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Geochemical Behavior of Cs, Sr, Tc, Np, and U in Saline Groundwaters: Sorption Experiments on Shales and Their Clay Mineral Components

Progress Report

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NUCLEAR AND CHEMICAL WASTE PROGRAMS
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ABSTRACT

The Sedimentary Rock Program at the Oak Ridge National Laboratory is investigating shale to determine its potential suitability as a host rock for the disposal of high-level radioactive wastes (HLW). In support of this program, preliminary studies were carried out on sorption of cesium, strontium, technetium, neptunium, and uranium onto Chattanooga (Upper Dowelltown), Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales under oxic conditions (air present). Three simulated groundwaters were used. One of the groundwaters was a synthetic brine made up to simulate highly saline groundwaters in the Pumpkin Valley Shale. The second was a 100/1 dilution of this groundwater and the third was 0.03 M NaHCO$_3$. Moderate to significant sorption was observed under most conditions for all of the tested radionuclides except technetium. Moderate technetium sorption occurred on Upper Dowelltown Shale, and although technetium sorption was low on the other shales, it was higher than expected for Tc(VII), present as the anion TcO$_4^-$. Little sorption of strontium onto the shales was observed from the concentrated saline groundwater. These data can be used in a generic fashion to help assess the sorption characteristics of shales in support of a national survey.

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1. INTRODUCTION

The Sedimentary Rock Program (SERP) at the Oak Ridge National Laboratory (ORNL) is investigating the use of sedimentary rocks (other than salt) as part of a national effort to broaden the range of choices of hydrologic environments and rock types available to the U. S. Department of Energy (DOE) as a potential second host medium for a high-level waste repository. Recent geochemical investigations at ORNL have focused on shales as possible host rocks for the disposal of high-level radioactive wastes (HLW).

Shales are among the most common and widespread rock types in the United States (Gonzales and Johnson, 1984). Thick deposits of shale can be found in almost every state of the United States, and these deposits encompass a wide range of geologic times, from the Precambrian, (0.6 - 3.0) x 10^9 years B.P. (before the present) to the Miocene Epoch of the Cenozoic Era, (1.3 - 2.5) x 10^7 years B.P. Clastic sedimentary rocks, even those as fine-grained as shales, may exhibit a great diversity in chemical composition. For example, on the small scale of a hand specimen of shale from the Green River Formation (Garfield County, Colorado), local fluctuations in composition are visible as laminae resulting from variations in the rate of sedimentation as the rock was formed (Longwell et al., 1969). Thus, it was expected that the various shales to be investigated in the SERP would show a number of interesting geochemical differences, with important implications for nuclear waste repository performance.

The interactions of radionuclides, groundwaters, and host rocks provide the dominant controls for limiting the mobility of radionuclides that will be released from the waste packages of a HLW repository. The extent of the interactions will be determined by the geochemical conditions of the repository environment (e.g., temperature, pressure, groundwater chemistry, pH, redox conditions, host-rock mineralogy and chemistry). The geochemical conditions associated with the shales being evaluated in the SERP show a number of differences among the members of the group, and the shales themselves may prove to have varying capabilities for the retention of radionuclides.

2. OBJECTIVE AND SCOPE

The objective of the work presented here is to acquire data to begin the characterization of the sorption properties of shales. Therefore, sorption tests are being performed to identify some of the more important geochemical parameters that contribute to the retention of radionuclides. By selecting shales representative of compositional extremes and using a variety of synthetic groundwater compositions, this type of sorption information can be used to plan further experiments designed to aid in a national survey to help select the most suitable shales for detailed site-specific consideration.

The first series of tests performed was designed to begin to elucidate the sorption behavior of cesium, strontium, technetium, uranium, and neptunium from appropriate synthetic groundwaters onto montmorillonite and illite. These two clay minerals are present in many shales and probably constitute the principal sorbing phases in many shales. The second series of sorption tests was made using the same elements with Chattanooga (Upper Dowelltown) Shale, Pierre Shale, shales from the Green River Formation, and with Nolichucky and Pumpkin Valley Shales from the Conasauga Group. The mineralogies of these shales, which are being determined in a companion study (Lee, et al., 1987), are representative of the compositional extremes of shales; a summary of the mineralogies is presented below. A limited number of tests were conducted with shales that had been heated in air at 250°C for six months in an attempt to acquire preliminary data on the effects of the heating of shale likely to occur in a HLW repository.

One of the most important parameters to the retention of radionuclides is the ionic strength and chemical composition of groundwater. Groundwaters associated with shales are highly variable in composition and range from dilute bicarbonate types to concentrated NaCl brines (Von Damm, 1987). Considerable literature exists on the geochemical behavior of radionuclides in dilute groundwaters in contact with typical rocks being considered for HLW repositories (e.g., basalt, granite, tuff). However, there is relatively little information on the interaction of shale-related minerals and radionuclides, especially in concentrated brines. The synthetic groundwaters selected for study were designed to be representative of the groundwaters found in various shale formations.

Cesium and strontium, although not key elements for long term storage of HLW, were chosen for study because they typically sorb by ion exchange, and their sorption behavior is therefore indicative of the extent to which the shales act as ion exchange sorbents. Also, cesium is thought to be permanently fixed by the illitic clays present in many shales, while strontium is normally sorbed reversibly. Uranium is a key radionuclide because spent fuel is expected to be stored in the repositories. Technetium normally exists as an anion under oxidizing conditions and was chosen to model anion behavior. Neptunium, uranium, and technetium are all sensitive to redox conditions to some extent, and their behavior can serve to indicate the ability of shales to reduce the valence of these radionuclides and thereby decrease their mobility. From the results of these preliminary tests, it will be possible to design more sophisticated tests to measure the ability of shales to retard nuclides. Such tests might include tests in anoxic environments, migration of elements through columns of shale, and systematic variation of groundwater composition parameters such as pH and concentration. As these data are obtained, other types of experiments may be found to be helpful.

3. MATERIALS AND METHODS

3.1 SHALES

The five core samples of Chattanooga Shale, Pierre Shale, Green River Formation Shale, Nolichucky Shale, and Pumpkin Valley Shale were characterized by Lee, et al. (1987), and the description below summarizes their conclusions.

The Chattanooga Shale sample was from the Upper Dowelltown Member of the shale in Fentress County, Tennessee, at a depth of 141-142 m. This unit may be described as interbedded medium light gray claystone and dark gray shale beds, varying in thickness, but only 3 - 12 cm thick.

The samples of Pierre Shale were representative of the Mobridge Member of Pierre Shale in Gregory County, South Dakota and were retrieved from a drill hole at a depth of 88.2 to 88.9 m. Lee, et al. (1987) have described the cores as claystone, thickly bedded to massive, nonfisslo, slightly to moderately calcareous, soft, moist, medium gray with slight olive tinge, dense, solid, bedding at low angle, nonweathered.

The samples from the Green River Formation originated in Garfield County, Colorado, and were drilled from the roof of the Colony mine. The samples were described as thinly bedded calcareous marl, very hard and compact.

Samples of Nolichucky and Pumpkin Valley Shales were from the Joy 2 well, in Oak Ridge, Tennessee, at depths of 181 to 182 and 604 to 605 m, respectively. Both shales are part of the Conasauga Group, a complex sequence of Middle to Upper Cambrian clastic and carbonate strata. The Nolichucky section is described as a gray to brown shaley limestone with discontinuous parallel bedding. The Pumpkin Valley section is maroon to gray, glauconitic, laminated silty mudstone.

The approximate mineralogical composition of the five whole-rock samples is given in Table 3.1, from the summary by Lee, et al. (1987). All of the shales contain organic matter; the Green River Formation Shale appears to have the most, while the representatives of the Conasauga Group, Nolichucky and Pumpkin Valley Shales, appear to have the least. Some of the experiments to be described were carried out with shales that had been heated to 250°C in air for six months. Analyses of the heated shales are not yet complete, but such treatment should oxidize or volatilize most of the organic matter, possibly oxidize sulfides and other reduced material, and alter the layer-type clays.

Table 3.1. Estimated mineralogical composition of whole-rock samples[a]

Component	Percent by Weight[b]				
	Chattanooga Shale	Pierre Shale	Green River Formation Shale	Nolichucky Shale	Pumpkin Valley Shale
Organic Matter	11	5	13	t	t
Chlorite/Kaolinite	4	t	t	14	15
Illite	49	t	10	43	57
Micas	t	4	t	t	t
Smectite	nd	59	nd	nd	nd
Carbonates	t	15	42	11	t
Quartz/Feldspars	25	11	28	29	22
Pyrite	6	2	t	t	t
Weight Loss (105°C)	1	4	2	2	2

[a]Lee, et al. (1987)

[b]t = trace ($\leq$ 2%), observed from thin section and electron micrographs; nd = not detectable.

3.2 GROUNDWATER

A synthetic brine groundwater was prepared to simulate saline groundwaters found at the 427-m depth of test wells in the Pumpkin Valley Shale. The composition of the synthetic groundwater is given in Table 3.2. This groundwater has a density of about 1.13 and can be characterized as an acidic, highly saline groundwater containing considerable quantities of alkaline earth ions. The ionic strength of this groundwater is 3.30 mol/L or about 3.42 mol/kg H_2O. Sorption tests were made with this groundwater (concentrated brine) and a 100-fold dilution (dilute brine), each adjusted initially to pH 5. To simulate alkaline carbonate conditions, measurements were also made with 0.03 mol/L $NaHCO_3$ (bicarbonate). A few sorption measurements with clays were made with a 10-fold dilution (intermediate brine) of the concentrated brine; it was also adjusted initially to pH 5.

Table 3.2. Composition of synthetic brine groundwater

Component	Concentration	
	(eq/L)	(g/L)
Na	2.00	46.00
K	0.0089	0.348
Mg	0.230	2.79
Ca	0.599	12.0
Sr[a]	0.027	1.20
Cl	2.86	101.29
Br	0.009	0.71

pH adjusted to 5 with HCl

[a]In some of the experiments to measure strontium sorption, the
strontium was eliminated from the synthetic groundwater so that
trace levels of strontium could be studied.

