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The sorption and desorption behavior of radionuclides in groundwater-interbed systems of the Columbia River basalt formation was investigated. Radionuclides chosen for study were those of concern in assessing the safety of a high-level radioactive waste repository in basalt (isotopes of technetium, neptunium, plutonium, uranium, americium, cesium, strontium, and radium). Sandstone and tuff materials from selected interbed layers between basalt flows were used in these experiments. Effects of groundwater composition and redox potential (Eh) on radionuclide sorption and desorption on the geologic solids were studied. Sodium, potassium, and calcium in the groundwater decrease sorption of cesium, strontium, and radium by ion exchange reactions. Groundwater Eh strongly affects sorption of technetium, neptunium, plutonium, and uranium since chemical species of these elements containing the lower oxidation states are more extensively sorbed by chemisorption than those containing higher oxidation states. Effects of radionuclide complexation by groundwater anions on sorption were not observed except for neptunium carbonate (or bicarbonate) complexes and plutonium sufate complexes.

Sorption and desorption isotherms were obtained for sorption of radionuclides under oxidizing and reducing conditions. The Freundlich equation accurately describes most of these isotherms. Most radionuclides are apparently irreversibly sorbed on each of the geologic solids since the slopes of sorption and desorption isotherms for a given radionuclide are different. This hysteresis effect is very large and will cause a significant delay in radionuclide transport. It, therefore, should be included in modeling radionuclide transport to accurately assess the isolation capabilities of a repository in basalt.

The groundwater transport of radionuclides through water-bearing interbed layers in the Columbia River basalt formation will be controlled by reactions of the radionuclides with groundwater and interbed solids. These interactions must be understood to predict possible migration of radionuclides from a proposed radioactive waste repository in basalt. Precipitation and sorption on interbed solids are the principle reactions that retard radionuclide movement in the interbeds. The objective of the work described herein was to determine the sorption and desorption behavior of radionuclides important to safety assessment of a high-level radioactive waste repository in Columbia River basalt. The effects of groundwater composition, redox potential, radionuclide concentration, and temperature on these reactions were determined.

Geochemical models of sorption and desorption must be developed from this work and incorporated into transport models that predict radionuclide migration. A frequently used, simple sorption (or desorption) model is the empirical distribution coefficient, K_d. This quantity is simply the equilibrium concentration of sorbed radionuclide divided by the equilibrium concentration of radionuclide in solution. Values of K_d can be used to calculate a retardation factor, R, which is used in solute transport equations to predict radionuclide migration in groundwater. The calculations assume instantaneous sorption, a linear sorption isotherm, and single-valued adsorption-desorption isotherms. These assumptions have been shown to be erroneous for solute sorption in several groundwater-soil systems (1-2). A more accurate description of radionuclide sorption is an isothermal equation such as the Freundlich equation:

$$S = KC^N \tag{1}$$

where

S = the equilibrium concentration of sorbed radionuclide in moles/g
C = the equilibrium concentration of radionuclide in solution in moles/L
K and N = empirical constants.

This equation has been successfully applied to many sorption and desorption reactions of dissolved metals and organic compounds. In the case of irreversible sorption (hysteresis), sorption and desorption isotherms are not identical. However, both sorption and desorption Freundlich isotherm equations can be substituted into the transport equation(2):

$$\rho \frac{S}{t} - \frac{\partial C}{\partial t} = \frac{D\partial^2 C}{\partial x} - v \frac{\partial C}{\partial x} \tag{2}$$

where

D = dispersion coefficient
v = average pore water velocity
ρ = bulk density
ϕ = saturated water content
x = distance in the direction of flow
t = time.

This equation can be used to describe one-dimensional transport of radionuclides through porous media (e.g. radionuclide elution curves from laboratory columns packed with interbed solids) assuming instantaneous sorption and desorption. Van Genuchten and coworkers have demonstrated the importance of using both sorption and desorption isotherms in this equation when hysteresis is significant. Isotherm data for sorption and desorption reactions of radionuclides with interbed materials are presented in this paper which can be used to predict radionuclide transport.

Experimental

Materials. The groundwater compositions of waters in the major water bearing zones of the Columbia River basalts at the Hanford Site have been determined (3). There are two distinct groundwaters present in the basalts: a sodium-bicarbonate buffered groundwater (pH 8 at 25°C) characteristic of the Saddle Mountains and Upper Wanapum basalts and a sodium-silicic acid buffered groundwater (pH 10 at 25°C) characteristic of the Lower Wanapum and Grande Ronde Basalts. Synthetic groundwater compositions have been established that simulate these two groundwater types. The compositions of the synthetic groundwaters used in the sorption experiments are given in Table I. The GR-1A groundwater simulates the groundwater composition of the Mabton Interbed in the Saddle Mountain Basalts. The GR-2 and GR-2A groundwaters simulate the dominant groundwaters in the Lower Wanapum and Grande Basalts. Synthetic groundwaters are used rather than actual groundwaters in order to ensure the availability of a stable, compositionally consistent groundwater for the sorption experiments.

Table I. Synthetic Groundwater Compositions.

Constituents	Concentration (mg/L)		
	GR-1A	GR-2	GR-2A
Na^+	107	225	246
K^+	11.2	2.5	2.5
Ca^{2+}	2.0	1.06	1.01
Mg^{2+}	0.4	0.07	0
Cl^-	50*	131	152
CO_3^{2-}	0	59	28.8
HCO_3^-	215	75	36.6
F^-	1.3	29	37
SO_4^{2-}	2.4	72	108
SiO_2	30	108	82
pH	8.5	10.0	10.0
Ionic strength	-	0.014	-

*In experiments having reducing conditions, Cl^- content increased to 479 mg/L due to addition of HCl to neutralize N_2H_4 to obtain pH = 8.5.

