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Effects of High-pH and High-Ionic-Strength Groundwater on Iodide, Pertechnetate, and Selenate Sorption to Hanford Sediments: Final Report for Subtask 3a

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Prepared for the U.S. Department of Energy
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Summary

As part of the Immobilized Low-Activity Waste-Performance Assessment, three experiments were conducted to evaluate the effect of the expected near-field chemistry on the sorption of iodide, selenate, and pertechnetate onto a sediment obtained from the Hanford Site. These experiments were performed in fiscal year 1998 at the Pacific Northwest National Laboratory.[1]

During these experiments, attention was directed at the identification of the chemical mechanisms controlling the sorption processes to provide technical defensibility for the selection of the distribution coefficients (K_d) to be used in the remainder of the performance assessment. It was found, during the conduct of the experiments, that selenium and technetium K_ds increased as ionic strength increased. The cause for this is most likely to be that the higher ionic strength caused the double layer around the particles to decrease, thereby permitting greater interaction with the mineral surfaces. Further, the pH level had an effect on the sorption of these anions.

These are the first-ever experiments conducted with Hanford Site sediment in which the K_ds were measured as a function of ionic strength and pH. Overall, the observed trends were consistent with more generalized geochemical principles. One of the most important contributions of these experiments was that they quantified the K_d changes induced by variations in ionic strength and pH that are expected to exist in the near field.

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

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1.0 Introduction

1.1 Background

A performance assessment is under way to evaluate the suitability of the unsaturated zone of the Hanford Site for the long-term immobilization of vitrified low-activity waste. This assessment will predict the transport of radionuclides and/or contaminants from a source to a receptor via pathways that are considered credible. Previous analyses for proposed disposal actions on the Hanford Site show that groundwater transport presents the greatest potential for long-term dose uptake by humans (Mann et al. 1998). Furthermore, these previous analyses have shown that the key risk drivers at the proposed disposal site include ^{79}Se, ^{99}Tc, ^{129}I, ^{234,235,238}U, and ^{237}Np.

It is expected that the leachate from the glass waste forms used for the immobilized low-activity waste (ILAW) will have very high-pH and ionic-strength properties (Mann et al. 1998). The effect of high-ionic strength and pH on the tendency of dissolved key radionuclides to sorb to sediments is not known. This lack of knowledge could adversely affect the performance assessment by increasing the uncertainty and requiring that unrealistically conservative estimates be used as input parameters.

pH has been shown to have a large effect on adsorption tendencies of radionuclides to pure mineral phases (Zachara and McKinley 1993, Waite et al. 1994) and natural sediments (Koss 1988, Johnson et al. 1995, Kaplan et al. 1998). These studies indicate that cation sorption tends to increase as pH increases to ~10. Above this pH value, several complex geochemical reactions occur, including dissolution of several silicate-containing minerals, reprecipitation of secondary mineral phases, radionuclide adsorption to primary minerals and to the newly formed secondary minerals, incorporation of radionuclides into the structure of some of these secondary phases, incorporation of radionuclides into carbonate phases (carbonate mineral formation increases as pH increases), and increased competition for sorption sites resulting from the higher ionic strength of the aqueous solution. It is difficult to determine *a priori* whether radionuclide movement would tend to be retarded more or less in these chemically and mineralogically altered systems than in natural, nontransformed systems.

Elevated solution ionic strength, or salt concentration, has been shown to have significant effects on sorption processes (Serne and Relyea 1981, Kaplan et al. 1998, Stumm and Morgan 1998). Generally, as the ionic strength increases, adsorption of cationic and anionic contaminants decreases because there is greater competition for adsorption sites and the activity of the sorbed species decreases. However, high-ionic strengths can occasionally have the opposite effect (i.e., as the ionic strength increases, solute interactions with the solid phase also increases [Stumm and Morgan 1998]). The cause for this has been attributed to precipitation and/or coprecipitation.

As part of the ILAW project, the effects of ionic strength and pH on U(VI) sorption were evaluated through a series of batch-type laboratory experiments (Kaplan et al. 1996, 1998). The results show that U(VI) adsorption remained constant between 3.3 and 100 µg/L UO_2^{2+} at pH 8.3 and ionic strength of

0.02 M. This result suggests that the simple distribution coefficient (K_d) model could be used to describe adsorption in this concentration range. In a separate study, U(VI) K_d and solubility values did not change as the ionic strength was increased with $NaClO_4$ to 0.014 M. U(VI) K_d values essentially doubled from 1.07 to 2.22 mL/g as the pH of the system increased from 8.3 to 9.3. Above pH 10.3, precipitation of U(VI)-containing solids occurred, resulting in apparent K_d values of >400 mL/g. Precipitation did not occur unless a sediment was present. This suggests that heterogeneous precipitation occurred. Thus, in carbonate systems with a pH ≥10.5, U(VI) mobility may be much less than in near-neutral pH systems. These results have significant ramifications for the performance assessment, in that in areas where high-pH levels are expected (e.g., near the glass logs, quite high K_d values for U[VI] can be justified).

The effect of ionic strength on anion sorption is not well understood. Routson et al. (1977) measured K_d values for TcO_4^- as a function of sodium bicarbonate concentrations and reported values of -0.05 ± 0.01, -0.03 ± 0.01, 0.01 ± 0.04, and 0.02 ± 0.06 mL/g, with an average of -0.014 mL/g (the standard deviation of this mean was not reported). Serne et al. (1993) reported 17 TcO_4^- K_d values for 3 sediments from the Hanford Site measured under varying experimental conditions. Ten K_d values were negative, ranging from -0.6 ± 0.1 to -0.1 ± 0.8, while 7 were positive, ranging from 0.8 ± 0.8 to 0.02 ± 0.3 mL/g. The standard deviations of the TcO_4^- K_d values reported by Serne et al. (1993) were large and generally included 0 mL/g. Gee and Campbell (1980) reported comparatively large negative K_d values in sediments collected from the Hanford Site and in aqueous phases of high-ionic-strength solutions: -3 ± 2 and -1 ± 2 mL/g. In a separate set of batch K_d experiments in which the aqueous-phase chemical composition was varied, they measured 24 TcO_4^- K_d values from 2 sediments. The K_d values ranged from -2.77 to 1.27, with 14 negative determinations. The positive distributions of TcO_4^- K_d values (i.e., x + 1s, reported by Gee and Campbell [1980] rarely included 0 mL/g). The TcO_4^- K_d values tended to be greater for solution with higher ionic strength than for lower ionic strength. The impact of pH on TcO_4^- or I^- sorption to Hanford Site sediments has not been studied.