3.3 NUCLIDES

The tracers used in this study are listed in Table 3.3, along with some
of the pertinent data on their radioactive decay properties.

Concentrations of strontium, cesium, and technetium were determined by
measuring the gamma radiation of aliquots of traced solutions with a
well-type NaI(Tl) scintillation detector and comparing the counting
rates to those of reference standard solutions of the same tracer
nuclide. The K-series x-rays from the electron-capture decay of ^{235}Np
were also determined with the well-type NaI(Tl) detector and compared to
reference standard solutions of this nuclide. The concentrations of
uranium solutions were determined by liquid scintillation alpha counting
of tracer ^{233}U in solutions of natural uranium. Limitations imposed by
detection sensitivity and specific activity were such that
concentrations of ^{233}U less than about 10^{-6} mol/L could not be used as
starting solutions.

Table 3.3. Half-lives, decay modes, and radiations emitted by tracers used in this study[a]

Nuclide	Half-Life	Principal Decay Mode	Radiations Detected
[8 5]Sr	64.84 d	Electron capture	514.0-keV gamma ray
[1 3 7]Cs	30.17 y	Beta decay	661.6-keV gamma ray (in decay of [1 3 7 m]Ba)
[9 5 m]Tc	61 d	Electron capture	204.1-keV gamma ray
[2 3 5]Np	396.2 d	Electron capture	No gamma; K-series x-rays at 94.7, 98.4, and 111 keV
[2 3 3]U	1.59 x 10^{5} y	Alpha decay	4.824- and 4.783-keV alpha particles

[a]Data from Kocher (1981).

3.4 EXPERIMENTAL PROCEDURES

Sorption of the radionuclides was measured by determining the sorption ratio after exposure of the sorbent to traced groundwaters. The sorption ratio, which is here designated R_s, is defined as the concentration of the nuclide in the sorbent divided by the concentration of the nuclide in the groundwater, each determined after the test. In this study, the unit for concentration in the sorbent is moles/kg, and that in the solution is moles/L. Thus, the units of R_s are L/kg. The amount adsorbed is determined by comparison of the concentrations of the sorbate (adsorbing nuclide) in the solution before and after the test. It is then assumed that any reduction in concentration in the solution is a result of sorption onto the sorbent. Control experiments are carried out simultaneously with solutions that do not contain the solid sorbent to see whether there are other processes such as sorption on the container or precipitation that could remove the sorbate from the solution.

The sorption ratios are calculated from the equation

$$R_s = \frac{(C_i - C_f) \times V}{C_f \times W} \tag{1}$$

where C_i is the initial concentration of the sorbate in the solution,

C_f is the final concentration in the solution, V is the initial volume of groundwater, and W is the weight of the shale sorbent (shale).

In most of the experiments, 2 mL of groundwater was used. The amount of shale used depended upon the amount of sorption expected in the experiment. Enough shale is needed to cause substantial sorption, but too much of a highly-sorbing shale removes essentially all of the nuclide and a precise value of R_s cannot be determined.

A typical procedure is as follows: The shale samples are added to tared tubes and the tubes are reweighed to determine the shale weight. The groundwater is then added and the tubes are reweighed; the groundwater volume is calculated from the weight and density. All determinations of groundwater volume are based on weight. The tubes are weighed at the beginning and end of every equilibration to determine any solution loss.

The tubes containing the shale and groundwater are then shaken for a three day preequilibration period. After each preequilibration, the solutions are centrifuged and the supernatant is carefully decanted to avoid loss of sorbent. The shales, which at this time are packed at the bottom of the tube, are resuspended in fresh groundwater and the pre-equilibration is repeated twice. In general, atomic absorption analyses of the centrifugates for the principal cations in the groundwaters have shown that three preequilibration periods are sufficient to reach compositions within 5% of the initial composition.

After the preequlibration periods, traced groundwater is added along with enough untraced groundwater to bring the volume to the desired level. The preequilibrated shale and the traced groundwater are then gently shaken, usually for 14 days. Tests with clay samples were shaken for 3 days because only a short time is generally necessary to reach equilibrium with the clay samples that we used (Shiao et al., 1979). Test samples and controls (tubes containing traced groundwater but no sorbent) are done in triplicate. After the test contact period, the samples are centrifuged and the tracer content of the final solutions is assayed. Values of R_s are then calculated using Eq. 1.

Desorption ratios are determined from samples that have been equilibrated and the sorption ratios calculated. As much as possible of the groundwater is then carefully decanted after which the tube is weighed to determine the amount of solution still in the test tube. Enough untraced groundwater is then added to make up to a solution volume equal to that used in the sorption portion of the experiment. The amount of tracer present at the beginning of the desorption experiment is equal to the volume of the residual groundwater times the final concentration in the sorption experiment plus the amount on the solid, which is calculated from the sorption ratio. The tubes are then shaken for an appropriate length of time and the concentration of the tracer in the solution is then determined. Desorption ratios are calculated from Eq. 1; C_i is calculated by dividing the amount of tracer originally present by the solution volume.

Values of R_s can be calculated on the basis of the initial radionuclide concentration of the standard solution (corrected for decay if necessary) or of the radionuclide concentration of control samples carried along with the test samples. Because of sorption on tube walls or precipitation, there will sometimes be a reduction in the radionuclide concentration of the control samples. In the presence of a sorbing phase, sorption on tube walls may not be significant compared to the sorption on the sorbing phase. Also, because the final pH of the control samples is often different from the final pH of the test samples, it is not known whether precipitation occurs with the test samples. Ideally, the sorbing phase should be removed and the tracer concentration on it should be determined directly. However this is difficult to do and could easily lead to large errors. For these reasons in these initial tests, we chose to report sorption ratio values calculated using the initial radionuclide concentration of the standard solutions as C_i. Values given are averages of three determinations; standard deviations are also provided.

All equilibrations were carried out at room temperature, approximately 23°C, in the presence of air. Thus, the groundwaters were oxidizing. In most cases, no attempt was made to keep the pH of the solutions constant during the experiment, but it was allowed to adjust to a value determined by the interactions between the shale and the groundwater. As shown below the pH changed during the experiments, sometimes significantly.

In the measurements of the effect of the pH on cesium and strontium sorption, the pH in the first equilibration was allowed to "float," then it was adjusted upward by adding sodium hydroxide solution to the same samples, and finally it was adjusted downward by adding hydrochloric acid solution. The samples were equilibrated for at least seven days at each value.

4. RESULTS AND DISCUSSION

The experiments summarized in the sections below are preliminary investigations of the sorption of cesium, strontium, technetium, neptunium, and uranium onto samples of montmorillonite, illite, and shale. In these acidic groundwaters, cesium and strontium are expected to exist as the singly- and doubly-charged aquo ions, respectively. Because the experiments were carried out under mildly oxidizing conditions, technetium is expected to be present as the pertechnetate ion, TcO_4^-, and neptunium as the neptunyl ion, NpO_2^+. Uranium was added as the uranyl ion, UO_2^{2+}. The extent of complexation in these groundwaters, if any, has not yet been determined or calculated.

It should be stressed that only a limited number of shale samples were studied, and only batch contact sorption techniques were used. A

complete study of sorption using batch contact techniques should include investigation of desorption, kinetics, and anoxic conditions. Further, only a limited number of solution variables were studied, and in most cases the pH was allowed to "float" to a final value without any control. Thus, some of the experiments reported here can only be considered to be indicative and serve mostly to suggest future investigations. Nevertheless, the results from these tests have proved to be useful and informative.

The pH of the concentrated brine and the intermediate brine was adjusted initially to 5. In general, the pH of the concentrated brine increased to 6.5 - 7.0 during the course of the experiments for the Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales. The pH of the intermediate brine generally increased significantly more than the pH of the concentrated brine. The groundwaters in contact with the Chattanooga (Upper Dowelltown) Shale became quite acidic with time, an effect which can be attributed to the production of acid by oxidation of the large amount of pyrite (FeS_2) and to the very small concentration of carbonate in the shale. (Carbonate neutralizes acid, and, if present in sufficient concentration, could prevent the solution from becoming acidic.) The production of acid by the oxidation of pyrite to ferric sulfate is illustrated by Eq. 2.

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-} \tag{2}$$
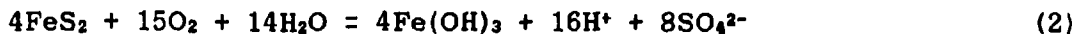
In this equation we have assumed that ferric iron in the groundwaters is present as $Fe(OH)_3$; this is a simplification because at the pH levels of the final solutions (ca. 3 to 4), hydrolytic aqueous species of Fe(III) will be present. The pH of the 0.03 M $NaHCO_3$ solution remained above pH 8 for the tests with Upper Dowelltown Shale because of the buffering action of the bicarbonate ion.

4.1 CESIUM

The data presented in Table 4.1 show that cesium sorbs strongly on montmorillonite and illite. It is important to note that sorption was more pronounced on illite than on montmorillonite and that sorption increased with dilution of the brine. Such a trend with dilution is strongly suggestive of an ion exchange mechanism. These observations will be important in the discussion below, because the five shales chosen for study contain varying amounts of clays (Table 3.1).

Sorption ratios obtained for cesium on the five shales are given in Tables 4.2 - 4.6 and in Figs. 4.1 and 4.2 for a relatively wide range of conditions and types of experiments. Examination of these data shows that cesium is sorbed rather strongly under all conditions, although relatively low sorption ratios were observed for Green River Formation Shale in the concentrated brine. For the diluted brine, the sorption ratios were consistently higher, usually by approximately two orders of magnitude, suggestive of a simple ion exchange mechanism. The mineralogy of the shale samples summarized in Table 3.1 shows some

interesting correlations with these results. The relatively low sorption ratios observed for the Green River Formation Shale appear to correlate with the low clay mineral content. The other shales, which show stronger sorption of cesium, either are high in illite (Chattanooga, Nolichucky, Pumpkin Valley) or are high in smectite (Pierre).

