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CHEMISTRY DIVISION

EFFECTS OF EXPERIMENTAL PARAMETERS ON THE SORPTION
OF CESIUM, STRONTIUM, AND URANIUM FROM SALINE
GROUNDWATERS ONTO SHALES

PROGRESS REPORT

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ABSTRACT

The Sedimentary Rock Program at the Oak Ridge National Laboratory has been investigating shale to determine its potential suitability as a host rock for the disposal of high-level radioactive wastes (HLW). This report concerns an extension of the first series of experiments on the sorption properties of shales and their clay mineral components reported earlier. Studies on the sorption of cesium and strontium were carried out on samples of Chattanooga (Upper Dowelltown), Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales that had been heated to 120°C in a 0.1-mol/L NaCl solution for periods up to several months and on samples of the same shales which had been heated to 250°C in air for six months, to simulate limiting scenarios in a HLW repository. To investigate the kinetics of the sorption process in shale/groundwater systems, strontium sorption experiments were done on unheated Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales in a diluted, saline groundwater and in 0.03-mol/L NaHCO₃, for periods of 0.25 to 28 days. Cesium sorption kinetics tests were performed on the same shales in a concentrated brine for the same time periods. The effect of the water/rock (W/R) ratio on sorption for the same combinations of unheated shales, nuclides, and groundwaters used in the kinetics experiments was investigated for a range of W/R ratios of 3 to 20 mL/g. Because of the complexity of the shale/groundwater interaction, a series of tests was conducted on the effects of contact time and W/R ratio on the pH of a 0.03-mol/L NaHCO₃ simulated groundwater in contact with shales. Experiments on the solubility of uranium(VI) in a diluted brine groundwater as a function of pH and over a concentration range of 10⁻⁴ to 10⁻⁶ mol/L were carried out in preparation for further studies of U(VI) sorption. The results of these studies can now be applied to the design of more detailed experiments in support of any future national surveys to select the most suitable shales for site-specific consideration.

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1. INTRODUCTION

The Sedimentary Rock Program (SERP) at the Oak Ridge National Laboratory (ORNL) has been investigating the properties 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) and exhibit a range of chemical compositions. Thick deposits of shale can be found in almost every state of the United States, and the ages of these deposits encompass a wide range of geologic times, from the Precambrian, $(0.6 - 3.0) \times 10^9$ years B.P. (before the present) to the Miocene Epoch of the Cenozoic Era, $(1.3 - 2.5) \times 10^7$ years B.P. Sedimentary rocks frequently show large variations in chemical composition. Clastic rocks such as shales are known to manifest such variations, even on a localized scale, as can be seen qualitatively in a hand specimen of shale from the Green River Formation (Garfield County, Colorado), in which 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 geochemical conditions of the repository environment such as temperature, pressure, groundwater chemistry, pH, redox conditions, host-rock mineralogy and chemistry. The geochemical conditions associated with the shales evaluated in the SERP show a number of differences among the members of the group, and the shales themselves have been shown to have varying capabilities for the retention of radionuclides.

2. OBJECTIVE AND SCOPE

The objective of the work presented here was to acquire data for characterization of the sorption properties of shales. Extensive series of sorption tests were 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, the sorption information which was obtained can be used to plan further,

more detailed experiments in support of any future national surveys to select the most suitable shales for detailed site-specific consideration.

The first series of experiments on the sorption behavior of shales and their clay mineral components was reported by Meyer et al. (1987). In these initial studies, tests were carried out 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 if substantial quantities are present. The second series of sorption tests was made using the same elements with Chattanooga (Upper Dorelltown) 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 were 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 also was 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.

The work reported below was an extension of the investigations just described. Experiments with heated shales proved to be of sufficient interest to justify further tests. Accordingly, studies of the sorption of cesium and strontium were begun on samples of Chattanooga (Upper Dorelltown) Shale, Pierre Shale, shales of the Green River formation, and with Nolichucky and Pumpkin Valley Shales from the Conasauga Group that had been heated to 120°C in a 0.1-mol/L NaCl solution for periods up to several months, and on samples of the same shales which had been heated to 250°C in air for six months. To answer questions regarding the kinetics of the sorption process in shale/groundwater systems, strontium sorption measurements were carried out on Pierre, Green River, Nolichucky, and Pumpkin Valley Shales in a diluted brine groundwater and in 0.03-mol/L NaHCO₃ for periods of 0.25 to 28 days. Cesium sorption experiments in a concentrated brine were performed on the same shales over the same time periods. The effect of the water/rock (W/R) ratio on sorption was investigated for the same combinations of shales, nuclides, and groundwaters used in the kinetics experiments by measuring sorption ratios for a range of W/R ratios of 3 to 20. To investigate the difficulties in preparing stable solutions for the sorption studies reported for uranium in Meyer et al. (1987), the stability and solubility of uranium in aqueous solutions was investigated as a function of pH. Because of the chemical complexity of the shale/groundwater interaction, a series of tests was conducted on the effects of contact time and water/rock ratio on the pH of a bicarbonate groundwater in contact with shales.

Two important parameters influencing the retention of radionuclides are the ionic strength and chemical composition of groundwater. In all of the studies we have carried out on shales, it was important to recall that 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 which have been considered for HLW repositories, e.g., basalt, granite, and 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 this study were chosen 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 in the work reported last year in Meyer et al. (1987). 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 the preliminary tests reported earlier and those of the current experiments, it now should be possible to design more sophisticated tests on the ability of shales to retard nuclides. Such additional tests, for example, might include tests in anoxic environments, migration of elements through columns of shale, and correlations of observed chemical behavior with mineral compositions of the shales.

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 Dowlstown 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, nonfissile, 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 in 0.1-mol/L NaCl solution at 120°C for 43-85 days, or heated to 250°C in air for six months. The latter heat 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				
	Upper Dowelltown 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

^aLee, et al. (1987)^bt = trace ($\leq 2\%$), observed from thin section and electron micrographs;
nd = not detectable.

3.2 GROUNDWATER

In all of the sorption studies on shales conducted under the SERP, synthetic groundwaters were used which simulated natural shale groundwaters, ranging from saline waters of high ionic strength to those of dilute carbonate composition. 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 g/mL 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 H₂O. Sorption tests were made with this groundwater (concentrated brine) and a 100-fold dilution (diluted brine), each adjusted initially to pH 5. To simulate alkaline carbonate conditions, measurements were also made with 0.03 mol/L NaHCO₃ (bicarbonate).

Table 3.2. Composition of synthetic brine groundwater

Component	Concentration	
	(mol/L)	(g/L)
Na	2.00	46.00
K	0.0089	0.348
Mg	0.115	2.79
Ca	0.299	12.0
Sr ^a	0.014	1.20
Cl	2.86	101.29
Br	0.0089	0.71
pH adjusted to 5 with HCl		

^aIn 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 TRACER NUCLIDES

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

Radioactive concentrations of strontium and cesium were determined by measuring the gamma radiation of aliquots of traced solutions of natural strontium and cesium 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 concentrations of uranium solutions were determined by liquid scintillation alpha counting of tracer ²³³U in solutions of natural uranium. Limitations imposed by detection sensitivity and specific activity were such that concentrations of ²³³U 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
⁸⁵ Sr	64.84 d	Electron capture	514.0-keV gamma ray
¹³⁷ Cs	30.17 y	Beta decay	661.6-keV gamma ray (in decay of ^{137m} Ba)
²³³ U	1.59 x 10 ⁵ y	Alpha decay	4.824- and 4.783-keV alpha particles

^aData from Kocher (1981).

3.4 GENERAL EXPERIMENTAL PROCEDURES

Typical procedures for measurement of sorption and desorption ratios were described in the earlier report by Meyer et al. (1987), and so only an outline of the experimental methods will be included here.

Prior to the sorption experiments, each shale sample was contacted with untraced groundwater for three cycles of three days each. The previous study by Meyer et al. (1987) showed that the initial groundwater composition remained constant within $\leq 5\%$ after the third contact cycle. The phases were separated by centrifugation, followed by decantation of the groundwater. The tube containing the solid then was weighed to determine the amount of groundwater remaining with the shale, and a calculation was performed to determine the amount of traced groundwater required for the water/rock (W/R) ratio desired. All determinations of groundwater volume were based on weight. The shale and traced groundwater then were gently shaken for a period of time appropriate to the test. In the studies described below, contact times ranged from 0.25 to 35 d, and W/R ratios from about 3 to 20. At the conclusion of the test, the samples were centrifuged, and the tracer content of the final solutions was assayed. Test samples and controls (tubes containing traced groundwater but no sorbent) were prepared and measured in triplicate.

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 was moles/kg, and that in the solution was moles/L. Thus, the units of R_s were L/kg. The amount adsorbed was determined by comparison of the concentrations of the sorbate (adsorbing nuclide) in the solution before and after the test, which assumed that any reduction in concentration in the solution was a result of sorption onto the sorbent.

The sorption ratios were calculated from the equation

$$R_s = \frac{(C_i - C_f)}{C_f W} \times V_s \quad (1)$$

where C_i is the initial concentration of the sorbate in the solution, C_f is the final concentration in the solution, V_s is the initial volume of groundwater, and W is the weight of the sorbent (shale). For each of the experiments discussed below, the weights of the shale samples, the volume of the groundwater, and the contact time are given.

Desorption ratios were determined from samples that had been contacted with traced groundwater and the sorption ratios calculated. As much as possible of the groundwater was carefully decanted, after which the tube was weighed to determine the amount of solution remaining. Enough untraced groundwater then was 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 was computed as equal to the volume of the residual groundwater times the final concentration in the sorption experiment plus the amount on the solid, which was calculated from C_i and C_f as in Eq. 1. The tubes then were shaken for an appropriate length of time and the concentration of the tracer in the solution determined. The desorption ratio R_d , defined as the ratio of the radioactive concentration in the solid after desorption divided by the radioactive concentration in the groundwater after desorption C_d , may be calculated from Eq. 2,

$$R_d = \frac{C_f V_r + (C_i - C_f) V_s - C_d V_d}{C_d W}, \quad (2)$$

where C_i , C_f , V_s , and W have the same meanings as defined above for Eq. 1; V_r is the volume left in the tube after the sorption experiment and after removal of nearly all of the aqueous phase; and V_d is the volume of aqueous phase before desorption. As for R_s , the units of the desorption ratio R_d are mL/g or L/kg.

All sorption experiments were carried out at room temperature, approximately 25°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.

4. EXPERIMENTS WITH HEATED SHALES

In our previous report (Meyer et al., 1987) we discussed a limited number of tests conducted with shales that had been heated in air to 250°C for six months in an effort to acquire preliminary data on the effects of one scenario for heating shale in a HLW repository. Comparisons between sorption results on heated and unheated shales proved to be informative, but because a limited number of solution compositions were used on shales heated by only one method, it was felt that further studies on the sorption properties of heated shales would be useful.

Accordingly, it was decided to prepare five shales heated by two methods and to study the sorption of cesium and strontium on samples of these five shales for comparison with the well-characterized sorption behavior reported by Meyer et al. (1987) on unheated samples of the same shales.

4.1 PREPARATION OF HEATED SHALES

The five shales used for these experiments were heated according to two procedures. The first set of shale samples, heated in a 0.1-mol/L NaCl solution for 43-85 days at 120°C, were intended as analogs of shales in a HLW repository exposed to groundwater of relatively low ionic strength after considerable radioactive decay had occurred. The second set of samples was heated in air to 250°C for six months, intended as analogs of shales heated early in the history of a repository, when the temperature is expected to be relatively high and before any intrusion by groundwater. Details of each procedure are given below.

Fifty grams each of the <180 μ m fraction of Upper Dowlstown, Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales were added to a Teflon container containing ~200 g of a 0.1-mol/L NaCl solution adjusted to a pH of 7.5. The containers were sealed, placed in an oven at a temperature of 120°C, and shaken vigorously once a day, for 43 to 85 days. Unfortunately, some of the containers leaked at the cover seals. It was assumed that any weight loss observed was due to escape of water vapor only, and so whenever the weight loss amounted to 20 g, i.e., 10% of the weight of the NaCl solution, the affected vessel was cooled and distilled water was added to make the total solution 200 g. In Table 4.1 are summarized the treatment histories of the five shale samples processed as described. After this initial processing was complete, the shale samples were washed with distilled water and dried.

The shale samples to be heated in air were from the same starting materials as described above. In this procedure, 15 g of each of the five shale samples were weighed into porcelain crucibles, covered, and heated to consistent weight in a drying oven at 110°C. Then, as an approximation to a thermogravimetric analysis, each sample was heated stepwise to 150, 200, and 250°C in a muffle furnace. Upon reaching 250°C, the temperature was maintained at that value for six months.

Table 4.1. Treatment history of shales heated to 120°C in 0.1-mol/L NaCl solution.^a

Shale	Time at Temperature (days)	Remarks
Upper Dowltown	43	Vessel failed; lost water.
Pierre	78	Vessel failed; lost some water.
Green River Formation	63	Vessel failed; lost water.
Nolichucky	85	Recovered all of the solution.
Pumpkin Valley	85	Recovered all of the solution.

^aShale samples were 50 g of the < 180-micrometer size fraction in ~200 g of 0.1-mol/L NaCl solution, heated to 120°C for the times indicated. Data from Jacobs (1988).

The results of the stepwise heating are summarized in Table 4.2 and Fig. 4.1. The greatest weight loss at the highest temperature was observed for the Upper Dowltown Shale, while the Pierre and Green River Formation Shales exhibited a smaller, but similar, weight loss. The weights of the Nolichucky and Pumpkin Valley Shales remained essentially constant throughout the temperature range. These results correlate only qualitatively with the amounts of organic matter shown in Table 3.1. The trace of organic matter estimated in Table 3.1 for Nolichucky and Pumpkin Valley Shales is consistent with their absence of weight loss upon heating. However, the amount of organic matter shown in Table 3.1 for Upper Dowltown is slightly less than that of Green River Formation, and larger than that of the Pierre Shale. Thus, a more quantitative comparison between the data of Tables 3.1 and 4.2 does not appear possible.