As part of this performance assessment project, Kaplan and Serne (1998) measured ~30 TcO_4^- K_d values using sediments from the 200 Areas on the Hanford Site. The average K_d value was -0.04 ± 0.02 mL/g over a wide range of initial TcO_4^- activities and soil types. They attributed the negative values to anion exclusion; this was supported by literature and theoretical considerations. However, one thing that is not known is the effect of ionic strength on the K_d value of Tc or any other anion, including SeO_4^{2-}. All the TcO_4^- K_d values that have been measured to date using Hanford Site sediments have been with solutions of low ionic strength, <0.05 M. It is possible that as the ionic strength increases, the diffuse double layer that extends the negative charge of the sediments into the surrounding groundwater would collapse, thereby decreasing the anion exclusion from the mineral surfaces and permitting the TcO_4^- anion to come into contact and sorb to the mineral surfaces. The importance of this to the performance assessment is that higher K_d values may, in fact, exist for anions in near-field, high-ionic-strength systems than the reported K_d values that pertain to far-field, low-ionic-strength systems.

1.2 Objectives

The objectives of this study were to determine the effects of high pH and ionic strength on technetium (as TcO_4-), iodine (as I^-), and selenate (as SeO_4^-) sorption to 200-East Area sediments. These sediments contain carbonate phases that provide sorption sites and maintain high concentrations of total carbonate (CO_3^{2-} and bicarbonate [HCO_3^-]) in the aqueous phase. Total dissolved carbonates can greatly influence dissolved cationic radionuclide speciation (e.g., UO_2^{2+}) and can potentially compete with anionic species for sorption sites on mineral surfaces. A series of batch experiments were conducted to simulate various near-field and far-field environments influenced by a plume emanating from a glass waste form. The intent of these experiments was to provide a conceptual model of the I^-, SeO_4^-, and TcO_4^- geochemistry in the plume as a function of distance from the glass waste form and to provide quantified sorption values in the form of K_d values.

1.3 Scope

This study consisted of three experiments: 1) the preliminary experiment of detection interferences and sorption competition of $^{125}I^-$, $^{75}SeO_4^-$, and $^{99}TcO_4^-$; 2) the ionic-strength experiment; and 3) the pH experiment. The first was designed to determine whether the three radionuclides of interest (technetium [as $^{99}TcO_4^-$], iodine [as $^{125}I^-$], and selenium [as $^{75}SeO_4^{2-}$]) could be combined in one sediment/water system to measure K_d values without causing any analytical interferences or chemical competition for sorption sites on the sediment surface. If the radionuclides could be tested concurrently, then a great deal of time would be saved in conducting these measurements.

The experiments were designed to evaluate the effects that the ionic-strength and pH conditions expected in the near field would have on K_d values. These two batch sorption experiments were conducted with a 200 Areas sediment (from trench AE-3) that was previously characterized as part of this project (Kaplan et al. 1996). NaOH and $NaClO_4$ additions to an uncontaminated Hanford Site groundwater were used in the pH and ionic-strength experiments, respectively. The NaOH additions in the pH experiment were expected to change the ionic strength and pH of the solutions, whereas the $NaClO_4$ additions were expected to change only the ionic strength, not the pH, of the solutions. This difference would permit separating the effects of ionic strength from those of pH. In addition to measuring K_d values under various pH and ionic-strength conditions, the filtration index was determined to provide a measure of the solubility of the TcO_4^-, I^-, and SeO_4^{2-} under these various groundwater conditions.

1.4 Document Outline

This report consists of five chapters. The materials and methods used to conduct these experiments are given in Chapter 2.0. The results and discussion are given in Chapter 3.0. The conclusions and implications for the performance assessment are contained in Chapter 4.0, followed by the references cited in the text (Chapter 5.0).

2.0 Materials and Methods

2.1 General Batch Sorption Procedure

Three experiments were conducted: preliminary experiment of detection interferences and sorption competition of $^{125}I^-$, $^{75}SeO_4^-$, and $^{99}TcO_4^-$; ionic-strength experiment; and pH experiment. The general procedure used in each experiment was identical, except that one parameter was systematically changed.

Groundwater collected from well 699-S3-25, located in an uncontaminated portion of the Hanford Site, was used as the aqueous phase in all experiments (Table 1). The groundwater was analyzed using standard techniques. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), having an analytical precision of $\leq \pm 4\%$ at 5 mg/L, was used to determine dissolved cation concentrations. Ion chromatography (IC), having an analytical precision of $\leq \pm 4\%$ at 5 mg/L, was used to determine dissolved anion concentrations. Analysis for ^{99}Tc was by liquid scintillation counting (LSC), using a quench-calibrated Wallac® 1415 LSC and Packard® Opti-fluor™ LSC cocktail (Wallac Instruments, Inc. and Packard Instruments, Meriden, Connecticut). Analyses for ^{75}Se and ^{125}I were by gamma energy analysis using a Wallac® 1480 Wizard™ 3-in. NaI automatic gamma detector. All analytical methods were performed to 3% combined error, with systematic error accounting for <1% of the total.