Over the range of initial cesium concentrations tested (Tables 4.2 and 4.3), there appear to be no significant differences in the sorption ratios determined at cesium concentrations of 1×10^{-8} and 5×10^{-11} mol/L.

Experiments on the desorption of cesium from these shales are instructive, since it might be suspected that sorption processes involving clay minerals, which manifest large sorption ratios, might not be reversible, and so would tend to "fix" cesium. However, the data in Table 4.4 do not show any systematic or significant differences between sorption ratios and desorption ratios in the concentrated brine. This indicates that a nearly reversible, ion-exchange-like process is involved. For the other groundwaters, the values of R_d are consistently higher than the values of R_s. This observation suggests a nonequilibrium process.

Table 4.5 shows a comparison between the sorption of cesium on unheated shales and on shales heated for six months at 250°C. Unfortunately, the amount of heated shale available was insufficient for conducting experiments with all of the groundwater compositions shown in the other tables. Thus, it was decided to carry out experiments only with the concentrated brine groundwater composition. Except for the Green River Formation Shale, which contains little illite or smectite, heating of the shales consistently resulted in an increase in the sorption ratio for cesium, which suggests that cesium sorption occurs on the mineral (i.e., inorganic) components of the shales.

The results of studies on the pH dependence of cesium sorption from the diluted brine are summarized in Table 4.6. To date, only a limited range of pH has been covered in these experiments, and the errors are large, especially for the large values of the sorption ratio. The data have been plotted in Figs. 4.1 and 4.2 to guide the reader in discerning trends in the data. The results for the Green River Formation Shale appear to show little pH dependence above pH 6, while the results for the other three shales appear to show a general increase in sorption ratio with increasing pH. However, because of the poor precision resulting from the almost complete removal of cesium from the groundwater, it is not possible to analyze the pH dependence quantitatively on the basis of these results.

Table 4.1. Cesium(I) sorption on montmorillonite and illite from concentrated and diluted brine groundwater.[a]

Groundwater[b]	Initial Cs concentration (mol/L)	Montmorillonite R_s (L/kg)		Illite R_s (L/kg)	
		avg	std dev	avg	std dev
Concentrated	1×10^{-8}	14.5	2	308	22
Intermediate	1×10^{-8}	106	8	3740	123
Dilute	1×10^{-8}	476	28	>10000	--
	8×10^{-11}	610	30	>10000	--

[a]Solid/solution ratios were 0.10 for concentrated brine, 0.025 for intermediate brine, and 0.005 for dilute brine. The samples were preequilibrated three times for three days each, and the final equilibration was for three days at 25°C. Samples were separated by centrifugation at 25,000 rcf for 30 minutes.

[b]Concentrated groundwater composition is given in Table 3.2.

Table 4.2. Cesium(I) sorption on shale samples.[a]
Initial Cs concentration: 1×10^{-8} mol/L.

| | | | Rs (L/kg) | |
| | | Final | | std |
Shale	Groundwater[b]	avg pH	avg	dev
Upper Dowelltown	concentrated brine	3.90	152	2.4
	diluted brine	4.24	>10000	--
	bicarbonate	8.31	>10000	--
Pierre	concentrated brine	6.37	107	9.1
	diluted brine	7.86	>10000	--
	bicarbonate	8.00	9493	993
Green River	concentrated brine	6.93	5.2	2.4
Formation	diluted brine	8.31	182	4.7
	bicarbonate	9.03	1317	565
Nolichucky	concentrated brine	6.95	93.9	1.1
	diluted brine	8.27	>10000	--
	bicarbonate	9.16	6570	1363
Pumpkin Valley	concentrated brine	6.55	70.0	14.6
	diluted brine	6.79	>10000	--
	bicarbonate	8.79	>10000	--

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater. The samples were preequilibrated three times for at least three days each, and the final equilibration was for 15 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Composition of the concentrated brine is given in Table 3.2. The diluted brine is a 100/1 dilution of the concentrated brine, and the concentration of the bicarbonate solution is 0.03 mol/L.

Table 4.3. Cesium(I) sorption on shale samples.[a]
Initial Cs concentration: 5 x 10^{-11} mol/L.

Shale	Groundwater[b]	Final avg pH	Rs (L/kg) avg	std dev
Upper Dowelltown	concentrated brine	3.81	123	3.2
	diluted brine	3.82	>10000	--
	bicarbonate	8.22	8260	1107
Pierre	concentrated brine	6.12	102	3.5
	diluted brine	7.87	>10000	--
	bicarbonate	8.36	7740	601
Green River Formation	concentrated brine	6.87	12.1	4.1
	diluted brine	8.35	413	39.7
	bicarbonate	9.05	683	61.0
Nolichucky	concentrated brine	6.76	94.5	6.1
	diluted brine	8.58	>10000	--
	bicarbonate	9.10	2635	351
Pumpkin Valley	concentrated brine	6.77	79.1	10.3
	diluted brine	6.93	>10000	--
	bicarbonate	9.37	9580	1086

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater. The samples were preequilibrated three times for at least three days each, and the final equilibration was for 15 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Composition of the concentrated brine is given in Table 3.2. The diluted brine is a 100/1 dilution of the concentrated brine, and the concentration of the bicarbonate solution is 0.03 mol/L.

Table 4.4. Cesium(I) sorption and desorption on shales.[a]

| Groundwater[b] | Shale | Sorption | | | Desorption | | |
| | | pH | Rs (L/kg) | | pH | Rd (L/kg) | |
			avg	std dev		avg	std dev
Concentrated brine	D	6.77	331	1.4	4.18	321	5.7
	P	6.97	238	5.8	6.37	234	1.5
	G	6.88	4.0	0.1	6.67	4.9	0.1
	N	6.76	251	2.1	6.63	238	3.7
	V	6.89	149	6.2	6.46	149	2.9
Dilute brine	D	5.09	2677	117	3.70	3927	655
	P	7.30	2442	119	7.31	3036	521
	G	7.51	61.0	1.1	7.56	75.0	2.2
	N	7.38	3130	205	7.49	4582	500
	V	7.23	2146	192	7.26	2484	237
Bicarbonate	D	8.05	6668	1492	7.39	>10000	--
	P	8.05	>10000	--	7.47	>10000	--
	G	8.60	1452	45.8	7.93	1791	117
	N	8.69	1333	443	8.06	5483	1267
	V	8.57	721	59.4	7.97	1224	181

[a]The symbols for the shales are: D, Upper Dowelltown; P, Pierre; G, Green River Formation; N, Nolichucky; V, Pumpkin Valley. The samples contained approximately 0.2 g of shale and 2 mL of groundwater with an initial Cs concentration of 1×10^{-8} mol/L. The samples were preequilibrated 3 times for at least 3 days each and the final equilibration was for 14 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Composition of the concentrated brine is given in Table 3.2. The diluted brine is a 100/1 dilution of the concentrated brine, and the concentration of the bicarbonate solution is 0.03 mol/L.

Table 4.5. Comparison of cesium(I) sorption on heated and unheated shales from concentrated brine groundwater.[a]

| Shale | Heated shale | | | Unheated shale | | |
| | final pH | Rs (L/kg) | | final pH | Rs (L/kg) | |
		avg	std dev		avg	std dev
Upper Dowelltown	3.48	226	1.0	3.90	152	2.4
Pierre	6.74	143	0.9	6.37	107	9.1
Green River Formation	6.95	1.8	0.1	6.93	5.2	2.4
Nolichucky	6.71	181	1.0	6.95	93.9	1.1
Pumpkin Valley	6.62	111	2.1	6.55	70.0	14.6

[a]The solid/solution ratios were about 0.05 kg/L with heated shales and 0.10 kg/L with unheated shales. Shales were heated in air for six months at 250°C. The initial Cs concentration was 1×10^{-8} mol/L at initial pH 5. The samples were preequilibrated three times for at least three days each and the final equilibration was for 15 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

Table 4.6. Effect of pH on cesium sorption from brine groundwater diluted 100/1.[a]

Shale	pH		Rs (L/kg)	
	avg	std dev	avg	std dev
Pierre	7.50	0.01	5098	262
	8.30	0.03	5955	864
	8.93	0.03	6730	592
	7.24	0.03	4989	196
	6.25	0.04	3110	171
	5.16	0.03	2786	66
Green River Formation	8.03	0.02	244	3
	8.21	0.01	216	3
	8.80	0.01	257	7
	7.36	0.01	250	4
	6.41	0.04	248	5
	5.53	0.02	161	3
Nolichucky	8.16	0.07	6889	659
	8.33	0.05	6056	489
	8.89	0.04	9865	2014
	7.21	0.03	8243	717
	6.34	0.03	4955	63
	5.41	0.02	6174	784
Pumpkin Valley	8.16	0.04	6437	468
	8.48	0.05	>10000	---
	8.94	0.04	7255	254
	7.00	0.09	5111	439
	3.69	0.02	3250	109
	5.12	0.00	5007	697