Three interbed materials from the Columbia River Basalt Group have been investigated in the radionuclide sorption experiments. Interbeds are porous sedimentary layers located between many of the basalt flows in the Columbia River Basalt Group and comprise a potential preferential pathway for groundwater and, therefore, radionuclide transport.

Two interbed samples, a sandstone and a tuff, were taken from as outcrop of the Rattlesnake Ridge Interbed above the Pomona basalt flow. A third interbed sample was taken from drilling cores of the Mabton Interbed, located between the Saddle Mountains and Wanapum Basalts. The Mabton Interbed is the first continuous, major interbed above the candidate repository horizons in the Grande Ronde Basalts. Mineralogical characteristics of the interbed materials are summarized in Table II. A more complete discussion of the characteristics of the interbed materials may be found in Reference (4).

Procedures. Batch equilibrations of interbed solids (Mabton Interbed, Rattlesnake Ridge sandstone, or tuff), tracers, and groundwaters were used to measure radionuclide distributions between solid and liquid phases. Triplicate measurements were made for each combination of temperature, redox condition, tracer concentration, tracer type, groundwater composition, and interbed sample. Constant temperatures were maintained by placing the mixtures in environmental shaker air baths (New Brunswick Scientific Company) set at 23°C, 60°C, or 85°C. For experiments under reducing conditions, 0.05M hydrazine was added to the groundwater to establish an Eh of -0.8 V at the pH values used. This Eh value was calculated from the standard potential for hydrazine oxidation in basic solution (-1.16 V) assuming a pH of 9.0, N_2 pressure of 1 atmosphere and a hydrazine concentration of 0.05M.

Details of the procedure are as follows: 2.00 ± 0.02 g of disaggregated interbed material was added to a 1-oz polyethylene bottle. These interbed materials were soft and easily broken up using gentle action with mortar and pestle. Twenty milliliters of unspiked groundwater (reducing or oxidizing, as appropriate) were added to the bottle and the mixture was gently shaken overnight to preequilibrate the system. The bottle was centrifuged and the supernate discarded. This preequilibration was repeated and the bottle - interbed - solution weighed to estimate the volume of residual solution. Spiked groundwater solutions were prepared by dissolving a measured amount of solid tracer (obtained by evaporating stock tracer solution) in the appropriate groundwater solution. The spiked solution was filtered through a 0.3-um Millipore filter to remove any undissolved solids and analyzed. The spiked solution was added to the bottle from the preequilibration step, and the bottle was capped and shaken gently for 14 days at the appropriate temperature. The contents were then filtered through a 30 Angstrom Amicon 50A ultra-filter. The filtrates were analyzed for tracer concentrations using standard counting techniques.

For desorption measurements, the above procedure was used to load tracer radionuclides onto the interbed solid sample. The solution-solid mixture was centrifuged and the supernate carefully removed to avoid removing any solids with it; it was then filtered through a 30 Angstrom Amicon 50A filter before analysis. Fresh groundwater solution was added to the separated solid and this mixture was equilibrated for 1 week at the same temperature as during the loading of the tracer. The solution was separated as before and the concentration of desorbed tracer determined. The tracer-loaded solid was equilibrated with fresh groundwater 10 to 13 consecutive times. Each time the resulting solution was analyzed for tracer concentration.

Table II. Sources and Characteristics of Interbed Materials.

Source/Characteristic	Interbed sandstone	Interbed sandstone/ claystone	Interbed tuff
Source	Rattlesnake Ridge Interbed	Mabton Interbed	Rattlesnake Ridge Interbed
Size fraction	0.25 to 0.5 mm	16% = <250 mesh 60% = 40 to 250 24% = <40	0.5 to 1.0 mm
Surface area[a]	50.9 ± 0.8 m^2/g	not available	188 ± 3 m^2/g
Cation exchange capacity[b]	9.9 ± 0.2 meq/100 g	not available	52.2 ± 4.2 meq/100 g
Minerals present[c]	Quartz	Quartz	Smectite Clay
	Plagioclase	Albite	Glass
	Orthoclase	Anorthite	
	Hornblende	Nontronite	
	Muscovite	Biotite	
	Biotite	Orthoclase	
	Clinopyroxene (Also basalt fragments)	Illite	

[a]Ethylene glycol method (5).
[b]Strontium cation exchange (6).
[c]By X ray diffraction and electron microprobe.

Changes in groundwater composition (major ion concentrations) during equilibration of the synthetic groundwaters with interbed solids were measured as follows. Either 20 or 40 g of interbed solids were added to 16-oz polyethylene bottles along with 400 mL of reducing or oxidizing groundwater. The bottles were placed in the environmental shakers set at either 23°C or 60°C. Each bottle was sampled weekly by turning off the shaker, allowing the solids to settle for several hours, and then decanting approximately 20 mL into 30 Angstrom Amicon 50A ultra-filter cones for filtration. The filtrates were analyzed for cations by an inductively coupled plasma spectrometer (ICP; Applied Research Laboratory) and anions by anion chromatography (Dionex, Inc.). It was found that groundwater-interbed solid reactions were fast, reaching steady-state concentrations after less than 1 week. Concentrations of major cations increased over this time; however, interbed solids control the groundwater composition to such a great extent that initial groundwater composition is not very significant.

