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PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS: REPORT FOR APRIL 1986 - SEPTEMBER 1987

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ABSTRACT

Information that is being developed by projects within the Department of Energy (DOE) pertinent to the potential geochemical behavior of radionuclides at candidate sites for a high-level radioactive waste repository is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). During this report period, all experiments were conducted with tuff from the proposed high-level nuclear waste site at Yucca Mountain, Nevada. Batch sorption ratio determinations were conducted for strontium, cesium, uranium, and technetium onto samples of tuff using real and synthetic groundwater J-13. There were no significant differences in sorption ratios in experiments with real and synthetic groundwater. Columns 1 cm in diameter and about 5 cm long were constructed, and experiments were conducted with the objective of correlating the results of batch and the column experiments. The characteristics of the columns were tested by determination of elution curves in J-13 containing tritium and technetium as the TcO_4^- ion. For strontium and cesium, fairly good correlation between values of the sorption ratio obtained by the two methods was observed. Little or no technetium sorption was observed with either method. The elution peaks obtained with neptunium and uranium were asymmetrical and the shapes were often complex, observations which suggest irreversibilities in the sorption reaction. An experiment was performed to provide information on the compositions of the first groundwaters that will contact waste canisters in a tuff-hosted repository after very near field temperatures have cooled to below 100°C. Synthetic groundwater J-13 was slowly dripped onto a slab of tuff maintained at 95 - 100°C, and the result was a thin encrustation of solids on the slab as the water evaporated. Fresh J-13 groundwater was then allowed to contact the encrustation in a vessel maintained at 90°C. The principal result of the experiment was a significant loss of calcium and magnesium from the fresh J-13 groundwater.

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1. EXECUTIVE SUMMARY

Information that is being developed by projects within the Department of Energy (DOE) pertinent to the potential geochemical behavior of radionuclides at candidate sites for a high-level radioactive waste repository is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). During this report period all experiments dealt with the Yucca Mountain, Nevada, site. Information pertinent to this site is the responsibility of the Nevada Nuclear Waste Storage Investigations (NNWSI) managed by the Nevada Operations Office of the DOE.

The rock samples used in this study were prepared from Topopah Spring tuff, core from well USW-G1 and material from the Busted Butte outcrop. The materials had been chemically analyzed and characterized by X-ray diffraction and petrographic analysis. A major difference between the core and the outcrop is that core samples contain significant quantities of smectite (approximately 10% by weight), whereas the outcrop material from Busted Butte contains only trace amounts of smectite. No major differences in bulk or clay mineralogy were detected among the five size fractions prepared from Busted Butte outcrop material.

To evaluate the methods that NNWSI used to acquire sorption data, the first elements studied, strontium and cesium, were selected because their aqueous solution chemistry is relatively simple. Experiments described in the last report (Meyer et al. 1987) had the objective of studying the effects of pH, particle size, pretreatment of the tuff, and other factors that might influence sorption behavior. Using the knowledge gained from experience with these relatively well-behaved elements, studies were initiated with europium which has considerably more complicated behavior in groundwaters. Europium was selected because it was extensively studied by NNWSI and because it can be used as a "stand-in" for americium, an important element in high-level nuclear waste (HLW). Other important nuclides in HLW, technetium and uranium, were studied in the current report period.

In the initial stages of the work, batch sorption studies were used to determine the sorption ratio of the elements on tuff. During the current report period considerable emphasis was placed upon determination of sorption ratios by using columns of tuff. In general,

there was good agreement between sorption ratios determined by the batch method with those determined by the column method for strontium, cesium, and technetium.

For neptunium and uranium at the flow rates used in the columns, the sorption ratios calculated from the positions of the peaks of the elution curve were consistently lower than those measured by the batch method, and the elution curves were asymmetrical and usually exhibited considerable tailing. Further study is needed to understand the behavior of these elements in column experiments.

Considerable difficulty was experienced with europium. Significant losses of europium from solution with time were observed when standard solutions containing various concentrations of europium were prepared. The cause of these losses is not known, but formation of colloidal material is a possibility. A batch experiment with a solution of europium that appeared to have stabilized at a concentration of 10^{-11} mol/L gave somewhat confusing results. In a column experiment, no europium was detected in the effluent after 2400 mL had passed through a column with a void volume of only ~ 2 mL. Later it was found that all but a small fraction of the europium was on a 25- μ m teflon frit at the entrance of the column. The remaining europium was found in the first sections of the column. Thus, it is difficult to interpret the behavior of europium on the basis of sorption ratios.

A two-stage preliminary experiment was completed to provide information on the composition of the first groundwaters that would be expected to contact waste canisters in a tuff-hosted HLW repository after very near field temperatures have cooled to below 100°C. In the first stage of the experiment, synthetic groundwater was slowly evaporated to dryness at 95-100°C on a small slab of Topopah Spring tuff. A thin, irregular layer of solid material was deposited on the tuff during this stage. In the second stage of the experiment, this slab of tuff was immersed in a fresh batch of synthetic J-13 groundwater in a vessel held at 90°C. A substantial fraction of the solid material that had precipitated on the tuff during stage one redissolved into J-13 groundwater. Samples of the hot groundwater were taken at regular intervals to monitor the rate at which the precipitated material redissolved and to follow the composition of the groundwater. Neither of the alkaline earth elements magnesium and calcium, which precipitated in the first stage of the experiment, redissolved from the precipitate, and the magnesium and calcium in the J-13 groundwater used for leaching precipitated rapidly during the second stage. Most of the sodium, potassium, and chloride that precipitated in the first stage of the experiment redissolved in the leach solution during the second stage of the experiment. Thus, the effect of the precipitation/dissolution was primarily to reduce the concentration of alkaline earth elements in the water in contact with the tuff.

2. INTRODUCTION

The Oak Ridge National Laboratory (ORNL) is providing technical support to the Nuclear Regulatory Commission (NRC) in their analysis of geochemical information pertinent to radionuclide migration at candidate sites for high-level nuclear waste (HLW) repositories being developed by the Department of Energy (DOE). The purpose of the project is to supply the NRC with an independent laboratory evaluation of the assumptions, methods, and results of DOE related to the geochemical behavior of radionuclides at the candidate HLW site, Yucca Mountain, Nevada. The NRC can then utilize this information in their review and analysis of the DOE site characterization plan and may be able to resolve important technical issues before the final licensing activities.

Most DOE site projects are anticipated to rely on experimental determinations and, to a lesser extent, geochemical modeling of key parameters pertinent to radionuclide migration. Solubility controls and sorption processes are expected to make significant contributions to the performance of the geologic site component of the multiple barrier system. Therefore, this project is predominantly a laboratory effort, complemented by geochemical modeling where appropriate, to evaluate the DOE information for its uncertainty, accuracy, and/or conservatism. This project (FIN B0290) is closely integrated with another NRC project at ORNL (FIN B0287) which provides technical assistance to the NRC by reviewing and assessing available DOE information. Through project B0287, key geochemical information is identified and independent laboratory investigations are then planned and executed via project B0290. These independent laboratory analyses allow the NRC to evaluate alternative experimental methods, to identify potential systematic errors or experimental bias in the DOE methods, and to assess the impact of alternative conceptual models on the interpretation of DOE results. These projects are also related to another NRC project at ORNL (FIN B0462), which deals with subjects that have been identified through the activities under FIN B0290 and FIN B0287 as needing further research for an appropriate level of understanding of sorption, solubility, and other phenomena related to nuclide migration.