[a]Each sample contained approximately 1.5 g shale and 1.15 mL groundwater. The samples were preequilibrated three times for three days each and the first equilibration was for 7 days at 25°C. The initial Cs concentration was 1×10^{-8} mol/L at initial pH 5. The samples were separated by centrifugation at 5000 rcf for 90 minutes. The pH was then increased by adding sodium hydroxide solution to the same samples and then it was decreased by adding hydrochloric acid solution. The samples were equilibrated for at least 7 days at each pH.
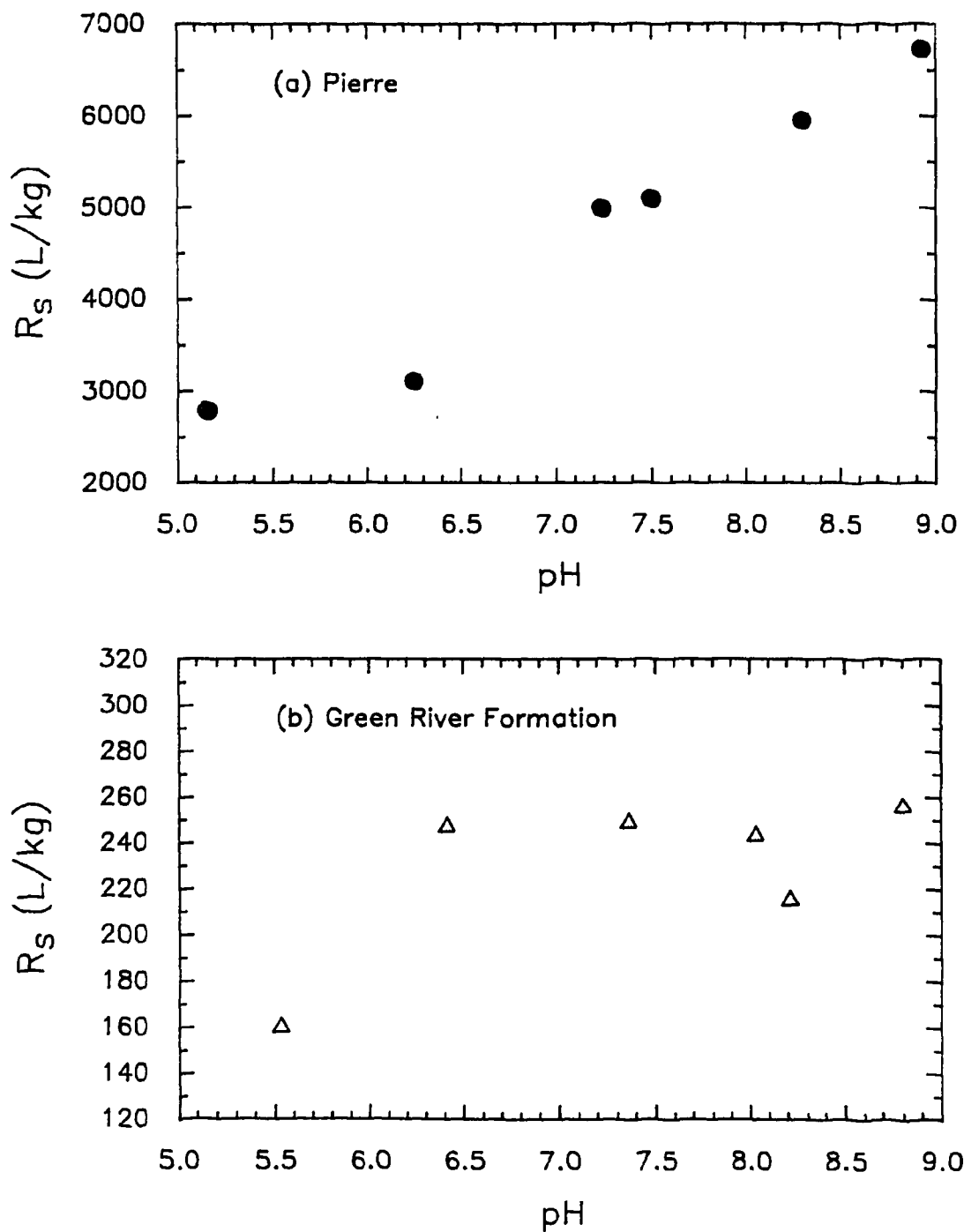
Fig. 4.1. Effect of pH on sorption of cesium(I) from brine groundwater
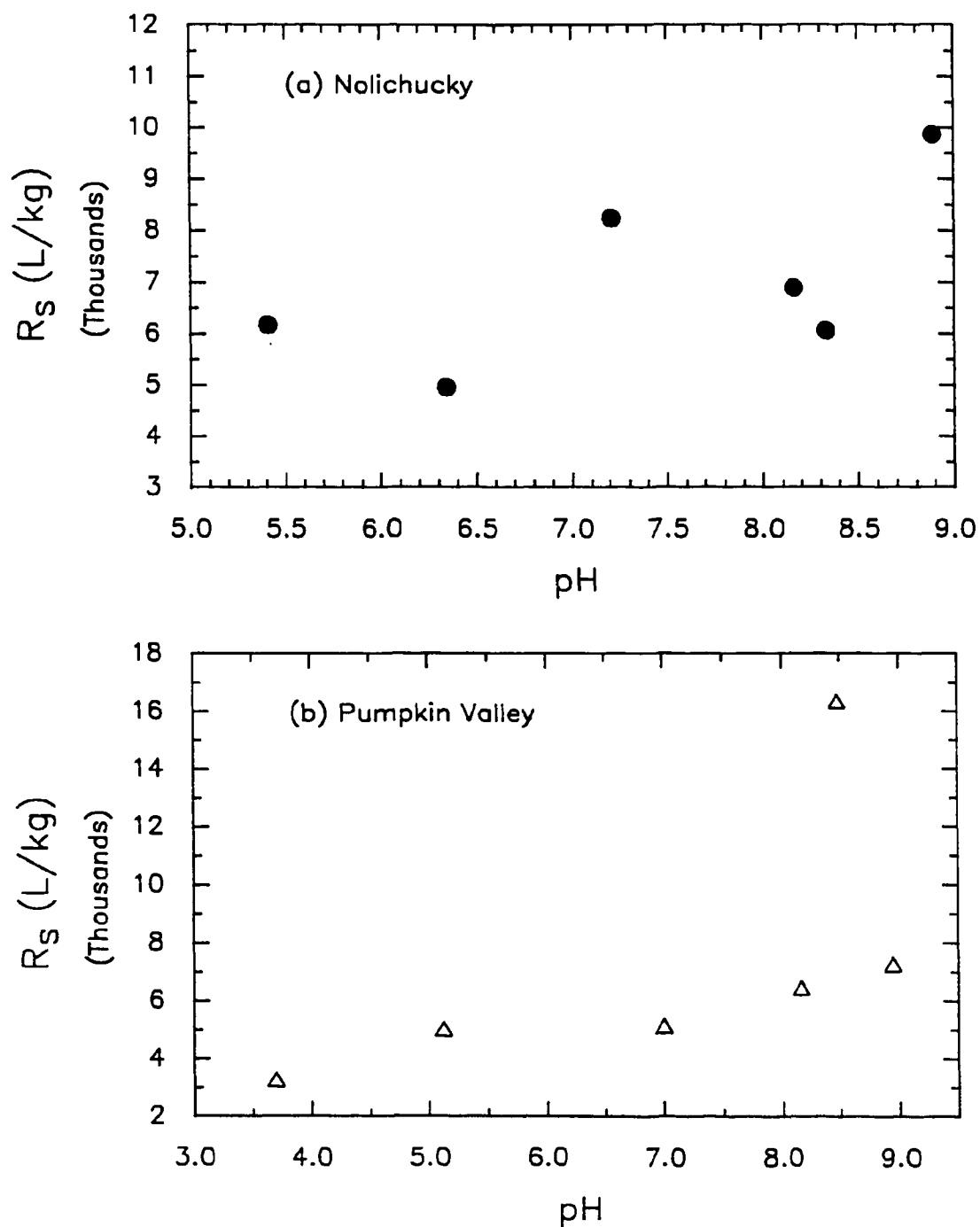diluted 100/1 on (a) Pierre Shale, and (b) Green River
Formation Shale.

Fig. 4.2. Effect of pH on sorption of cesium(I) from brine groundwater diluted 100/1 on (a) Nolichucky Shale, and (b) Pumpkin Valley Shale.

4.2 STRONTIUM

Results of experiments to measure sorption of strontium, assumed to be present as the aquo ion Sr^{2+}, on montmorillonite and illite are given in Table 4.7. Little sorption was observed from the concentrated brine groundwater. However, as the groundwater was diluted, the values of the sorption ratios increased significantly, consistent with ion exchange behavior. For strontium, the sorption ratios were consistently higher on montmorillonite than on illite.

The data from a series of tests designed to study the sorption of strontium on the five shale samples are shown in Tables 4.8-4.11 and in Figs. 4.3 and 4.4. Unlike cesium, significant sorption of strontium was observed only from the 0.03 M $NaHCO_3$ solutions, and sorption ratios for the concentrated brine groundwater were particularly low (cf., Table 4.8). As mentioned earlier, all of the shales except the Pierre shale contain significant amounts of illite, which was found to sorb strontium relatively poorly. The Pierre shale, on the other hand, contains smectite (montmorillonite), which sorbs Sr^{2+} more readily than illite (Table 4.7), and this may account for the larger sorption ratio in Table 4.8 from the diluted brine groundwater. The higher sorption ratios observed with 0.03 M $NaHCO_3$ solutions might be expected to be a consequence of the higher values of pH associated with the presence of bicarbonate ions; however, the studies of the effect of pH on sorption of Sr^{2+} discussed later indicate that the pH alone does not appear to account for all of the increased sorption observed in the bicarbonate solutions. A better understanding of the sorption behavior in bicarbonate solutions will require additional studies.

The sorption and desorption experiments summarized in Table 4.9 did not reveal any meaningful trends in the concentrated brine, since the sorption and desorption ratios were too small and the errors large in proportion. However, in the diluted brine and in the 0.03 M $NaHCO_3$ solution, values of the desorption ratios R_d were consistently larger than the corresponding values of the sorption ratios R_s, which implies that some of the strontium is "fixed" to the shales and is not sorbed and desorbed by an equilibrium ion exchange process. Such a nonequilibrium process would work to immobilize a portion of the available strontium in the presence of a dilute groundwater.

The comparison between the sorption of strontium on heated and unheated shales is shown in Table 4.10. As shown previously, there is very little sorption by the unheated shales from concentrated brine groundwater. After the shale was heated in air at 250°C for six months, there was no strontium sorption at all; in fact, slightly negative sorption ratios were measured, an observation which might be due to experimental error but which could also be due to some ion exclusion by the shales. Thus, the little sorption ability for strontium possessed by the shales was apparently lost by heating.