Results and Discussion

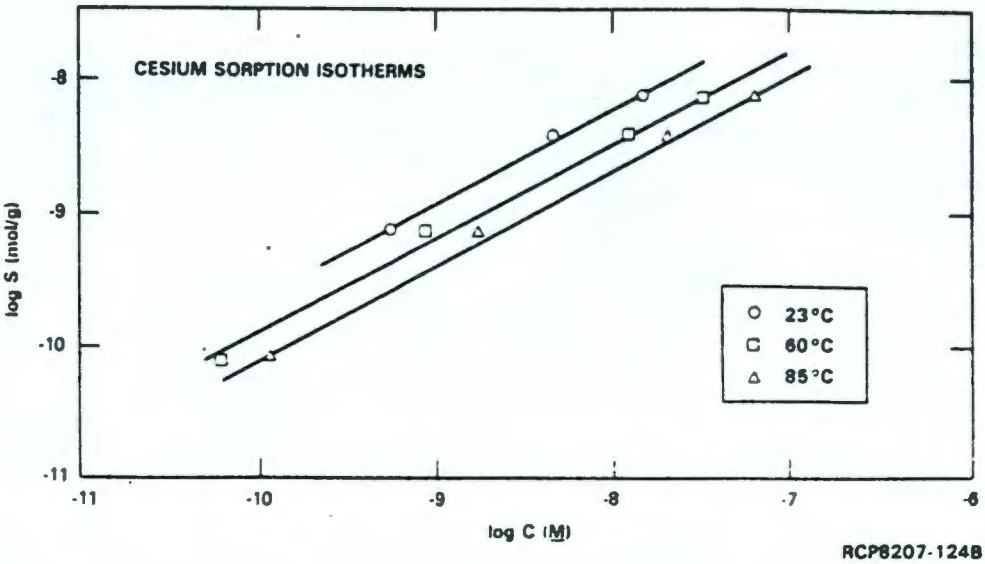
Sorption and Desorption Isotherms. To model radionuclide transport in groundwater through geologic media, it is necessary to mathematically describe sorption and desorption in terms of isotherms. The Freundlich isotherm was found to accurately describe sorption and desorption of all radionuclides studied in the interbed-groundwater systems, except when precipitation of the radionuclide occurred.

In addition to describing sorption and desorption, isotherms can be used to estimate the solubilities of radionuclides in the groundwater-radionuclide-geologic solid system. For radionuclides that form slightly soluble compounds (e.g., $SrCO_3$, $PuO_2 \cdot H_2O$) in these systems, isotherms can define the approximate concentrations above which precipitation, rather than sorption, dominates removal from solution.

Sorption of cesium, strontium, selenium, technetium, radium, uranium, neptunium, and americium on the standard Rattlesnake Ridge sandstone interbed material was measured using the GR-2 groundwater composition. Reducing conditions (0.05M N_2H_4) were used for selenium, technetium, uranium, and neptunium. Freundlich plots for cesium and uranium at 23°C, 60°C, and 85°C are shown as examples in Figure 1. Precipitation was observed in the cases of selenium and technetium at 23°C. Selenium begins to precipitate at 10^{-5}M and technetium precipitates at concentrations above 10^{-7}M. At the higher temperatures, technetium solubility increases and selenium sorption increases so that precipitation is not observed.

Freundlich constants and ranges of K_d values for radionuclide sorption on the Rattlesnake Ridge sandstone are given in Table III. The constants K and N were calculated using linear regression. Linear sorption isotherms (N = 1.0) are observed only for strontium, selenium, and radium.

Sorption isotherms were also measured for sorption of selenium, technetium, tin, radium, uranium, neptunium, plutonium, and americium on the reference Mabton Interbed solids. The GR-1A groundwater composition was used in these experiments. Two temperatures (23°C ± 2°C and 60°C ± 1°C) were used, and both oxidizing and reducing conditions were used for each radionuclide. Tin and americium were so extensively sorbed under all conditions that isotherm data could not be obtained. These elements are not significantly mobile in the Mabton Interbed aquifer. Values of Freundlich constants for technetium, radium, uranium, neptunium, and plutonium are given in Table IV. The Freundlich equation did not



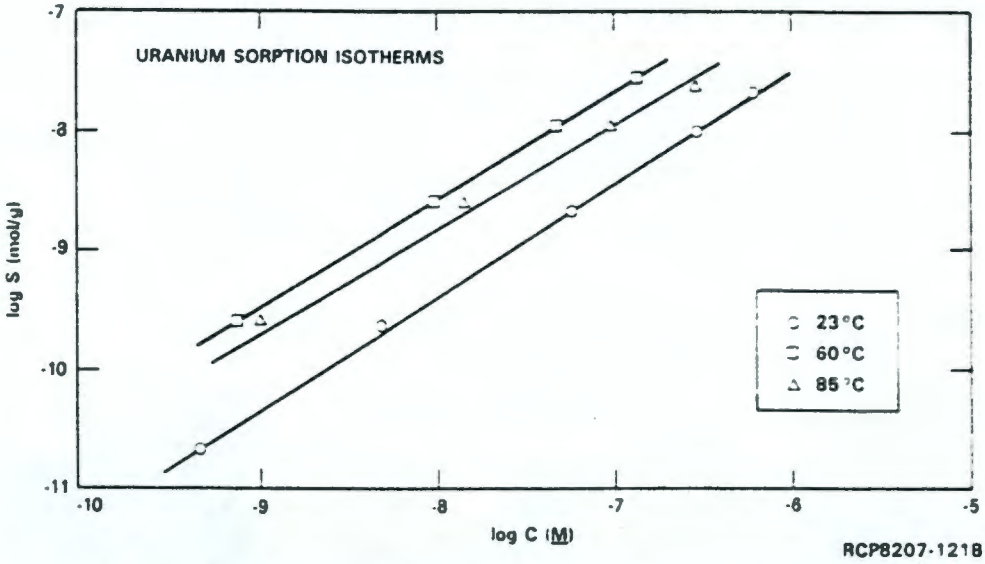


FIGURE 1. Cesium and Uranium Isotherms for Sorption on Sandstone at 23°(o), 60°(□), and 85°C(Δ). (Oxidizing conditions were used for cesium and reducing conditions for uranium.)

Table III. Freundlich Constants for Radionuclide Sorption (Molar Basis) on Sandstone.

