = \text{Sn}(\text{OH})_2^{2+} + 2\text{H}^+$	0.63
$\text{Sn}^{4+} + 3\text{H}_2\text{O} = \text{Sn}(\text{OH})_3^+ + 3\text{H}^+$	0.36
$\text{Sn}^{4+} + 4\text{H}_2\text{O} = \text{Sn}(\text{OH})_4^{\circ}(\text{aq}) + 4\text{H}^+$	-0.86
$2\text{Nb}(\text{OH})_5(\text{aq}) = \text{Nb}_2\text{O}_5(\text{am}) + 5\text{H}_2\text{O}$	9.60
$\text{Nb}(\text{OH})_5(\text{aq}) + \text{H}^+ = \text{Nb}(\text{OH})_4^+ + \text{H}_2\text{O}$	-0.79
$\text{Nb}(\text{OH})_5(\text{aq}) + \text{H}_2\text{O} = \text{Nb}(\text{OH})_6^- + \text{H}^+$	-7.82
$\text{Sm}^{3+} + \text{H}_2\text{O} + \text{CO}_3^{2-} = \text{Sm}(\text{OH})\text{CO}_3(\text{c}) + \text{H}^+$	8.50
$\text{Sm}^{3+} + 3\text{H}_2\text{O} = \text{Sm}(\text{OH})_3(\text{c}) + 3\text{H}^+$	-16.50
$\text{Sm}^{3+} + \text{H}_2\text{O} = \text{SmOH}^{2+} + \text{H}^+$	-7.719
$\text{Sm}^{3+} + 2\text{H}_2\text{O} = \text{Sm}(\text{OH})_2^+ + 2\text{H}^+$	-16.855
$\text{Sm}^{3+} + 3\text{H}_2\text{O} = \text{Sm}(\text{OH})_3^{\circ}(\text{aq}) + 3\text{H}^+$	-26.101
$\text{Sm}^{3+} + 4\text{H}_2\text{O} = \text{Sm}(\text{OH})_4^- + 4\text{H}^+$	-36.115
$\text{Sm}^{3+} + \text{CO}_3^{2-} = \text{SmCO}_3^+$	7.851
$\text{Sm}^{3+} + 2\text{CO}_3^{2-} = \text{Sm}(\text{CO}_3)_2^-$	12.985
$\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{c}) + \text{H}^+$	-3.30
$\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$	-8.30
$\text{NpO}_2^+ + 2\text{H}_2\text{O} = \text{NpO}_2(\text{OH})_2^- + 2\text{H}^+$	-19.40
$\text{NpO}_2^+ + \text{CO}_3^{2-} = \text{NpO}_2\text{CO}_3^-$	4.51
$\text{NpO}_2^+ + 2\text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)_2^{3-}$	6.86

NICKEL SOLUBILITY

The solubility of Ni was determined using existing thermodynamic data contained within the MINTEQ database. Calculations indicate that the most stable solid phase of Ni in both Hanford groundwater and cement leachate should be $\text{Ni}(\text{OH})_2(\text{c})$. The solubility of Ni in natural Hanford groundwater was determined to be 2.8×10^{-4} M, assuming equilibrium with $\text{Ni}(\text{OH})_2(\text{c})$. In the cement leachate the solubility of Ni decreases to 9.9×10^{-8} M. The thermodynamic data for Ni^{2+} appear to be reliable.

NICKEL ADSORPTION

Nickel adsorption studies conducted for this project on Trench-8 sediment are reported in Section 5.0 of the main text. The results of this work, which were determined at trace Ni concentrations for two equilibration periods (5 and 44 days), are as follows: for Hanford groundwater the average R_d values were determined to be 440 mL/g after 5 days and 2350 mL/g after 44 days; the average values determined in a cement-waste leachate solution (which also contained significant concentrations of dissolved organic carbon) were 3 mL/g after 5 days and 6 mL/g after 44 days.

More recently adsorption work has been conducted on Trench-94 soil as a function of Ni concentration (see Rhoades et al. 1992). Results for a 10-day equilibration period ranged from 48 mL/g at a final Ni concentration in a solution of approximately 1000 ppb to 337 mL/g at a final Ni concentration of approximately 2 ppb. Nickel adsorption onto Trench-94 soil from Hanford groundwater was found to fit a Freundlich isotherm, $X = KC^N$, where X is the concentration of Ni adsorbed to soil ($\mu\text{g/Kg}$) and C is the concentration of Ni in solution ($\mu\text{g/Kg}$), and K and N are constants. Linear regression of the Ni adsorption data onto Trench-94 soil from Hanford groundwater yielded the following constants: $\log K = 2.38$ and $N = 0.845$.