Small samples of each of the shales treated by both methods were washed three times, for one day each time, and the pH and the sodium concentrations of the wash solutions were determined after each wash. After three washes the sodium concentration of the wash solutions was not significant when compared to the sodium concentration of the groundwaters used in the sorption tests to be discussed below.

A significant additional observation is that after the heat treatment at 250°C in 0.1-mol/L NaCl, the wash water for the Upper Dowltown Shale

reached a pH value of 2.63. Normally several weeks are required for groundwaters, initially adjusted to pH 5, to reach comparably acidic pH levels in contact with Upper Dowlletown Shale.

Table 4.2. Results of stepwise heating of dry shale samples in air.

Shale	Temperature (°C)	Time at Temperature (hr)	Fraction Remaining
Upper Dowlletown	110	68	0.9939
	150	48	1.0050
	200	190	1.0099
	250	4385	0.8873
Pierre	110	68	0.9616
	150	48	0.9594
	200	190	0.9435
	250	4385	0.9214
Green River Formation	110	68	0.9979
	150	48	0.9982
	200	190	0.9656
	250	4385	0.9250
Nolichucky	110	68	0.9881
	150	48	0.9866
	200	190	0.9854
	250	4385	0.9850
Pumpkin Valley	110	68	0.9893
	150	48	0.9889
	200	190	0.9884
	250	4385	0.9862

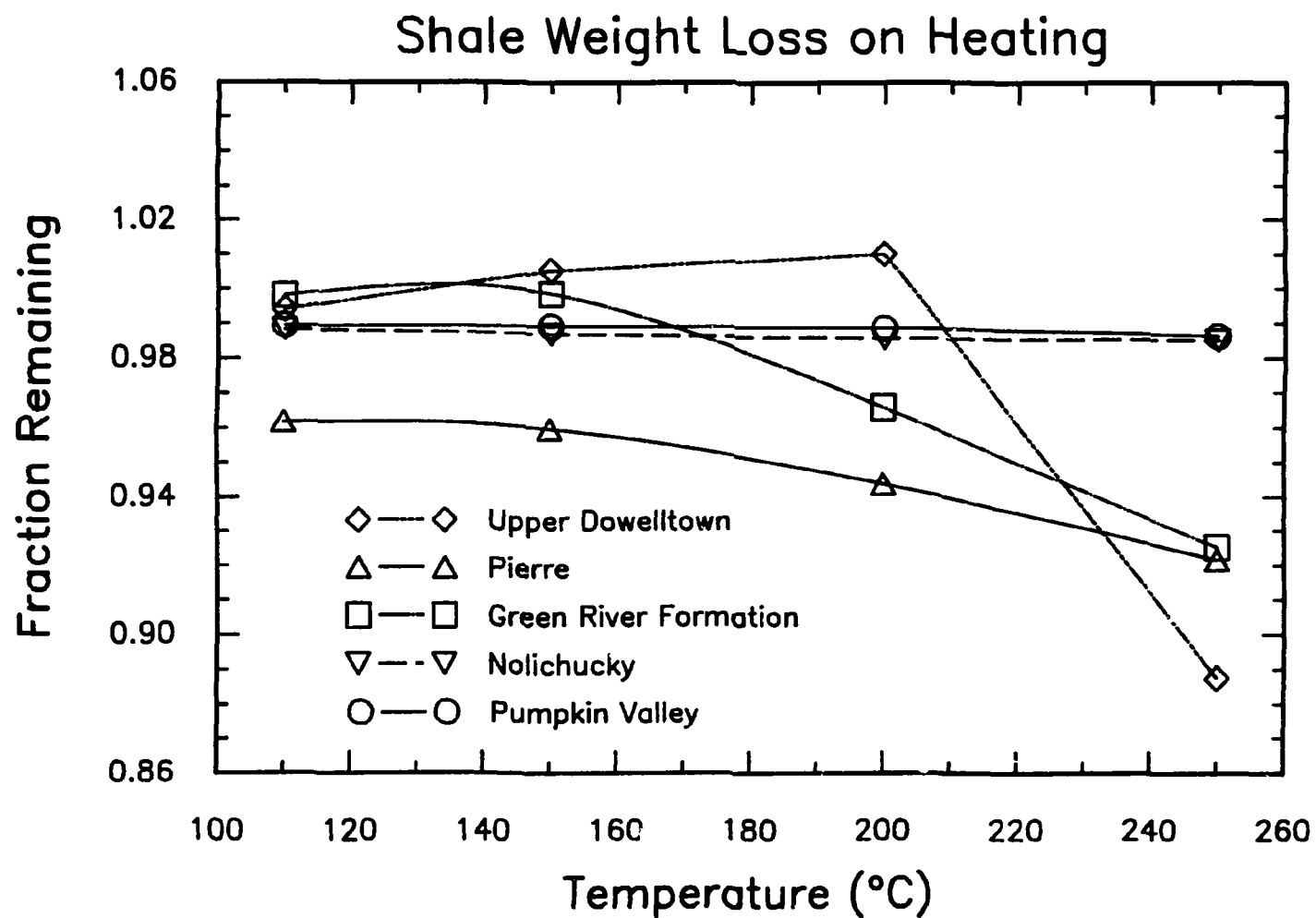


Fig. 4.1. Weight change on heating to 250°C for samples of Upper Dowlstown, Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales. Data from Table 4.2.

4.2 CESIUM SORPTION

Our preliminary survey of the sorption of cesium onto heated and unheated shales (Meyer et al., 1987) led to a number of conclusions. A simple ion exchange mechanism was suggested by the observed increase in the sorption ratio with decreasing ionic strength, i.e., with dilution of the brine, and by the absence of any systematic differences between the sorption and desorption ratios. There appeared to be no significant difference in the sorption ratios determined at initial cesium concentrations of 1×10^{-8} and 5×10^{-11} mol/L. Finally, the sorption ratios correlated with the clay mineral content of the shales.

The previous report by Meyer et al. (1987) only included data on measurements of cesium sorption from the concentrated brine groundwater onto shales heated to 250°C in air. When samples of shales heated by two methods became available, it was decided to carry out a set of measurements using the groundwater diluted 100/1 (ionic strength 0.033 mol/L), at a cesium concentration of 1×10^{-8} mol/L, and to determine both sorption and desorption ratios. Each sorption measurement used about 2 mL of groundwater and about 0.2 g of shale, for a W/R ratio of 10. Samples of shales heated by both methods were used, and each sample was contacted three times with untraced, diluted brine groundwater for at least three days each. The contact time for the sorption tests using traced groundwater was 14 days at 25°C. Following the sorption tests, desorption measurements were conducted for 14 days, as discussed above in Section 3.4.

The results are summarized in Table 4.3 and may be compared with the data reported by Meyer et al. (1987) on cesium sorption and desorption onto unheated shales in the same groundwater. Also of interest in the same report is a comparison between cesium sorption on unheated shales and on shales heated to 250°C for six months. At the time of those measurements, the amount of heated shale available was insufficient for conducting experiments with several groundwater compositions, and so the concentrated brine was used.

In the concentrated brine, Meyer et al. (1987) reported that, 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 occurred on the mineral (i.e., inorganic) components of the shales. Table 4.3 shows that, in the diluted brine, all of the cesium sorption and desorption ratios are very large, except those of the Green River Formation Shale, and subject to relatively large errors. Such large errors are to be expected, because when sorption ratios are large, only a very small fraction of the original tracer remains in the solution after sorption, and errors in measuring the concentration of tracer left in solution become significant. The results in Table 4.3 are consistent with the earlier tests on unheated shales in the diluted brine groundwater. In fact, there appears to be little difference in the sorption properties of the shales due to the heat treatment. Since the sorption and desorption ratios are large, it is not possible to make

Table 4.3. Cesium(I) sorption and desorption in diluted brine groundwater for shales heated by two methods.^a

Shale ^b	Heating Method ^c	Sorption			Desorption		
		pH	Rs (L/kg)		pH	Rd (L/kg)	
			avg	std dev		avg	std dev
D	1	2.26	9293	2282	2.25	2870	7469
P	1	7.68	>10000	---	7.66	>10000	---
G	1	7.90	189	1	7.82	197	4
N	1	7.86	>10000	---	7.79	>10000	---
V	1	6.37	>10000	---	6.34	>10000	---
D	2	2.94	6272	1835	2.90	9680	386
P	2	7.67	5979	411	7.75	6206	518
G	2	8.04	118	1	8.02	129	3
N	2	7.85	>10000	---	7.88	>10000	---
V	2	7.42	8518	3548	7.34	11889	3766

^aComposition of the concentrated brine is given in Table 3.2. The brine used here was a 100/1 dilution of the concentrated brine.

^bThe symbols for the shales are: D, Upper Dowlstown; P, Pierre; G, Green River Formation; N, Noliuchucky; and V, Pumpkin Valley. Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial cesium concentration of 1×10^{-8} mol/L. The samples of shale were contacted three times with the untraced, diluted brine groundwater for at least three days each, and the final contact time for sorption was 14 days at 25°C. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

^cHeating methods: (1) Heated at 120°C for varying times in the presence of 0.1-mol/L NaCl solution; (2) Heated for six months at 250°C in air. See text.

very accurate comparisons between them; however, because they appear to be quite similar in magnitude, there does not seem to be any identifiable irreversibility in the sorption/desorption process for these heated shales in this aqueous system. Thus, the two forms of heat treatment do not appear to impair the ability of the shales to sorb cesium.

4.3 STRONTIUM SORPTION

The earlier report by Meyer et al. (1987) showed that strontium, and probably other divalent elements with similar chemical properties such as radium, exhibited little sorption from the concentrated brine. The shales tested had little ability to retard strontium from solutions of high ionic strength, and preliminary tests with heated shales indicated that there would be even less sorption for shales heated under aerobic conditions. Strontium has a greater tendency to be sorbed as the pH increases, which suggested a greater likelihood for retention of strontium by alkaline groundwaters.

Results are presented in Table 4.4 from a series of tests designed to measure the sorption and desorption of strontium in the diluted brine groundwater for the shales heated by two methods, as for cesium sorption. A detailed comparison between the data in Table 4.4 and the earlier work by Meyer et al. (1987) shows generally good agreement with the trends observed. The sorption and desorption ratios for the heated shales are generally somewhat smaller than for the unheated shales in the same solution. This trend was noted in the earlier work using the concentrated brine and shales heated in air for six months at 250°C. There are some small, individual differences between the sorption and desorption ratios measured for the two methods of heat treatment, but no significant trend is evident. In Table 4.4 values of the desorption ratios R_d are consistently somewhat larger than the corresponding values of the sorption ratios R_s , which suggests that some of the strontium is "fixed" to the shales and is not sorbed and desorbed by an equilibrium process. Such a nonequilibrium process could prove to be an advantage, since it would work to immobilize a portion of the available strontium in the presence of a dilute groundwater.

Thus, the small differences in sorption behavior between the heated and unheated shales would not be expected to diminish significantly the ability of the shales to sorb strontium.

Table 4.4. Strontium(II) sorption and desorption in diluted brine groundwater for shales heated by two methods.^a

Shale ^b	Heating Method ^c	Sorption			Desorption		
		pH	Rs (L/kg)		pH	Rd (L/kg)	
			avg	std dev		avg	std dev
D	1	2.26	1.2	0.0	2.26	3.3	0.2
P	1	7.62	34.3	0.2	7.63	43.4	0.6
G	1	7.74	7.8	0.2	7.80	11.8	0.1
N	1	7.75	10.9	0.4	7.78	14.4	0.6
V	1	6.37	11.7	0.0	6.44	14.9	0.1
D	2	2.81	2.9	0.3	2.81	6.5	1.1
P	2	7.65	21.3	0.3	7.68	36.3	0.5
G	2	7.99	5.5	0.1	7.95	9.6	0.3
N	2	7.80	12.1	0.3	7.93	15.8	0.3
V	2	7.60	11.8	0.2	7.52	15.8	0.4

^aComposition of the concentrated brine is given in Table 3.2. The brine used here was a 100/1 dilution of the concentrated brine.

^bThe symbols for the shales are: D, Upper Dowlstown; P, Pierre; G, Green River Formation; N, Nolinucky; and V, Pumpkin Valley. Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial strontium concentration of 1×10^{-8} mol/L. The samples of shale were contacted three times with the untraced, diluted brine groundwater for at least three days each, and the final contact time for sorption was 14 days at 25°C. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

^cHeating methods: (1) Heated at 120°C for varying times in the presence of 0.1-mol/L NaCl solution; (2) Heated for six months at 250°C in air. See text.

5. EFFECT OF CONTACT TIME ON SORPTION

A series of tests was designed to give information on the effects of contact time on the values of sorption ratios. The systems studied included sorption of cesium from concentrated brine groundwater, strontium from diluted brine groundwater, and strontium from 0.03-mol/L NaHCO_3 . Previous experience (Meyer et al., 1987) had shown that these combinations of tracers and groundwaters would yield sorption ratios amenable to measurement with adequate precision. Four shales were chosen, namely, Pierre, Green River Formation, Nolichucky, and Pumpkin Valley. Upper Dowelltown Shale was omitted from the series because it was known to exhibit a significant variation in pH with time. The pH of a rock-groundwater system containing Upper Dowelltown Shale was found to show a slow change in pH during an induction period, after which it dropped dramatically. To study the effect of contact time on sorption for Upper Dowelltown Shale would require a special series of measurements over an extended period. Such measurements were precluded by the limited time and resources available.

5.1 EFFECT OF CONTACT TIME ON CESIUM SORPTION

The data obtained on the effect of contact time on the sorption of cesium onto the four unheated shales from the concentrated brine groundwater are listed in Table 5.1 and shown graphically in Fig. 5.1. Sorption ratios were determined over a range of contact times of 0.25 - 28.0 days, while most previous experiments had been contacted for 14 days, largely due to time constraints. The concentration of cesium was 1.00×10^{-8} mol/L, and the water/rock (W/R) ratio was about 10 mL/g. These data are a subset from a larger test matrix which included the W/R ratio as one of the variables, which will be discussed in Section 6.