Data from studies on the pH dependence of strontium sorption from the dilute (100/1) groundwater are presented in Table 4.11 and in Figs. 4.3

and 4.4. As was the case with cesium, only a limited range of pH values has been investigated to date; however, in spite of the differences in sorption between the shales already discussed, all of the shales manifested a rise in sorption ratio with increasing pH. On some sorbents, the sorption ratio for strontium has been shown to increase sharply with increasing pH (Shiao, et al., 1981), similar to the behavior shown in Table 4.11 and in Figs. 4.3 and 4.4. A comparison of this pH dependence with the strontium sorption from 0.03 mol/L $NaHCO_3$ solutions in Table 4.8 shows that the pH effect alone does not seem to account for all of the sorption observed for the cases shown in Table 4.8. Further work remains to be done in attempting to model this complex system in terms of chemical speciation.

Table 4.7. Strontium(II) sorption on montmorillonite and illite from concentrated and diluted brine groundwater.[a]

Groundwater[b]	Initial Sr concentration (mol/L)	Montmorillonite Rs(L/kg)		Illite Rs(L/kg)	
		avg	std dev	avg[c]	std dev
Concentrated	1×10^{-8}	0.55	0.2	-0.26	0.1
10/1 dilution	1×10^{-8}	6.8	1.0	0.29	0.5
	0.0135	10.8	0.8	2.7	0.4
100/1 dilution	1×10^{-8}	97.2	6.3	10.7	2.7
	0.0135	112	5	19.5	6.8

[a]Solid/solution ratios:

(1) For 1×10^{-8} mol/L initial Sr, the solid/solution ratios in preequilibration were 0.025 for concentrated brine, 0.0125 for intermediate brine, and 0.005 for dilute brine; the ratios in the final equilibration were 0.050 for concentrated brine, 0.025 for intermediate brine, and 0.010 for dilute brine.

(2) For 0.0135 mol/L initial Sr, the solid/solution ratios in preequilibration and final equilibration were 0.025 for intermediate brine and 0.005 for dilute brine.

The samples were preequilibrated three times for three days each and the final equilibration was for three days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 30 minutes.

[b]Concentrated groundwater composition is given in Table 3.2.

[c]Negative sorption ratios could be an indication either of small experimental errors or ion exclusion by the sorbents.

Table 4.8.   Strontium(II) sorption on shale samples[a]

Shale	Groundwater[b]	Final avg pH	Rs (L/kg) avg	Rs (L/kg) std dev
Upper Dowelltown	concentrated brine	5.46	1.3	0.2
	diluted brine	3.37	3.5	0.3
	bicarbonate	8.69	146	18
Pierre	concentrated brine	6.22	1.2	1.5
	diluted brine	7.21	36.6	0.5
	bicarbonate	8.41	534	245
Green River Formation	concentrated brine	6.86	3.9	3.5
	diluted brine	7.52	3.3	1.4
	bicarbonate	9.09	138	12
Nolichucky	concentrated brine	6.97	0.7	0.4
	diluted brine	7.73	13.8	0.7
	bicarbonate	9.42	390	74
Pumpkin Valley	concentrated brine	6.88	4.0	2.8
	diluted brine	7.65	10.9	0.8
	bicarbonate	9.45	713	117

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial Sr concentration of 1×10^{-8} mol/L.   The samples were preequilibrated three times for at least three days each and the final equilibration was for 19 days at 25°C.   The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]The strontium normally present in the concentrated brine and the dilute brine was omitted in these tests.   Composition of the concentrated brine is given in Table 3.2.   The diluted brine is a 100/1 dilution of the concentrated brine, and the bicarbonate solution is 0.03 mol/L.

Table 4.9. Strontium(II) sorption and desorption on shales.

Groundwater[b]	Shale[a]	pH	Sorption Rs (L/kg) avg	std dev	pH	Desorption Rd (L/kg) avg	std dev
Concentrated	D	4.33	0.0	0.0	3.64	0.0	1.0
brine	P	6.83	0.0	0.0	6.78	0.4	0.3
	G	6.80	0.0	0.0	6.82	0.3	0.6
	N	6.69	0.0	0.0	6.57	0.0	0.4
	V	6.84	-0.1	0.1	6.70	-0.4	1.7
Diluted	D	3.21	3.3	0.1	2.75	11.2	0.4
brine	P	7.61	38.1	1.1	7.63	48.7	2.9
	G	7.77	4.9	0.1	7.73	10.1	0.2
	N	7.54	17.1	0.1	7.54	22.2	0.0
	V	7.52	12.4	0.1	7.49	16.3	0.1
Bicarbonate	D	8.30	122	2.6	8.40	185	3.7
	P	8.33	522	19.5	8.54	832	18.8
	G	8.84	478	31.9	8.99	1101	106
	N	8.79	161	2.8	8.87	245	1.8
	V	8.69	220	4.2	8.79	280	15.2

[a]The symbols for the shales are: D, Upper Dowelltown; P, Pierre; G, Green River Formation; N, Nolichucky; and V, Pumpkin Valley. Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial Sr concentration of 1×10^{-8} mol/L. The samples were preequilibrated 3 times for at least 3 days each, and the final equilibration was for 14 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Composition of the diluted brine is given in Table 3.2. The diluted brine is a 100/1 dilution of the concentrated brine, and the bicarbonate solution concentration is 0.03 mol/L.

Table 4.10. Comparison of strontium(II) sorption on heated and unheated shales from concentrated brine groundwater.[a]

| | Heated shale | | | Unheated shale | | |
| | | Rs (L/kg) | | | Rs (L/kg) | |
Shale	final pH	avg	std dev	final pH	avg	std dev
Upper Dowelltown	3.54	-0.6	0.1	5.46	1.3	0.2
Pierre	6.84	-0.2	0.1	6.22	1.2	1.5
Green River Formation	--	--	--	6.86	3.9	3.5
Nolichucky	7.00	-0.6	0.3	6.97	0.7	0.4
Pumpkin Valley	6.74	-0.4	0.2	6.88	4.0	2.8

[a]The solid/solution ratio was about 0.05 kg/L with heated shales and 0.10 with unheated shales. The shales were heated in air for six months at 250°C. The initial Sr concentration was 1×10^{-8} mol/L at initial pH 5. The samples were preequilibrated three times for at least three days each and the final equilibration was for 14 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

Table 4.11. Effect of pH on strontium(II) sorption
from dilute brine groundwater.[a]

Shale	pH		Rs (L/kg)	
	avg	std dev	avg	std dev
Pierre	7.32	0.01	40.9	0.5
	8.27	0.01	244	0.0
	8.96	0.01	519	1.6
	7.12	0.09	63.1	0.3
	6.25	0.00	17.3	0.4
	5.73	0.01	10.6	0.1
Green River	7.95	0.00	5.2	0.1
Formation	8.29	0.00	20.5	0.5
	9.02	0.02	53.3	0.9
	7.06	0.09	8.4	0.3
	6.23	0.01	3.0	0.1
	5.84	0.01	4.5	0.1
Nolichucky	8.07	0.02	20.2	0.0
	8.30	0.00	32.7	0.2
	9.00	0.02	55.3	0.5
	7.12	0.10	14.5	0.1
	6.25	0.00	5.0	0.1
	5.97	0.05	4.6	0.1
Pumpkin Valley	8.10	0.01	15.0	0.1
	8.35	0.01	22.0	0.2
	8.99	0.05	35.7	0.6
	7.00	0.13	12.6	0.1
	6.12	0.13	9.6	0.0
	4.34	0.18	7.3	1.2

[a]Each sample contained approximately 1.5 g shale and
15 mL groundwater. The samples were preequilibrated
three times for three days each and the first
equilibration was for 7 days at 25°C. The initial
Sr concentration was 1×10^{-6} mol/L at initial pH
5. The samples were separated by centrifugation at
5,000 rcf for 90 minutes. The pH was then
increased by adding sodium hydroxide solution to
the same samples and then it was decreased by
adding hydrochloric acid solution. The samples
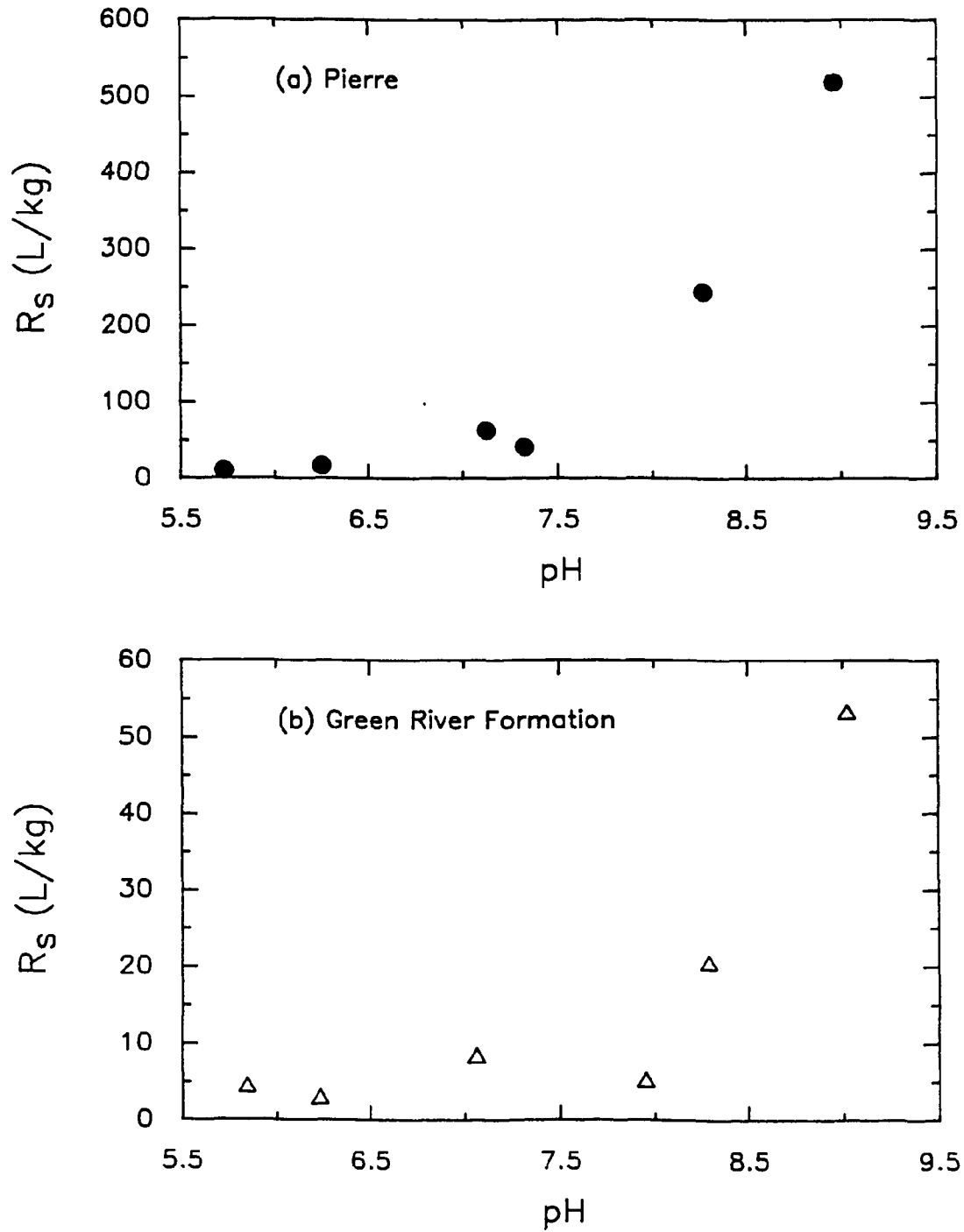were equilibrated for at least 7 days at each pH.