Table 1. Chemical Composition of Uncontaminated Hanford Site Groundwater (<0.45-µm filter)

Constituent	Concentration (mg/L)
pH	8.4 (unitless)
Cl^-	24
NO_3^-	1.7
SO_4^{-2}	109
Total organic carbon	0.73
Total alkalinity (as CO_3^{2-})	160
Al	0.14
B	0.05
Ba	0.069
Ca	58
Fe	0.14
K	14
Mg	16
Mn	0.046
Na	30
Si	16.2

The sediment used in these studies was collected from the side wall of trench AE-3 located in the 200-West Area burial grounds on the Hanford Site (Table 2). The sediment was collected at a depth of ~10 m. The sediment characterization was conducted using standard methods: cation-exchange capacity was determined by the Na^+-exchange ion method (Rhodes 1987), surface area using N_2 adsorption by the BET method (Carter et al. 1987), particle-size distribution by the pipette method (Gee and Bauder 1987), particle density by the submersion method (Blake and Hartge 1987), hydraulic conductivity by the constant head method (Klute and Dirksen 1987), carbonate concentration by acid neutralization of the carbonate followed by back titration of the excess acid (Nelson 1987), pH by the 1:1 solid:solution method (McLean 1987), and mineralogy by x-ray diffraction (Whittig and Allardice 1987).

Trench AE-3 sediment has the texture of a silty loam (see Table 2). The mineralogy of the clay-size fraction is dominated by smectite, illite, and vermiculite. X-ray diffraction analysis of the samples revealed that the carbonate phase was dominated by calcite. The hydrous iron oxide concentration of this sediment was not measured, but was based on measurements made on nearby sediments that contained between 0.2% to 0.5% (wt) amorphous Fe_2O_3 (Kaplan et al. 1996).

Table 2. Selected Properties of the Trench AE-3 Sediment

Constituent	Trench AE-3
Texture	Silty loam
pH	8.3
Cation-exchange capacity (CEC) (meq/100 g)	6.4
Surface area (m^2/g)	14.8
In situ gravel (%)[(a)]	<1
In situ sand (%)	41
In situ silt (%)	50
In situ clay (%)	9
<2-mm sand (%)[(b)]	41
<2-mm silt (%)	50
<2-mm clay (%)	9
Particle density (g/cm^3)	2.74
Saturated hydraulic conductivity (cm/s)	6E-6
$CaCO_3$ (as inorganic C) (mg/L)	1.92
Dominant mineral in clay fraction	Smectite (57%) Illite (19%) Vermiculite (14%)

(a) In situ compositions refer to the total sediment as it exists in the ground. This sediment was not used in the adsorption experiments.

(b) The <2-mm fraction was used in the sorption experiments.

The experiments were conducted on a laboratory bench in contact with air (i.e., not in a CO_2-free chamber) in an attempt to simulate better actual conditions in a subsurface environment. The sediment was first preequilibrated with groundwater. This was accomplished by adding groundwater to the sediments, shaking the suspensions overnight, centrifuging, pouring off the supernatant, and then measuring the pH of the supernatant. This was repeated until the pH of the groundwater did not change before and after contact with the sediment, usually three washes. The purpose of this pre-equilibration step was to isolate the radionuclide adsorption reaction from the large number of other reactions that may occur while sediments and aqueous solutions come to chemical equilibrium. This has been shown to be a critical step for accurately measuring adsorption values and minimizing precipitation and/or coprecipitation of several radiotracers (Serne and Relyea 1981).

$^{99}TcO_4^-$, $^{125}I^-$, and $^{75}SeO_4^{2-}$ were added to uncontaminated Hanford Site groundwater and then the solutions were placed on a platform shaker for 7 days, a period selected to ensure that steady-state conditions were achieved. These solutions were then passed though a 0.20-μm filter, and the filtrates were analyzed for pH, electrical conductivity, and total dissolved radionuclide activity.

An index of the solubility of the radionuclides in the various treatment solutions was estimated by the filtration ratio:

$$\text{Filtration Rate} = \frac{A_{\text{final}}}{A_{\text{initial}}} \tag{1}$$

where A_{final} is the radionuclide activity in the <0.20-μm filtrate and A_{initial} is the radionuclide activity added to the groundwater. No sediment was added to the solutions used to calculate the filtration ratios. The purpose of gathering this information was to help in differentiating between radionuclide removal from solution by precipitation or by adsorption. If the filtration ratio is <1, then precipitation or container wall adsorption likely occurred.

A 20-mL aliquot of the filtered radionuclide solutions was then added to 10 g of preequilibrated sediment. The radionuclide/groundwater/sediment suspensions were placed on a slow-moving platform shaker for 14 days. This duration was selected to ensure that the system was in a steady state. Preliminary experiments showed that U and I^- sorption to trench AE-3 sediment remained constant between 2 and 14 days (Kaplan et al. 1996). The suspensions were centrifuged and the supernatants were then passed through 0.20-μm filters. Radionuclide activity, pH, and electrical conductivity of the filtrates were measured.

The K_ds (mL/g) were calculated using the following equation.

$$K_d = \frac{\left(A_{\text{spike}} \times V_{\text{spike}}\right) - A_{\text{final}}\left(V_{\text{spike}} + V_{\text{excess}}\right)}{A_{\text{final}} \times M_{\text{sediment}}} \tag{2}$$

where A_{spike} is the initial radionuclide activity in the spike solution (mCi/L), V_{spike} is the volume of radionuclide solution (mL), V_{excess} (mL) is the volume of excess solution left after the third preequilibration wash (weight of excess solution divided by solution density), A_{final} is the radionuclide activity in the effluent solution after equilibration (mCi/L), and $M_{sediment}$ is the sediment mass (g).

A sediment:solution ratio of 1:2 was used in these experiments. This high ratio was used to improve K_d measurement accuracy. As can be seen from Equation (2), the activity of adsorbed radionuclide is determined by subtracting the radionuclide activity in solution before, A_{spike}, and after, A_{final}, contact with the sediment. If little adsorption takes place, then the difference between A_{spike} and A_{final} will be small. Thus, one of the difficulties in determining low-K_d values is that two large numbers must be subtracted from each other to determine a small value, a poorly poised mathematical situation. To obtain a greater difference between A_{spike} and A_{final}, the sediment:solution ratio was increased in these experiments.