TIN SOLUBILITY

Few thermodynamic data are available for Sn. The solubility of Sn was determined by assuming that solubility was controlled by formation of $\text{SnO}_2(\text{c})$. The solubility and hydrolysis data were obtained from Baes and Mesmer (1976). The solubility of Sn in both Hanford groundwater and cement leachate was

calculated to be 5.5×10^{-10} M using MINTEQ. The data used to determine this value are considered as estimates only.

TIN ADSORPTION

No data were found for the adsorption of Sn onto Hanford soil. Gerritse et al. (1982) measured R_d values for Sn adsorption onto a sandy top soil and a sandy loam top soil in equilibrium with a dilute inorganic solution. The R_d results ranged between approximately 1000 and 3000 mL/g for the sandy top soil and 4400 and 11,000 mL/g in the sandy loam. Trace concentrations of $^{113}\text{Sn}^{4+}$ were used in these experiments to determine R_d values.

NIOBIUM SOLUBILITY

Thermodynamic data available in Baes and Mesmer (1976) for the solubility of Nb_2O_5 and the hydrolysis species of Nb^{5+} were input to the MINTEQ database and subsequently used to determine the solubility of Nb^{5+} in both Hanford groundwater and cement leachate. These calculations indicate that the solubility of Nb^{5+} in Hanford groundwater is 4.9×10^{-5} M and 0.32 M in cement leachate, assuming Nb_2O_5 is the solubility controlling solid. The data used in these calculations were considered by Baes and Mesmer (1976) to be very approximate. These data were measured on freshly precipitated Nb_2O_5 (Babko et al. 1963), which was uncharacterized and likely to have been amorphous. Because well-crystallized materials tend to have lower solubilities than amorphous precipitates, the solubility estimate provided above may overestimate the actual solubility of Nb in the environment.

NIOBIUM ADSORPTION

Rhodes (1957) reported R_d values for Zr-Nb adsorption onto Hanford subsoil that ranged from 90 mL/g at pH 6.0 to >1980 mL/g at pH values of 2.7, 3.5, 4.4, 8.4, and 9.3. These data are not particularly useful because we cannot determine if they are most appropriate for describing the adsorption of Zr or Nb.

SAMARIUM SOLUBILITY

A complete set of thermodynamic data necessary to calculate Sm^{3+} solubility in Hanford groundwater is not available. Thermodynamic data are available for the solubility of $\text{Sm}(\text{OH})_3(\text{c})$ and the hydrolysis of Sm^{3+} (Baes and

Mesmer 1976), but not for the solubility of SmOHCO_3 or carbonate complexation of Sm^{3+} . Other phases and complexes are not likely to be important in natural Hanford groundwater.

Due to the similarity in electronic structure, ionic radius, and chemical properties, the trivalent lanthanides have often been used as chemical analogs for the trivalent actinides (Cantrell 1988; Allard 1982; and Krauskopf 1986). In this case, we will use solubility data determined for $\text{AmOHCO}_3(\text{c})$ as an analog for SmOHCO_3 . It has been shown that that $\text{AmOHCO}_3(\text{c})$ is the thermodynamically stable phase for Am under existing conditions in Hanford groundwater (Felmy et al. 1990). In addition, we will use carbonate stability constants for Sm^{3+} determined using an estimation technique based on data determined for several other lanthanide ions (Cantrell and Byrne 1987).

Using the thermodynamic data discussed above (i.e., assuming $\text{Sm}(\text{OH})\text{CO}_3$ is the solubility controlling phase), and the groundwater composition listed in Table A.1, the solubility of Sm was determined to be 4.9×10^{-9} M. In cement leachate Sm solubility increases to 3.3×10^{-8} M. Based on our knowledge of other lanthanides and actinides, these estimates are likely to be reliable.

SAMARIUM ADSORPTION

Data specific to Hanford are not available for Sm; however, as indicated above, analogous behavior is expected for other trivalent lanthanides and actinides. Sheppard et al. (1976) reported R_d values for Am between two Hanford soils and a solution (apparently distilled water) containing $^{241}\text{Am}^{3+}$ to be 125 mL/g and 833 mL/g, respectively. These values are likely to be larger than values appropriate for Hanford groundwater because of the strong tendency of Sm to form carbonate complexes that will inhibit adsorption. The adsorption of Sm onto Hanford soil in contact with cement leachate cannot be predicted from the available data.