Radionuclide	Redox	Temperature (°C)	K	N	r^2*
Cesium	Oxidizing	23	0.0023	0.70	0.99
		60	0.0029	0.72	0.96
		85	0.0013	0.72	0.99
Strontium	Oxidizing	23	0.78	1.02	0.99
		60	1.17	1.03	0.99
		85	12.2	1.18	0.99
Selenium	Reducing	23	0.010	1.03	0.98
		60	0.053	0.97	0.99
		85	0.70	1.06	0.99
Technetium	Reducing	23	1,056	1.50	0.92
		60	5.6	1.30	0.99
		85	0.2	1.09	0.99
Radium	Oxidizing	23	0.62	0.94	0.98
		60	0.48	0.95	0.98
		85	83.1	1.16	0.98
Uranium	Reducing	23	0.013	0.94	0.99
		60	0.046	0.91	0.99
		85	0.0037	[illegible]9	0.99
Neptunium	Reducing	23	3.5	1.03	0.99
		60	–	–	–
		85	1,743	1.36	0.99
Americium	Oxidizing	23	0.030	0.89	0.99
		60	2.89	1.03	0.99
		85	–	–	–

*Coefficient of determination.

Table IV. Freundlich Constants (Molar Basis) for Radionuclide Sorption on Mabton Interbed Solids.

Radionuclide	Redox	Temperature (°C)	K	N	r^2*
Technetium	Oxidizing	23	2.96×10^{-4}	0.91	0.978
		60	9.40×10^{-4}	0.99	0.979
	Reducing	23	4.36×10^{-1}	1.09	0.978
		60	1.14×10^{-4}	0.58	0.974
Radium	Oxidizing	23	1.83×10^{2}	1.18	0.971
		60	9.64	0.99	0.919
	Reducing	23	5.56×10^{-2}	0.91	0.994
		60	8.40×10^{-2}	0.98	0.990
Uranium	Oxidizing	23	3.97×10^{-4}	0.74	0.993
		60	2.52×10^{-1}	0.96	0.992
	Reducing	23	1.30×10^{-2}	0.88	0.997
		60	1.51×10^{-2}	0.79	0.990
Neptunium	Oxidizing	23	2.82×10^{-4}	0.69	0.994
		60	5.50×10^{-4}	0.68	0.997
	Reducing	23	3.35×10^{-2}	0.80	0.996
		60	1.64×10^{-2}	0.87	0.995
Plutonium	Oxidizing	23	5.06×10^{-1}	0.95	0.967
		60	1.44×10^{-2}	0.78	0.874

*Coefficient of determination.

fit the selenium sorption data very well probably because of slow sorption kinetics or precipitation. Precipitation was also observed for technetium at 23°C for concentrations above 10^{-7}M. This is about the same solubility observed for technetium in the sandstone isotherm measurements. Linear isotherms were observed only in the case of radium sorption. In general, sorption on the Mabton Interbed was greater than on the Rattlesnake Ridge sandstone. This is probably due to the greater clay content of the Mabton standard.

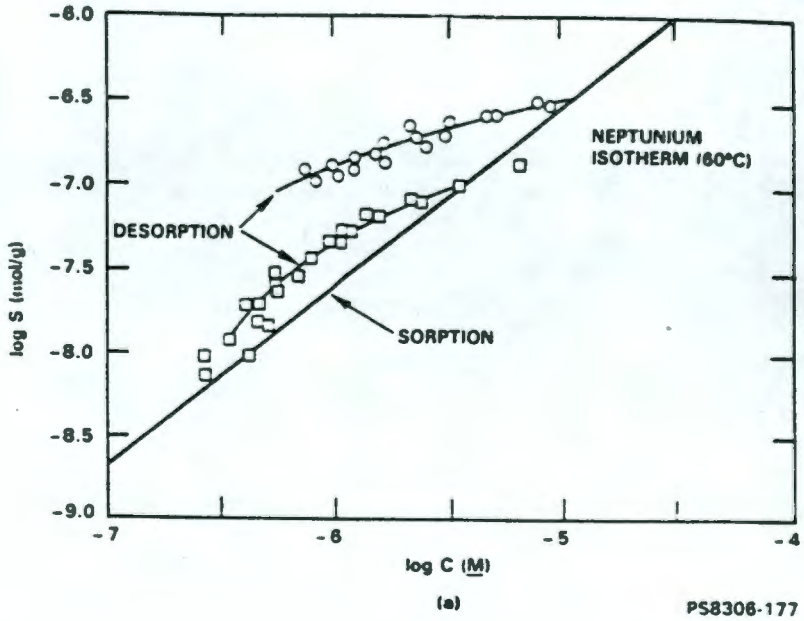
The Freundlich equation requires the assumption that sorption reactions are reversible. However, several studies (7) have recently shown that K and N depend on sorption direction, i.e., whether sorption or desorption occurred. In each case, N was less and K was greater for desorption than sorption.

This chemical hysteresis will, of course, affect radionuclide transport. For example, if hysteresis occurs during a column experiment in which a pulse of tracer is added to the influent, the effluent curve will show heavy tailing and a reduction in peak concentration. Ignoring hysteresis effects could cause serious errors in predicting radionuclide movement.

Desorption isotherms for selenium, technetium, neptunium, uranium, and radium have been measured for the Mabton Interbed materials under both oxidizing and reducing conditions at 60°C using the Grande Ronde groundwater composition, GR-1A. The reason for measuring desorption isotherms is to determine whether or not the sorption reactions are reversible (i.e., exhibit hysteresis). An example of the results of desorption isotherm measurements is shown in Figure 2. These curves are Freundlich plots of the sorption and desorption data for neptunium at 60°C under oxidizing and reducing conditions. The two desorption curves were obtained using different tracer loadings (initial S values). Both plots show hysteresis since the slopes of the desorption curves are less than the sorption curves. Hysteresis is a much greater effect for neptunium sorption under reducing conditions, however. The ratio of Freundlich exponents N_s/N_d, where N_s and N_d are the measured exponents for sorption and desorption, respectively, is a measure of the magnitude of hysteresis. Larger values for N_s/N_d indicate greater hysteresis effects. For neptunium sorption under oxidizing conditions $N_s/N_d = 2$ and for reducing conditions $N_s/N_d = 435$.