For the Pierre Shale, sorption ratios increased during the first week, then remained constant within experimental error. The sorption ratios of the Green River Formation Shale were much smaller than those of the other shales, as was observed in a similar system for a 14-day contact time (Meyer et al., 1987); equilibrium was apparently never established, even after 28 days. The sorption ratios of the Nolichucky and Pumpkin Valley Shales, although different in their absolute values, reached a constant value after two weeks. During all of the contact times shown in Table 5.1, the value of the pH varied only slightly.

Table 5.1. Effect of contact time on sorption of cesium(I) onto four unheated shales in concentrated brine groundwater.^a

Shale	Water/Rock Ratio (mL/g)	Contact Time (d)	R _s (L/kg)	Std. Deviation (L/kg)	pH
Pierre	10.0	0.25	84.6	2.5	6.53
	9.9	1.00	90.9	1.0	6.44
	9.9	3.00	121.7	3.1	6.58
	9.9	7.00	129.7	4.1	6.60
	10.0	14.00	127.8	7.3	6.68
	10.0	28.00	128.5	1.1	6.45
Green River Formation	9.8	0.25	0.87	0.05	6.76
	9.8	1.00	0.93	0.02	6.74
	9.9	3.00	1.20	0.06	6.69
	9.6	7.00	1.13	0.19	6.88
	9.8	14.00	1.26	0.02	6.79
	10.0	28.00	1.46	0.07	6.64
Nolichucky	9.9	0.25	36.7	0.6	6.79
	9.8	1.00	40.5	0.6	6.77
	10.0	3.00	38.4	1.5	6.87
	9.9	7.00	43.6	0.6	6.75
	10.0	14.00	48.5	1.1	6.74
	9.7	28.00	47.1	2.2	6.58
Pumpkin Valley	9.7	0.25	58.6	0.3	6.70
	9.9	1.00	64.3	0.5	6.60
	9.8	3.00	63.3	1.1	6.78
	9.9	7.00	70.8	0.5	6.67
	9.8	14.00	77.3	0.6	6.61
	9.8	28.00	75.6	1.3	6.48

^aComposition of the concentrated brine is given in Table 3.2. Each sample contained approximately 0.2 g of shale and 2 mL of groundwater and an initial cesium concentration of 1×10^{-8} mol/L. The samples of shale were contacted three times with the untraced, concentrated brine groundwater for at least three days each, and the final contact times for sorption were as indicated. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

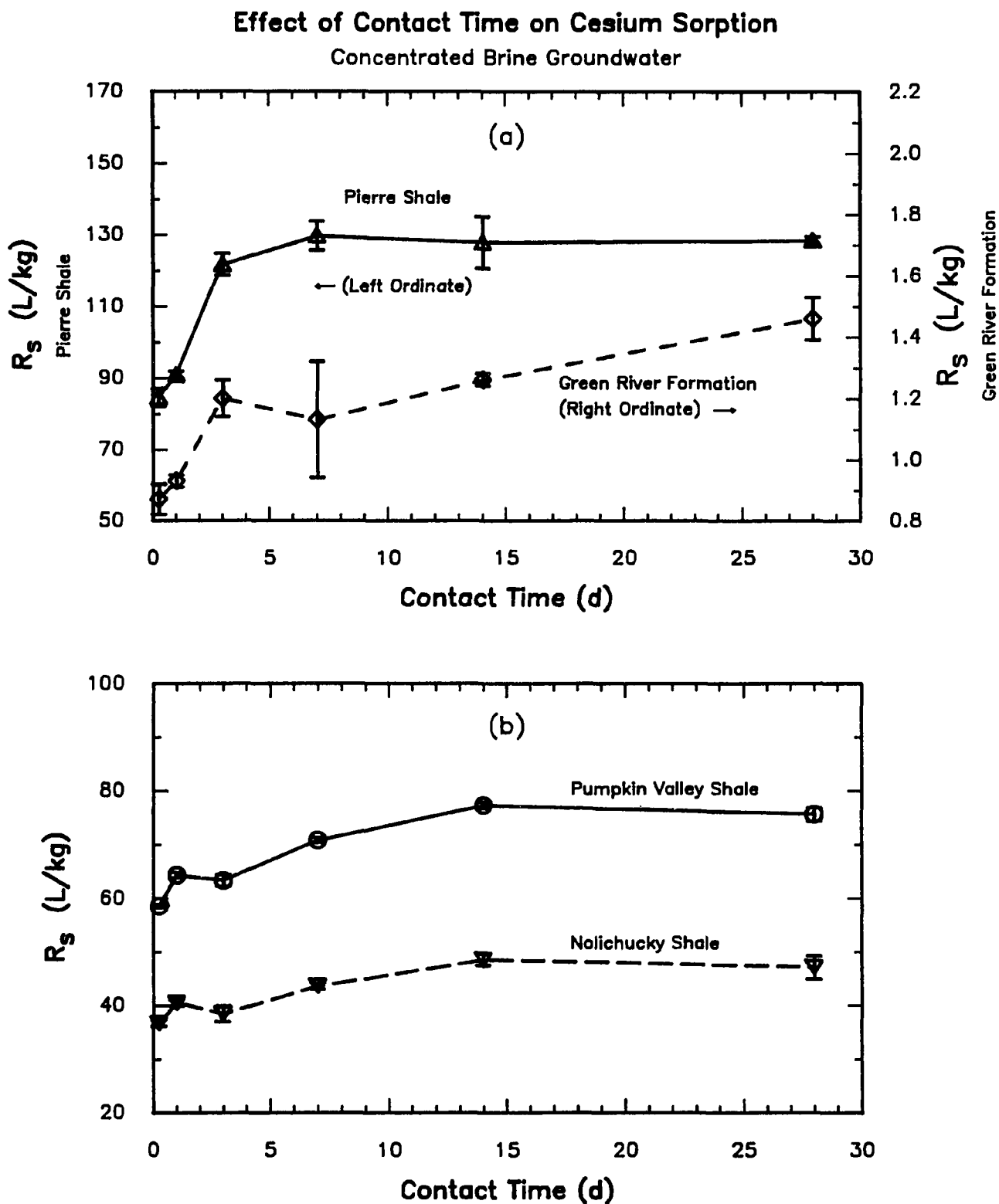


Fig. 5.1. Effect of contact time on sorption of cesium(I) onto unheated shales from concentrated brine groundwater. (a) Pierre and Green River Formation Shales, (b) Nolichucky and Pumpkin Valley Shales. Data from Table 5.1.

5.2 EFFECT OF CONTACT TIME ON STRONTIUM SORPTION

In studying the effect of contact time on the sorption of strontium(II), the four unheated shales were contacted with the diluted brine groundwater. As was done for cesium sorption, sorption ratios for strontium(II) were measured over a range of 0.25 - 28 days, with an initial strontium concentration of 1.00×10^{-8} mol/L, and a W/R ratio of about 10 mL/g. The effect of varying the W/R ratio will be addressed in Section 6. Most of the previous sorption ratios had been measured for a contact time of 14 days.

The data on the effects of contact time on strontium(II) sorption are listed in Table 5.2 and displayed graphically in Fig. 5.2. For Pierre Shale, there appears to be an early increase in the sorption ratio, followed by a gradual decline up to 28 days. However, the values of the sorption ratios at 7, 14, and 28 days are not significantly different, in view of the standard deviations of these last three determinations. The rapid initial rise implies a rapid approach to equilibrium, probably because the ground shale contained 59% smectite (Table 3.1). The slight decrease in the value of the sorption ratio following the early increase may imply slow chemical reactions. The sorption ratios for Green River Formation Shale gradually increased over the range of contact times investigated and never appeared to achieve equilibrium. Sorption ratios for the Nolichucky and Pumpkin Valley Shales increased rapidly and remained constant within the limits of experimental error.

The results for strontium sorption from 0.03-mol/L NaHCO_3 as a function of contact time were more varied, as can be seen from the data of Table 5.3 and the graphs shown in Fig. 5.3. The sorption ratio for Pierre Shale rose to a peak after three days, then decreased to a minimum value after 28 days. On the other hand, the sorption ratio for the Green River Formation Shale increased over the entire period of 0.25 - 28.0 days. The sorption ratio of the Nolichucky Shale increased to an equilibrium value at 14 days and remained constant within experimental error at 28 days. Equilibrium was established rapidly for the Pumpkin Valley Shale and remained constant from 7 to 28 days.

Table 5.2. Effect of contact time on sorption of strontium(II) onto four unheated shales in diluted brine groundwater.^a

Shale	Water/Rock Ratio (mL/g)	Contact Time (d)	Rs (L/kg)	Std. Deviation (L/kg)	pH
Pierre	10.1	0.25	31.9	0.6	7.66
	10.1	1.00	32.7	0.4	8.21
	10.0	3.00	32.5	0.4	7.63
	10.1	7.00	31.2	0.3	7.67
	9.9	14.00	30.3	1.0	7.44
	9.8	28.00	27.3	2.1	7.49
Green River Formation	9.7	0.25	2.33	0.10	8.05
	9.7	1.00	2.50	0.06	8.55
	9.5	3.00	2.83	0.07	8.04
	9.7	7.00	2.97	0.10	7.99
	9.7	14.00	3.26	0.07	8.01
	9.8	28.00	3.60	0.08	7.88
Nolichucky	10.2	0.25	8.5	0.1	7.92
	10.2	1.00	8.3	0.2	7.98
	10.1	3.00	8.9	0.2	7.94
	10.1	7.00	8.8	0.2	7.81
	10.0	14.00	8.8	0.3	7.89
	10.1	28.00	9.1	0.3	7.84
Pumpkin Valley	9.9	0.25	12.0	0.1	7.77
	9.7	1.00	11.7	0.1	7.75
	9.8	3.00	12.1	0.1	7.77
	9.7	7.00	11.7	0.9	7.70
	10.0	14.00	11.7	0.7	7.65
	9.9	28.00	11.5	0.1	7.63

^aComposition of the concentrated brine is given in Table 3.2. The brine used here was a 100/1 dilution of the concentrated brine. Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial strontium concentration of 1×10^{-8} mol/L. The samples of shale were contacted three times with the untraced, diluted brine groundwater for at least three days each, and the final contact times for sorption were as indicated. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

Effect of Contact Time on Strontium Sorption Diluted Brine Groundwater

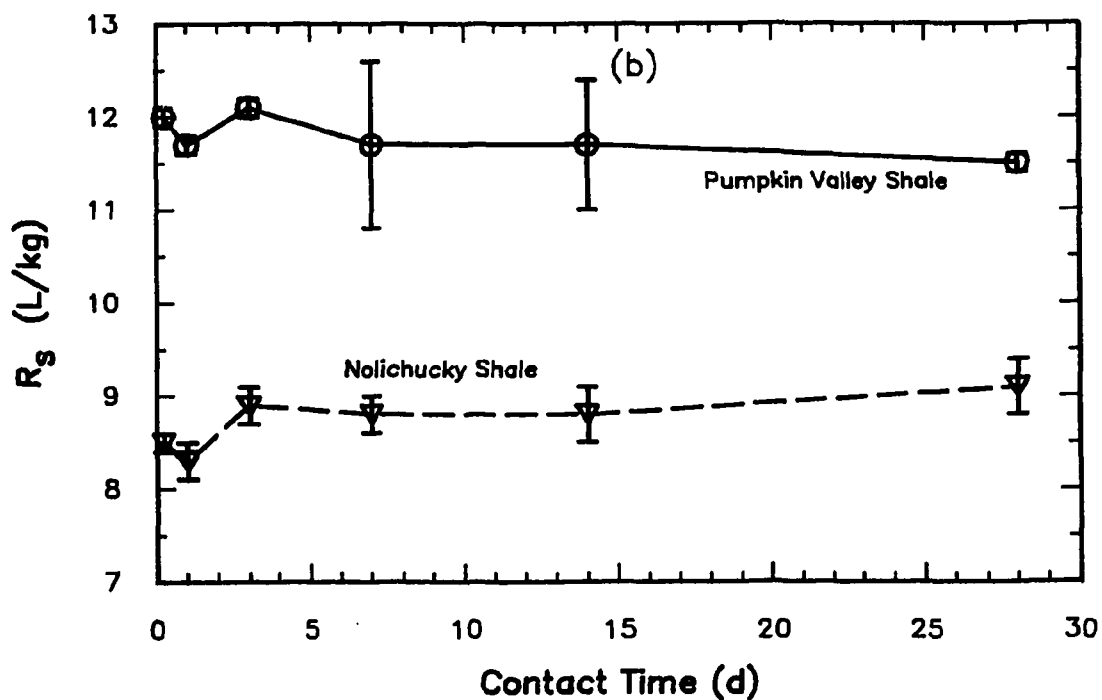
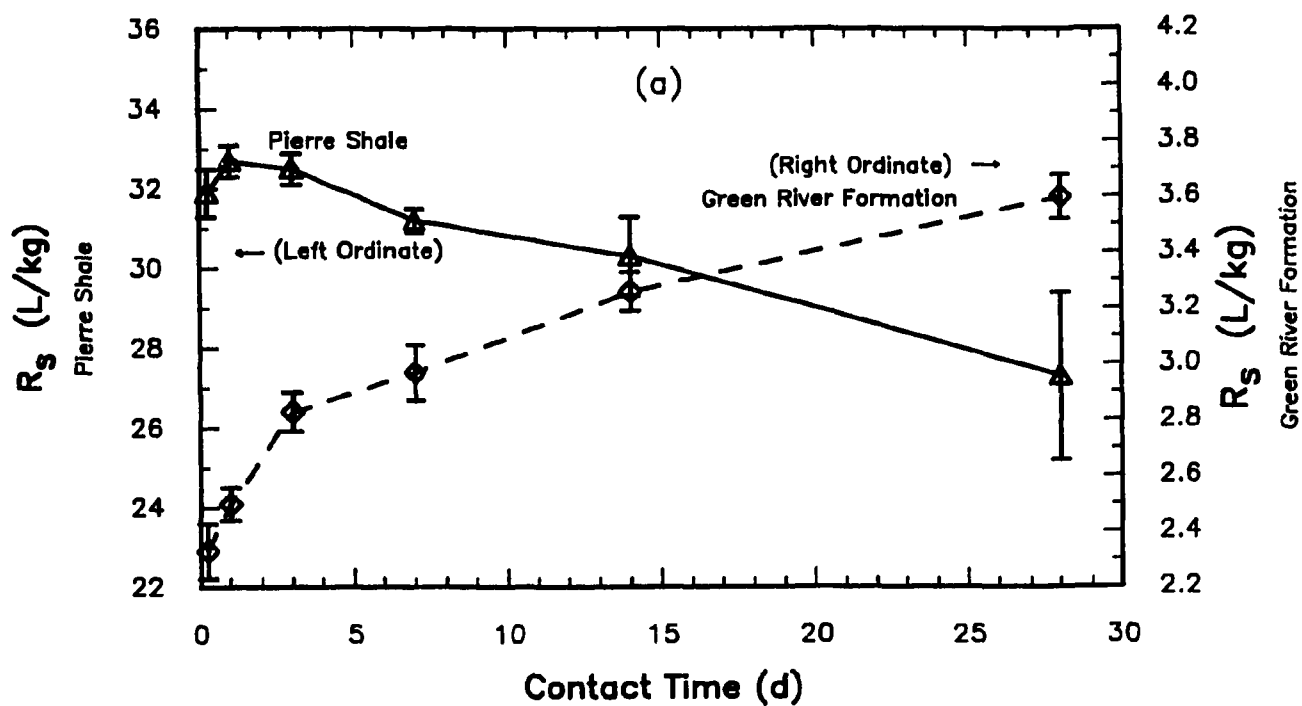


Fig. 5.2. Effect of contact time on sorption ratios for strontium(II) on unheated shales in diluted brine groundwater. (a) Pierre and Green River Formation Shales; (b) Nolichucky and Pumpkin Valley Shales. Data from Table 5.2.