URANIUM SOLUBILITY

Uranium solubility was determined using thermodynamic data available in MINTEQA. Uranium solubility was assumed to be controlled by schoepite ($\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$). In Hanford groundwater UO_2^{2+} solubility was determined to be

2.7×10^{-4} M. In cement-leachate solution the solubility was determined to be 1.2×10^{-8} M. The reliability of these data are considered fair (Newton and Sullivan 1985).

PLUTONIUM SOLUBILITY

The aqueous chemistry of Pu is complex, and the thermodynamic data needed to describe Pu chemistry in groundwaters are incomplete and sometimes unreliable. One of the main barriers to obtaining reliable thermodynamic data for Pu is the difficulty in maintaining Pu in solution in a single oxidation state. Pu can exist as Pu^{3+} , Pu^{4+} , PuO_2^+ , and PuO_2^{2+} .

Plutonium (IV) oxide and amorphous hydrous oxide are the Pu compounds most likely to precipitate and be present in nuclear wastes (Rai and Ryan 1982). Although thermodynamic considerations dictate that the $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ will eventually convert to $\text{PuO}_2(\text{c})$, radiolytic effects oppose the crystallization process, causing the crystallinity of the equilibrium solid phase to be somewhere between $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ and $\text{PuO}_2(\text{c})$, depending on the radiation field (Rai and Ryan 1982). Because $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ is the more soluble phase, its solubility can be used to set maximum limits on the Pu concentration in solution. Data from Rai et al. (1980) and Rai (1984) indicate that the solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in CO_2 free solution at a pH of 8.2 is approximately 1×10^{-8} M. The data also indicate that practically all of the dissolved Pu is oxidized to PuO_2^+ .

Because carbonate is a good complexing agent for actinide ions and is ubiquitous in groundwaters, it is possible that carbonate could significantly affect the solubility of Pu in groundwater. If we assume that $\log \beta_1 = 4.5$ for $\text{PuO}_2(\text{CO}_3)^-$, the same as that determined for $\text{NpO}_2(\text{CO}_3)^-$ at zero ionic strength (Bidoglio et al. 1987), then carbonate complexation should increase the solubility of PuO_2^+ to approximately 2×10^{-8} M in Hanford groundwater.

It has been demonstrated that high carbonate concentrations stabilize the Pu(IV) oxidation state in solution (Eiswirth et al. 1985; Lierse and Kim 1984; Kim et al. 1983). It is not known, however, if this is also true for the lower carbonate concentrations existing in groundwater. In a solubility study of the Np(IV) hydrous oxide system in which dissolved Np was stabilized as Np(IV), it has been demonstrated that addition of 0.01 M total carbonate does

not increase the solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ (Rai and Ryan 1985). Because $\log K_{\text{sp}}$ for the reaction: $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am}) = \text{Pu}^{4+} + 4\text{OH}^+ + (x-2)\text{H}_2\text{O}$ is smaller than that for $\text{Np}(\text{IV})$, the data of Rai and Ryan (1985) should provide an upper bound to the solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$, if Pu is stabilized in the Pu(IV) oxidation state. The solubility of $\text{Np}(\text{IV})$ determined by Rai and Ryan (1985) in 0.01 M total CO_2 was approximately 5×10^{-9} M, both at pH = 8.2 (pH of groundwater) and at pH = 12.1 (pH of cement leachate). In addition to the Pu oxides and hydrous oxides, it is possible that $\text{Pu}(\text{OH})_2\text{CO}_3$ forms; however, if this phase does form it will have a solubility less than that of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ or $\text{PuO}_2(\text{c})$, whichever is present. We can therefore conclude that the maximum solubility of Pu in Hanford groundwater and cement leachate should be less than 2×10^{-8} M. Actual values, however, cannot be ascertained from the available data.

NEPTUNIUM SOLUBILITY

The MINTEQ database was modified by adding thermodynamic data for the solubility of $\text{NpO}_2\text{OH}(\text{c})$ and data for hydrolysis and carbonate complexation of NpO_2^+ (Nakayama et al. 1988; Bidoglio et al. 1987). The solubility of NpO_2^+ was calculated to be 3.2×10^{-5} M in Hanford groundwater and 1.1×10^{-4} in cement leachate solution. The reliability of these data is considered to be fair.