The sorption and desorption behavior of uranium is similar to neptunium. Figure 3 shows that hysteresis is more important for uranium sorption under reducing conditions than under oxidizing conditions. Values of N_s/N_d are 10 and approximately 200 for oxidizing and reducing conditions, respectively.

Results for selenium and technetium under oxidizing conditions show that these reactions are fully reversible. However, under reducing conditions, sorption reactions of these radionuclides show significant hysteresis (Figure 4). Sorption of radium also shows a large hysteresis effect. Table V gives a summary of N_s/N_d values for each radionuclide sorption-desorption reaction with Mabton Interbed material at 60°C. These data show that the reduced species of selenium, technetium, neptunium, and uranium are more irreversibly sorbed on Mabton Interbed material than the oxidized species. The reducing environment expected in the interbed layers found in basalt formations at depth should significantly decrease the mobility of these radionuclides and thus provides an additional safety factor for waste storage.



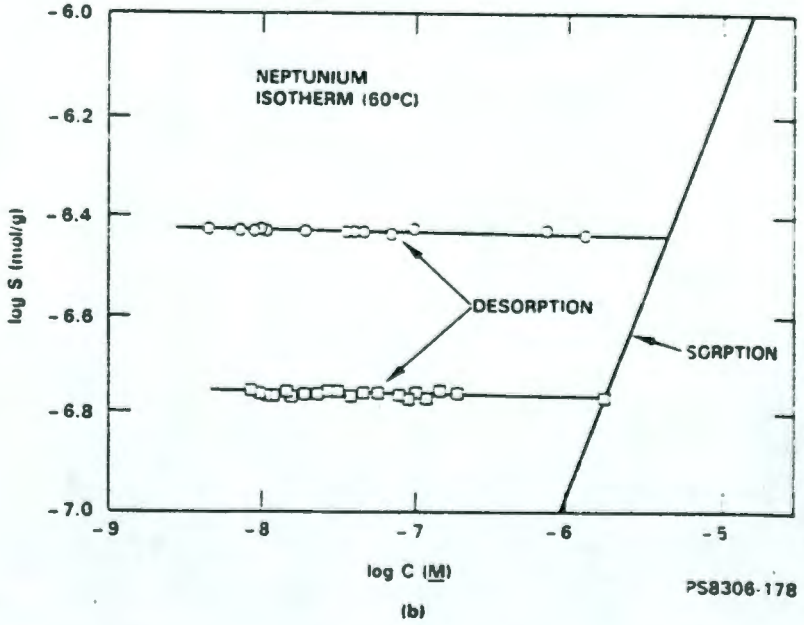
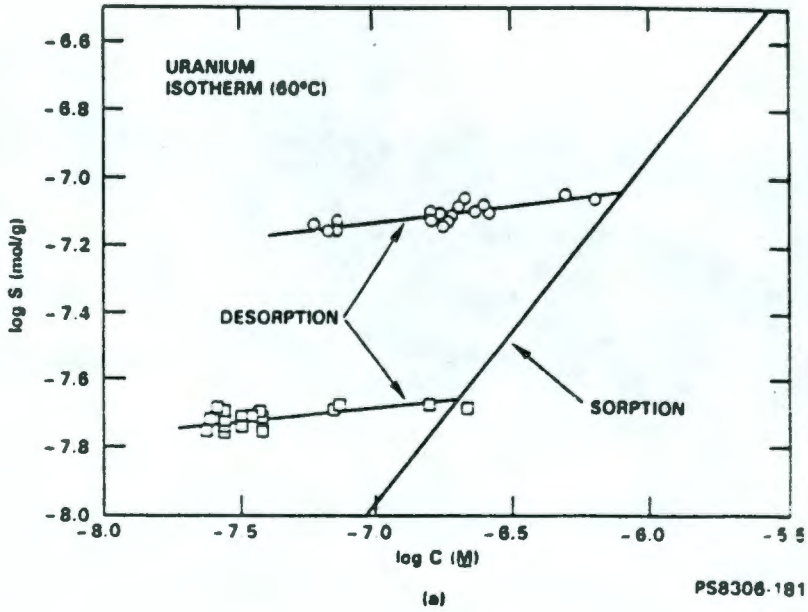


FIGURE 2. Sorption and Desorption Isotherms for Neptunium Sorption on Mabton Interbed Solids: (a) Oxidizing Conditions. (b) Reducing Conditions.