Table 5.3. Effect of contact time on sorption of strontium(II) onto four unheated shales in 0.03-mol/L NaHCO_3 .^a

Shale	Water/Rock Ratio (mL/g)	Contact Time (d)	Rs (L/kg)	Std. Deviation (L/kg)	pH
Pierre	10.2	0.25	565.9	14.1	8.50
	10.2	1.00	606.5	32.6	8.59
	10.2	3.00	688.7	86.8	8.48
	10.2	7.00	510.8	34.2	8.30
	10.2	14.00	440.9	8.4	8.26
	10.1	28.00	397.3	16.3	8.06
Green River Formation	9.8	0.25	87.0	2.9	8.89
	9.8	1.00	110.3	1.6	8.86
	9.6	3.00	153.4	1.4	8.85
	9.6	7.00	215.0	6.0	8.80
	9.8	14.00	264.9	21.8	8.80
	9.7	28.00	308.3	29.1	8.72
Nolichucky	9.9	0.25	261.9	0.6	8.90
	9.8	1.00	290.0	2.9	8.95
	9.7	3.00	305.3	5.1	8.95
	10.4	7.00	319.9	9.9	8.90
	9.8	14.00	341.2	22.5	8.93
	9.9	28.00	337.1	13.3	8.95
Pumpkin Valley	10.0	0.25	212.0	2.6	8.90
	9.8	1.00	226.2	6.5	8.97
	9.8	3.00	213.4	3.3	8.91
	9.7	7.00	224.6	2.4	8.93
	9.8	14.00	224.9	1.3	8.82
	9.9	28.00	226.4	9.0	8.88

^aThe synthetic groundwater used here was 0.03-mol/L NaHCO_3 . Each sample contained approximately 0.2 g of shale and 2 mL of groundwater with an initial strontium concentration of 1×10^{-8} mol/L. The samples of shale were contacted three times with the untraced, bicarbonate groundwater for at least three days each, and the final contact times for sorption were as indicated. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

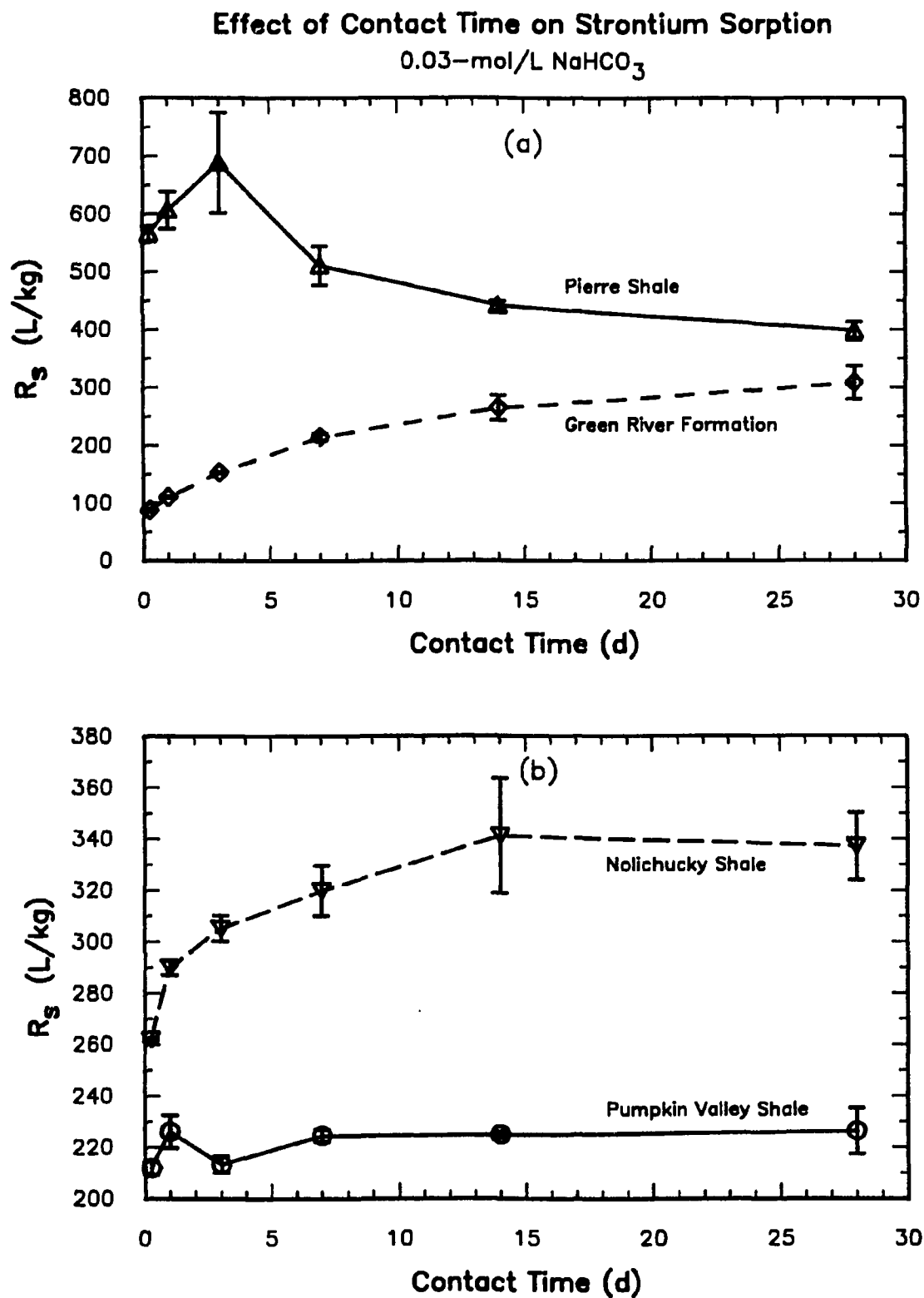


Fig. 5.3 Effect of contact time on sorption of strontium(II) onto unheated shales from 0.03-mol/L NaHCO_3 . (a) Pierre and Green River Formation Shales; (b) Nolichucky and Pumpkin Valley Shales. Data from Table 5.3.

6. EFFECTS OF THE WATER/ROCK RATIO ON SORPTION

Experiments to determine the effect of the W/R ratio on the measured sorption ratio were carried out with the measurements of sorption ratio as a function of contact time, discussed above in Section 5. Samples of Pierre, Green River Formation, Nolichucky, and Pumpkin Valley Shales were contacted for 14 days with 2 mL of traced groundwater at W/R ratios of about 3, 6, 10, and 20 mL/g. In most of our previous measurements, we used a contact time of 14 days and a W/R ratio of 10.

6.1 EFFECT OF THE WATER/ROCK RATIO ON CESIUM SORPTION

The results on the effect of the W/R ratio on the sorption ratios of cesium(I) from the concentrated brine groundwater onto the four unheated shales are listed in Table 6.1 and presented graphically in Fig. 6.1. Sorption ratios for the Pierre Shale decreased slightly as the W/R ratio increased, while sorption ratios for the Green River Formation Shale remained fairly constant. For the Nolichucky and Pumpkin Valley Shales, the sorption ratios decreased slightly overall as the W/R ratio increased, although within experimental error there was no significant change in the sorption ratio for either shale between W/R ratios of 10 and 20. In all of these experiments the pH of the groundwater remained almost constant as the W/R ratio changed by a factor of almost seven.

6.2 EFFECT OF THE WATER/ROCK RATIO ON STRONTIUM SORPTION

Data were obtained on the sorption of strontium(II) onto the four unheated shales from the diluted brine groundwater and from the 0.03-mol/L NaHCO_3 groundwater. The variation in the sorption ratios obtained in the two groundwaters as a function of the W/R ratio was quite complex and distinct from the results for cesium.

The data are summarized in Table 6.2 and plotted in Fig. 6.2 for the diluted brine groundwater. After 14 days of contact time, the strontium(II) sorption ratio for the Pierre Shale rapidly increased as the W/R ratio was increased. A practical implication of this strong, positive dependence of sorption ratio on W/R ratio is that in a repository of Pierre Shale, the W/R ratio for matrix flow, for example, might be expected to be considerably smaller than the sorption ratio measured at our usual W/R ratio of 10 mL/g. There was no significant variation in the strontium(II) sorption ratio for the Green River Formation Shale with changes in the W/R ratio. For the Nolichucky Shale, the slight initial decrease in the sorption ratio with increasing W/R ratio may be real, but the differences between the data points for W/R ratios of 10.0 and 19.8 mL/g are not significant in view of their standard deviations. Similarly, although there seems to be a declining trend in the strontium sorption ratios for Pumpkin Valley Shale as the W/R ratio increases, such a trend is not statistically significant.

Table 6.1. Effect of water/rock ratio on sorption of cesium(I) onto four unheated shales in concentrated brine groundwater.^a

Shale	Contact Time (d)	Water/Rock Ratio (mL/g)	Rs (L/kg)	Std. Deviation (L/kg)	pH
Pierre	14.0	3.1	144.7	7.3	6.65
	14.0	6.3	140.2	2.6	6.62
	14.0	10.0	127.8	7.3	6.68
	14.0	20.2	124.2	1.7	6.64
Green River Formation	14.0	3.0	1.24	0.02	6.75
	14.0	6.0	1.27	0.06	6.82
	14.0	9.8	1.26	0.02	6.79
	14.0	19.5	1.32	0.03	6.81
Nolichucky	14.0	3.0	53.3	1.9	6.71
	14.0	6.1	48.1	2.4	6.71
	14.0	10.0	48.5	1.1	6.74
	14.0	19.2	47.0	1.0	6.74
Pumpkin Valley	14.0	3.0	83.6	1.6	6.60
	14.0	6.0	80.7	2.8	6.62
	14.0	9.8	77.3	0.6	6.61
	14.0	19.6	76.6	0.4	6.59

^aComposition of the concentrated brine is given in Table 3.2. Each sample contained 2 mL of groundwater with an initial cesium concentration of 1×10^{-8} mol/L and sufficient shale to yield the water/rock ratios shown. The samples of shale were contacted three times with the untraced, concentrated brine groundwater for at least three days each, and the final contact time for sorption was 14 days at 25°C. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