RADIUM SOLUBILITY

Radium salts of strong acids, such as HCl and HNO_3 , are quite soluble (Molinari and Snodgrass 1990). Radium salts of sulfate, carbonate, and phosphate are less soluble. Thermodynamic solubility products for Ra are available only for sulfate (Sillen and Martell 1964). The solubility product of RaSO_4 is $10^{-10.37}$ at 20°C and zero ionic strength (Sillen and Martell 1964). Stability constants for Ra complexation are available for both sulfate and carbonate. $\log K_1$ values for these constants are 2.43 and 2.48 at 25°C and zero ionic strength, respectively (Benes et al 1982).

MINTEQ calculations indicate that for a typical Hanford groundwater (Table A.1, sulfate concentration of 75 mg/L or 7.8×10^{-4} M), the solubility of Ra is controlled by RaSO_4 . The solubility controlled maximum Ra concentration was determined to be 1.6×10^{-7} M. The proposed EPA maximum concentration level for adjusted gross alpha emitters is 20 picocuries per liter for

^{226}Ra plus ^{228}Ra . This is equivalent to a concentration of 6×10^{-14} M, assuming all Ra is ^{226}Ra . Solubility calculations in cement leachate, using the composition listed in Table A.2 for a 12-week leaching period, indicate an equilibrium Ra concentration of 1.0×10^{-5} M. These calculated solubility constraints are considered fairly reliable.

Radium is also known to coprecipitate with barite, and a mixing model that describes the correlation between Ra and Ba concentrations during precipitation has been used with reasonable success (Beaucaire and Toulhoat 1987). The solubility product for BaSO_4 is $10^{-9.96}$ (Sillen and Martell 1964). The concentration of Ba in Hanford groundwater at equilibrium with barite was calculated to be 3.6×10^{-7} M (0.05 ppm) using the MINTEQ geochemical code. This value lies within the range of Ba concentrations measured in Hanford groundwater (Table A.1), suggesting that Hanford groundwaters are in equilibrium with barite. Although coprecipitation could occur, it is unlikely because the saturation index of barite in groundwater will actually decrease as it mixes with cement leachate solution. If barite does not precipitate, Ra will not coprecipitate.

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APPENDIX B

UNSATURATED TRANSPORT IN TRENCH-8 SOILS

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UNSATURATED TRANSPORT IN TRENCH-8 SOILS

SUMMARY

Diffusion coefficients (D), hydraulic conductivity values (K), and retardation factors (R_f) were experimentally determined in unsaturated Trench-8 soil from the proposed solid low-level radioactive waste burial ground to be located in the currently operated W-5 Burial Ground in 200 West Area of the Hanford Site to help quantify the release and transport of contaminants in the vadose zone. New unsaturated flow technologies were used that significantly decrease the time required to obtain this type of data. Water contents (wt%) ranged from 5 to 24% with respective D values from 2×10^{-7} to 4×10^{-6} cm²/sec and K values from 6×10^{-8} to 4×10^{-2} cm/sec. The D values are consistent with the recent observations on natural materials that D is a function only of volumetric water content and not of the characteristics of the material, e.g., texture, grain size, fracture-aperture widths, and distributions (Conca and Wright 1991). Hydraulic conductivity values obtained with the UFA™ agree very closely with traditional column experiments, long-term field lysimeter measurements, and van Genuchten-Campbell/Mualem relationships curve-fitted to laboratory water-retention data on the same soils.

This study demonstrates the applicability of the UFA™ technology to site characterization studies of unsaturated subsurface environments and that the UFA™ can be used to determine the primary transport parameters: $D(\theta)$, $K(\theta)$, and R_f .

INTRODUCTION

Modeling the transport of contaminants in vadose zones surrounding nuclear and hazardous waste repositories requires knowledge of the material characteristics under unsaturated conditions. The primary transport parameters D , K , and R_f are not well-known under unsaturated conditions but are key input parameters to existing and developing models of contaminant release and migration in vadose zones (Pigford and Chambré 1988). Knowledge of D and K as

functions of the volumetric water content (θ) is particularly important in the near-field transition zone around waste sites, in either high-level or low-level disposal situations, where changes in temperature, water content, compaction of backfill, infiltration of fines, and secondary mineralization will alter transport characteristics. Knowledge of R_f is essential to predicting contaminant migration under the myriad field conditions that can affect speciation and mobility. This study experimentally determined the D , K , and R_f behavior of unsaturated soil as a function of water content.