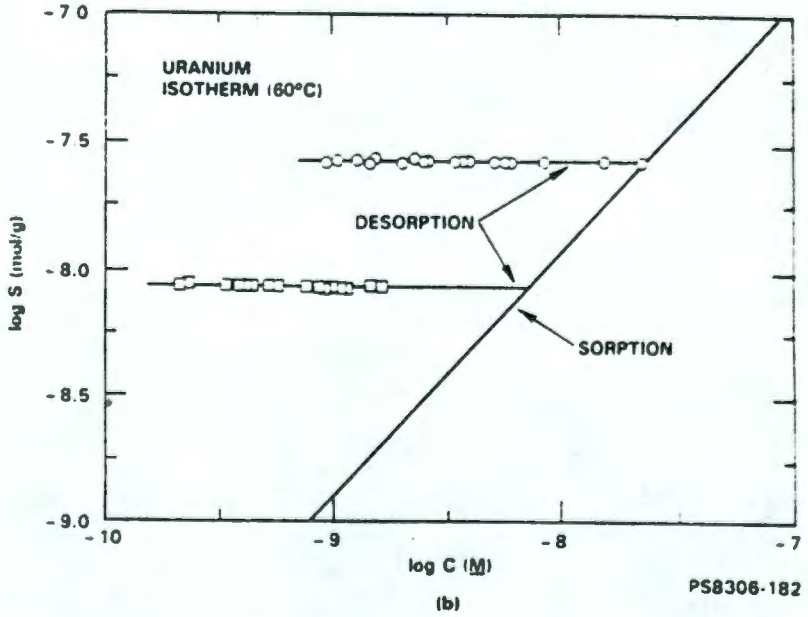
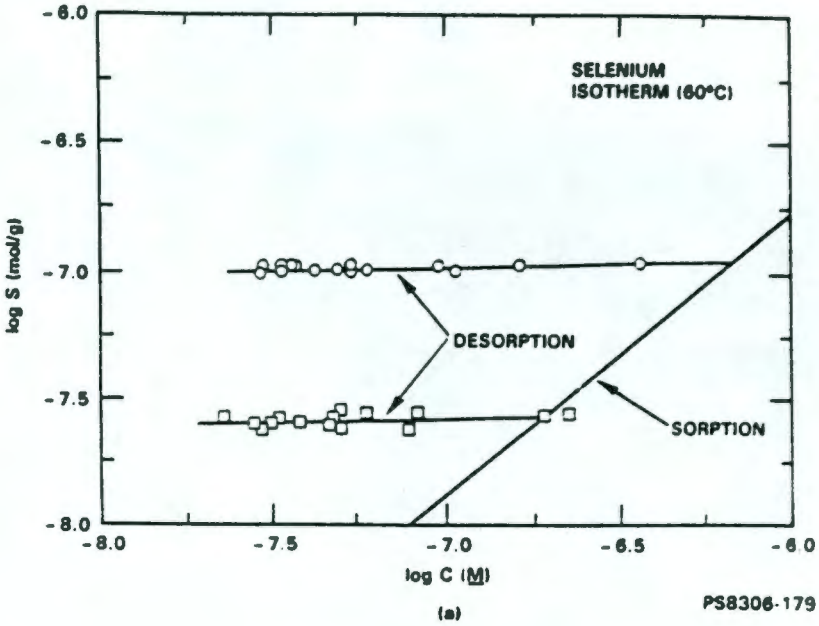


FIGURE 3. Sorption and Desorption Isotherms for Uranium Sorption on Mabton Interbed Solids: (a) Oxidizing Conditions. (b) Reducing Conditions.



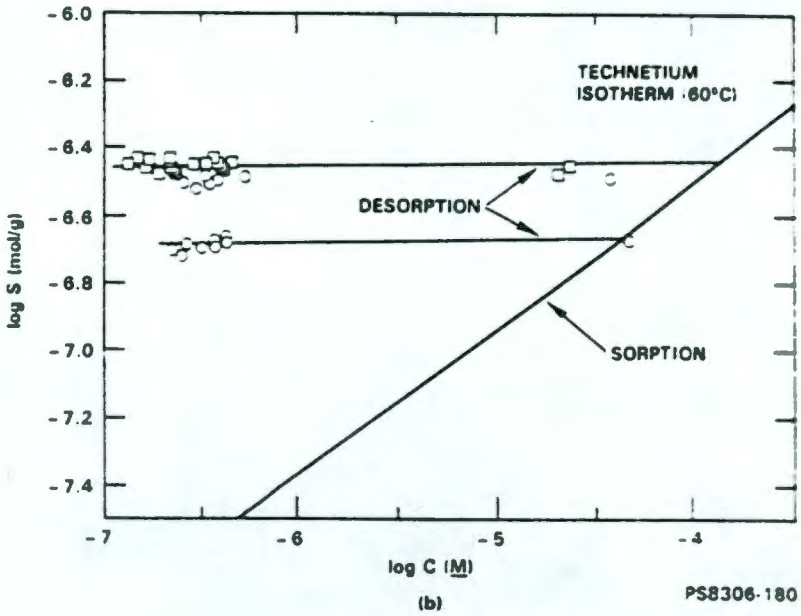


FIGURE 4. Sorption and Desorption Isotherms for (a) Selenium and (b) Technetium Sorption on Mabton Interbed Solids under Reducing Conditions.

Table V. Freundlich Constants for Radionuclide Sorption-Desorption on Mabton Interbed at 60°C.

Isotope	Redox	S_o (mol/g)	N_s	N_d	N_s/N_d
Selenium	Reducing	1.11×10^{7} 2.76×10^{-8}	1.0	0.018 0.027	56 37
Technetium	Reducing	1.88×10^{7} 3.50×10^{-7}	0.58	0.018 0.003	32 193
Neptunium	Oxidizing	3.13×10^{7} 1.38×10^{-7}	1.0	0.45 0.91	2.2 1.1
Neptunium	Reducing	3.84×10^{7} 1.81×10^{-7}	0.87	0.002 0.002	435 435
Uranium	Oxidizing	8.88×10^{-8} 2.11×10^{8}	0.96	0.093 0.074	10 13
Uranium	Reducing	2.70×10^{8} 8.58×10^{7}	0.79	0.008 0.003	100 263
Radium	Reducing	7.65×10^{-10} 1.81×10^{10}	0.98	0.016 0.087	61 11

Effects of Groundwater Composition and Eh. Radionuclide sorption on geologic solids is dependent on the chemical composition of the groundwater solution and the redox potential (Eh) of the solid-groundwater system. Aquifers at various depths in the Columbia Plateau formation have been observed to have significant differences in composition. To accurately model radionuclide migration, it is necessary to understand the effects of chemical components and Eh on sorption and solubility of key radionuclides. An additional benefit of this work is to better understand the mechanisms of sorption and desorption of the radionuclides.