Three or four replicates of each K_d measurement were made. Two types of control treatments were included in each experiment: a negative and a positive. The positive control, containing the radionuclide-spiked groundwater and no sediment, was used to evaluate radionuclide sorption to labware and filters. The negative control contained sediment and groundwater without the added radionuclides and served to account for background radionuclide activity in the uncontaminated sediment and groundwater.

2.2 Preliminary Experiment of Detection Interferences and Sorption Competition of $^{125}I^-$, $^{75}SeO_4^-$, and $^{99}TcO_4^-$

The objective of this experiment was to determine whether ^{125}I, ^{75}Se, and ^{99}Tc could be combined in one sorption test without causing analytical interferences or sorption competition. This study had a full-factorial experimental design and consisted of four radionuclide treatments (^{125}I, ^{75}Se, ^{99}Tc, and $^{125}I/^{75}Se/^{99}Tc$ combined), two soil treatments (with and without soil), and four replicates. The four radionuclide treatments were made by adding ~15 µCi/L of each radionuclide to the Hanford Site groundwater. Once the radionuclides were permitted to equilibrate for 7 days with the groundwater, they were passed through a 0.20-µm filter, counted for radioactivity, and then added in 20-mL aliquots to 10 g of preequilibrated trench AE-3 sediment (see Table 2). These suspensions were placed on a slow-moving platform shaker for 14 days to equilibrate. The liquid and solid phases were then separated by centrifugation, followed by filtration (0.20-µm filter), and then the effluent was counted for radioactivity.

2.3 Ionic-Strength Experiment

The effect of solution ionic strength on solubility (as estimated by the filtration index, Equation [1]) and K_d values of Tc (as TcO_4^-) and Se (as SeO_4^-) were evaluated by varying the amount of $NaClO_4$ added to the groundwater/sediment suspensions. The effect of $NaClO_4$ concentration on I^- filterability and K_d values was not evaluated because ClO_4^- would oxidize the I^- to iodate (IO_3^-). IO_3^- has an appreciably different geochemical behavior than I^- (e.g., it sorbs much more strongly to mineral surfaces [Couture and Seitz 1983, Ticknor and Cho 1990, Muramatsu et al. 1993]). $NaClO_4$ was selected as the salt to vary ionic strength because Na will likely be the dominant cation emanating from most glass waste forms and ClO_4^- is a noncomplexing ligand. Thus, it was expected that ClO_4^- would increase the ionic strength without greatly affecting the pH and the chemical speciation. $NaClO_4$ treatment solutions of 0.05, 0.10, 0.50, and 1.00 M were prepared in Hanford Site groundwater. The trench AE-3 sediment was preequilibrated with the $NaClO_4$ treatment solutions as described in Section 2.1. Approximately 15 µCi/L of $^{99}TcO_4^-$ and $^{75}SeO_4$ were prepared using the $NaClO_4$ treatment solutions. The radionuclide/groundwater solutions with variable ionic strength were permitted to equilibrate for 7 days and then filtered through a 0.20-µm filter. These filtered solutions and preequilibrated sediments were then used in sediment-sorption experiments, using the procedure described in Section 2.1.

2.4 pH Experiment

The pH values of five groundwater solutions were adjusted with 0.1 M NaOH to pH values ranging from 8.1 (no addition) to 11.9. Once the pH values remained stable (pH ± 0.03) for a period of 7 days, the solutions were spiked with 15 µCi/L $^{99}TcO_4^-$, $^{125}I^-$, or $^{75}SeO_4^-$ and then equilibrated for another 7 days. The solutions were passed through a 0.20-µm filter, and the pH and radionuclide activities of the filtrate were measured. These solutions and preequilibrated sediments were then used in sediment-sorption experiments using the procedure described in Section 2.1.

3.0 Results and Discussion

3.1 Preliminary Experiment of Detection Interferences and Sorption Competition of $^{125}I^-$, $^{75}SeO_4^-$, and $^{99}TcO_4^-$

A preliminary experiment was conducted to evaluate whether $^{125}I^-$, $^{75}SeO_4^-$, and $^{99}TcO_4^-$ could be combined in the same batch test to measure K_d values. At issue was whether these three radionuclides 1) would interfere with the analytical detection of each other or 2) would compete with each other for sorption sites on the mineral surfaces. To address the first issue, an experiment was conducted in which the radionuclides were added to separate solutions and combined in one solution. As can be seen by comparing the first two columns of Table 3, the activity of ^{125}I and ^{75}Se was similar irrespective of whether these radionuclides were separated or combined in solutions. Interference of ^{99}Tc was detected in the presence of the other radionuclides. Close examination of the spectra revealed that a secondary ^{75}Se peak overlapped the primary ^{99}Tc peak. Time-consuming chemical separation, or possibly deconvolution of spectrum peaks, may permit independently measuring ^{75}Se and ^{99}Tc in the same solution.

Table 3. Detection Interference and Sorption Competition of ^{125}I, ^{75}Se, and ^{99}Tc Experiment

Constituent	Solution Activity (µCi/L)[(a)]		K_d (mL/g)[(b)]	
	Radionuclides in Separate Solutions	^{125}I, ^{75}Se, and ^{99}Tc in Same Solution	Radionuclides in Separate Tubes	^{125}I and ^{75}Se in Same Tube
^{125}I	46.0 ± 0.3	47.4 ± 0.4	0.06 ± 0.02	0.07 ± 0.02
^{75}Se	43.2 ± 0.2	43.5 ± 0.4	8.31 ± 1.02	9.6 ± 0.61
^{99}Tc	58.5 ± 0.7	65.7 ± 0.9	--[(c)]	--[(c)]

(a) Means ± standard deviation of four replicates; solution spiked with $^{125}I^-$, $^{75}SeO_4^{2-}$, and $^{99}TcO_4^-$ and permitted to equilibrate with Hanford Site groundwater for 14 days.
(b) Spike solution and sediment equilibration period groundwater = 14 days; 1:2 sediment mass:spike groundwater ratio; sediment was preequilibrated with Hanford Site groundwater.
(c) ^{99}Tc K_d measurements were not conducted because it was determined earlier that ^{99}Tc detection in the presence of ^{75}Se was not practical.