Traditional methods of investigating unsaturated systems require very long times to attain homogeneous distributions of water because normal gravity does not provide a large-enough driving force relative to the low hydraulic conductivities that characterize highly unsaturated conditions. An unsaturated flow apparatus (UFA™) based on open centrifugation was developed in which hydraulic steady state can be achieved rapidly in most geologic materials at low water contents (Conca and Wright 1990). Soil was placed in the UFA™ to achieve hydraulic steady state with Hanford groundwater, distilled water, or a 0.1 M KCl electrolyte solution, depending on the experimental goals. The D , corrected to infinite dilution, was determined from the measured electrical conductivity of the equilibrated, partially saturated sediment sample using the Nernst-Einstein equation.

WATER CONTENT AND CENTRIFUGATION

The use of steady-state centrifugation to fix the water content in soils has recently been demonstrated by Nimmo and co-workers (Nimmo et al. 1987). There are specific advantages to using a centripetal acceleration as a fluid driving force. Because it is a body force similar to gravity, it acts simultaneously over the entire system and independently of other driving forces, e.g., gravity or matric suction. The UFA™ developed for this study consists of an ultracentrifuge, sample cell, effluent collection cell, and ultralow constant-rate flow pump that provides any liquid or gas to the sample surface through a rotating seal assembly and microdispersal system (Figure 1). Accelerations up to 20,000 g are attainable at temperatures up to 150°C and flow rates as low as 0.1 ml/hr. The effluent is collected in a transparent,

FIGURE 1. UFA™ Rotor and Seal Assembly

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volumetrically-calibrated container at the bottom of the sample assembly where it can be observed during centrifugation using a strobe light.

Under a centripetal acceleration in which the water is driven by both the matric potential and the centrifugal force per unit volume ($\rho\omega^2r$), Darcy's Law is given by

$$q = -K(\Psi)(d\Psi/dr - \rho\omega^2r) \quad (1a)$$

where q = the flux density into the sample

K = the hydraulic conductivity, which is a function of the matric suction (Ψ) and therefore of water content (θ)

r = the radius from the axis of rotation

ρ = the fluid density

ω = the rotation speed.

Soils reach steady state in 1 to 4 hours depending on the intrinsic permeability. Moisture distributions in samples run in the UFA™ are uniform to within 3%. Appropriate values of rotation speed and flow rate into the sample are chosen to obtain desired values of flux density, water content, and hydraulic conductivity within the sample. At speeds above 400 rpm, provided that a sufficient flux density exists, $d\Psi/dr \ll \rho\omega^2r$ and Equation (1a) reduces to $q = K(\Psi)(\rho\omega^2r)$ or

$$K(\Psi) = q/\rho\omega^2r \quad (1b)$$

As an example, a 45-gram sample of silt accelerated to 2000 rpm with a flow rate into the silt of 3 ml/hr achieved hydraulic steady state in 2 hours at a volumetric water content of 22.4% and an unsaturated hydraulic conductivity of 2.5×10^{-7} cm/sec. The linear dependence of K on flux and the second-order dependence on rotation speed has been verified for Equation (1b) (Nimmo et al. 1987; Conca and Wright 1990).

There are several issues surrounding flow in an acceleration field that are frequently raised and that have been successfully addressed by previous and on-going research. These include uniformity of moisture distribution,

deviation of the driving force with position in the sample due to deviations in the curvatures of air-water interfaces, and compaction due to acceleration (Nimmo and Mello 1991; Nimmo and Akstin 1988; Nimmo et al. 1987; Conca and Wright 1990). Studies in this project have shown that 1) compaction caused by acceleration is negligible in sediment samples packed at more than 1.0 g/cm^3 (bulk densities in all samples have remained constant because a whole-body acceleration does not produce high-enough point pressures to further compact the samples); 2) three-dimensional deviations of the driving force with position in the sample are less than 1%; and 3) moisture distribution in the sample holder is uniform to within 3% for repacked Hanford sand sediments (see Figure 2 for an example). In heterogeneous samples or stratified systems (e.g., clay lenses in sands), each component reaches its own hydraulic conductivity and water content at steady state, as occurs in the field (capillary bundle theory still holds in the UFA™). This last effect (i.e., unique water contents and conductivity in each material) cannot be reproduced with pressure-driven techniques, but only under a whole-body acceleration field such as produced by gravity or centrifugal methods.