Effect of Water/Rock Ratio on Cesium Sorption Concentrated Brine Groundwater

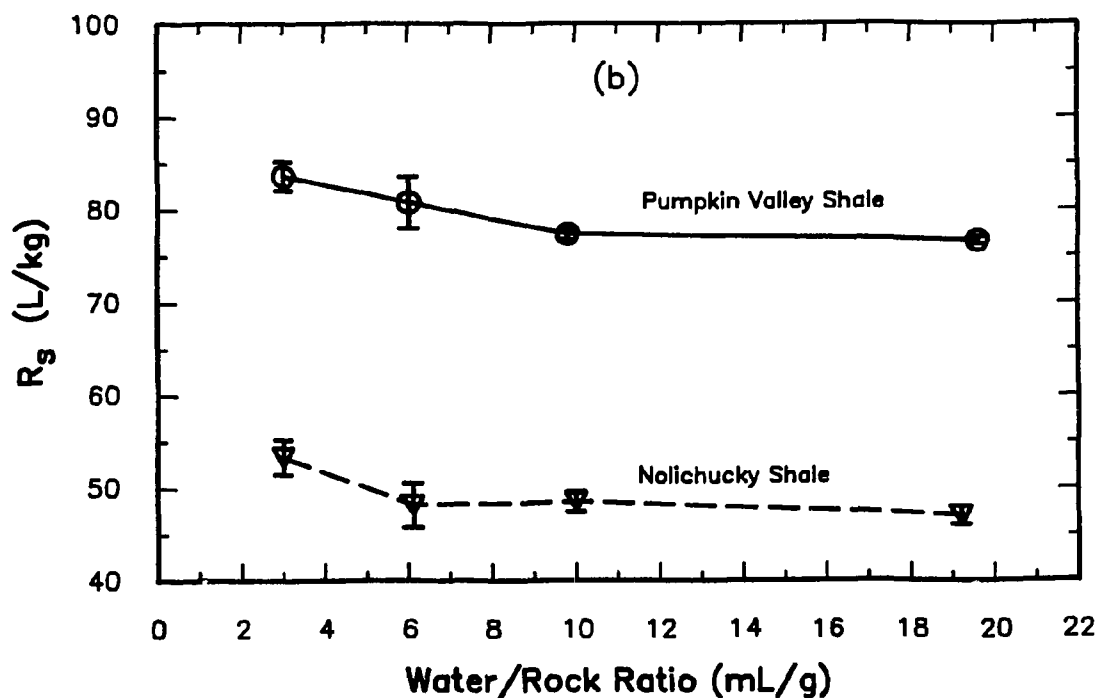
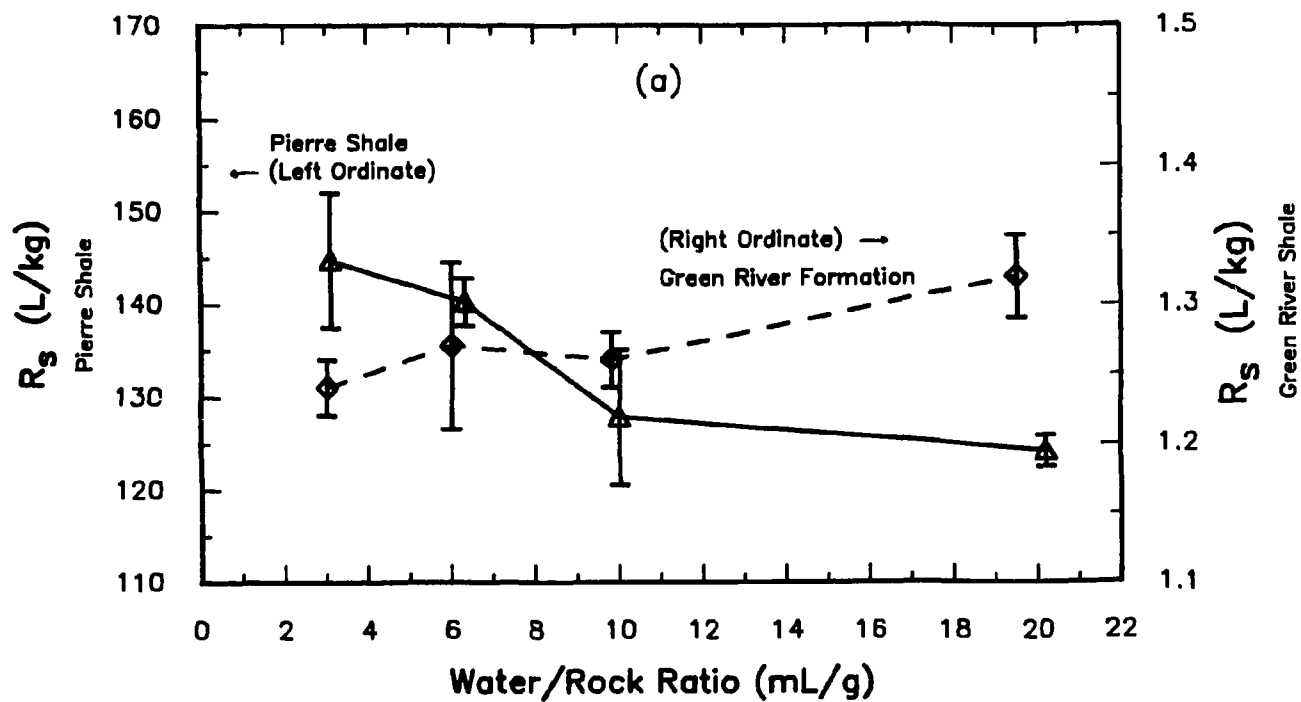


Fig. 6.1. Effect of the W/R ratio on sorption of cesium(I) onto four unheated shales in concentrated brine groundwater.
(a) Pierre and Green River Formation Shales; (b) Nolichucky and Pumpkin Valley Shales. Data from Table 6.1.

The dependence of the strontium(II) sorption ratio on the W/R ratio of the four unheated shales in the 0.03-mol/L NaHCO_3 solution showed a very different range of behavior from that just discussed for the diluted brine groundwater. The sorption ratio for Pierre Shale shows an increase with the W/R ratio that is much steeper over the range investigated than that observed above for the diluted brine groundwater system. During the measurements, the value of the pH changed overall by 0.88 unit. In contrast to the strontium sorption from the diluted brine, the sorption ratio for the Green River Formation Shale increased in the bicarbonate groundwater at a substantial rate with respect to the W/R ratio. The overall increase in the pH in this case was about 0.4 unit.

In the bicarbonate groundwater, the Nolichucky Shale was the only shale to reach a limiting value of the strontium sorption ratio, which occurred at a W/R ratio of about 10. There was a continual increase in the sorption ratio for the Pumpkin Valley Shale as the W/R ratio increased, but there was no indication that a limiting value had been reached. For both of these shales, the pH of the bicarbonate groundwater increased with the value of the W/R ratio, but the magnitudes of the pH changes were not as large as those observed for the Pierre Shale.

Sorption ratios for strontium(II) are consistently larger in the bicarbonate groundwater than in the diluted brine groundwater (see Tables 5.2, 5.3). Larger values of the sorption ratios in the bicarbonate groundwater may be a consequence of the higher pH of the 0.03-mol/L bicarbonate solution, as experience has shown that strontium is generally sorbed more strongly as the pH increases (Meyer, et al., 1987).

Table 6.2. Effect of water/rock ratio on sorption of strontium(II) onto four unheated shales in diluted brine groundwater.^a

Shale	Contact Time (d)	Water/Rock Ratio (mL/g)	Rs (L/kg)	Std. Deviation (L/kg)	pH
Pierre	14.0	3.1	7.8	0.1	7.20
	14.0	6.2	24.6	0.3	7.41
	14.0	9.9	30.3	1.0	7.44
	14.0	19.3	33.1	2.6	7.47
Green River Formation	14.0	3.0	3.20	0.04	7.98
	14.0	6.0	3.39	0.06	8.00
	14.0	9.7	3.26	0.07	8.01
	14.0	19.3	3.04	0.21	7.99
Nolichucky	14.0	3.1	9.7	0.1	7.80
	14.0	6.3	9.0	0.2	7.80
	14.0	10.0	8.8	0.3	7.89
	14.0	19.8	8.2	0.4	7.90
Pumpkin Valley	14.0	3.0	12.1	0.1	7.83
	14.0	6.1	11.7	0.3	7.72
	14.0	10.0	11.7	0.7	7.65
	14.0	19.4	11.3	1.0	7.58

^aComposition of the concentrated brine is given in Table 3.2. The brine used here was a 100/1 dilution of the concentrated brine. Each sample contained 2 mL of groundwater with an initial strontium concentration of 1×10^{-8} mol/L and sufficient shale to yield the water/rock ratios shown. The samples of shale were contacted three times with the untraced, diluted brine groundwater for at least three days each, and the final contact time for sorption was 14 days at 25°C. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

Effect of Water/Rock Ratio on Strontium Sorption
Diluted Brine Groundwater

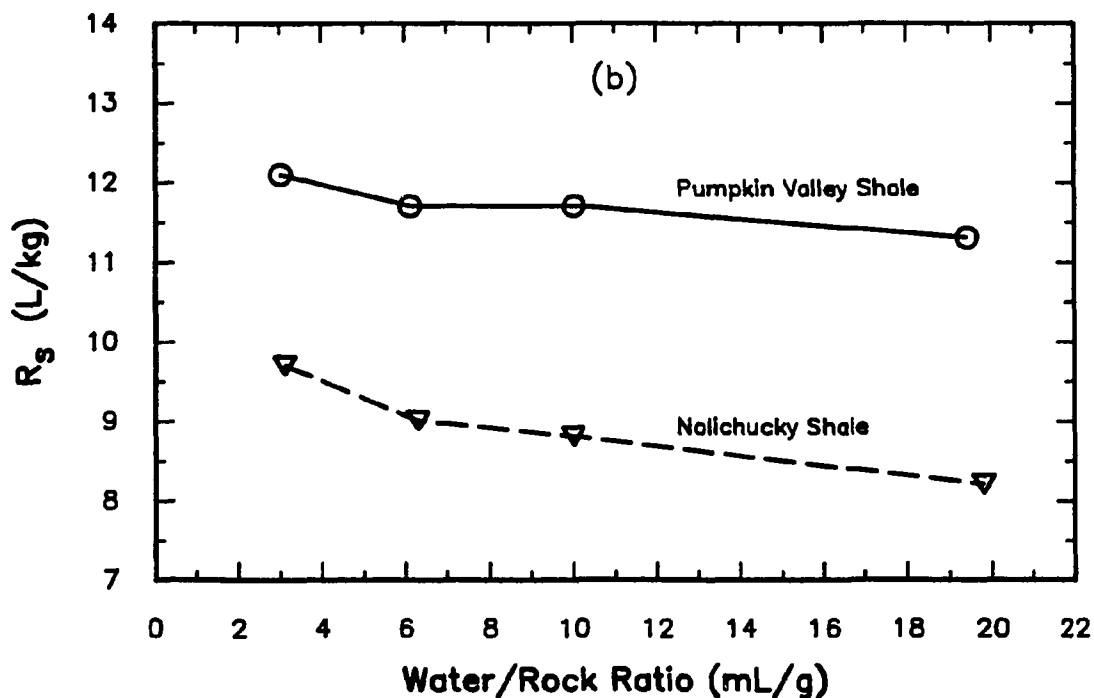
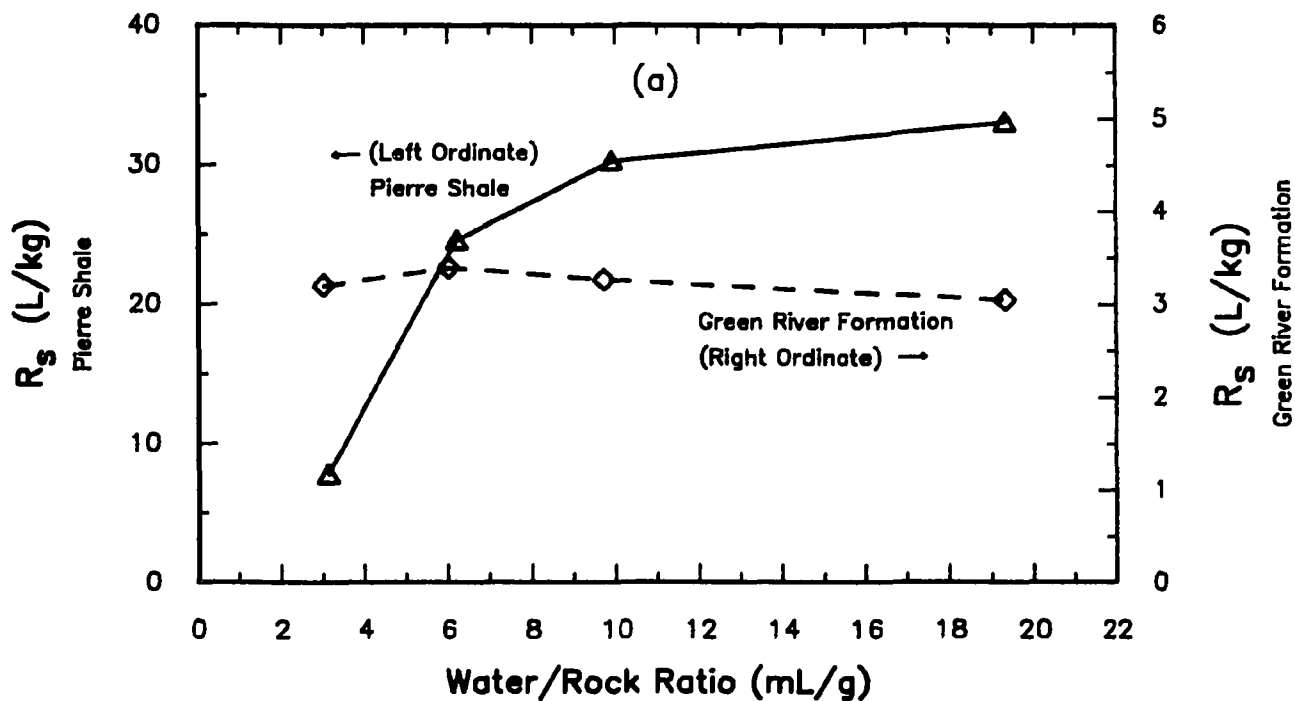


Fig. 6.2. Effect of W/R ratio on sorption of strontium(II) onto four unheated shales in diluted brine groundwater. (a) Pierre and Green River Formation Shales; (b) Nolichucky and Pumpkin Valley Shales. Data from Table 6.2.

Table 6.3. Effect of water/rock ratio on sorption of strontium(II) onto four unheated shales in 0.03-mol/L NaHCO_3 .^a

Shale	Contact Time (d)	Water/Rock Ratio (mL/g)	Rs (L/kg)	Std. Deviation (L/kg)	pH
Pierre	14.0	3.1	48.2	1.2	7.66
	14.0	6.3	289.1	31.6	8.14
	14.0	10.2	440.9	8.4	8.26
	14.0	19.9	750.6	39.4	8.54
Green River Formation	14.0	3.0	95.8	1.5	8.53
	14.0	6.0	198.8	10.5	8.68
	14.0	9.8	264.9	21.8	8.80
	14.0	19.8	320.2	30.0	8.89
Nolichucky	14.0	3.0	228.0	9.2	8.70
	14.0	6.0	281.7	2.5	8.83
	14.0	9.8	341.2	22.5	8.93
	14.0	19.1	343.5	8.9	8.91
Pumpkin Valley	14.0	3.0	168.7	6.2	8.59
	14.0	6.1	202.0	4.0	8.75
	14.0	9.8	224.9	1.3	8.82
	14.0	19.3	272.9	5.4	8.91

^aComposition of the synthetic groundwater was 0.03-mol/L NaHCO_3 . Each sample contained 2 mL of groundwater at an initial strontium concentration of 1×10^{-8} mol/L and sufficient shale to yield the water/rock ratios shown. The samples of shale were contacted three times with the untraced, bicarbonate groundwater for at least three days each, and the final contact time for sorption was 14 days at 25°C. The phases were separated by centrifugation at 10,000 rcf for 90 minutes.