Based on statistical evaluations, the K_d values of ^{125}I and ^{75}Se did not change significantly ($P \leq 0.05$) when they were measured separately or together in the same test vessel (see Table 3). Had competition for sorption sites been occurring in this system, then the K_d values would have decreased when measured in the presence of the other radionuclide anion. Based on the data in Table 3, it was decided to measure $^{99}TcO_4^-$ K_d values in one set of reaction vessels and $^{125}I^-$ and $^{75}SeO_4^-$ K_d values in a second set of reaction vessels.

3.2 Ionic-Strength Experiment

The objective of this experiment was to determine the effect of ionic strength on SeO_4^{2-} and TcO_4^- K_d values. Another intent of this experiment was to provide information that could be used to assist in differentiating between the effects of pH and ionic strength on K_d values in the pH experiment (Section 3.3), in which pH and ionic strength were varied concomitantly. I^- was not evaluated in this experiment because it was expected that the $NaClO_4$ used to adjust the ionic strengths would oxidize the I^- to IO_3^-, thereby increasing its propensity to adsorb to sediments (Couture and Seitz 1983, Ticknor and Cho 1990, Muramatsu et al. 1993).

The rather wide range of ionic strengths (or more specifically $NaClO_4$ concentrations) used in this experiment had no significant effect on the final activity of Se and Tc remaining in solution, as indicated by the filtration ratio data presented in Table 4. This provides indirect evidence that neither SeO_4^{2-} nor TcO_4^- precipitated from solution once they were added to the treatment solutions. It is also important to note that the final pH values of the four $NaClO_4$-amended solutions after the 14-day contact time were essentially identical, indicating that ionic strength increased independently of pH in these experiments.

Table 4. Selenium and Technetium Filtration Ratios and K_d Values of Groundwater Treated with Varying Concentrations of $NaClO_4$

	Solution Chemistry at End of Spike/Groundwater Equilibration Period		Filtration Ratio (unitless)[(a)]		K_d (mL/g)[(b)]	
$NaClO_4$ Added (M)	pH[(c)]	Electrical Conductivity (mS/cm)	Se	Tc	Se	Tc
0.05	7.74	9.06	0.99	1.00	3.31 ± 0.57	-0.16 ± 0.04
0.10	7.76	10.94	0.99	0.95	4.49 ± 0.19	-0.13 ± 0.00
0.50	7.73	11.05	0.99	0.97	4.47 ± 0.06	-0.28 ± 0.01
1.00	7.70	>20	0.97	1.01	4.11 ± 0.06	3.94 ± 0.99

(a) Initial ^{75}Se (as $^{75}SeO_4^{2-}$) and ^{99}Tc (as $^{99}TcO_4^-$) activity ~15 µCi/L; equilibration period for ^{75}Se or ^{99}Tc spike in groundwater = 14 days; filter = 0.20 µm; no sediment included in these systems; filtration ratio is defined in Equation (1); one replicate.

(b) Initial ^{75}Se (as $^{75}SeO_4^{2-}$) and ^{99}Tc ($^{99}TcO_4^-$) activity ~15 µCi/L; spike solution and sediment equilibration period groundwater = 14 days; 1:2 sediment mass:spike groundwater ratio; three replications.

(c) pH measured with a solid-state chip electrode (Sentron, 2001 pH; CP Instruments, Bishop's Stratford, Herts, United Kingdom) to reduce potential problems associated with measuring pH in high-ionic-strength solutions.

The filtered $NaClO_4$-amended solutions used to generate the filtration index data in Table 4 were reused in the Se and Tc sorption experiments. The Se and Tc K_d values did not remain constant as a function of $NaClO_4$ concentrations (see Table 4). The Se K_d value for the lowest $NaClO_4$ concentration, 0.05 M NaClO4, was ~1 mL/g less than for the higher $NaClO_4$ treatments. Similarly, the Tc K_d values were less for the lower $NaClO_4$ treatments, ≤0.50 M $NaClO_4$, and greater for the higher treatment, 1.00 M $NaClO_4$. The Tc K_d values for the ≤0.50 M $NaClO_4$ solutions were negative, ranging from -0.28 ± 0.01 to -0.16 ± 0.04 mL/g. The Tc K_d value for the 1.00 M $NaClO_4$ treatment was positive and significantly greater than the other treatments, 3.94 ± 0.99 mL/g.

Negative Tc K_d values have been frequently reported in the past (Routson et al. 1977, Gee and Campbell 1980, Serne et al. 1993). These negative K_d values have generally been attributed to experimental error associated with a nonadsorbing solute (i.e., a solute with a K_d of 0 mL/g). Recently, Kaplan and Serne (1998) measured ~30 Tc K_d values, using sediments from the 200 Areas on the Hanford Site. The average K_d value was -0.04 ± 0.02 mL/g over a wide range of initial Tc activities and soil types. However, and important, the ionic strength of all of these tests were <0.05 M. The negative K_d values were attributed to the negative charge of the sediments, repulsing the anions from the clay surface, creating an exclusion volume immediately around the clay particle, and thereby, concentrating the TcO_4^- anion in the nonexclusion solution volume that was sampled to calculate K_d values (Kaplan and Serne 1998).

The cause for the substantial increase in the Se and Tc K_d value at higher-ionic-strength solutions is not known. The most likely explanation is that the higher ionic strength caused the double layer around the sediment particles to decrease, thereby permitting greater TcO_4^- mineral interactions. The greater contact of the TcO_4^- with the mineral surface increased the likelihood that the TcO_4^- anion would come into contact with positive sorption sites. The Hanford Site sediment has few positive sorption sites at pH 8.1; however, these few sites may play an important role in sorbing anions. The presence of negative sorption sites, albeit there are very few, is especially important at the extremely low TcO_4^- concentrations used in the test solutions and expected in the proposed ILAW site, on the order of 10^{-10} M TcO_4^-. The increased removal of SeO_4^{2-} and TcO_4^- in the higher-ionic-strength solutions likely did not occur as a result of homogeneous precipitation (precipitation in solution). Na and ClO_4 tend to form very soluble salts with TcO_4^- and SeO_4^{2-}. Calculated solubility indices indicated that neither of the radionuclides likely formed precipitates in the test solutions (this will be discussed in greater detail below). Additionally, the filtration indices (see Table 4) showed that no filterable Tc or Se material was formed in the higher $NaClO_4$ concentration treatments. It is possible that heterogeneous precipitation occurred. Heterogeneous precipitation is precipitation that occurs only in the presence of a solid phase. In this process, the solid phase lowers the energy barrier for precipitation to occur by providing nucleation sites or by increasing the concentration of solute near the surface. This is not an especially likely mechanism because the calculated saturation indices were extremely low, indicating that precipitation in homogeneous systems was unlikely.