In our previous report (Meyer et al. 1987), efforts were described concerning the preparation of test materials and the establishment of basic methodologies that will be used for specific evaluations of key sorption and solubility information pertinent to the Yucca Mountain site. Information pertinent to this site is the responsibility of the Nevada Nuclear Waste Storage Investigations (NNWSI) managed by the Nevada Operations Office of the DOE. In this report, emphasis is placed upon establishment of column methodologies and comparison of sorption information obtained by us with that obtained by NNWSI.

3. MATERIALS AND METHODS

3.1 TUFF SAMPLES

The Topopah Spring tuff samples used in the tests described in this report were prepared from either Busted Butte outcrop or core, lithophysal zone, from the 1189.7 to 1190.3 ft level of well USW-G1. The tuff was ground and sieved to -70 mesh size before use. The characterization and preparation of the samples were described previously (Meyer et al. 1986, Meyer et al. 1987). Characterizations of the samples were done by semi-quantitative XRD and petrographic analyses at the University of Utah Research Institute (UURI). The analytical techniques employed and the results of the analyses are described in UURI report ESL-85026-RTR entitled "Petrographic Evaluation of Five Felsic Tuff Samples from Yucca Mountain, Nevada Test Site." The full text of this report appears as the Appendix in Meyer et al. (1987). The major results of this study are summarized below:

1. Topopah Spring tuff from Busted Butte is similar texturally to the samples of Topopah Spring tuff from borehole USW-G1, but the outcrop material and core material differ somewhat mineralogically. For example, the two core samples were found to have lower quartz/cristobalite ratios. More importantly, however, the core samples contain significant quantities of smectite (approximately 10% by weight), whereas the outcrop material from Busted Butte contains only trace amounts of smectite.

2. No major differences in bulk or clay mineralogy were detected among five size fractions prepared from Busted Butte outcrop material. In fact, the samples exhibited only one minor mineralogic variation: an apparent decrease in quartz and a concomitant increase in alkali feldspar with decreasing grain size.

3.2 GROUNDWATER

Either actual or synthetic J-13 well water was used. The composition of the well water is given in Table 3.1; the procedures used to prepare the synthetic well water were described previously (Meyer et al. 1986). All of the experiments were conducted in a controlled atmosphere glove box containing 1.5% CO₂ in air to maintain the pH of the well water at 6.8 to 7.1. The controlled atmosphere box, the CO₂ monitor, and the control system have already been described (Meyer et al. 1986).

3.3 BATCH CONTACT METHODOLOGY

The batch contact experiments described in this report were done using the methods and techniques described earlier for similar work related to basalt from the Hanford Site (Kelmers et al. 1985). In most of the

tests, 0.4 g of crushed tuff was contacted with 4 mL of traced groundwater under gentle agitation. Before contact with the traced groundwater, the tuff was usually preequilibrated three times with untraced groundwater to assure that the groundwater composition did not change during contact with the traced groundwater.

Table 3.1 Composition of synthetic J-13 well water

Constituent	Composition (mg/L)
Mg	2.1
Si	28.5
Fe	0.4
Sr	0.05
Ba	0.003
Ca	14.0
Li	0.05
K	4.9
Al	0.03
Na	51.0
F ⁻	2.2
Cl ⁻	7.5
PO ₄ ³⁻	0.12
NO ₃ ⁻	5.6
SO ₄ ²⁻	22.0
CO ₃ ²⁻	0.0
HCO ₃ ⁻	120
pH = 7.1	

3.4 COLUMN CONTACT METHODOLOGY

A number of sorption tests was made using a 1.0 cm diameter column of crushed tuff outcrop or core. A few of the early column tests were made with synthetic J-13 well water; however, we found that a small amount of material precipitated from the synthetic well water, even for times as short as a day after it had been prepared. This material apparently caused flow problems by plugging the column inlet frit. Consequently, most of the column tests were made with actual J-13 well water. Before use, the well water was filtered through a 0.2- μ m membrane and the pH was adjusted to between 6.8 and 7.0 by sparging with CO₂ or with air.

To prepare the columns, 5 g of dry crushed tuff was placed in the column and the end fittings were adjusted to compress the tuff to a bed depth of 4.7 to 4.8 cm. The void volume of the column was measured by circulating water from a weighed reservoir through the tuff until all the air was displaced and the weight of water in the reservoir stabilized. The void volume was calculated from the weight and density

of the water removed from the reservoir, adjusted for the dead volume (volume of tubing, fittings, etc.) of the system.

The packed columns were preequilibrated by pumping at least 20 bed volumes of J-13 wellwater upflow through the tuff at a flow rate of 0.20 mL/min. Atomic absorption analysis of the column effluent for the principal cations in J-13 wellwater indicated that the composition of the effluent was within 5% of the composition of the wellwater after this volume passed through the column.

With each column, the calculated void volume was checked by measuring the void volume of the system with tritiated J-13 wellwater. If the measured void volume did not agree within 10 to 15%, the column was abandoned and a new one was prepared. Examples of elution curves for tritium from improperly and properly packed columns are given in Fig. 3.1. The elution peak should be nearly symmetrical and show no signs of early breakthrough, which can cause the appearance of a "shoulder" in the elution curve. In the elution peak shown in Fig. 3.1b, the position of the peak corresponds to a void volume of 1.91 mL, and the calculated void volume was 1.81 mL. All properly packed columns gave equivalent results; periodically, columns were checked by remeasuring the void volume and technetium sorption.

The J-13 well water flow rate for most of the tests was 0.20 mL/min, equivalent to a velocity through the column of 4.2×10^{-3} cm/sec. The column length to diameter ratio was 5, and the column diameter to packing material maximum particle size ratio was 47. All of these parameters are well within the ranges recommended in Relyea (1982) for column sorption measurements.

For measurement of radionuclide sorption, a small volume of J-13 wellwater containing the radionuclide of interest was pumped into the bottom of the column, and the radionuclide was then eluted from the column by pumping J-13 wellwater upflow through the tuff. In most cases, 0.20 mL of the radionuclide spike solution was prepared, and 0.10 mL was transferred to a separate tube for addition to the column; counting standards were prepared from the remaining 0.10 mL. For elements such as uranium with potential stability problems, the spike solutions were prepared as nearly as practical (usually within 30 min) to the time of injection into the column. The column effluent was collected in appropriately sized fractions, and each fraction was analyzed for the radionuclide.

The radionuclide concentration in the effluent was plotted as a function of the effluent volume to determine the elution volume for the radionuclide, and the sorption ratio was calculated as described below. In the figures given below on column experiments, the flow rates are also plotted vs effluent volume. Occasionally, the flow rate decreased sharply and then returned to normal, cf. Fig. 5.2. This effect was probably due to a temporary blockage of flow somewhere in the system.