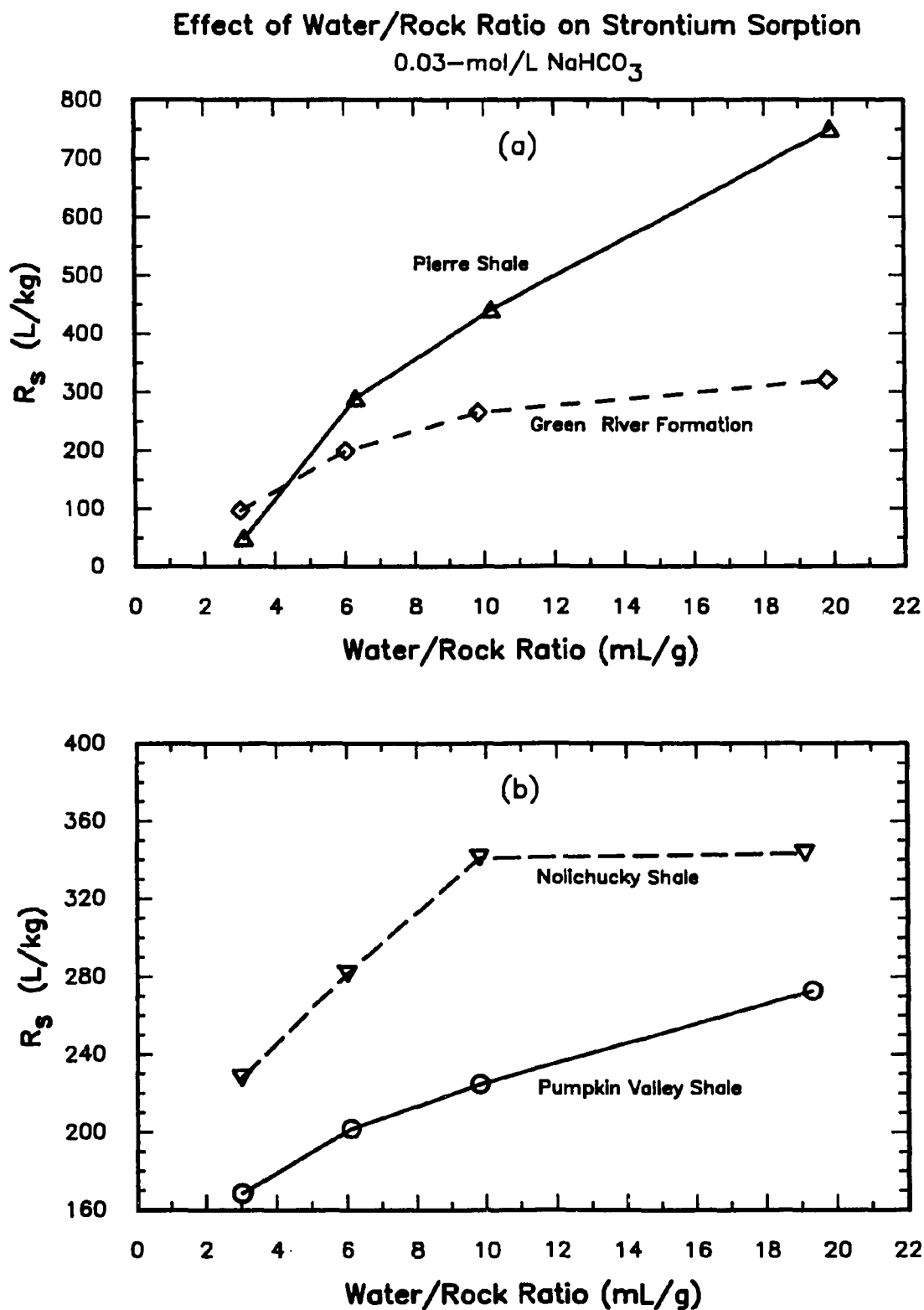


Fig. 6.3. Effect of W/R ratio on sorption of strontium(II) onto four unheated shales in 0.03-mol/L NaHCO_3 . (a) Pierre and Green River Formation Shales; (b) Nolichucky and Pumpkin Valley Shales. Data from Table 6.3.

7. EFFECTS RELATED TO THE pH

7.1. EFFECT OF CONTACT TIME ON THE pH OF SHALE-GROUNDWATER SYSTEMS

Some effects of the contact time on sorption were discussed earlier in Section 5. In Tables 5.1 - 5.3 are listed the values of pH obtained during the sorption experiments. However, in these experiments the pH was allowed to "drift," and it seemed desirable to design a test matrix in which the four unheated shales used in the tests of Sections 5 and 6 and a control sample containing no shale would be measured at each value of contact time and W/R ratio of interest. These tests used no radioactive tracer, and the parameters of contact time and W/R ratios were varied over a wide range. The results of these first tests, which have only been carried out in 0.03-mol/L NaHCO_3 so far, are given in Table 7.1.

The effect of contact time on the pH is plotted over the range of 1 - 35 days in Figs. 7.1 and 7.2 for W/R ratios of 3, 6, 10 and 20 mL/g, and for the control samples which contained groundwater only. In Fig. 7.1, it can be seen that the values of the pH as measured for Pierre Shale were relatively constant up to 35 days of contact time; however, the pH of the control samples increased about 0.26 of a pH unit, probably because there was an insufficient partial pressure of CO_2 to stabilize the pH of the control samples. The effect of the partial pressure of CO_2 on the Pierre Shale-bicarbonate system is difficult to predict, but may be small. The variation in the pH with contact time for the Green River Formation Shale was relatively small for W/R ratios of 10 or 20, but exhibited larger variations at lower W/R ratios, being largest at a W/R ratio of 3, where the system showed an initial smooth decline over the first two weeks and then remained relatively constant.

The effect of contact time on pH for the Nolichucky and Pumpkin Valley Shales is shown in Fig. 7.2. The Nolichucky Shale system, somewhat like the Green River Formation Shale, was relatively stable in pH, with negative changes, somewhat larger in magnitude, at the lowest W/R ratio of 3. The slope of the pH function for the Pumpkin Valley Shale with time ranged from slightly positive to slightly more negative at the lower W/R ratios.

Table 7.1. Effects of contact time and water/rock ratio on the pH of a 0.03-mol/L NaHCO_3 solution in contact with four unheated shales at 25°C.^a

Shale	Contact Time (d)	Values of pH for Water/Rock Ratios: ^b				
		3 mL/g	6 mL/g	10 mL/g	20 mL/g	Control
Pierre	1.0	6.87	7.55	7.90	8.25	8.62
	3.0	6.89	7.52	7.84	8.16	8.67
	7.0	6.89	7.55	7.87	8.16	8.75
	14.0	6.88	7.49	7.79	8.11	8.75
	21.0	6.86	7.42	7.71	8.02	8.83
	28.0	6.89	7.47	7.71	8.02	8.83
	35.0	6.82	7.46	7.75	8.09	8.88
Green River Formation	1.0	8.46	8.57	8.61	8.64	8.62
	3.0	8.33	8.51	8.59	8.64	8.67
	7.0	8.20	8.46	8.58	8.66	8.75
	14.0	8.07	8.36	8.52	8.63	8.75
	21.0	8.01	8.31	8.48	8.64	8.83
	28.0	8.00	8.31	8.49	8.64	8.83
	35.0	7.98	8.27	8.45	8.62	8.88
Nolichucky	1.0	8.54	8.59	8.58	8.58	8.62
	3.0	8.53	8.60	8.64	8.65	8.67
	7.0	8.48	8.56	8.62	8.68	8.75
	14.0	8.39	8.52	8.59	8.66	8.75
	21.0	8.30	8.47	8.59	8.67	8.83
	28.0	8.27	8.49	8.60	8.70	8.83
	35.0	8.28	8.50	8.62	8.72	8.88
Pumpkin Valley	1.0	8.50	8.55	8.59	8.59	8.62
	3.0	8.49	8.57	8.59	8.62	8.67
	7.0	8.45	8.52	8.54	8.63	8.75
	14.0	8.34	8.38	8.50	8.62	8.75
	21.0	8.25	8.30	8.49	8.63	8.83
	28.0	7.94	8.26	8.51	8.65	8.83
	35.0	7.99	8.15	8.54	8.69	8.88

^a Each sample contained 10 mL of the bicarbonate groundwater and sufficient shale to yield the water/rock ratios shown. The samples of shale were contacted three times with the untraced groundwater for at least three days each, prior to the final sorption contacting times.

^b Water/Rock (W/R) ratios were generally within 1-2% of the nominal values shown, except for a few cases of 3-5%. Decreases in the W/R ratios due to volume lost in the pH measurements were all in the range 1-2%, except for one determination on Pierre Shale, which began at a W/R ratio of 3.10 mL/g and showed a decrease of 8.4%, due to a leaking sample vial.

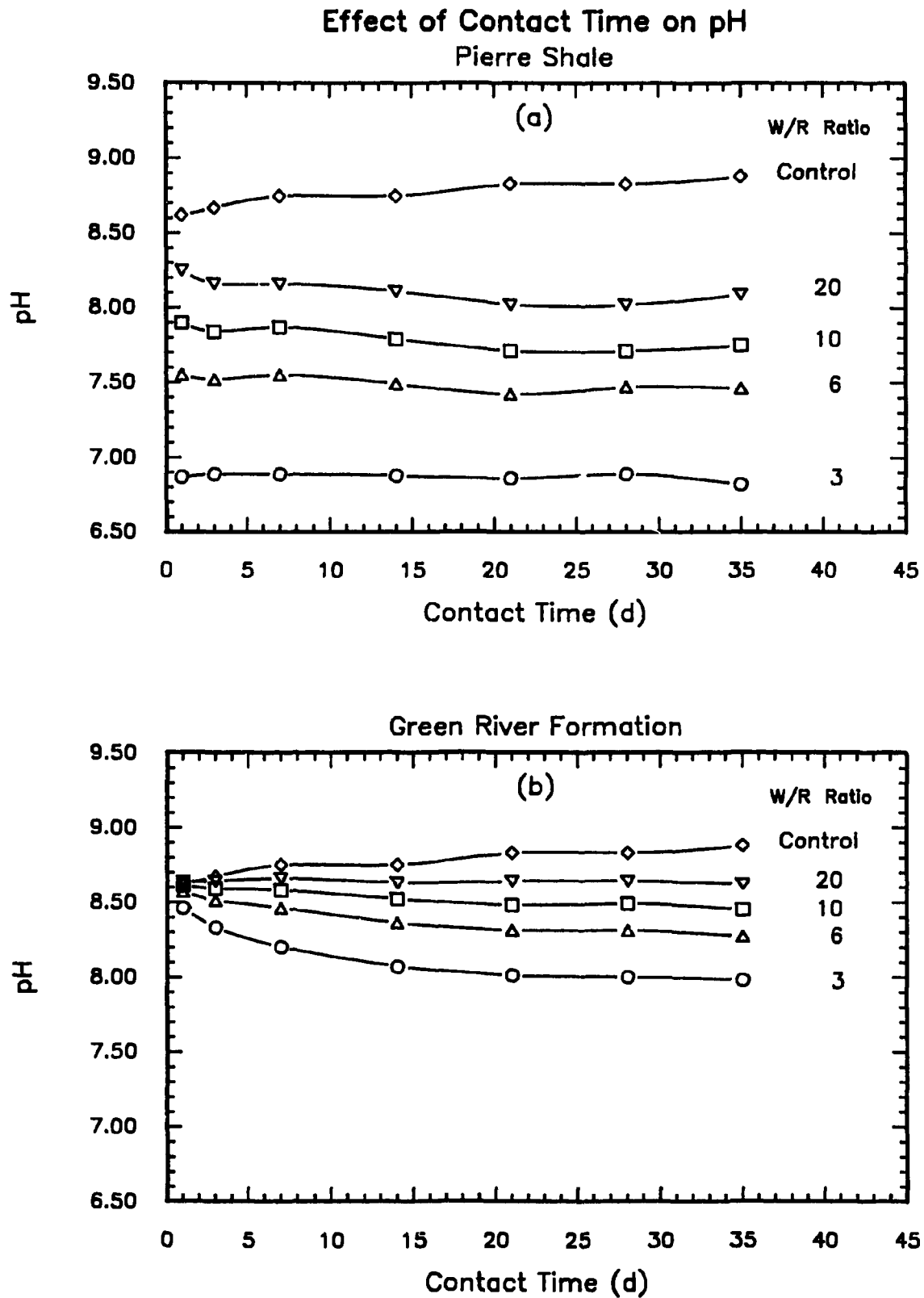


Fig. 7.1. Effect of contact time on pH, for 0.03-mol/L NaHCO_3 in contact with shales. (a) Pierre Shale; (b) Green River Formation Shale. Data from Table 7.1.