Also, the lower boundary condition where the sediment sample drains into the effluent collection cup and the relationship of $d\Psi/dr$ to $\rho\omega^2r$ need to be mentioned. In the UFA™, $d\Psi/dr = 0$ only after the sample has reached hydraulic steady state. But even before that occurs, as during initial infiltration into a dry sample, $d\Psi/dr \ll \rho\omega^2r$ for all speeds above about 300 rpm, and this includes the lower boundary. Unlike the gravity drain situation, there is no moisture buildup at the air-water interface under a centripetal acceleration because $d\Psi/dr \ll \rho\omega^2r$ at all points within the system. The lower boundary of such aggregate samples as soil is a filter paper between the sample bottom and a perforated plastic plate. Additionally, the boundary condition issue of flow channeling down the sample container interior sides, circumventing the sample, and affecting $K(\theta)$ has not been observed to occur in the UFA™. Flow down the sample container's exterior sides and subsequent accumulation in the collection cup is prevented by O-ring seals.

It should be noted that the dry-bulk densities obtained using procedures developed for the UFA™ appear to be very close to those existing in the field for soils and sediments.

FIGURE 2. Water Distribution in a Trench-8 Soil Sample after Only 1 Hour at 1200 rpm with a Flow Rate of 20 ml/hr

SIMPLE DIFFUSION COEFFICIENTS

Electrical conductivity methods measure the simple diffusion coefficient. The distribution coefficient (R_d) or the extent of retardation (R_f) for different systems needs to be determined separately for each specific ionic species, media, and fluid composition and will result in a decrease in the simple diffusion coefficient as measured by the electrical conductivity method. Numerical models using $D(\theta)$ as an input parameter require the simple diffusion coefficient, as measured by the electrical conductivity method. It is difficult for traditional half-cell methods to completely eliminate all advection, retardation, reaction, and osmotic effects over the long experimental durations needed to acquire sufficient data at low water contents.

In the absence of physicochemical processes, simple diffusion coefficients for most ionic aqueous species are similar, differing by, at most, a

factor of four from the self-diffusion coefficient of water in relatively dilute solutions, which is $2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 25°C . Within this small range of diffusion coefficients, there are some general groupings (Robinson and Stokes 1959). K^+ , Tl^+ , NH_4^+ , Cs^+ , Rb^+ , Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , and TcO_4^- all cluster near $2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 25°C because their size is in the critical range [~ 1.3 - 2.2 angstroms ($\text{\AA}$)]. At smaller sizes ions acquire permanent hydration shells that decrease their mobilities by as much as a factor of two (Li^+ , Na^+ , Ca^{2+} , Sr^{2+} , IO_3^- , and F^-). At larger sizes ions exhibit lower mobilities also by as much as a factor of two (carboxylic acid anions). Such multivalent anions as SO_4^{2-} and $\text{P}_3\text{O}_{10}^{5-}$ have substantially higher mobilities by as much as a factor of 1.5 times $2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 25°C because shielding of the nuclei by their oxygen atoms prevents significant hydration (Robinson and Stokes 1959). For similar reasons, multivalent complex ions, e.g., $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Co}(\text{NH}_3)_6^{3+}$, have substantially higher mobilities, also by as much as a factor of 1.5, as a result of shielding by the ligand groups.

Therefore, simple diffusion coefficients in porous media that are less than $10^{-5} \text{ cm}^2/\text{sec}$ result from mechanisms or conditions other than the inherent mobility differences between the ions themselves. If these mechanisms and conditions are sufficiently known, barriers can be engineered to minimize the transport of contaminants away from the waste package by choosing materials and conditions that minimize D and K while maximizing R_d and R_f .

ELECTRICAL CONDUCTIVITY AND MEASUREMENT OF THE DIFFUSION COEFFICIENT

It was anticipated that diffusive fluxes through unsaturated soil would be much lower than in pure solution, resulting in inordinately long time periods needed to collect sufficient data from transient-state experiments. Additionally, the maintenance of proper boundary conditions and the difficulty of experimental setup for direct steady-state techniques necessitated the search for an indirect method to measure diffusion coefficients. The most widely used indirect method is the measurement of electrical conductivity in a potentiostatic or galvanostatic mode, which provides reliable estimates of diffusion coefficients in dilute electrolyte solutions (Miller 1972). A variation of the two-electrode method was developed for this study (Rhoades and Oster 1986).