Fig. 4.3. Effect of pH on sorption of strontium(II) from brine groundwater diluted 100/1 on (a) Pierre Shale, and (b) Green River Formation Shale.
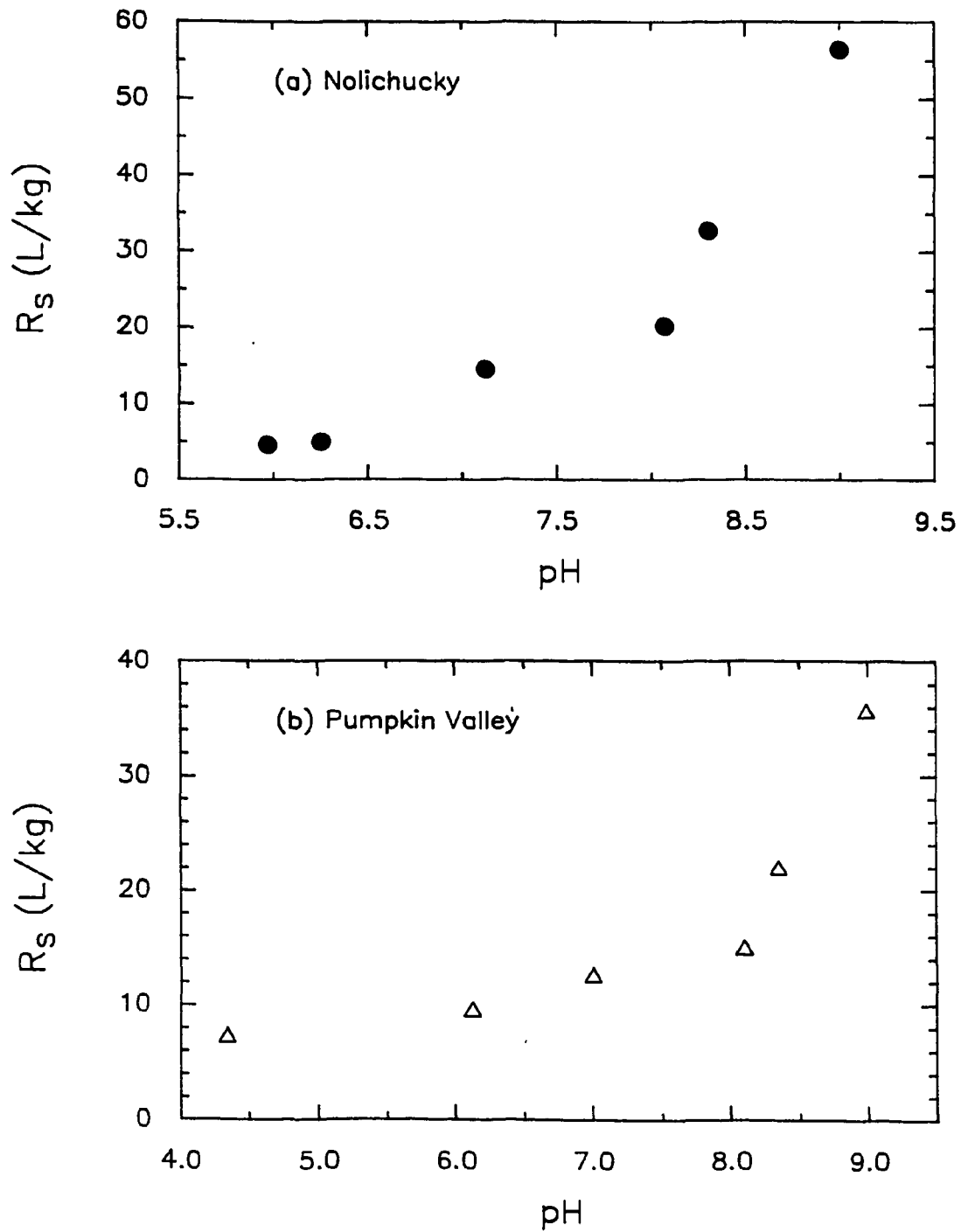
Fig 4.4. Effect of pH on sorption of strontium(II) from brine groundwater diluted 100/1 on (a) Nolichucky Shale, and (b) Pumpkin Valley Shale.

4.3 TECHNETIUM

For elements like technetium, which exists as Tc(VII) in oxidizing environments and in lower valence states if conditions are sufficiently reducing, there could be a significant difference between anoxic and oxic tests with minerals or groundwaters that have reducing properties. For the experiments reported here with relatively pure montmorillonite and illite, and a synthetic groundwater that contains no possible redox-active agents, reduction of Tc(VII) would not be expected even if anoxic conditions were used. The results for technetium given in Table 4.12 show that essentially no sorption was observed, i.e., $R_s < 1$ for all cases studied. This result is not surprising, because Tc(VII) exists as the pertechnetate anion TcO_4^- under these conditions. Anions are not sorbed significantly by illite or montmorillonite, which sorb mainly by a cation-exchange process.

Small but measurable sorption of technetium occurred on all of the shales except the Chattanooga (Upper Dowelltown) Shale, and relatively high sorption ratios were measured for this shale from both of the brine groundwaters and from the bicarbonate groundwater (cf., Table 4.13). These results were surprising, because little or no technetium sorption was expected under the oxic conditions of the tests. Sorption onto the shales could occur if components of the shale had sufficient reducing ability. Under these conditions, lower valence states of technetium could be produced, and insoluble oxides or other compounds could be formed. Such a reduction might be a consequence of reactions between the technetium and the organic components of the shales. The observation that all of the shales showed at least some capability of removing technetium from both of the brine groundwaters suggests that a material common to all the shales is responsible. Since all of the shales lost their ability to remove technetium from the concentrated brine after they had been heated to 250°C for an extended period (cf., Table 4.14), the organic material, which is expected to have been greatly reduced by the heating, appears to be the most likely reductant or adsorbent. Evidently the Upper Dowelltown shale contains more of this unknown component than the other shales. A companion study (Ho and Meyer, 1987) is underway to separate and identify the organic constituents in these shales. Technetium sorption measurements with these separated materials when they become available will be needed to determine whether organic compounds are responsible for the technetium sorption, and if so, to identify the compound(s).

Another possibe reason for the high technetium sorption with Upper Dowelltown shale may be the relatively high pyrite content of this shale (cf., Table 3.1). However, the current experiments were run under oxic conditions (air present), and Palmer and Meyer (1981) measured a technetium sorption ratio of only 1.6 L/kg under oxic conditions with samples of pyrite in 0.1 mol/L NaCl. This is more than two orders of magnitude lower than the sorption ratio measured with Upper Dowelltown shale from the diluted brine. This difference does not necessarily eliminate pyrite as the reason for the high sorption ratio on the Upper Dowelltown shale because the experimental conditions were not exactly

the same for the two different results. Yet another explanation may be that some components of the shale may be acting as ion exchangers under the acidic conditions found for the brine groundwaters, although sorption from the bicarbonate groundwater might not be expected if this were the case.

The shale was leached with 1 mol/L HCl to look for reduced technetium adsorbed on the shale. The leached technetium in the HCl was then subjected to valence analysis by extracting the solution with tetraphenylarsonium chloride in chloroform (Meyer, et al., 1984). This extractant removes all of the TcO_4^-, leaving reduced technetium in the solution. After 12 hours of leaching, only about 5 to 10% of the technetium present on the shales was removed, and of the amount removed all but a few percent was TcO_4^-. These operations were carried out in a controlled atmosphere of argon containing less than 1 ppm O_2. Nevertheless, the adsorbed technetium could have been reduced and remained bonded strongly to the shales. Further experimentation is required to determine whether the adsorbed technetium was actually reduced.

Technetium sorption from the concentrated brine groundwater was also studied on heated and unheated shales. The results (Table 4.14) show that the ability of the shales to sorb technetium was lost in heating. As discussed above, the organic fraction of the shales is suspected to be the most likely reductant for technetium, and loss of the organic fraction during heating is likely to have caused the loss of sorption ability. The slightly negative sorption ratios observed for the heated shales may be indicative of ion exclusion effects as was proposed for the strontium experiments.