The objectives of this work were to determine effects of the major groundwater components found in the Grande Ronde formation (Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, F^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}) on radionuclide sorption on geologic solids expected in the flow path. Interbed materials lying between basalt layers are of particular importance because of their porous nature. Interbed sandstone and tuff were studied because of their abundance in Columbia River basalt interbeds. The effect of Eh was examined by adding a chemical redox buffer, hydrazine, as a variable. Hydrazine lowered the Eh from about +0.6 V (air saturated solution) to about -0.8 V at pH 9. Because of the large number of variables to be studied, it was necessary to use statistical methods to design the experiments. An efficient design for screening the nine solution variables is the 20-run Plackett-Burman design (8). This is fractional, 2-level, factorial design that is used to identify significant variables and determine their effects. The application of this design is discussed in detail by Barney (4). The design requires a high and low value for each parameter (groundwater component concentration or Eh). Values were chosen to cover the range of concentrations found in the Grande Ronde formation.

Table VI compares the values used in these experiments to those actually found in the Grande Ronde aquifers. The 20-run experimental design requires preparation of 20 solutions, each with a different combination of groundwater parameters and having the high and low values given in Table VI. Silicate (0.001M) was added to each solution so that steady-state silicate concentrations would be approached more rapidly during equilibration. Since the interbed solids will control silicate concentration, it was not possible to study it as a variable. The final pH of interbed-equilibrated solutions ranged from 8.6 to 9.8 for sandstone and 8.5 to 9.2 for tuff.

Variables found to be significant for sorption of cesium, strontium, technetium, selenium, neptunium, plutonium, americium, and radium on sandstone and tuff at 23°C are given in Table VII. They are ranked in order of significance where more than one variable was found to be significant. The (+) and (-) signs indicate whether sorption is increased or decreased.

Table VII shows that for cesium sorption, both KCl and N_2H_4 are significant for the two geologic solids studied. The negative values indicate that the presence of either KCl or N_2H_4 lowers sorption. Both appear to be competing with Cs^+ ion for sorption sites. Competition between K^+ and Cs^+ ions for sorption sites on mica-like minerals is well known. However, displacement of Cs^+ by hydrazine was surprising since N_2H_4 should exist mainly as a neutral species at pH 9-10. A small amount (0.0005M to 0.005M) will be protonated and apparently competes with Cs^+. Ammonium ion is known to effectively compete with Cs^+ for mineral sorption sites. Hydrazinium ion with a similar molecular structure should also displace Cs^+. Since hydrazine will not reduce or complex Cs^+, the only possible effects on cesium sorption is to compete for sorption sites or to alter the surface of the solid minerals. No evidence of surface alteration (change in color or texture) was observed. Therefore, it appears that an Eh buffer is not required for Cs^+ sorption studies and hydrazine only interferes with the sorption reaction.

Table VI. Comparison of Experimental and Measured Parameters.

Concentration parameter	Experimental range	Measured range*
Na^+	0.002 to 0.022M	0.009 to 0.016M
K^+	0.0 to 0.0005M	0.00001 to 0.0004M
Ca^{2+}	0.0 to 0.0001M	0.00002 to 0.0001M
Mg^{2+}	0.0 to 0.00002M	<0.0000002 to 0.00001M
Cl^-	0.001 to 0.011M	0.001 to 0.008M
F^-	0.0 to 0.002M	0.001 to 0.002M
SO_4^{2-}	0.0 to 0.003M	0.0008 to 0.002M
CO_3^{2-}	0.0 to 0.001M	0.0 to 0.001M
HCO_3^-	0.0 to 0.001M	0.0 to 0.001M
SiO_3^{2-}	0.001M	0.001 to 0.002M

*Based on unpublished analyses of Grande Ronde groundwater by T. E. Jones.

Table VII. Significant Variables for Radionuclide Sorption at 23°C*.

Radio-nuclide	Solid	Variables								
		NaCl	NaF	Na_2SO_4	Na_2CO_3	$NaHCO_3$	$CaCl_2$	MgCl	KCl	N_2H_4
^{137}Cs	sandstone	–	–	–	–	–	–	–	-1	-2
	tuff	-3	–	–	–	–	–	–	-2	-1
^{85}Sr	sandstone	-1	-3	-2	–	–	-4	–	–	-5
	tuff	-1	-5	-2	–	–	-4	–	–	-3
^{95m}Tc	sandstone	–	–	–	–	–	–	–	–	+ 1
	tuff	–	–	–	–	–	–	–	–	+ 1
^{75}Se	sandstone	–	–	–	-1	–	+ 2	–	+ 3	–
	tuff	-2	–	–	-3	–	+ 4	–	+ 1	–
^{237}Np	sandstone	–	–	–	-2	-3	–	–	–	+ 1
	tuff	–	–	–	–	-2	–	–	–	+ 1
^{238}Pu	sandstone	–	–	–	–	–	+ 2	-3	–	+ 1
	tuff	–	–	-1	–	–	+ 3	–	–	+ 2
^{241}Am	sandstone	+ 3	–	–	+ 1	-2	–	–	–	–
	tuff	+ 1	–	–	–	–	–	–	–	–
^{226}Ra	sandstone	4	–	3	–	–	–	–	-2	-1
	tuff	–	–	1	–	–	–	–	-2	-3

*The number indicates ranking of importance (1 is the most important). A plus sign indicates that the presence of the variable increases sorption, a minus sign that its presence decreases sorption.

Table VII shows that for strontium sorption, sodium salts lower K_d values significantly. Those sodium salts that contribute the largest concentrations of Na^+ (NaCl and Na_2SO_4) are the most significant. There is a linear correlation between the ln of total Na^+ concentration and ln strontium K_d values in these experiments.