The chemical composition of the $NaClO_4$-amended groundwater used in this experiment is presented in Table 5. Other than the Na and ClO_4^- concentrations, the rest of the chemistry remained largely unchanged. With increased additions of $NaClO_4$, there was a decrease in Ca and K concentration in the aqueous phase. This likely is the result of an exchange reaction with the added Na. There was also a decrease in Si concentration with increased additions of $NaClO_4$. The cause of this trend is not known.

Table 5. Chemical Composition (mg/L) of $NaClO_4$-Amended Groundwater Solutions after Contact with Sediment[(a)]

Constituent	Added $NaClO_4$			
	0.05 M	0.10 M	0.50 M	1.00 M
pH	7.74	7.76	7.73	7.70
ClO_4^-	4,125	7,719	25,236	52,397
SO_4^{2-}	40.45	40.68	40.63	40.75
Alkalinity (as $CaCO_3$)	96.6	130	62.5	35.5
Ca	66.48	83.98	95.27	83.65
Fe	<0.04	<0.04	0.04	0.09
K	13.26	17.23	23.06	30.81
Mg	14.68	16.94	17.60	15.29
Na	958	1,793	5,863	12,173
Si	16.62	15.4	12.73	9.83

(a) The initial ^{75}Se (as $^{75}SeO_4^{2-}$) and ^{99}Tc ($^{99}TcO_4^-$) activity was 15 µCi/L; spike solution and sediment equilibration period was 14 days; 1:2 solid:liquid ratio; one replication.

Chemical speciation calculations were conducted using the data in Table 5 and the results are presented in Table 6. These calculations indicate that most of the Se and Tc in the system existed as free ions; namely, SeO_4^{2-} and TcO_4^-, respectively. As more Na was added, more of the SeO_4^{2-} formed $NaSeO_4^-$; however, the concentration of this species never exceeded 36% of the total SeO_4^{2-} pool. Although not presented, the saturation indices calculated using the data from Tables 5 and 6 indicated that TcO_4^- or SeO_4^{2-} mineral phases were very unlikely to form (i.e., the saturation indices of these minerals were appreciably less than zero).

3.3 pH Experiment

The effect of increasing pH values of Hanford Site groundwater and sediment by adding NaOH on the filtration ratio and K_d values (Equations [1] and [2], respectively) were evaluated in this experiment. The pH and the electrical conductivity, an indirect measure of ionic strength, increased with increased pH treatments (Table 7). It is important to note that the highest electrical conductivity value reported for this study was less than the lowest treatment, 0.05 M $NaClO_4$ in the ionic-strength experiment (see Table 4). The filtration ratios for all three anions were approximately equal to unity, suggesting that little filterable precipitates formed as a result of the NaOH additions.

The I and Se K_d values decreased as the pH treatment increased. This trend can likely be attributed to the sediments in the higher pH systems having greater negative surface charge. The greater negative surface charge not only increases the repulsion of the anions from the surface but also resulted in the conversion of positively charged surface sites to negatively charged surface sites.

Table 6. Calculated Speciation of the SeO_4^{2-} and TcO_4^- in the Solutions used in the Ionic Strength Experiment[(a)]

$NaClO_4$ Added (M)	Calculated Ionic Strength (mM)	SeO_4^{2-} Species (%)				TcO_4^- Species (%)
		SeO_4^{2-}	$CaSeO_4^0$	$MgSeO_4^0$	$NaSeO_4^-$	TcO_4^-
0.05	47	84	6	2	8	100
0.10	85	81	5	1	12	100
0.50	262	70	3	<1	26	100
1.00	536	62	1	<1	36	100

(a) Bulk chemical composition of the solutions were presented in Table 5. The sum of the speciation percentages for a particular solute may not equal 100% because only the species with concentrations >1% are presented in the table. The SeO_4^{2-} speciation calculations were conducted with the software GEOCHEM (Sposito and Mattigod 1980). The stability constants used in these calculations were from the GEOCHEM database, Smith and Martell (1976), and Dyrssen et al. (1968); and values calculated using the method described by Nieboer and McBryde (1973). The TcO_4^- speciation calculations were conducted with the software MINTEQA2 (Allison et al. 1991). The stability constants used in the TcO_4^- speciation calculations were from the MINTEQA2 database and Lemire and Jobe (1996).

Conversely, the Tc K_d values tended to increase as the pH of the system increased. The cause for this is not known and is contrary to the expected trend. It is possible that this trend may be attributed to the concomitant increase in ionic strength (or electrical conductivity) as the pH was increased (see Table 7). However, in the ionic-strength experiment (see Section 3.2), it was shown that ionic strength, per se, did not increase Tc K_d values until the electrical conductivity was >11.04 mS/cm (>0.5 M $NaClO_4$; see Table 4). The highest electrical conductivity measured in the Tc pH treatments was 6.14 mS/cm (see Table 7), which is less than the 11.04-mS/cm critical value.