For a column of given length operated at a given flow rate, the elution

Fig. 3.1 Elution of tritium in synthetic J-13 groundwater from column of Busted Butte outcrop. The flow rate was 0.2 mL/min. (a) The elution curve is highly asymmetrical because of poor packing. (b) The elution curve is symmetrical.

volume or the volume required to transport a radionuclide through the column is inversely proportional to the transport velocity. The elution volume for groundwater or an unretarded radionuclide is equal to the void volume of the column. The method used to calculate the value of the sorption ratio from the shape of the elution curve is shown in Eqs. 1 to 6. If the elution curve shows a peak which is nearly symmetrical, the position of the top of the peak may be used for the radionuclide elution volume, V_r . Many of the peaks we have obtained are not symmetrical; under these conditions, the centroid of the peak (the volume where 50% of the tracer is eluted) is probably a better indication of V_r (Relyea 1982). Sorption ratios calculated in this report were computed from the centroid unless otherwise stated.

$$R_f = S_p/S_r \quad (1)$$

$$= V_r/V_p = 1 + \frac{pR_s}{e} \quad (2)$$

$$e = V_p/V_b \quad (3)$$

$$p = W/V_b \quad (4)$$

$$e/p = V_p/W \quad (5)$$

$$R_s = \frac{V_r - V_p}{W} \quad (6)$$

where R_f = retardation factor
 S_p = groundwater velocity
 S_r = radionuclide velocity
 V_r = radionuclide elution volume, mL
 V_p = void volume or pore volume, mL
 p = bulk density of tuff, g/mL
 R_s = sorption ratio, mL/g or L/kg
 e = porosity of tuff
 V_b = bed volume, mL
 W = weight of tuff, g

4. PUBLISHED INFORMATION ON SORPTION ONTO YUCCA MOUNTAIN TUFF

A great deal of information has been obtained by NNWSI concerning sorption of radionuclides onto Yucca Mountain tuff. These data are described in a series of quarterly progress reports (e.g., Ogard and Vaniman 1985) and in topical and summary reports (e.g., Daniels et al. 1982). Daniels et al. (1982) provide a summary and tabulation of sorption data obtained prior to 1982. A general review and tabulation of Yucca Mountain site data is given by Tien et al. (1985). Sorption data are also tabulated and discussed in the Environmental Assessment (EA) for the Yucca Mountain Site (DOE 1986).

In Table 4.1 average values of the sorption ratio published in the EA for Yucca Mountain site are shown for Sr(II), Cs(I), Eu(III), Np(V), U(VI), and Tc(VII), the elements studied in this report period. These data are given for various depths in the Topopah Spring Member, which contains the recommended repository horizon (DOE 1986). Considerable data are also given by NNWSI for other types of tuff located in strata below the Topopah Spring tuff. Data from these strata are important because the flow path of the water from the repository horizon could include these strata. Only NNWSI data relevant to the Topopah Spring tuff are briefly summarized and discussed here. If samples of other tuffs are investigated, then the sorption data for them will be summarized and discussed as appropriate.

Table 4.1 Sorption of Cs(I), Sr(II), Eu(III), Np(V), U(VI), and Tc(VII) onto Topopah Spring Tuff (DOE 1986)

NNWSI Sample Designation	Depth (ft)	Sorption Ratio (L/kg)					
		Cs(I)	Sr(II)	Eu(III)	Np(IV)	U(VI)	Tc(VII)
YM-22	848	290 ±30	53 ±4	1390 ±110	7.0 ±1.0	1.8 ±0.2	0.3 ±0.14
GU3-1203	1203	350 ±30	42 ±1	190 ±2	2.7 ±0.1	0 -	0 -
G1-1292	1292	430 ±28	200 ±6	140 ±14	-	-	-
GU3-1301	1301	160 ±40	28 ±4	45 ±12	5.0 ±0.1	0 -	0.03 ±0.001
YM-30	1264	855 ±5	260 80	160,000 ±50,000	-	-	-
JA-18	1420	16,000 ±1,000	17,000 ±3,000	1,400 ±200	-	2.5 ±0.4	-

Unless otherwise noted, J-13 well water was used in the NNWSI determinations, and the experiments were conducted at room temperature under oxic conditions. Little information is given in NNWSI reports on the final pH of the well water. Apparently, for most, if not all, of these determinations, no attempt was made to control the atmosphere above the test samples, although in later experiments cited by Tien et al. (1985, p. 112) the atmosphere was controlled. If there is no control of CO₂ over the experiment, there will be a loss of CO₂ from the well water with a consequent rise in pH.

For cesium, the values of the sorption ratio in Table 4.1 range from 160 to 855 L/kg for the first five samples listed; for the last sample, JA-18, the much larger value 16,000 L/kg was observed. Similarly for strontium, the range in sorption ratios was 28 to 260 L/kg for the first five samples, and for sample JA-18 a value 17,000 L/kg was observed. Sample YM-30 has somewhat higher values for strontium and cesium than those of the first four samples and a much higher value for europium. For neptunium, low values of the sorption ratio are reported for the three tested samples. For uranium and technetium all values are very small. Mineralogical descriptions of four of these samples are given in Daniels et al. (1982). Their composition, as determined by X-ray diffraction analysis with respect to major minerals, is given in Table 4.2.

Table 4.2 Major mineralogy of tuff samples (Daniels et al. 1982)

NNWSI Sample Designation	Composition (wt. %)						
	Smectite	Illite	Clinoptil- olite	Quartz	Cristo- balite	Alkali Feldspar	Glass
YM-22	5-10	<2	--	30-50	--	30-50	--
YM-30	5-10	5	5-10	40-60	5-10	30-50	--
G1-1292	Trace	--	--	--	5-10	10-20	80-90
JA-18	5	5	10-20	--	30-50	30-50	40

The data in Table 4.2 provide no obvious reason why the sorption ratios for cesium and strontium onto JA-18 are so much higher than for the other samples. The significant differences are the presence of considerable cristobalite and clinoptilolite. Cristobalite would not normally be expected to sorb significant quantities of strontium and cesium unless it was highly hydrated. Although sample JA-18 contains 10-20% clinoptilolite, more than the other samples, the increase in sorption ratio seems too large compared to the sorption ratios for sample YM-30 which contains roughly half as much clinoptilolite. NNWSI has attempted to correlate the observed sorption ratios with mineral content, especially with the amount of zeolites present (Daniels et al. 1982). This correlation is only moderately successful for the elements

cesium and strontium, and not at all successful for neptunium, europium, and americium.

In Table 4.3, average values of sorption ratios as tabulated by Tien et al. (1985) for the "host rock" are given for the six elements that we have studied so far. The host rock corresponds to the Topopah Spring tuff from well USW-GU3 (LANL samples GU-3-433 for cesium, strontium, and europium, and GU-3-916 for neptunium). These samples are classified as devitrified tuff. These data show that for cesium and strontium there is little difference between sorption and desorption ratios. The sorption ratios for cesium in Table 4.3 seem to agree with the values in Table 4.1 for the top four samples; the values for strontium are similar to those for samples YM-22, GU3-1203, and GU3-1301. The sorption ratios for neptunium are low, but the desorption ratio in Table 4.3 is somewhat higher than the sorption ratio. The sorption ratios for europium show wide variations in Table 4.1 and little variation in Table 4.3. The values of R_s for uranium in Table 4.3 are 0 and 10 L/kg. The latter value is somewhat higher than the values shown in Table 4.1. For technetium, all values in both tables are consistently less than one.