Table 4.12. Technetium(VII) sorption on
montmorillonite and illite from concentrated and
diluted brine groundwater.[a]

Groundwater[b]	Montmorillonite Rs (L/kg)		Illite Rs (L/kg)	
	Rs	std dev	Rs	std dev
Concentrated	0.41	0.22	0.42	0.22
Intermediate	0.20	0.07	0.44	0.14
Dilute	-0.47	0.50	0.35	0.24

[a]Solid/solution ratios in preequilibration were
0.1; in final equilibration the ratios were 0.075
for concentrated and intermediate brines, and 0.10
for dilute brine. The initial Tc concentration was
1×10^{-8} mol/L at initial pH 5. The samples were
preequilibrated three times for three days each and
the final equilibration was for three days at 25°C.
The samples were separated by centrifugation at
25,000 rcf for 30 minutes.

[b]Composition of the concentrated brine is given in
Table 3.2. The intermediate brine is a 10/1 dilution
of the concentrated brine and the dilute brine is a
100/1 dilution.

Table 4.13. Technetium(VII) sorption on shale samples.[a]

Shale	Groundwater[b]	Final avg pH	Rs (L/kg) avg	Rs (L/kg) std dev
Upper Dowelltown	concentrated brine	3.68	22.9	3.1
	diluted brine	3.54	266	18.1
	bicarbonate	8.42	14.8	1.1
Pierre	concentrated brine	6.57	4.1	1.8
	diluted brine	--	3.0	0.7
	bicarbonate	8.52	1.7	0.4
Green River Formation	concentrated brine	6.98	1.6	0.6
	diluted brine	--	1.8	0.0
	bicarbonate	9.09	0.3	0.3
Nolichucky	concentrated brine	6.99	0.5	0.3
	diluted brine	--	1.2	0.3
	bicarbonate	9.61	1.3	0.3
Pumpkin Valley	concentrated brine	6.93	1.1	0.9
	diluted brine	--	0.9	0.5
	bicarbonate	9.59	1.0	1.0

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial Tc concentration 1×10^{-8} mol/L. The samples were preequilibrated three times for at least three days each and the final equilibration was for 19 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Composition of the concentrated brine is given in Table 3.2. The diluted brine is a 100/1 dilution of the concentrated brine, and the concentration of the bicarbonate solution is 0.03 mol/L.

Table 4.14. Comparison of technetium(VII) sorption on heated and unheated shales from concentrated brine groundwater.[a]

| | Heated shale | | | Unheated shale | | |
| | | Rs (L/kg) | | | Rs (L/kg) | |
Shale	final pH	avg	std dev.	final pH	avg	std dev
Upper Dowelltown	3.55	-0.9	0.0	3.68	22.9	3.1
Pierre	6.79	-0.8	0.1	6.57	4.1	1.8
Green River Formation	--	--	--	6.98	1.6	0.6
Nolichucky	6.92	-0.9	0.2	6.99	0.5	0.3
Pumpkin Valley	6.71	-1.0	0.0	6.93	1.1	0.9

[a]Solid/solution ratios were about 0.05 kg/L with heated shales and 0.10 with unheated shales. Shales were heated in air for six months at 250°C. The initial Tc concentration was 1 x 10⁻⁸ mol/L at initial pH 5. The samples were preequilibrated three times for at least three days each and the final equilibration at 25°C was 14 days for heated shale and 19 days for unheated shale. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

4.4 NEPTUNIUM

Because of limited availability of ^{235}Np, no experiments   ,   one for
neptunium sorption on montmorillonite and illite. We   . that it
would be more informative to use the limited amount of   Np for
experiments with the shales.

For most of the test conditions listed in Tables 4.15 and 4.16, sorption
of neptunium, introduced as NpO_2^+, was significant. As observed for
cesium, the sorption ratio for the dilute brine was always significantly
larger than that of the concentrated brine, which is suggestive of
sorption by an ion exchange process. However, the very high sorption
ratio for the dilute brine obtained with the Green River shale, which
has a very low clay content, suggests that other mechanisms may be
involved. Perhaps the organic material in the shales interacts with
Np(V).

A comparison between the sorption of neptunium on heated and unheated
shales from concentrated brine groundwater is summarized in Table 4.16.
The large, singly-charged NpO_2^+ ion seems to behave like Cs^+ on the
Pierre and Nolichucky shales, as slightly higher sorption occurred on
the heated shales. However, heating reduced the ability of the Pumpkin
Valley Shale to sorb neptunium, in a manner somewhat analogous to the
behavior observed for strontium and technetium. Data are lacking for
the sorption of neptunium on heated Green River Formation and on
unheated Chattanooga (Upper Dowelltown) Shales, so that comparisons
cannot be made. Further information is therefore needed for comparison
of heated and unheated samples of these two shales.

Table 4.15. Neptunium(V) sorption on shale samples.[a]

Shale	Groundwater[b]	Final avg pH	Rs (L/kg) avg	Rs (L/kg) std dev
Upper Dowelltown	concentrated brine	--	--	--
	diluted brine	--	--	--
	bicarbonate	7.79	145	8.4
Pierre	concentrated brine	6.66	151	5.5
	diluted brine	7.38	1980	216
	bicarbonate	7.67	1470	335
Green River Formation	concentrated brine	6.85	137	4.2
	diluted brine	7.78	>10000	--
	bicarbonate	8.29	2620	746
Nolichucky	concentrated brine	6.81	33.2	0.7
	diluted brine	7.88	472	27.1
	bicarbonate	8.17	368	110
Pumpkin Valley	concentrated brine	6.84	6.7	0.1
	diluted brine	7.73	59.6	2.1
	bicarbonate	8.33	42.5	0.7

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater at an initial Np(V) concentration of 5×10^{-11} mol/L. The samples were preequilibrated three times for at least three days each and the final equilibration was for 19 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Composition of the concentrated brine is given in Table 3.2. The diluted brine is a 100/1 dilution of the concentrated brine, and the concentration of the bicarbonate solution is 0.03 mol/L.

Table 4.16. Comparison of neptunium(V) sorption on heated and
unheated shales from concentrated brine groundwater.[a]

| | Heated shale | | | Unheated shale | | |
| | final pH | Rs (L/kg) | | final pH | Rs (L/kg) | |
Shale		avg	std dev.		avg	std dev
Upper Dowelltown	3.42	-1.1	0.1	--	--	--
Pierre	6.74	300	6.2	6.66	151	5.5
Green River Formation	--	--	--	6.85	137	4.2
Nolichucky	6.90	37.0	0.3	6.81	33.2	0.7
Pumpkin Valley	6.62	1.5	0.0	6.84	6.7	0.1

[a]Solid/solution ratios were about 0.05 with heated shales and 0.10
with unheated shales. The shales were heated in air for six
months at 250°C. The initial Np concentration was 5 x 10^{-11} mol/L
at an initial pH 5. The samples were preequilibrated three times for
at least three days each, and the final equilibration was for 14 days
at 25°C. The samples were separated by centrifugation at 25,000 rcf
for 90 minutes.

4.5 URANIUM

Determinations of sorption ratios for uranium on montmorillonite and illite were more complicated than for the other ions, because losses of uranium were observed from the control solutions. The losses were much larger for the 10^{-6} mol/L solutions, in some cases as much as 70%. For the 10^{-4} solutions, the losses were much lower. Losses could be caused either by sorption on the tube walls or by precipitation, and the losses appear to be a function of pH with the greatest losses around pH 6. Above and below pH 6, losses gradually decrease. Therefore, sorption ratios for monmorillonite and illite were calculated both by using the original concentration (10^{-6} mol/L) and the concentration in the control solution after three days ($\sim 7 \times 10^{-7}$ mol/L) as the term C_i in Eq. 1. The data from these studies are summarized in Table 4.17.

The results for sorption of uranium on shales are given in Tables 4.18 and 4.19 for two different initial uranium concentrations. The values of the sorption ratio were calculated assuming that the original standard concentration (10^{-4}) was equal to the term C_i in Eq. 1. The uranium was present in the form of U(VI) and added as UO_2^{2+}. For the initial uranium concentration of 10^{-4} mol/L, moderate sorption was observed for most cases; comparatively low sorption ratios (2.3 to 2.5 L/kg) were observed from 0.03 M $NaHCO_3$ for the Nolichucky, Pumpkin Valley, and Chattanooga (Upper Dowelltown) Shales. At the pH of these tests (8.40 to 9.27), the uranium is probably, at least in part, in the form of a negatively-charged carbonate complex which would not be expected to sorb strongly. To obtain an adequate understanding of the effects of speciation, these experiments should be extended by measuring sorption as a function of pH.

For the smaller concentration of 10^{-6} mol/L, the results varied significantly among the shale/groundwater combinations. Losses from the control solutions suggest that precipitation and/or sorption on the tube walls were occurring. However, the term C_i was assumed to be 10^{-6} mol/L. It is evident that the uranium/shale system is quite complicated, and further experimentation with careful control of pH is required to understand the processes involved.

In the experiments discussed above for sorption of uranium onto montmorillonite and illite, significantly larger sorption ratios were observed in most cases compared to those shown in Tables 4.18 and 4.19 for sorption onto shales in the concentrated and diluted brines. Thus, for uranium it is difficult to correlate the sorption results with the data shown in Table 3.1 for the illite content of the shales.

Table 4.17. Uranium(VI) sorption on montmorillonite and illite from concentrated and diluted brine groundwater.[a]

Groundwater	Initial U concentration[b] (mol/L)	Montmorillonite Rs (L/kg)		Illite Rs (L/kg)	
		avg	std dev	avg	std dev
Concentrated	1×10^{-6}	519	51	243	16
	$\sim 7 \times 10^{-7}$	334	33	154	11
	1×10^{-4}	142	7	24.3	1.8
Intermediate	1×10^{-6}	1830	118	673	136
	$\sim 7 \times 10^{-7}$	1190	77	430	89
	1×10^{-4}	350	21	32.6	7.5
Dilute	1×10^{-6}	>10000	--	2870	390
	$\sim 7 \times 10^{-7}$	6840	85	1655	235
	1×10^{-4}	613	145	51.5	2.8

[a]Solid/solution ratios in preequilibration were 0.025 for concentrated brine, 0.0125 for intermediate brine and 0.005 for dilute brine; in the final equilibration the ratios were 0.050 for concentrated brine, 0.025 for intermediate brine and 0.010 for dilute brine. The samples were preequilibrated three times for three days each and the final equilibration was for three days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 30 minutes.