Conductivity measurements of aqueous solutions actually measure the impedance (the AC analog of DC resistance) at the impressed frequency. Impedance is a complex variable vector sum of the real in-phase (resistive) and the imaginary out-of-phase (reactive) components of the system response. For conductivity measurements (conductivity is the reciprocal of resistivity) using AC excitation, the in-phase component of impedance is a measure of the true solution resistivity (or conductivity) and can be used to represent the migration of ions in the solutions that form thin films and pendular element droplets in geologic material. Therefore, the impedance must be totally resistive, i.e., no capacitive elements, for diffusion coefficients to be determined from electrical conductivity measurements. This was verified for unsaturated geologic systems with a 1 kHz bridge using electrochemical impedance spectroscopy, which gives direct information about the real and imaginary components of impedance as a function of excitation frequency (Conca and Wright 1990). The impedance in geologic systems is a constant, frequency-independent quantity in the 600 to 7,000 Hz region and is totally resistive in the 400 to 10,000 Hz region. Thus, the measured impedance at 1 kHz on unsaturated geologic systems is a good measure of the true system resistance and its reciprocal, conductivity, and will give reliable values for diffusion coefficients. In addition, we have determined $D(\theta)$ on the same soils using the UFA-EC method and using Kemper's empirically-derived relationship (Bresler et al. 1982) and the results are in excellent agreement.

The standard unit of conductivity is reciprocal ohms·cm or mhos/cm. Once electrical conductivity measurements are made, they can be related to the diffusion coefficient through the Nernst-Einstein equation (Jurinak et al. 1987). For the experimental design of this study, the Nernst-Einstein equation is

$$D_i = \frac{RT}{F^2} \times \frac{KGt_i}{Z_i C_i} \quad (2)$$

where D_i = the diffusion coefficient of the i th ion (cm^2/sec)
 R = the gas constant (J/deg mol)
 T = the absolute temperature (Kelvin)
 F = Faraday's constant (coul/mol)
 K = the cell constant for the UFA™ conductivity cell sample holder (cm^{-1})
 G = the measured conductance on the conductivity bridge (mhos)
 t_i = the transport or transference number of the i th ion ($t_{K^+} = 0.4898$ 0.1 M)
 Z_i = the charge number on the i th ion (dimensionless)
 C_i = the molar concentration of the i th ion.

To be applicable to the Hanford Site vadose zone, the diffusion coefficients determined from Equation (2) must also be corrected for the solution non-ideality at 0.1 M and were done so in this study using the extended Debye-Hückel approximation (Stumm and Morgan 1981). For 0.1 M KCl solutions, the activity coefficient is 0.76, giving a correction factor of approximately 1.12, which was applied to the diffusion coefficients calculated from Equation (2).

The electrical conductivity cell designed for use in the UFA™ fits inside the centrifuge sample chamber and has two stainless-steel ring electrodes 2.5 cm apart. Stainless-steel electrodes are ideal for the low water contents and the current densities used in these experiments ($\leq 1\text{mA}/\text{cm}^2$; Geddes et al. 1971).

SAMPLE AND SOLUTION DESCRIPTION

The material selected for this experimental study was a sediment from the Hanford Site, W-5 Burial Ground, Trench-8. This soil is a coarse- to medium-grained fluvioglacial soil of a dominantly volcanic source lithology, composed of 87% sand, 7% silt, and 6% clay by weight for the <2 mm size fraction. (See Section 2 of this report for detailed characterization information.) The solution used in these experiments to measure hydraulic conductivity was 0.1 M KCl. The electrical conductivity of the effluent solutions was monitored during the experiments to observe any changes in conductivity resulting from water/sediment interactions that could affect the determination of the diffusion coefficient. Initial contact with the solutions resulted in minor cation exchange in the soils, which ceased after interaction with several pore volumes. During determinations of the diffusion coefficients, the electrical conductivity of the effluent solutions never varied by more than 0.0005 mhos or 2% of the conductivity of the infiltrating 0.1 M KCl solution.

COMPARISON OF UFA™-DETERMINED $K(\theta)$ TO TRADITIONAL TECHNIQUES

Hydraulic conductivities of unsaturated sediments from the Hanford Site, W-5 Burial Ground, Trench-8 and from the Buried Waste Test Facility (BWTF) site were determined over the water content range from 5 to 40% using the UFA™ method and traditional techniques. The BWTF sediments are similar to the Trench-8 soils in that they are coarse- to medium-grained fluvioglacial soils of a dominantly volcanic source lithology, composed of approximately 85-90% sand, 5-10% silt, and 3-6% clay by weight for the <2 mm size fraction.