Table 4.3 Average sorption ratios for Cs(I), Sr(II), Np(V), Eu(III), U(VI), Tc(VII) onto devitrified tuff (Tien et al. 1985, p. 335-336)

Element	Sorption Ratio (L/kg)	Desorption Ratio (L/kg)
Cs(I)	630 $\pm$ 20	530 $\pm$ 50
	400 $\pm$ 40	510 $\pm$ 20
Sr(II)	61 $\pm$ 6	44 $\pm$ 5
	30 $\pm$ 2	34 $\pm$ 2
Eu(III)	100 $\pm$ 14	120 $\pm$ 20
	68 $\pm$ 14	150 $\pm$ 20
Np(V)	4.9 $\pm$ 0.1	-
	4.9 $\pm$ 1	33 $\pm$ 1
	5.3 $\pm$ 1.0	-
U(VI)	0	-
	10 $\pm$ 0.1	-
Tc(VII)	0	-
	0.7 $\pm$ 0.02	-
	0.72 $\pm$ 0.2	-
	0.81 $\pm$ 0.5	-

Two replications for each sample, 42 d contact time, 75-500 micron particle size.

Because there are wide variations in the mineralogy of tuff, it is difficult to compare data among various samples. Additional information on the specific sorbing minerals in the various tuff samples is needed to provide meaningful comparisons.

Much of the NNWSI sorption data taken using crushed tuff columns was summarized by Treher and Raybold (1982). The volumes of the columns ranged from 0.226 mL to 1.571 mL, and the flow rates ranged from 0.017 mL/hour to 18 mL/hour; most of the flow rates were less than 0.1 mL/hour. Values of R_s obtained by batch and column methods were compared. In general, the agreement was satisfactory for strontium, cesium, and technetium. For europium, the agreement was satisfactory except that some of the europium apparently passed through the column with little or no retention. The amount of europium retained on the column was determined by sectioning the column after the experiment, and the value of R_s determined by the distribution of europium in the column. R_s values were calculated from the volume at which 50% of the tracer had passed through; this did not usually correspond to the volume at the top of the elution peak, because the peaks often exhibited considerable tailing.

Some preliminary data on neptunium column experiments were reported in Rundberg, Ogard, and Vaniman (1985) along with data for plutonium and americium. For these elements, it was observed that a portion of the tracer passed through the column without being adsorbed although the batch experiments indicated high values for the sorption ratios. Slow kinetics of sorption were postulated to explain these results, and kinetic experiments using batch contact techniques were reported to have been started to help verify this postulate.

5. EVALUATION OF SORPTION DATA

5.1 INTRODUCTION TO SORPTION DATA

It is not the objective of this project to conduct experiments with all of the types of tuff under all of the conditions studied by NNWSI. Rather, the objective is to evaluate their data through careful selection of experiments designed to examine the key conclusions from the sorption studies of NNWSI concerning the Yucca Mountain tuffs. To investigate the methods used by NNWSI to acquire sorption data, it is best to select for initial study those elements whose behavior in groundwaters is relatively simple, such as strontium, cesium, and neptunium. Therefore, the initial experiments on tuff described in the previous report in this series (Meyer et al. 1987) with these elements had the objective of studying the effects of pH, particle size, pretreatment of the tuff, and other factors that might influence sorption behavior. A few experiments with europium were also described; europium was selected because it was extensively studied by NNWSI and because it is a good analog for americium.

In the current report period (July 1986 to September 1987), additional experiments with Cs(I), Sr(II), Eu(III), and Np(V) were performed, and Tc(VII) and U(VI) were added. A major effort in this report period is the comparison of sorption results obtained with the batch method to the results calculated from elution peaks obtained by passage of the element through columns filled with crushed tuff. If the results from the two methods agree for a particular element, then it is possible to use relatively simple models to calculate transport of the element through crushed tuff. If the results do not agree, then a much more elaborate model may be necessary. Thus, the column experiments were designed to point out areas of difficulty in the application of batch sorption ratios to the calculation of radionuclide transport and to evaluate whether small column experiments with crushed tuff can be used for meaningful evaluation of retardation.

5.2 DETERMINATION OF SORPTION CAPACITY OF TUFF

Experiments were conducted to measure the sorption capacity of the tuff samples that were used. For the determination of the capacity with respect to monovalent ions, the procedure was to contact the Busted Butte outcrop and Topopah Spring core tuffs with 0.1 M NaCl. For the determination with respect to divalent ions, 0.1 M SrCl₂ was used. The sodium and strontium concentrations of the resulting solutions were then determined by atomic absorption analysis. This procedure was repeated until the analyses showed that the concentrations of Na and Sr remained constant, indicating that the tuff was at equilibrium with respect to the ion in question. To determine capacities, tracer amounts of ²²Na were then added to the tubes containing the tuff samples and the NaCl solution; similarly, tracer amounts of ⁸⁵Sr were added to the samples

containing the SrCl_2 solution. Capacities then were determined by isotopic exchange of the tracers between the Na and Sr on the tuffs and in the solutions. These experiments indicated Na capacities of approximately 8×10^{-3} equivalents/kg for the outcrop and 6×10^{-2} equivalents/kg for the core. Strontium capacities were 1.4×10^{-2} equivalents/kg for the outcrop and 2×10^{-1} equivalents/kg for the core. The capacities of the core for these ions were significantly higher than those for the outcrop, an observation which is probably caused by the significantly higher smectite content of the core compared to that of the outcrop. The capacities for strontium were higher than those for sodium for both the outcrop and the core.

5.3 SORPTION OF STRONTIUM ONTO TUFF

To determine the effect of preequilibration on sorption tests with the core material, strontium experiments were completed with and without preequilibration. A 14-day sorption isotherm in synthetic J-13 was completed for the non-preequilibrated case during the previous report period, and the preequilibrated case was completed during the current report period. The final pH of all solutions for both cases was between 6.7 and 6.9. The results of these two sets of experiments are compared in Table 5.1.

Table 5.1 Comparison of sorption ratios of strontium from real J-13 onto preequilibrated and non-preequilibrated Topopah Spring core (well USWG1, 1189.7-1190.3 ft level)

Initial Conc. (mol/L)	Preequilibrated Sorption Ratio (L/kg)	Non-preequilibrated Sorption Ratio (L/kg)
2×10^{-12}	85.9 ± 0.4	75.9 ± 0.7
1×10^{-8}	105.1 ± 1.0	70.4 ± 2.6
1×10^{-6}	105.0 ± 1.4	76.1 ± 0.4
1×10^{-4}	101.5 ± 2.2	65.4 ± 0.9

Test conditions: Batch contact experiment with 0.4 g tuff in 4 mL synthetic groundwater J-13. For preequilibration, tuff was contacted three times with J-13 three days each time. Contact period was 14 d at 25°C in a controlled-atmosphere box containing air with 1.5% CO_2 . Separation of solid was carried out by 30 min centrifugation at 25,000 rcf. The uncertainty is based on the standard deviation of triplicate samples.

As shown in Table 5.1, the strontium sorption ratios at comparable initial concentrations for the preequilibrated case were all somewhat higher than those for the non-preequilibrated case. The strontium sorption ratios were much higher for the core material than those for

the outcrop which were determined earlier (Meyer et al. 1987) and were in the range of 5 to 12 L/kg. This is probably a result of the much higher smectite content of the core material (cf. section 3.1). In another comparison test, strontium sorption isotherms determined from real and synthetic J-13 were compared. As shown in Table 5.2 and Fig 5.1, there was only a small difference between the values of R_s and the two isotherms. (In Fig. 5.1, a few values are included from non-preequilibrated tuff for the synthetic J-13. On the log-log scale used in Fig. 5.1, there is no significant difference.)