[b]The uranium concentration decreased from 1×10^{-6} mol/L to about 7×10^{-7} mol/L soon after the solutions were prepared. The results in the 10^{-6} mol/L row were calculated assuming C_i (Eq.1) to be 10^{-6} mol/L. The results in the 7×10^{-7} mol/L row were calculated from the measured concentration of the control solutions at the end of the tests (three days).

Table 4.18. Uranium(VI) sorption on shale samples.[a]
Initial U concentration 1 x 10^{-4} mol/L.

Shale	Groundwater[b]	Final avg pH	Rs (L/kg) avg	Rs (L/kg) std dev
Upper Dowelltown	concentrated brine	3.25	6.5	0.9
	diluted brine	2.90	4.0	3.3
	bicarbonate	8.40	2.3	0.4
Pierre	concentrated brine	6.47	19.2	1.3
	diluted brine	7.75	21.1	2.5
	bicarbonate	8.58	9.5	2.6
Green River Formation	concentrated brine	6.70	10.9	0.9
	diluted brine	7.99	44.4	6.7
	bicarbonate	9.10	19.3	1.7
Nolichucky	concentrated brine	6.88	8.6	1.9
	diluted brine	7.67	6.0	1.3
	bicarbonate	9.27	2.3	0.1
Pumpkin Valley	concentrated brine	6.70	10.6	1.7
	diluted brine	7.77	182	17
	bicarbonate	9.16	2.5	0.3

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater. The samples were preequilibrated three times for at least three days each and the final equilibration was for 15 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes.

[b]Compositions of groundwaters are the same as for Table 4.15.

Table 4.19. Uranium(VI) sorption on shale samples.[a]
Initial U concentration 1 x 10⁻⁶ mol/L.

Shale	Groundwater[b]	Final avg pH	Rs (L/kg) avg	Rs (L/kg) std dev
Upper Dowelltown	concentrated brine	3.16	6.4	0.7
	diluted brine	2.80	1.9	0.4
	bicarbonate	8.63	6.0	0.7
Pierre	concentrated brine	6.45	39.0	3.1
	diluted brine	7.59	96.2	2.3
	bicarbonate	8.34	23.7	2.6
Green River Formation	concentrated brine	6.78	53.6	0.9
	diluted brine	8.01	4880	145
	bicarbonate	9.18	1042	107
Nolichucky	concentrated brine	6.83	7.3	1.3
	diluted brine	8.24	71.8	6.0
	bicarbonate	9.30	11.5	0.3
Pumpkin Valley	concentrated brine	6.80	10.4	6.4
	diluted brine	8.12	267	29.4
	bicarbonate	9.45	19.3	1.1

[a]Each sample contained approximately 0.2 g of shale and 2 mL of groundwater. The samples were preequilibrated three times for 12, 13, and 22 days, respectively, and the final equilibration was for 15 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes. Significant amounts of uranium were lost from the control solutions, possibly by precipitation.

[b]Compositions of the groundwaters are the same as for Table 4.15.

Table 4.20. Comparison of uranium(VI) sorption on heated and unheated shale samples.[a]

Shale	Groundwater[b]	Heated shale		Unheated shale	
		pH	Rs (L/kg)	pH	(L/kg)
Upper Dowelltown	conc. brine	3.61	40.6	3.16	6.4
	diluted brine	2.74	9.9	2.80	1.9
	bicarbonate	8.18	15.5	8.63	6.0
Pierre	conc. brine	6.98	70.6	6.45	39.0
	diluted brine	7.69	318	7.59	96.2
	bicarbonate	8.42	4.3	8.34	23.7
Green River Formation	conc. brine	7.13	64.7	6.78	53.6
	diluted brine	8.02	4490	8.01	4880
	bicarbonate	8.60	57.4	9.18	1042
Green River Formation (uranium conc. 1 x 10^{-4} mol/L)	conc. brine	7.24	16.0	6.70	10.9
	diluted brine	8.02	153	7.99	44.4
	bicarbonate	8.60	7.4	9.10	19.3
Nolichucky	conc. brine	6.90	35.1	6.83	7.3
	diluted brine	7.78	68.4	8.24	71.8
	bicarbonate	8.61	1.6	9.30	11.5
Pumpkin Valley	conc. brine	6.64	773	6.80	10.4
	diluted brine	7.06	2680	8.12	267
	bicarbonate	8.56	7.2	9.45	19.3

[a]Each sample contained approximately 0.2 g of shale in 4 mL of groundwater. The shales were heated for six months in air at 250°C. The initial U(VI) concentration was 1 x 10^{-6} mol/L for all tests except the second with Green River shale. The samples were preequilibrated three times for at least three days each and the final equilibration was for 14 days at 25°C. The samples were separated by centrifugation at 25,000 rcf for 90 minutes. Significant amounts of uranium were lost, possibly by precipitation, from the control solutions that initially contained 1 x 10^{-6} mol/L uranium.

[b]Groundwater compositions are those of Table 4.15.

5. CONCLUSIONS AND RECOMMENDATIONS

For cesium, there was strong sorption for practically all conditions onto the shales that contained illite or smectite. Sorption ratios were relatively low only for Green River Formation Shale, which has a low or negligible clay mineral content as reported by Lee, et al. (1987). The sorption/desorption experiments demonstrated cesium is most probably sorbed by an ion exchange mechanism. Heating the shales generally resulted in an increase in sorption ratio. Thus, insofar as the shales selected may be representative of shales to be considered for a HLW repository, cesium would be retained by these shales.

For strontium, and probably for other divalent ions with similar chemical properties such as radium, little sorption would be expected if the groundwaters are concentrated brines. The tested shales had little ability to retard strontium from the concentrated solutions; the results with the heated shales suggest that there would be even less sorption for shales that have been heated under aerobic conditions such as could occur following emplacement of nuclear waste. Strontium tends to be sorbed by many sorbents more strongly at high pH levels; thus, if the groundwaters are alkaline, there is a much greater likelihood that strontium would be retained by the shales.

Small but measurable sorption of technetium occurred on all shales studied except the Chattanooga (Upper Dowelltown) Shale, which yielded comparatively high sorption ratios for all experimental conditions. It was expected that under oxic conditions technetium would be present as the pertechnetate ion, TcO_4^-, which would sorb very little. It is possible that organic material in the shales has the ability to reduce Tc(VII) to a lower oxidation state, which may immobilize the technetium by formation of insoluble compounds such as hydrous oxides, or to sorb TcO_4^-. When the organic constituents of shales have been identified, it will be important to determine the role of the organic compounds in technetium reduction/sorption. Another possibility is that the pyrite in the Chattanooga (Upper Dowelltown) Shale contributed to the retention of technetium. Studies of technetium sorption under anoxic conditions would be very useful in measuring the shales' ability to reduce pertechnetate ion and fix the reduced technetium. Such studies might also elucidate the behavior of Np(V) and U(VI), both of which can be reduced to form relatively insoluble oxides. Thus, a primary recommendation of this study is to perform systematic experiments with reducible nuclides under anoxic conditions.

Neptunium was introduced into the groundwaters as the neptunyl ion, NpO_2^+, a large, singly-charged ion. Sorption was significant for all tested conditions. Sorption ratios were especially large for the Pierre Shale and the Green River Formation Shale. The Pierre Shale has considerable smectite which could sorb the neptunyl ion by an ion exchange mechanism. The Green River Formation Shale has a negligible clay mineral content but a high organic content. Perhaps the organic matter could act to reduce the neptunium to an insoluble oxide of a

lower valence state or affect the sorption ratio by complexation with organic ligands.

The results with uranium are indicative of a rather complex system. The key to understanding sorption of uranium is first to investigate the solution chemistry and speciation of U(VI) in the appropriate ground-water and then to conduct systematic experiments as a function of pH and other groundwater variables. Without this information, it is very difficult to interpret the results of sorption experiments with uranium.

Comparing the results of experiments with unheated and heated shales proved to be informative. Further experiments with the heated shales would be useful because only a limited range of solution compositions have been used for most of the elements tested. Also, only one method of heating has been used so far (heating in air at 250° for six months).

These experiments also have served to suggest the need for more detailed information on the organic constituents in shales. In particular, it will be important to nuclear waste repository performance to identify those organic compounds in shales which may be able to reduce polyvalent elements to insoluble compounds of lower oxidation state and to study the complexation of radionuclides by particular organic compounds, which might lead to mobilization of the nuclides in the groundwater.

More sytematic studies of groundwater parameters are needed. These include variation of ionic strength at constant pH and variation of pH at constant composition. These studies, in combination with the preliminary results presented in this report, should help elucidate the sorption mechanisms and provide better correlation of sorption with the mineral content of the clay.

In comparing the shales that we have studied so far, no one of them sorbs all of the tested elements strongly, and only one (Chattanooga Shale, Upper Dowelltown Member) exhibited any ability to sorb technetium. They all sorb cesium strongly and show fairly small sorption ratios for strontium. However, cesium and strontium are not key elements, and therefore the ability of the shales to sorb these elements is not a significant criterion for selection of a suitable shale. The Pierre Shale strongly sorbed neptunium and showed some of the higher sorption ratios for uranium and strontium; these observations may be correlated with the large percentage of smectite in this shale. The Pumpkin Valley Shale, which has the highest illite content among the tested shales, sorbed cesium very strongly, and except for technetium, sorbed the other tested elements moderately. It is interesting that the Green River Formation Shale, which according to Table 3.1 has the lowest clay content, also sorbed cesium, neptunium, and uranium with moderate to very large sorption ratios. Further studies which would attempt to correlate sorption with the mineralogy of the shales would be useful to help explain these effects.

ACKNOWLEDGMENTS

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