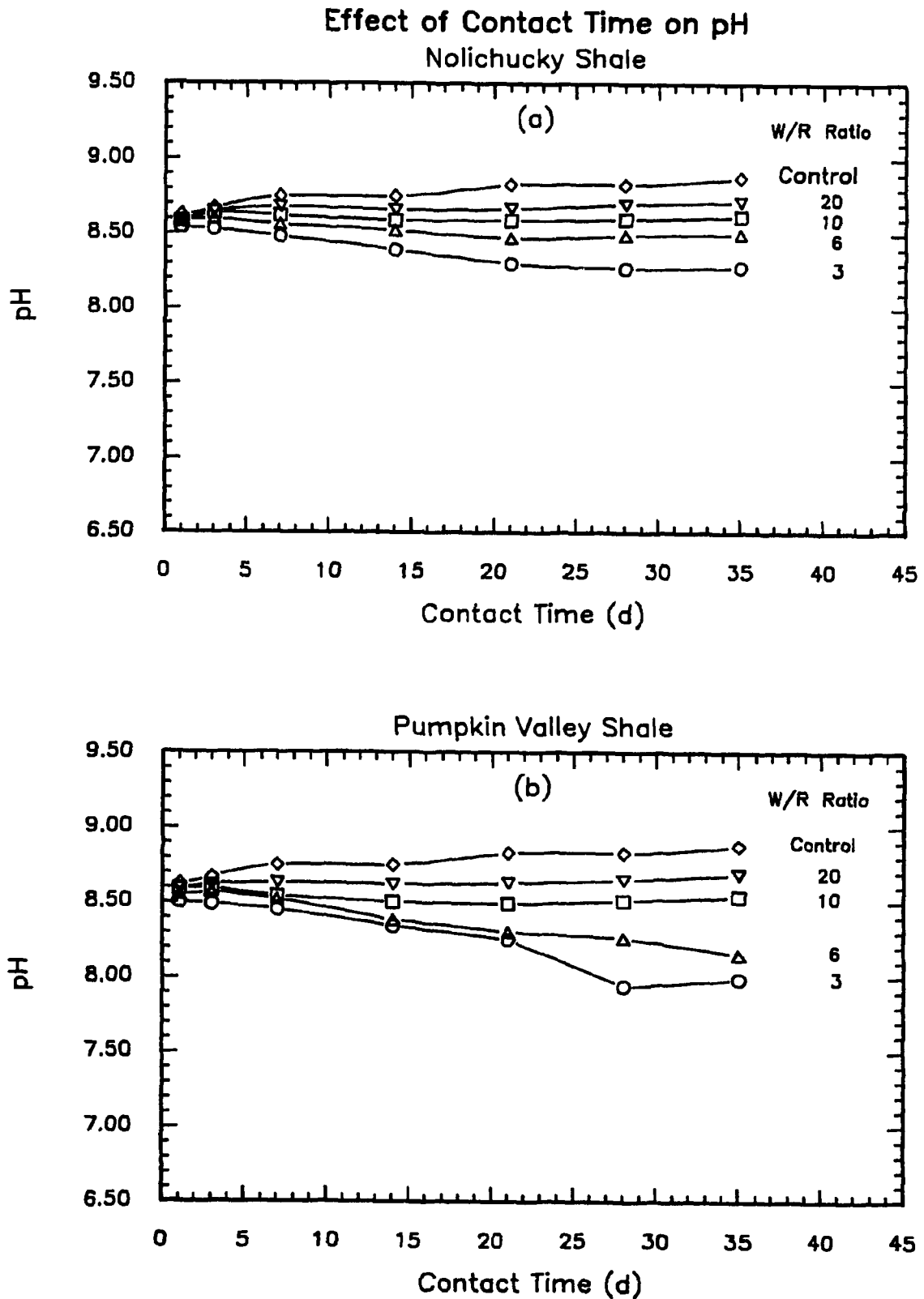


Fig. 7.2. Effect of contact time on pH, for 0.03-mol/L NaHCO_3 in contact with shales. (a) Nolichucky Shale; (b) Pumpkin Valley Shale. Data from Table 7.1.

7.2 EFFECT OF THE W/R RATIO ON THE pH OF SHALE-GROUNDWATER SYSTEMS

The data from the measurements of pH dependence on contact time and W/R ratio discussed above in Section 7.1 and shown in Table 7.1 have been plotted in Figs. 7.3 and 7.4 to show the variation in pH as the W/R ratio is increased from 3 to 20 mL/g for contact times of 1, 3, 7, 14, 21, 28, and 35 days. The dependence in Fig. 7.3(a) for Pierre Shale shows that the pH tends to increase with W/R ratio over the entire range investigated. The variation with contact time was relatively small, even at a W/R ratio of 20. The Green River Formation Shale [Fig. 7.3(b)] shows an interesting convergence of pH values, which show little variation with respect to contact time at our usual W/R ratio of 10 mL/g, and almost none at a W/R ratio of 20, the highest value of the W/R ratio investigated.

The pH dependence with respect to the W/R ratio shows an interesting similarity for the data of Nolichucky and Pumpkin Valley Shales, which are plotted in Fig. 7.4. Although both exhibit substantial variations in the pH from one contact time to another at low values of the W/R ratio, for W/R ratios of 10 to 20 the many values of the pH fall within a narrow band. Such results can be helpful in ascertaining whether variations in sorption ratios may be due to changes in the pH of a particular shale-groundwater system, if the pH dependence of the sorption ratio is known.

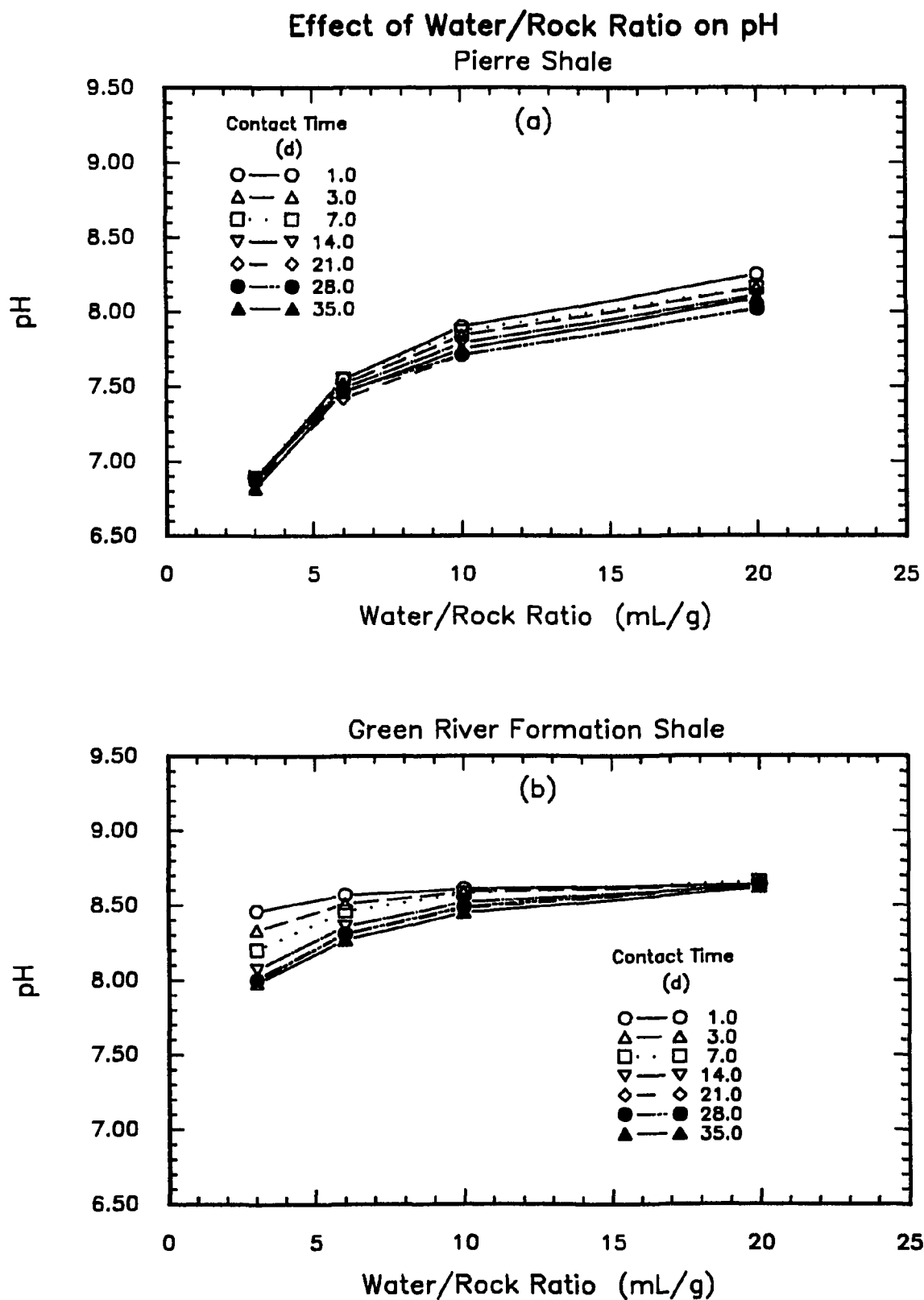


Fig. 7.3. Effect of W/R ratio on the pH of 0.03-mol/L NaHCO_3 in contact with shales. (a) Pierre Shale; (b) Green River Formation Shale. Data from Table 7.1.

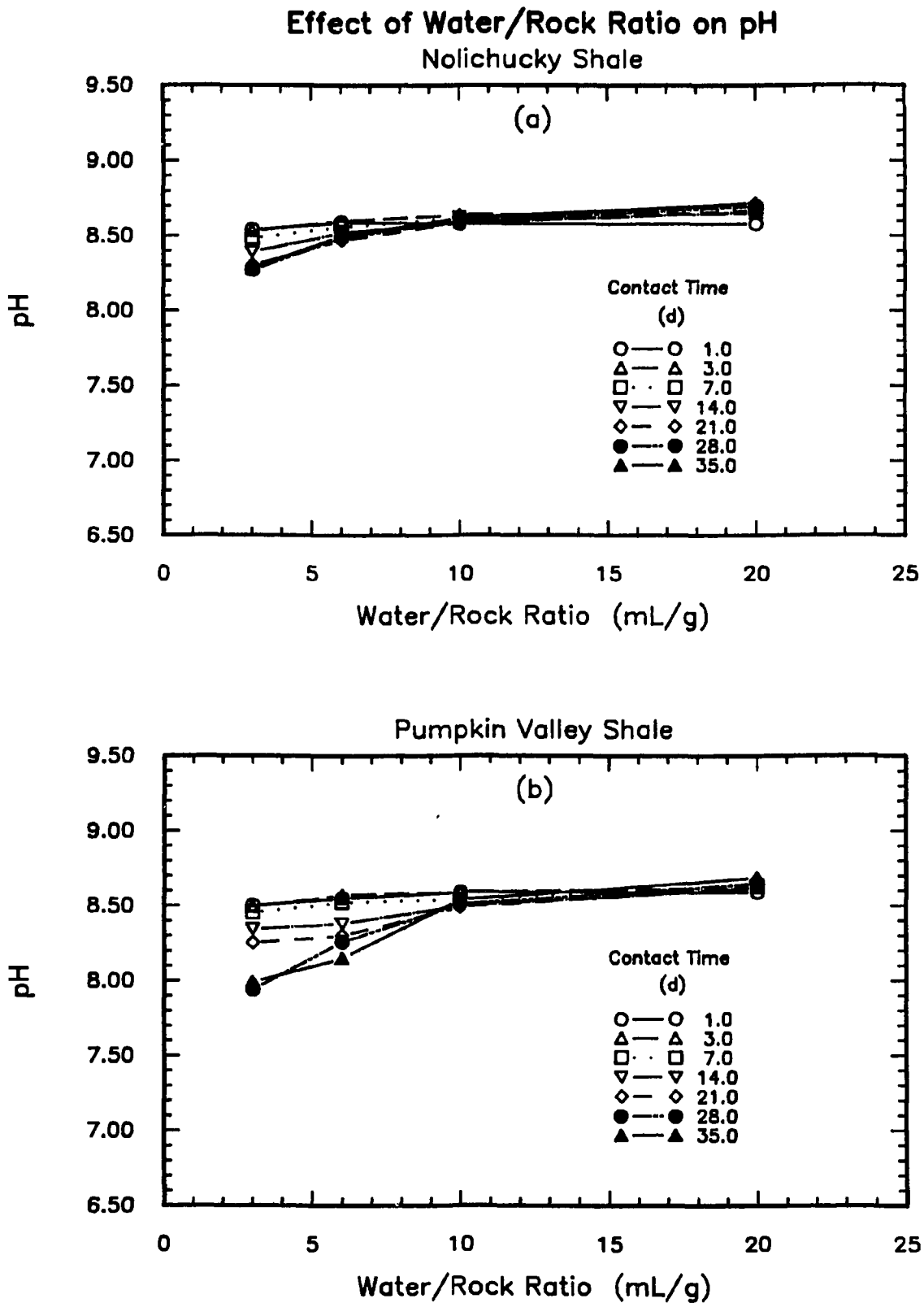


Fig. 7.4. Effect of W/R ratio on the pH of 0.03-mol/L NaHCO_3 in contact with shales. (a) Nolichucky Shale; (b) Pumpkin Valley Shale. Data from Table 7.1.

7.3 EFFECT OF pH ON THE STABILITY AND SOLUBILITY OF URANIUM

In the annual report for last year (Meyer et al., 1987), sorption results for uranium were presented which were indicative of a rather complex system. It was decided that, before undertaking any further sorption experiments on uranium, it was necessary to investigate the practical implications of the solution chemistry and speciation of U(VI) in appropriate groundwaters as a function of pH. Without such information, it would be very difficult to interpret the results of sorption experiments with uranium.

Several tests were carried out to measure the effect of pH on the stability of uranium-groundwater solutions. The pH of the solutions was varied from approximately 5.0 to 8.3, and the initial concentrations of uranium were 10^{-4} , 10^{-5} , and 10^{-6} mol/L. The results from a series of such measurements in the diluted brine groundwater are listed in Table 7.2 and plotted in Fig. 7.5. For these tests, the pH of the groundwater was initially 5 and then adjusted to higher values by small additions of NaOH, which had a negligible effect on the ionic strength of the solution. The samples were shaken gently for 7 days, as for sorption experiments. At the completion of this "equilibration" period, the sample tubes were weighed and an aliquot for counting was taken without delay and recorded as the "uncentrifuged solution." The tubes then were centrifuged for 30 min at 5000 rcf and aliquots of the groundwater were taken for counting and designated as the "centrifuged solution." This procedure was followed by another cycle of equilibration for 7 days, followed generally by the sampling and centrifugation just described. All data in Table 7.2 and Fig. 7.5 were recorded after the second equilibration.

The greatest losses of uranium were noted at all values of pH above about 5 from solutions with an initial concentration of 10^{-4} mol/L. Although the large decrease in concentration at pH 5.79 is about the same for the centrifuged and uncentrifuged samples, implying a possibly complex mechanism for removing uranium in this pH range, the large disparities between the concentrations in the centrifuged and uncentrifuged solutions at higher values of pH are clearly suggestive of the formation of a precipitate.

In the solution with an initial concentration of 10^{-5} mol/L, the losses of uranium were relatively smaller, about 12% or less. The uranium concentrations in the centrifuged and uncentrifuged solutions were about the same, which would imply that the losses are not necessarily due to precipitation.

Within experimental error, the solutions with an initial concentration of 10^{-6} mol/L showed no loss at values of pH above about 7.5; however, in the pH range of about 4.9 - 7.2, there were significant losses. No data are shown for the uncentrifuged solution at an initial concentration of 10^{-6} mol/L, since the centrifuged and uncentrifuged solutions were indistinguishable after the first equilibration, and no measurements on the uncentrifuged solution were made after the second procedure.