Table 5.2 Comparison of sorption ratios of strontium from real and synthetic J-13 well water onto pre-equilibrated Topopah Spring core (well USWG1, 1189.7-1190.3 ft level)

Initial Conc. (mol/L)	Real J-13 Sorption Ratio (L/kg)	Synthetic J-13 Sorption Ratio (L/kg)
2×10^{-12}	111.5 ± 1.7	101.5 ± 2.2
1×10^{-8}	107.7 ± 2.9	105.0 ± 1.4
1×10^{-6}	108.5 ± 2.7	105.1 ± 1.0
1×10^{-4}	90.4 ± 2.1	85.9 ± 0.4
5×10^{-4}	52.7 ± 0.4	-
5×10^{-3}	17.0 ± 0.2	-

Test conditions: Batch contact experiment with 0.4 g tuff in 4 mL synthetic groundwater J-13. For pre-equilibration, tuff was contacted three times with J-13 three days each time. Contact period was 14 d at 25°C in a controlled-atmosphere box containing air with 1.5% CO₂. Separation of solid was carried out by 30 min centrifugation at 25,000 rcf. The uncertainty is based on the standard deviation of triplicate samples.

A number of column experiments was performed with strontium in synthetic and actual J-13 well water. An early attempt using a 2.54 cm diameter column containing 40 g of Busted Butte outcrop tuff indicated a broad peak from which a value of the sorption ratio was estimated to be about 100 L/kg. This was much higher than values estimated earlier by the batch technique for the outcrop under similar conditions, where values were generally much lower, in the range of 5 to 12 L/kg, depending on conditions (Meyer et al. 1987). This experiment was repeated with a 1.0 cm diameter column after more experience was gained in packing columns. In an experiment comparing columns of Busted Butte outcrop and core tuffs, the sorption ratios were 100.1 L/kg for the core and 16.3 L/kg for the outcrop. However, flow problems were encountered in this experiment as shown in Figs. 5.2 and 5.3. This experiment was therefore repeated, but again flow problems were encountered; the value of R_s for the outcrop of 19.0 L/kg is in fair agreement with the value of 16.3 L/kg observed in the previous experiment. At this point, it was discovered that some component(s) of the synthetic J-13 was causing the

Fig. 5.1 Sorption isotherms for strontium from actual and synthetic J-13 well water onto Topopah Spring core tuff.

Fig. 5.2 Column determination of sorption ratio of strontium onto Busted Butte outcrop using synthetic J-13 well water. $R_s = 16.3$ L/kg. (a) Elution curve (b) Flow Rate.

Fig. 5.3 Column determination of sorption ratio of strontium onto Topopah Spring core using synthetic J-13 well water. $R_s = 100.7$ L/kg. (a) Elution curve (b) Flow Rate.

flow problems (cf. section 3.4), and the experiment was repeated with real J-13. There were no flow obstruction problems in this experiment (Fig. 5.4), and the sorption ratio was 15.9 L/kg. For the core tuff with strontium using actual J-13 well water, the value measured for R_s of 112 L/kg was in good agreement with the values obtained from batch experiments (Table 5.2). Some flow problems were encountered in this experiment (Fig. 5.5), but the peak was relatively symmetrical. Thus, for strontium it appears that the batch and column experiments give approximately the same values of R_s . Therefore, relatively simple models using the results from batch determinations could be used to calculate the transport of strontium through crushed tuff.

5.4 SORPTION OF CESIUM ONTO TUFF

To determine the effect of preequilibration on sorption with core material, cesium experiments with and without preequilibration were completed. A 14-day sorption isotherm in synthetic J-13 was completed for non-preequilibrated tuff during the previous report period, and the preequilibrated case was completed during the current report period. The final pH for both cases was between 6.6. and 6.8. The results of these two sets of experiments are compared in Table 5.3.

As shown in Table 5.3, the cesium sorption ratios were lower with the preequilibrated tuff for initial concentrations between 10^{-10} to 10^{-6} mol/L, but the sorption ratio was higher for an initial concentration of 10^{-4} mol/L. Within the uncertainty levels there was no significant difference in the measurements between the preequilibrated and non-preequilibrated cases. In another comparison test, sorption isotherms were determined for cesium onto Topopah Spring core in synthetic and in actual J-13 well water. The results are shown in Table 5.4 and in Fig. 5.6. Except at the lowest concentrations, there was generally little difference between the sorption ratios for the two cases; at the lower concentrations the sorption ratios were somewhat higher for the actual well water. (To extend the isotherm for the synthetic J-13 in Fig. 5.6, some results for cesium sorption on non-preequilibrated tuff are included. On the log-log scale used in Fig. 5.6, there is no significant difference.)

Because cesium tends to be fixed by sorbents, generally it was the last element tested before a new column was prepared. An elution curve was determined for cesium on a column prepared from Busted Butte outcrop material using real J-13 well water. As shown by the elution curve in Fig. 5.7, the curve had a long tail. The position of the top of the peak corresponds to a sorption ratio of approximately 115 L/kg, and the position of the centroid corresponded to 159 L/kg; the long tail shows that considerable cesium was held firmly by the tuff. Also some flow problems were encountered in this experiment, as shown by Fig. 5.7b. It would be difficult to predict the migration behavior of cesium in columns of crushed tuff from the R_s value determined by a batch technique. The concentration of cesium in the column is difficult to estimate precisely, but the amount introduced probably corresponds to

Fig. 5.4 Column determination of sorption ratio of strontium onto Busted Butte outcrop using actual J-13 well water.
 $R_s = 15.9$ L/kg. (a) Elution curve (b) Flow Rate.

Fig. 5.5 Column determination of sorption ratio of strontium onto Topopah Spring core using actual J-13 well water.
 $R_s = 112 \text{ L/kg}$. (a) Elution curve (b) Flow Rate.

Fig. 5.6 Sorption isotherms for cesium from actual and synthetic J-13 well water onto Topopah Spring core tuff.

Cs Sorption on Busted Butte Outcrop Column

Fig. 5.7 Column determination of sorption ratio of cesium onto Busted Butte outcrop using actual J-13 well water. $R_s = 159/\text{kg}$. (a) Elution curve (b) Flow Rate. The solid line through the points is a polynomial fit put in to guide the eye.

concentrations lower than the lowest concentration (2×10^{-10} mol/L) used in the batch tests. The R_s value of 159 L/g determined from the position of the centroid of the elution curve is smaller than the batch sorption ratio values for Busted Butte outcrop at low concentrations of cesium. For initial concentrations of cesium of 2×10^{-10} and 10^{-8} mol/L, the values of R_s for preequilibrated Busted Butte outcrop were 454(+17) and 448(+58) L/kg, respectively (Meyer et al. 1987). It is also small compared to the values reported above in Table 4.3 reported by NNWSI. To determine the position of the cesium remaining in the column, the tuff in this column was carefully removed and cut into ten sections, and each section was counted. The results are shown in Fig. 5.8a. The distribution shows a peak in section 3 and then a rise from section 6 to 10. Little cesium was found on the frits at the entrance and exit to the column. It is difficult to explain the distribution in the column, except perhaps in terms of an unequal distribution of a minor component of tuff that has very slow desorption kinetics. The crushed tuff was carefully homogenized before use, but it is possible that a minor component could have been distributed unequally in the column.