Samples were run at fixed speeds with variable flow rates and at fixed flow rates with variable speeds using the procedure developed for this study. Figure 3 is a comparison of the UFA™ method with traditional curve-fitting estimates for determining $K(\theta)$ for the Trench-8 soils. Open triangles in the right-hand portion of Figure 3 are direct measurements of $K(\theta)$ using the UFA™. Open circles in the left-hand portion of Figure 3 are laboratory-determined water-retention versus matric-potential data on the same Trench-8 soils. A Van Genuchten relationship (the solid curve in the matric potential field) was fit to the water-retention data and used to generate the Mualem relationship

FIGURE 3. A comparison of the UFA™ Method (Left-Hand Figure) and Water-Retention Methods (Right-Hand Figure)

(the solid curve in the conductivity field). The agreement of the UFA™ with the Mualem curve is very good. At the lower water contents, the UFA™ data indicate that a lower water-content boundary for advective flow is being reached, an effect observed in the field but not predicted by the retention data.

Figure 4 is another comparison of the UFA™ method; this time with three traditional techniques for determining $K(\theta)$ for the BWTF soils. The right-hand portion of Figure 4 contains the conductivity data. Open squares are direct measurements of $K(\theta)$ using the UFA™. All UFA™ data were obtained with only 24 work hours. Open triangles are direct measurements of $K(\theta)$ using traditional column-flow experiments under unit-gradient conditions, requiring about six weeks to achieve hydraulic steady states over this water content range. For the left-hand portion of Figure 4, open circles are laboratory-determined water-retention versus matric-potential data on the same BWTF soils. The open circle in the right-hand portion of Figure 4 is a traditional measurement of the saturated hydraulic conductivity. A Campbell relationship (the solid curve in the matric potential field) was fit to the water-retention data and used to generate the Mualem relationship (the solid curve in the conductivity field), which again slightly overpredicts hydraulic conductivity at the lower water contents. Also shown in Figure 4 (see the solid circle) is 13-year average hydraulic conductivity calculated from the BWTF field lysimeter, assuming unit-gradient conditions at field-measured water contents, a point which ties the laboratory data to the field conditions. The agreement of the UFA™ data with all three methods is excellent and demonstrates the feasibility and rapidity of the UFA™ method to measure hydraulic conductivity of samples at low moisture contents.

COMPARISON OF TRENCH-8 SOILS WITH OTHER HANFORD FORMATION SEDIMENTS

Figure 5 shows $K(\theta)$ determined using the UFA™ for the Trench-8 soils, BWTF soils, and undisturbed cores from Borehole 299-W7-9, which are also from the Hanford Formation. It can be seen that Hanford Formation soils cannot be described with a single characteristic behavior, and much field and laboratory work may be needed to adequately characterize this formation. Note, however, that at the lower water contents (5 to 7% volume) characteristic of field

FIGURE 4. Characteristic Curves for the BWTF Soil Investigated Using four Different Methods

FIGURE 5. UFA™-Generated Characteristic Curves for Hanford Formation Soils and Sediments

conditions, the curves for all the soils have the same shape and are more or less displaced by some simple factor. This suggests that a scaling parameter might be used to simplify characterization and predictive modeling of Hanford Site sediments. It is interesting to note in Figure 5 that at any fixed hydraulic conductivity, the water content of undisturbed cores from Borehole 299-W7-9 increases with depth. The dry-bulk densities do not reflect simple compaction as a possible explanation.

DIFFUSION COEFFICIENTS

Figure 6 shows the Trench-8 diffusion coefficients, along with recent results for a variety of soils, gravels, bentonite, and whole rock cores, as a function of water content. These results fit well with the observation that simple diffusion coefficients $[D(\theta)]$ in most unsaturated media are primarily a

FIGURE 6. Diffusion Coefficients as a Function of Water Content in Geologic Materials

function of water content and not material characteristics except where the characteristics affect or determine water content (Conca and Wright 1991). At high water contents $D(\theta)$ gradually declines as water content decreases, from $10^{-5} \text{ cm}^2/\text{sec}$ at a volumetric water content of about 50% to $10^{-7} \text{ cm}^2/\text{sec}$ at a volumetric water content of about 5%, followed by a sharp decline as surface water films become thin and discontinuous and pendular water elements become very small, from $10^{-7} \text{ cm}^2/\text{sec}$ at a volumetric water content of about 5% to $10^{-9} \text{ cm}^2/\text{sec}$ at a volumetric water content of about 0.5 to 1%.

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