Table 7.2. Effect of pH on the solubility of uranium^a.

Avg. pH	U Concentration in solution (mol/L)		U Loss (%)	
	Uncentrifuged Solution	Centrifuged Solution	Uncentr. Sol'n	Centr. Sol'n
<u>Initial U Concentration = 1.00×10^{-4} mol/L:</u>				
5.06	$(9.88 \pm 0.04) \times 10^{-5}$	$(9.99 \pm 0.04) \times 10^{-5}$	1.2	0.1
5.79	$(1.15 \pm 0.68) \times 10^{-5}$	$(1.16 \pm 0.68) \times 10^{-5}$	88.5	88.4
6.76	$(8.72 \pm 0.66) \times 10^{-5}$	$(1.24 \pm 0.19) \times 10^{-5}$	12.8	87.6
7.10	$(9.37 \pm 0.18) \times 10^{-5}$	$(1.40 \pm 0.03) \times 10^{-5}$	6.3	86.0
7.83	$(9.60 \pm 0.29) \times 10^{-5}$	$(3.08 \pm 2.27) \times 10^{-5}$	4.0	69.2
<u>Initial U Concentration = 1.00×10^{-5} mol/L:</u>				
4.96	$(9.41 \pm 0.16) \times 10^{-6}$	$(9.48 \pm 0.26) \times 10^{-6}$	5.9	5.2
6.03	$(8.92 \pm 0.08) \times 10^{-6}$	$(8.89 \pm 0.08) \times 10^{-6}$	10.8	11.1
7.00	$(8.79 \pm 0.20) \times 10^{-6}$	$(8.81 \pm 0.22) \times 10^{-6}$	12.1	11.9
7.50	$(9.43 \pm 0.38) \times 10^{-6}$	$(9.41 \pm 0.38) \times 10^{-6}$	5.8	5.9
7.71	$(9.49 \pm 0.12) \times 10^{-6}$	$(9.50 \pm 0.16) \times 10^{-6}$	5.2	5.0
<u>Initial U concentration = 1.00×10^{-6} mol/L:</u>				
4.89	---	$(7.95 \pm 1.21) \times 10^{-7}$	---	20.5
6.32	---	$(6.95 \pm 0.79) \times 10^{-7}$	---	30.5
7.16	---	$(9.02 \pm 0.20) \times 10^{-7}$	---	9.8
7.58	---	$(1.03 \pm 0.01) \times 10^{-6}$	---	-3.0
8.25	---	$(1.06 \pm 0.01) \times 10^{-6}$	---	-6.0

^aAbbreviations: Centr. = centrifuged; Uncentr. = uncentrifuged;
Sol'n = solution.

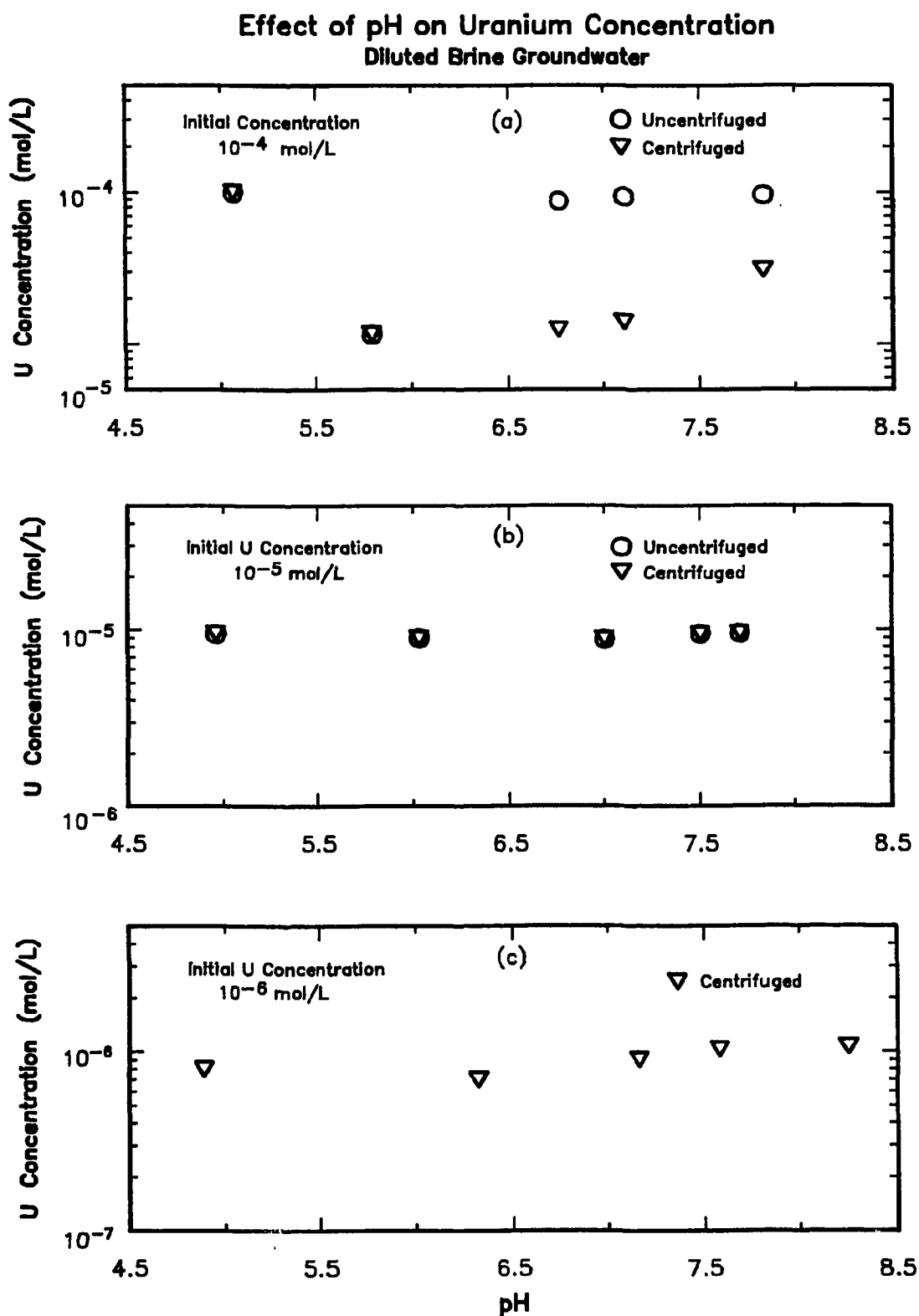


Fig. 7.5. Effect of pH on the concentration of uranium in diluted brine groundwater after two "equilibrations" of 7 days each. Initial uranium concentrations: (a) 10^{-4} , (b) 10^{-5} , (c) 10^{-6} mol/L. Data from Table 7.2.

8. CONCLUSIONS

The purpose of these studies was to acquire data for characterizing the sorption properties of shales representative of compositional extremes and to develop sufficient information for planning any future site-specific studies to determine whether a particular shale might be a suitable host for a HLW repository. Considerable effort this year was devoted to exploring the range of experimental parameters involved in performing sorption experiments on shales. These parameters included heat treatment, contact time, W/R ratio, and pH.

Sorption and desorption ratios of cesium on the heated shales were all very large, except for the case of the Green River Formation Shale, shown in Table 3.1 to be high in carbonate and organic matter, but low in smectite. From the report of Meyer et al. (1987) this might have been anticipated from earlier experiments on unheated shales in the diluted brine groundwater. Although the lowest sorption and desorption ratios were obtained for the Green River Formation shale, the ratios were still rather high (118 - 197 L/kg), and there was little difference either between sorption and desorption ratios or between methods of heat treatment.

As found earlier (Meyer et al., 1987), strontium exhibited less sorption generally than cesium. In the strontium sorption and desorption tests on shales heated by two methods, agreement with previous work was good, although in this case the sorption and desorption ratios were somewhat smaller for the heated shales than for unheated shales in the same solution. Of the heated shales, Pierre Shale sorbed strontium best, while Upper Dowlstown sorbed the least. This low retention of strontium for the Upper Dowlstown Shale is probably due to its low pH in the dilute groundwater (cf., Table 4.4). Again, there were some small, individual differences between the sorption and desorption ratios measured for the two methods of heat treatment, but no significant trend was evident.

Values of the desorption ratios were consistently somewhat larger than the corresponding values of the sorption ratios, suggesting that some of the strontium is "fixed" to the shales and is not sorbed and desorbed by an equilibrium process. Such a nonequilibrium process would work to immobilize a portion of the available strontium in the presence of a dilute groundwater. In summary, the small differences in sorption behavior between heated and unheated shales would not be expected to diminish significantly the ability of the shales to sorb strontium.

Most of the previous sorption experiments had been carried out for 14 days, generally because of time constraints. The data obtained on the effect of contact time on the sorption ratios for cesium and strontium on four unheated shales showed that, for most cases, 14 days provided adequate contact time. However, there were some exceptions. The cesium and strontium sorption ratios for the Green River Formation Shale increased, but never reached an equilibrium value in any of the groundwaters. Sorption ratios for strontium on unheated Pierre shale

showed significant decreases with time in the diluted brine and in 0.03-mol/L NaHCO_3 . In general, the shale/groundwater systems which showed a reluctance to equilibrate within the time period investigated also showed larger variations in pH during this same time interval.

The effects of the W/R ratio were investigated for the same shales, groundwaters, and radionuclides as for the tests on contact time. For most previous sorption experiments the W/R ratio was 10 mL/g, and this ratio was found to have been adequate for most circumstances. Sorption ratios for cesium on Pierre Shale decreased slightly with increasing W/R ratios in the concentrated brine, but did not change significantly above a W/R ratio of 10 mL/g. The sorption ratios for cesium on the Green River Formation Shale in the same groundwater were smaller by a factor of about 100. The sorption ratios for the Nolichucky and Pumpkin Valley Shales under the same conditions showed no significant change as the W/R ratio was increased from 10 to 20 mL/g. The pH of the concentrated brine groundwater remained remarkably constant for all four shales as the W/R ratio was changed by a factor of nearly seven.

Sorption ratios for strontium(II) onto four unheated shales in the diluted brine groundwater and in 0.03-mol/L NaHCO_3 exhibited behavior which was somewhat more complex and different from that just described for cesium. In the diluted brine, the sorption ratio for strontium(II) onto Pierre Shale showed a relatively rapid increase with increasing W/R ratio at low values of the W/R ratio, which implies that, at the low values of the W/R ratio appropriate to matrix flow, the sorption ratio might well be considerably lower than the values measured at a W/R ratio of 10 mL/g. For the Green River Formation, Nolichucky, and Pumpkin Valley Shales, variations in the sorption ratios for strontium(II) in the diluted brine ground water were relatively insignificant.

However, in the 0.03-mol/L NaHCO_3 solution, variations in the sorption ratio for strontium(II) with increases in the W/R ratio were much larger and more complex than in the diluted brine. The sorption ratio for Pierre Shale showed a large and continuous increase in the pH of 0.88 pH unit as the W/R ratio was increased from 3.1 to 19.9 mL/g. This behavior again shows the high buffering capacity of some shales. Similarly, the sorption ratio for the Green River Formation Shale increased with the W/R ratio, while the overall increase in the pH was about 0.4 unit. In this bicarbonate groundwater, the Nolichucky Shale was the only one of the shales to reach a limiting value of sorption ratio with respect to the W/R ratio, a point which was reached at about 10 mL/g. The pH also reached a limiting value and remained constant for W/R ratios of 10 to 20 mL/g, again suggesting the importance of the buffering effect of the shales on the measured sorption ratios. The Pumpkin Valley Shale showed a continual increase in the sorption of strontium(II) as the W/R ratio increased, and there was no indication that a limiting value was ever reached. The pH increased with the increase in the W/R ratio, but not quite to the extent observed, for example, in the case of the Pierre Shale.

As a means of investigating in more detail the effects of contact time and W/R ratio on the pH, a test matrix was designed to measure the variation in pH of a 0.03-mol/L NaHCO_3 solution in contact with four unheated shales, for contact times of 1 to 35 days and for W/R ratios of 3 to 20 mL/g. No radioactive tracer was employed. The pH of a set of control samples containing only 0.03-mol/L NaHCO_3 also was measured over the time span of 35 days. Over this time period, the pH of the control samples increased about 0.26 pH unit, probably because there was not a sufficient partial pressure of CO_2 present to stabilize the pH (Halperin, 1982). The buffering capacity of the shales is evident in the data of Table 7.1, because, even though the control samples manifested a shift toward more basic values, the solutions containing relatively large amounts of shale (i.e., low W/R ratios) showed a drift toward more acidic values of pH. This shift toward more acidic values was small at large (20 mL/g) W/R ratios; in the case of the Green River Formation Shale, there was no significant change at all. At low W/R ratios, alteration in the pH for Pierre shale was especially large and rapid, nearly 2 pH units in the first 24 hours.

An analysis of the variation in pH with the W/R ratio (Figs. 7.3-7.4) shows that the Pierre Shale exhibits an increase in the pH with increasing W/R ratio over the entire range of contact times investigated. However, the Green River Formation Shale shows an interesting convergence in the pH values, such that there is little variation in the pH between W/R ratios of 10 and 20 mL/g. A similar convergence in the values of the pH for the Nolichucky and Pumpkin Valley Shales is especially pronounced for all values of the contact time.

Some experiments were carried out on the practical implications of the solution chemistry of uranium, as a background to further sorption studies on uranium(VI). Solubility of uranium(VI) in the diluted brine groundwater was investigated as a function of pH for initial concentrations of 10^{-4} , 10^{-5} , and 10^{-6} mol/L. Large disparities between centrifuged and uncentrifuged samples with initial concentrations of 10^{-4} mol/L were indicative of precipitation. At the lower initial concentrations, the losses due to precipitation and other effects were much less, although in the near-neutral region of pH there were still some losses, perhaps through formation of hydrolysis products. Somewhat increased solubility at higher values of pH might be explained by hydroxycarbonate complexes. These results indicate the need for further studies on the behavior of uranium (VI) in other groundwaters, in order to help understand sorption data in this complex system.

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