Table 5.3 Comparison of sorption ratios of cesium from J-13 onto non-preequilibrated and preequilibrated Topopah Spring core (well USWG1, 1189.7-1190.3 ft level)

Initial Conc. (mol/L)	Preequilibrated Sorption Ratio (L/kg)	Non-preequilibrated Sorption Ratio (L/kg)
2×10^{-10}	191.7 ± 72	250.8 ± 141
1×10^{-8}	286.8 ± 147	330.3 ± 162
1×10^{-6}	304.3 ± 43	418.8 ± 59
1×10^{-4}	118.5 ± 4.7	106.7 ± 3.2

Test conditions: Batch contact experiment with 0.4 g tuff in 4 mL synthetic groundwater J-13. The tuff was contacted 14 d at 25°C in a controlled-atmosphere box containing air with 1.5% CO₂. Separation of the solid was carried out by 30 min centrifugation at 25,000 rcf. The uncertainty is based on triplicate samples.

Fig. 5.8 Distribution of (a) cesium, (b) europium, and (c) technetium on column of Busted Butte outcrop tuff. See text for details of experiment.

Table 5.4 Comparison of sorption ratios of cesium from real and synthetic J-13 well water onto preequilibrated Topopah Spring core (well USWG1, 1189.7-1190.3 ft level)

Initial Conc. (mol/L)	Real J-13 Sorption Ratio (L/kg)	Synthetic J-13 Sorption Ratio (L/kg)
2×10^{-10}	626.0 ± 76	191.7 ± 72
1×10^{-8}	537.4 ± 153	286.8 ± 147
1×10^{-6}	343.1 ± 28	304.3 ± 43
1×10^{-4}	100.6 ± 6.1	118.5 ± 4.7
5×10^{-4}	116.5 ± 5.8	-
2×10^{-3}	98.5 ± 8.6	-

Test conditions: Batch contact experiment with 0.4 g tuff in 4 mL synthetic groundwater J-13. For preequilibration, tuff was contacted three times with J-13 three days each time. Contact period was 14 d at 25°C in a controlled-atmosphere box containing air with 1.5% CO₂. Separation of solid was carried out by 30 min centrifugation at 25,000 rcf. The uncertainty is based on triplicate samples.

5.5 SORPTION OF TECHNETIUM ONTO TUFF

Technetium was introduced into the J-13 well water in the form of TcO₄⁻, and the experiments were always run in air containing 1.5 % CO₂. Technetium is not expected to sorb under these conditions. Thus, the elution curves for technetium should be similar to those for tritium. An example is given in Fig. 5.9 for a column made from the outcrop tuff using actual J-13 well water. The peaks were not always this symmetrical. However, in all cases the positions of the peaks indicated negligible sorption.

For the technetium experiments with the core material, essentially all of the technetium passed through the column based on material balances measured by summing the amount of technetium in each fraction collected. However, only 72% of the technetium was recovered in the experiment with the Busted Butte outcrop shown in Fig. 5.9. Later when the tuff from the column was removed and cut into sections, the technetium was found at the entrance to the column (Fig. 5.8c). This observation suggests that some component of the outcrop material, not present in the core, may have fixed the technetium, possibly by a reduction mechanism. However, this did not always occur; in other experiments with the Busted Butte material essentially all of the technetium was recovered. Thus, it appears that this component is not homogeneously distributed in the outcrop. We conclude therefore that technetium will not usually be adsorbed under oxic conditions and that the one experiment where technetium was fixed was not characteristic of all samples of Busted Butte outcrop.

Fig. 5.9 Column determination of sorption ratio of technetium onto Busted Butte outcrop using actual J-13 well water.
 $R_s = 0.03$ L/kg. (a) Elution curve (b) Flow Rate.

5.6 SORPTION OF NEPTUNIUM ONTO TUFF

Relatively few experiments were done with neptunium, primarily because our very small supply of ^{235}Np for use at low concentrations is difficult to prepare and extremely expensive. In the previous report period, an experiment was described in which the effect of particle size on sorption of neptunium was determined. Sorption ratios ranged from about 1.4 to 3.4 L/kg with only a small effect of particle size (Meyer et al. 1987).

Several column experiments with neptunium were completed; the elution curves are given in Fig. 5.10 for the Busted Butte outcrop and Fig. 5.11 for the core tuff. Neither elution curve was symmetrical, and tailing was observed. The position of the centroids of the elution curves always corresponded to values of R_s that indicated little or no sorption ($R_s = 0.13$ L/kg for outcrop and 0.22 L/kg for core). This observation and the asymmetry of the peaks show that some of the neptunium flowed through the column without being sorbed. A possible explanation for these observations is that the column was not packed correctly, and that channeling in the column allowed some of the neptunium to flow through rapidly. To test this a technetium experiment was completed immediately after the experiment shown in Fig. 5.11, but the resulting elution curve, shown in Fig. 5.12, is symmetrical and shows no evidence of channeling. Another possible explanation for the peak shapes in these experiments is that Np, introduced as the ion NpO_2^+ , interacts slowly with the tuff, and because of slow sorption kinetics, there is insufficient time to establish equilibrium.

5.7 SORPTION OF EUROPIUM ONTO TUFF

Preliminary to the study of americium sorption, the behavior of Eu(III) is being investigated as a stand-in for americium. As described in our last report (Meyer et al. 1987), as much as 98% of the europium was lost over periods of about a month from synthetic J-13 that initially contained 10^{-4} and 10^{-7} mol/L europium. Samples of the solutions were centrifuged for 30 min at 25,000 rcf before counting. Possible causes of these losses were sorption on tube walls, sorption of europium on colloidal particles to form pseudo-colloids, and formation of true colloids of europium. Because europium does not hydrolyze significantly below pH 8 (Schmidt et al. 1978, Baes and Mesmer 1976), it is probable that true colloids did not form in the systems that we studied. Most of the losses are probably caused by formation of pseudocolloids and adsorption on tube walls.

Further experiments were completed to test the stability of europium solutions in synthetic J-13. A 10^{-10} mol/L solution of europium in synthetic J-13 was prepared and allowed to remain in a stirred container in the glove box containing 1.5% CO_2 for about 4 months. Periodically, samples were taken and a portion of the sample was centrifuged; both centrifuged and non-centrifuged samples were then counted. The pH

Fig. 5.10 Column determination of sorption ratio of neptunium onto Busted Butte outcrop using actual J-13 well water. $R_s = 0.13$ L/kg. (a) Elution curve (b) Flow Rate.

Fig. 5.11 Column determination of sorption ratio of neptunium onto Topopah Spring core using actual J-13 well water.
 $R_s = 0.34$ L/kg (a) Elution curve (b) Flow Rate.