Calcium concentration can also affect strontium sorption on sandstone and tuff even through concentrations of Ca^{2+} are 30 to 220 times lower than Na^+. This is due to similar chemical behavior, ion charge, and size of Sr^{2+} and Ca^{2+}. Both ions are sorbed onto similar sites and effectively compete for these. Hydrazinium ions also exchange with Sr^{2+}. Ions of similar size effectively compete with both Cs^+ and Sr^{2+} for sorption sites.

Table VII shows that hydrazine is the only important variable for technetium sorption on each of the geologic solids. Hydrazine causes technetium to be removed from solution either by sorption or by precipitation of the reduced technetium species. Hydrazine is a powerful reducing agent and should reduce TcO_4^- to technetium(IV) according to standard half-cell potentials. No TcO_2 was observed; however, since the technetium passed through 0.45-m filters with the spiked solutions containing N_2H_4, it appears that technetium(IV) exists in solution as a positively charged species, possibly TcO^{2+} as proposed by Gorski and Koch (9).

Selenium is weakly sorbed on sandstone and tuff. Although selenium exists as an anion in these solutions, it is not sorbed by anion exchange on the solids. Their anion exchange capacity is very low at the pH of these experiments. Selenium must, therefore, be sorbed by chemisorption or precipitation. Calcium increases sorption while CO_3^{2-} decreases sorption. A slightly soluble calcium-selenium compound is apparently forming on the surface of solids. The effect of CO_3^{2-} is to reduce the concentration of Ca^{2+} in solution by formation of $CaHCO_3^-$ and $CaCO_3^0$ making the calcium unavailable for formation of the compound. Eh-pH diagrams for selenium predict reduction of SeO_3^{2-} to HSe^- by hydrazine under the conditions of these experiments. These anions apparently behave similarly since hydrazine is not a significant variable for selenium sorption.

Hydrazine is by far the most important variable controlling sorption/precipitation of neptunium. Hydrazine greatly increases removal of neptunium from solution. This is due to reduction of neptunium(V), which exists in oxygenated solutions, to neptunium(IV). Standard half-cell potentials for hydrazine and neptunium(V) indicate that neptunium(V) should be easily reduced. As with other actinides, the (IV) oxidation state should be sorbed more strongly than the (V) because of the greater complex-forming ability of the (IV) state. The effect of CO_3^{2-} and HCO_3^- is to decrease sorption due to formation of carbonate complexes by both neptunium(V) and neptunium(IV). Possible carbonated complexes are $NpO_2HCO_3^-$ for neptunium(V) and $Np(CO_3)_4^{4-}$ for neptunium(IV)(10). These neutral anionic species would not be expected to sorb as strongly as positively charged, noncomplexed neptunium species.

Sorption/precipitation of plutonium is greatly affected by the presence of hydrazine. Since hydrazine increases sorption, it appears that at least some of the plutonium is present initially as plutonium(V) or plutonium(VI) and is reduced to plutonium(IV) by hydrazine. According to standard half-cell potentials, both plutonium(VI) and plutonium(V) should be reduced to plutonium(IV) or plutonium(III) under the conditions of the experiments, assuming that the hydroxyl complexes are important at the pHs of the experiments.

Parameters affecting sorption of americium on sandstone were Na_2CO_3, $NaHCO_3$, and NaCl. It seems unlikely that a carbonate complex or solid is formed since Na_2CO_3 increases sorption and $NaHCO_3$ decreases sorption. If carbonate or bicarbonate take part in the reaction, both salts should affect sorption in the same

way. However, they do affect the pH differently--Na_2CO_3 slightly increasing pH and $NaHCO_3$ slightly lowering the pH. It appears that a slightly soluble americium compound is formed that is more soluble at low pH.

Significant parameters for radium sorption are Na_2SO_4, KCl, and N_2H_4. Each of these variables decrease sorption of radium by ion exchange competition. The effective ion diameter of Ra^{2+} is near those of Na^+ and $N_2H_5^+$ so that they compete for similar sorption sites.

Conclusions

Most of the sorption reactions of radionuclides with interbed materials were found to be irreversible (i.e., hysteresis was significant). Only selenium and technetium sorption under oxidizing conditions was found to be fully reversible. Sorption hysteresis was much greater for reduced species of selenium, technetium, neptunium, and uranium than for oxidized species. The Freundlich equation fit both sorption and desorption data quite well for most of the radionuclides studied. The ratio of Freundlich exponents for sorption and desorption, N_s/N_d, is a measure of the magnitude of the hysteresis effect. Values of this ratio have been calculated for selenium, technetium, neptunium, uranium, and radium. The large values obtained for each radionuclide under reducing conditions suggest that radionuclide transport will be significantly delayed due to sorption hysteresis in the reducing environment of the basalt interbeds. This effect is an important safety factor that should be considered in radionuclide transport modeling to accurately assess the safety of a nuclear waste repository in basalt.

Statistically designed experiments have identified groundwater components that affect sorption of key radionuclides on basalt interbed materials. Sodium, potassium, and calcium in the groundwater decrease sorption of cesium, strontium, and radium by competing with these radionuclides for sorption sites on the solids. These radiouclides are at least partially sorbed by ion exchange reactions. Groundwater Eh greatly affects sorption of technetium, neptunium, plutonium, and uranium. The reducing Eh values produced by hydrazine (-0.8 V) increased sorption of these elements by reducing them to lower oxidation states--technetium(IV), neptunium(IV), plutonium(III), and uranium(IV). The sorption mechanism for these elements (and for americium) is chemisorption. Over the range of groundwater component concentrations studied, metal complex formation with groundwater anions does not greatly affect sorption. The only evidence of this effect is for formation of neptunium carbonate (or bicarbonate) complexes and plutonium sulfate complexes. Hydrazine reduces SeO_3^{2-} to HSe^- in sorption experiments and these anions have similar sorption behavior. Since selenium should exist as elemental Se in basalt aquifers, a weaker reducing agent (e.g., thiosulfate) must be used to control the Eh in selenium sorption experiments.

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