The solution chemistry of the NaOH-amended groundwater is presented in Table 8. The pH 8.1 groundwater did not receive any NaOH. The other solutions that did receive NaOH showed a rather dramatic change in chemistry. As expected, the pH and Na concentration increased with NaOH additions. Substantial decreases in Ca, K, and Mg concentrations and increases in Si and CO_3^{2-} concentrations were also measured with increased pH treatments. The increase in carbonate levels is attributed to the direct interaction between hydroxide and CO_3^{2-} concentrations (Stumm and Morgan 1998). The

Table 7. Filtration Ratios and K_d Values of Iodine, Selenium, and Technetium in NaOH-Amended Groundwater

Constituent	Solution Chemistry at End of Spike/Groundwater Equilibration Period pH	Electrical Conductivity (mS/cm)	Filtration Ratio[(a)] (unitless)	K_d[(b)] (mL/g)
^{125}I	8.1	0.66	0.98	0.22 ± 0.01
	9.9	0.79	0.96	0.01 ± 0.01
	10.2	0.79	0.96	-0.02 ± 0.02
	11.0	1.15	0.99	-0.04 ± 0.02
	11.9	3.46	1.01	0.01 ± 0.01
^{75}Se	8.1	0.66	0.98	5.78 ± 0.28
	9.9	0.79	0.92	0.29± 0.03
	10.2	0.79	0.96	0.19 ± 0.00
	11.0	1.15	0.99	0.05 ± 0.02
	11.9	3.46	0.99	0.04 ± 0.00
^{99}Tc	8.1	0.59	0.97	-0.02 ± 0.01
	9.9	0.70	0.99	1.04 ± 0.06
	10.2	0.70	1.00	1.05 ± 0.02
	11.0	1.13	1.00	1.07 ± 0.05
	11.9	6.14	1.02	1.07 ± 0.03

(a) The initial ^{125}I (as $^{125}I^-$), ^{75}Se (as $^{75}SeO_4^{2-}$), and ^{99}Tc ($^{99}TcO_4^-$) activity was 15 µCi/L; equilibration period for the radionuclides with the groundwater was 14 days; filter = 0.20-µm; no sediment included in these systems; filtration ratio is defined in Equation (1).

(b) Initial ^{125}I (as $^{125}I^-$), ^{75}Se (as $^{75}SeO_4^{2-}$), and ^{99}Tc ($^{99}TcO_4^-$) activity ~15 µCi/L; spike solution and sediment equilibration period was 14 days; 1:2 sediment mass:spike groundwater ratio; three replications.

Table 8. Chemical Composition (mg/L) of NaOH-Amended Groundwater Solutions after Contact with Sediment[(a)]

	pH				
Treatment	8.1	9.9	10.2	11.5	11.9
Cl^-	38.96	75.25	42.07	73.72	33.08
SO_4^{2-}	39.10	39.22	39.41	39.36	39.93
PO_4^{3-}	0.05	0.03	0.12	0.12	0.12
Alkalinity (as $CaCO_3$)	149.8	199.2	232.5	386.6	523.4
Ca	42.68	1.63	1.51	1.58	1.71
Fe	0.19	0.06	0.07	0.02	0.03
K	14.38	8.06	6.60	6.77	5.79
Mg	10.29	0.13	0.11	0.08	0.10
Na	78.89	170.26	166.47	226.79	418.06
Si	18.89	22.37	31.73	59.58	121.92

(a) The initial ^{125}I (as $^{125}I^-$), ^{75}Se (as $^{75}SeO_4^{2-}$), and ^{99}Tc ($^{99}TcO_4^-$) activity was 15 µCi/L; spike solution and sediment equilibration period was 14 days; 1:2 solid:liquid ratio; one replication.

increase in Si concentration is likely the result of the higher pH, causing the dissolution of some silicates and aluminosilicates in the sediment. This silicate dissolution of Hanford Site sediments in high-pH systems has been reported previously (Kaplan et al. 1998). The dramatic decreases in Ca, K, and Mg can be attributed to the precipitation (Ca) or coprecipitation (K and Mg) of aragonite ($CaCO_3$) (Carlson 1983). The formation of calcium carbonate phases was observed during the titration and equilibration of the solutions with NaOH. These precipitates were filtered prior to adding the radionuclides. The filtration ratio data in Table 7 indicate that essentially none of the TcO_4^-, SeO_4^{2-}, or I^- precipitated from these solutions prior to contact with the sediment. However, it is possible that some TcO_4^- coprecipitation with $CaCO_3$ may have occurred after the sediment was introduced, thereby accounting for the increased removal from solution for higher pH treatments. The coprecipitation would involve TcO_4^- replacing the CO_3^{2-} ions in the structure of the $CaCO_3$. Because the SeO_4^{2-} and I^- Kd values decreased with increased pH, these anions may not fit into the crystalline structure of the $CaCO_3$.

The chemical speciation of the I^-, SeO_4^{2-}, and TcO_4^- added to the solutions described in Table 8 are presented in Table 9. These calculations show that TcO_4^- and I^- existed only as the free, uncomplexed species. SeO_4^{2-} also existed predominantly as the free, uncomplexed species but also formed $CaSeO_4^0$, $MgSeO_4^0$, and $NaSeO_4^-$. An important conclusion from these data is that the added anion tracers remained predominantly as anions and to a much smaller degree become uncharged once introduced into the sediment/groundwater systems. As expected, the anions did not form any cationic species as the pH increased from 8.1 to 11.9. This is an important conclusion because cations are more inclined to adsorb to sediments, especially at higher pH levels, than anions. Not shown in this table was that the saturation indices of solid phases containing I^-, SeO_4^{2-}, and TcO_4^- were very low. This indicates that precipitation of

Table 9. Calculated Speciation of I^-, SeO_4^{2-}, and TcO_4^- in the Solutions Used in the pH Experiment[(a)]

pH	Calculated Ionic Strength (mM)	I^- Species (%)	SeO_4^{2-} Species (%)				TcO_4^- Species (%)
			SeO_4^{2-}	$CaSeO_4^0$	$MgSeO_4^0$	$NaSeO_4^-$	
8.1	6	100	87	9	3	1	100
9.9	8	100	97	<1	<1	3	100
10.2	8	100	98	<1	<1	2	100
11.5	17	100	97	<1	<1	3	100
11.9	26	100	95	<1	<1	5	100

(a) Bulk chemical composition of the solutions were presented in Table 8. The sum of the speciation percentages for a particular solute may not equal 100% because only the species with concentrations >1% are presented in this table. The I^- and SeO_4^{2-} speciation calculations were conducted with the software GEOCHEM (Sposito and Mattigod 1980). The stability constants used in these calculations were from the GEOCHEM database, Smith and Martell (1976), and Dyrssen et al. (1968), and values calculated using the method described by Nieboer and McBryde (1973). The TcO_4^- speciation calculations were conducted with the software MINTEQA2 (Allison et al. 1991). The stability constants used in the TcO_4^- speciation calculations were from the MINTEQA2 database and Lemire and Jobe (1996).

these phases was not likely. The lack of precipitation is supported by the filtration index data in Table 7 that indicated there was essentially no filterable I^-, SeO_4^{2-}, and TcO_4^- formed in the test solutions.