Fig. 5.12 Column determination of sorption ratio of technetium onto Topopah Spring core using actual J-13 well water.
 $R_s = 0.0$ L/kg (a) Elution curve (b) Flow Rate.

varied over the four months but was almost always within 0.4 pH units of 7. The concentration of europium as a function of time is shown in Fig. 5.13. The concentration after centrifugation appears to have stabilized at a level on the order of 10^{-11} mol/L. Using this solution, a batch sorption experiment using Topopah Spring core was completed. Triplicate experiments were done with 0.1, 0.2, 0.4, and 0.8 grams of tuff; each sample contained 4 mL of the europium-traced J-13. The samples were equilibrated 14 days in the atmosphere box containing 1.5% CO_2 . The results of the experiment are shown in Figs. 5.14 and 5.15. In Fig. 5.14a, it is shown that after the 14 day equilibration period, the concentration of europium in the synthetic J-13 (without tuff) varied from about 3.8×10^{-12} to 5.5×10^{-12} mol/L, and that the amount of europium in solution decreased rapidly as the amount of tuff was increased. The same data are plotted in two different ways in Fig. 5.14b where the R_s value is plotted vs the amount of tuff and in Fig. 5.15 where the amount of europium on the tuff is plotted vs the solution concentration of europium. The values of R_s vary considerably but generally tend to decrease with amount of tuff. The concentration of europium in solution tends to decrease slightly with the amount of tuff.

An experiment with europium in real J-13 yielded results similar to those found with synthetic J-13. When enough europium was added to make an approximately 10^{-10} mol/L solution in real J-13, 98% of the europium was lost immediately from the solution after centrifugation twice for 30 min at 25,000 rcf. The non-centrifuged solution did not lose any europium immediately, but it lost about half of the europium after 5 days.

An experiment was completed for europium with a column made from Busted Butte outcrop and real J-13 that had been filtered through a 0.2- μm pore-size filter. After a total of almost 2,400 mL of solution had passed through the column at a flow rate of 0.2 mL/min, no europium was detected in the effluent. When the column was later taken apart and sectioned, essentially all of the europium was found on the 25- μm pore-size teflon frit at the entrance of the column. Very small amounts of europium were found in the first six of the ten sections of tuff from the column. The distribution of europium in the column is shown in Fig. 5.8b.

It appears from these experiments that it is not possible to measure sorption ratios with europium (and most probably americium) in the usual sense. Losses of europium were observed which were affected by the amount of tuff present, but the process causing the losses is not at all clear. Thus it would be difficult to model the transport of europium through tuff, or any rock.

5.8 SORPTION OF URANIUM ONTO TUFF

An uranium sorption isotherm was completed using the batch contact technique in synthetic J-13 wellwater. The results of the experiment are given in Table 5.6. Ground Topopah Spring core was used, and it was

Fig. 5.13 Concentration of europium in uncentrifuged and centrifuged solutions as a function of time. The initial europium concentration was 10^{-10} mol/L.

Fig. 5.14 Results of batch contact test for sorption of europium on Topopah Spring core tuff from synthetic J-13 groundwater. The initial concentration of europium was approximately 10^{-11} mol/L. (a) Concentration of europium as a function of weight of tuff after 14 day equilibration period. (b) R_s value as a function of weight of tuff.

Fig. 5.15 Results of batch contact test for sorption of europium on Topopah Spring core tuff from synthetic J-13 groundwater. The initial concentration of europium was approximately 10^{-11} mol/L.

not preequilibrated with J-13 groundwater.

Control experiments were carried along with the sorption experiments; for initial solution concentrations of 10^{-7} , 10^{-6} , 10^{-5} , and 10^{-4} mol/L of uranium in synthetic J-13, the losses were 7.6%, 8.5%, 9.0% and 4.0%, respectively. Losses could be caused by sorption on the tube walls, or by formation of particulates removable by the centrifugation. If we use the concentrations in the control solutions as the initial concentrations, then the values of R_s are slightly lower. There appears to be a slight trend in Table 5.6; values of R_s decrease regularly with increase in initial concentration. No further batch sorption experiments with uranium were completed during the current report period.

Table 5.6 Sorption of U(VI) from synthetic J-13 well water onto Topopah Spring core (well USWG1, 1189.7-1190.3 ft level)

Initial Conc. (mol/L)	final pH	R_s (L/kg)	Conc. in soln. (mol/L)	Conc. on tuff (mol/kg)
10^{-7}	6.92	4.77 ± 0.4	$(6.7 \pm 0.17) \times 10^{-8}$	$(3.2 \pm 0.19) \times 10^{-7}$
10^{-6}	6.95	3.98 ± 0.1	$(7.1 \pm 0.05) \times 10^{-7}$	$(2.8 \pm 0.04) \times 10^{-6}$
10^{-5}	6.89	2.29 ± 0.1	$(8.1 \pm 0.05) \times 10^{-6}$	$(1.9 \pm 0.05) \times 10^{-5}$
10^{-4}	6.83	2.19 ± 0.2	$(8.2 \pm 0.11) \times 10^{-5}$	$(1.8 \pm 0.12) \times 10^{-4}$

Test conditions: Batch contact experiment with 0.4 g tuff in 4 mL synthetic groundwater J-13. The tuff was not preequilibrated with synthetic J-13. The contact period was 14 d at 25°C in a controlled-atmosphere box containing air with 1.5% CO₂. The separation of solid was carried out by 30 min centrifugation at 25,000 rcf. The uncertainty is the standard deviation of triplicate samples.

A number of column experiments with uranium was completed during the report period with somewhat mixed results. The elution and flow rate curves for these experiments are shown in Figs. 5.16 to 5.22. Busted Butte outcrop and actual J-13 well water were used in the experiment shown in Fig. 5.16, and Topopah Spring Core was used in the experiments shown in Figs. 5.17 to 5.22. A new column was made after the experiment in Fig. 5.17. The experiment shown in Fig. 5.21 was carried out at a flow rate of 0.1 mL/min (half the usual flow rate of 0.2 mL/min). The results were mixed in that in two cases (Figs. 5.17 and 5.19) clearly discernible double peaks were observed. The material balances were always in the range of 85 to 90% which indicates that some of the uranium was fixed within the column. This loss of uranium could be related to the losses of uranium in the control samples of the batch experiments (Table 5.6). In every case, values of R_s calculated from the centroid position (from 1.43 to 1.92 L/kg) were smaller than those found in the batch experiments, and there was considerable tailing. Double peaks could be caused by channeling or by the transport of two

species not at equilibrium. Further investigations are being made to attempt to answer some of the questions raised by these experiments. The tailing indicates that some of the uranium is held strongly by the column. Therefore, measurements are being made in which the flow rate and the temperature of the column are varied to investigate kinetic processes occurring with this system.

Fig. 5.16 Column determination of sorption ratio of uranium onto Busted Butte outcrop using actual J-13 well water.
 $R_s = 1.43$ L/kg (a) Elution curve (b) Flow Rate.

Fig. 5.17 Column determination of sorption ratio of uranium onto Topopah Spring core using actual J-13 well water. $R_s = 1.59$ L/kg. (a) Elution curve (b) Flow Rate.

Fig. 5.18 Column determination of sorption ratio of uranium onto Topopah Spring core using actual J-13 well water.
 $R_s = 1.70$ L/kg (a) Elution curve (b) Flow Rate.

Fig. 5.19 Column determination of sorption ratio of uranium onto Topopah Spring core using actual J-13 well water. $R_s = 1.59$ L/kg. (a) Elution curve (b) Flow Rate.