4.0 Conclusions

A series of experiments were conducted to evaluate the effect of the expected near-field chemistry on the sorption of I^-, SeO_4^{2-}, and TcO_4^- onto a Hanford Site sediment. Particular attention was directed at quantifying the effect of pH and ionic strength (salt concentration) on K_d values for these radionuclides that are expected to have a large impact on calculated dose. Perhaps just as important, attention in these studies was directed at identifying the chemical mechanisms controlling the sorption processes, thereby providing technical defensibility to the selection of K_d values that will be selected for the ILAW performance assessment. In general, both parameters are known to have a significant effect on sorption processes. However, the magnitude of these two parameters on the adsorption of I^-, SeO_4^{2-}, and TcO_4^- under conditions similar to those expected in the ILAW disposal complex are clearly not known (Kaplan and Serne 1995, Kaplan et al. 1995).

In the first set of experiments, the ionic strength of a Hanford Site groundwater was increased by adding $NaClO_4$ to create ionic-strength levels expected in the near field (Mann et al. 1998). Na was selected as the cation because it will be the dominant cation in the glass effluent. ClO_4 was selected as the anion because it is a rather chemically inactive solute, thus it would increase the ionic strength while not interfering or competing with the targeted anions, I^-, SeO_4^{2-}, and TcO_4^-, for sorption sites or complexing cations. Se and Tc K_d values increased as ionic strength increased. In the case of Se, the K_d values increased from 3.31 ± 0.57 to 4.11 ± 0.06 mL/g, as the background solution increased in calculated ionic strength from 47 to 536 mM. Over the same increase in ionic strength, Tc K_d values increased from -0.16 ± 0.04 to 3.94 ± 0.99 mL/g. The cause for this increase in K_d values is likely that the higher ionic strength caused the double layer around the particles to decrease, thereby permitting greater TcO_4^- and I^- interaction with the mineral surfaces. The greater contact of TcO_4^- and SeO_4^{2-} anions with the mineral permitted greater contact with positively charged sorption sites. Hanford Site sediments have few positively charged sorption sites at pH 8.1; however, these few sites may play an important role, especially at the extremely low TcO_4^- and I^- concentrations, on the order of 10^{-10} M, used in these tests and expected in leachate emanating from breached repositories.

The pH level of solutions also had a significant effect on the sorption of these anions. As the pH increased from 8.1 (background) to 11.9, I^- K_d values decreased from 0.22 ± 0.01 to 0.01 ± 0.01 mL/g, whereas SeO_4^{2-} K_d values decreased from 5.78 ± 0.28 to 0.04 ± 0.00 mL/g. This pH K_d trend is consistent with the geochemical rule-of-thumb that anion sorption decreases as the pH increases. The reason for this trend is that, as the pH increases, the extent of negative surface charge increases on the sediment as a result of increased concentration of OH^- on the mineral surface. This trend was not observed with TcO_4^- K_d values. Instead, as the pH increased from 8.1 to 11.9, the TcO_4^- K_d values increased from -0.02 ± 0.01 to 1.07 ± 0.03 mL/g. The cause for this unexpected but very consistent trend is not known. One possible explanation is that the modest increase in ionic strength that concomitantly increased with pH increases may have been responsible for the enhanced removal of TcO_4^- from the aqueous phase. Precipitation is an unlikely removal mechanism; neither thermodynamic solubility calculations nor aqueous-phase filtration of pH 11.9 TcO_4^- solution support the likelihood for Tc precipitation.

These results have some important implications for the ILAW performance assessment. They include the following.

- A suite of K_d values for I^-, SeO_4^{2-}, and TcO_4^- were measured. These values can be used to technically defend the choice of K_d values to be used in the near-field ILAW environment. These results support the use of unique K_d values for specific pH and ionic-strength conditions likely to exist in the near field.

- The TcO_4^- K_d values in the near field are likely to be >0 mL/g, perhaps conservatively set at 0.2 to 0.6 mL/g. For conditions in which the pH is >10 and the ionic strength is >0.5 M, K_d values as high as 3.9 mL/g were measured. The cause for the greater degree of adsorption under near-field conditions is not clearly understood, but is likely the result of compression of the electrical double layer around the sediments leading to less anionic repulsion and more TcO_4^-/sediment interaction.

- The I^- and SeO_4^{2-} K_d values followed consistent but not simple trends with pH and ionic strength. K_d values of these radionuclides decrease when pH is >10. Conservative K_d values for I^- and SeO_4^- in pH-10 systems should be 0.2 and 0 mL/g, respectively. In pH-11 systems, conservative K_d values should be set to 0 mL/g. However, under conditions in which the pH remains ~8.0 (i.e., background level) and the ionic strength increases above 80 mM (perhaps only 2 times background), conservative estimates of I^- and SeO_4^{2-} K_d values would be 0.5 and 4 mL/g, respectively.

These are the first studies conducted with Hanford Site sediment in which the K_d values of I, Se, and Tc were measured as a function of ionic strength and pH. For the most part, the observed trends in K_d values were consistent with more generalized geochemical principles. One of the most important contributions of this study was that it quantified K_d value changes induced by variations in pH and ionic strength that are expected to exist in the near field. It is expect that these data will provide important guidance for selecting K_d values for the ILAW performance assessment.

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