Fig. 5.20 Column determination of sorption ratio of uranium onto Topopah Spring core using actual J-13 well water.
 $R_s = 1.79$ L/kg (a) Elution curve (b) Flow Rate.

Fig. 5.21 Column determination of sorption ratio of uranium onto Topopah Spring core using actual J-13 well water. Note that the flow rate is about half of that for previous experiments. $R_s = 1.92$ L/kg. (a) Elution curve (b) Flow Rate.

Fig. 5.22 Column determination of sorption ratio of uranium onto Topopah Spring core using actual J-13 well water. $R_s = 1.72$ L/kg. (a) Elution curve (b) Flow Rate.

6. NEAR-FIELD GROUNDWATER COMPOSITION

6.1 BACKGROUND

Geochemical characterization and modeling of rock-groundwater interactions in the near field and very near field of an HLW repository in an unsaturated tuff horizon during the early post closure period are currently hampered by a lack of data on the compositions of groundwaters in these environments. As descending vadose-zone groundwater approaches waste canisters during the containment period, changes in the chemical composition of the groundwater are likely owing to processes such as ion exchange, precipitation of solute material, and dissolution of rock material. Furthermore, as groundwater approaches the very near field of the repository during the early postclosure period, temperatures will be sufficiently high to induce boiling. Such boiling could simultaneously alter enclosing tuffaceous rock and induce precipitation of solid material from the boiling groundwater. Repeated incursions of fresh groundwater into the very near field followed by prolonged boiling of the groundwater could ultimately result in: (1) extensive alteration of the tuffaceous host rock, and (2) the formation of encrustations of precipitated solid material.

However, waste canisters will eventually cool to temperatures below 100°C and boiling of groundwater will cease. Flow of groundwater toward waste canisters will then no longer be repelled by boiling, and it is highly likely that ingressing groundwater will have sufficient residence time to redissolve at least part of the solid material precipitated during earlier boiling events. The preliminary experiment described in this report was designed to simulate possible geochemical conditions in the very near field of an HLW repository in an unsaturated tuff horizon immediately after repository temperatures have fallen below 100°C. The principal objective of the experiment was to obtain information on the compositions of groundwaters that will flow toward waste packages at this stage in the history of the repository.

6.2 EXPERIMENTAL PROCEDURE

The experiment was performed in two stages. In the first stage, 4.7 liters of synthetic J-13 were slowly evaporated to dryness at 95-100°C on the top surface of a slab of Topopah Spring tuff approximately 5 x 5 x 0.75 cm, depositing a thin irregular layer of precipitated material on the slab of tuff. In the second stage of the experiment, the slab of tuff with the dried precipitate material was immersed in a fresh, stirred batch of 1.76 liters of synthetic J-13 groundwater in a reaction vessel held at 90°C. This stage of the experiment was performed to determine the amount of precipitated material that would redissolve in the J-13 groundwater.

Samples of the hot groundwater were taken over a period of 360 hours to monitor the dissolution of the precipitate. Analyses for sodium,

potassium, and magnesium were made by atomic absorption; chloride concentrations were measured with a small potentiometric cell; and a number of elements were determined in the ORNL Analytical Chemistry Division by inductively-coupled-plasma mass spectrometry (ICP-MS).

6.3 RESULTS

Neither the magnesium nor the calcium that precipitated in the first stage of the experiment redissolved significantly. Furthermore, the magnesium and calcium in the synthetic J-13 groundwater used for leaching was rapidly removed from the solution during the second stage of the experiment. The concentrations of magnesium and calcium as a function of time of leaching by synthetic J-13 at 90°C are shown in Fig. 6.1. After a few hours, the magnesium concentration decreased to undetectable levels and the calcium concentration decreased to low levels. Further experiments are necessary to understand why the calcium and magnesium decreased in concentration. Experiments with a similar slab of tuff without any encrustation and with J-13 alone at 90°C are necessary to see if the precipitate formed on the slab of tuff affected the concentration of the magnesium and calcium in the J-13 leaching solution. In addition, tests with real J-13 groundwater are needed. It may be that the tuff causes these decreases; Daniels et al. (1982) report that the concentrations of calcium and magnesium decreased significantly when tuff and J-13 were contacted at 152°C for three weeks.

The analyses indicated that almost all of the sodium and most of the potassium that had precipitated during the first stage of the experiment redissolved into the leach solution during the second stage. The chloride concentration as a function of leaching time is shown in Fig. 6.2a. The dashed horizontal line represents the concentration of chloride ion that would be obtained if all of the chloride in the precipitate redissolved into the J-13 used in the second-stage leaching solution. The concentration of chloride rose above this level probably because of evaporation of some of the water. As shown in Fig. 6.2b, the boron concentration in the leach solution increased throughout the test and reached a concentration of about 8 mg/L after 360 hours at 90°C. This concentration is considerably greater than that initially present (indicated by the dashed horizontal line). This observation suggests leaching of the borosilicate glass vessel in which the experiment was conducted. It is also likely that some SiO₂ was leached from the walls of the reaction vessel.

Sulfate analyses by ion chromatography were obtained from the ORNL Analytical Chemistry Division. The results show that the sulfate precipitated from the synthetic J-13 well water in the first phase of the experiment redissolved in the second phase. Titration of the leach solutions with dilute HCl showed that the synthetic J-13 well water initially contained about 0.002 mol/L bicarbonate and that the bicarbonate was converted to carbonate and hydroxide as the leach solution lost dissolved CO₂ during the leach at 90°C. This conversion

resulted in an increase of the solution pH. These results point out that if additional tests of this type are needed, they should be done with actual J-13 well water in a more controlled atmosphere and in apparatus that will not be attacked by the 90°C leaching solution.

Fig. 6.1 Composition of magnesium and calcium in leaching J-13 groundwater at 90°C as a function of time.
(a) Magnesium (b) Calcium.

Fig. 6.2 Composition of chloride and boron in leaching J-13 groundwater at 90°C as a function of time.
(a) Chloride (b) Boron.

7. COMPARISON OF RESULTS WITH NNWSI DATA

Strictly speaking, there are no experiments reported by NNWSI directly comparable to ours because each section of tuff is unique. However, there are several approximate methods of comparison. One method is to compare our data to those reported by NNWSI for the same drill hole (USW-G1) at close to the same depth (~1200 ft). Another is to compare our data to NNWSI data for the same general classification of tuff. Preliminary comparisons were given in the previous report for strontium and cesium.

The data that were obtained in the current report period suggest that our data and data from NNWSI are roughly comparable for similar conditions. Our values for strontium on the core tuff, which are on the order of 100 L/kg, are somewhat larger than those in Tables 4.1 and 4.3, but considering the variability in the composition in tuff, these differences are not surprising. For the outcrop, our values ranged from 5 to 15 L/kg, somewhat lower than those in Tables 4.1 and 4.3. Our values for cesium are in the same range as those given in Tables 4.1 and 4.3. For uranium, we found values in batch tests ranging from 2.19 to 4.77 L/kg (Table 5.6) and values of 1.43 to 1.92 L/kg in our column tests. These values appear to be reasonably consistent with the values in Table 4.1 and 4.3. Although we have done no batch sorption experiments for technetium, the many column tests that we have run all suggest very low sorption. The one exception is the experiment with Busted Butte outcrop shown in Fig. 5.8 in which we recovered only 72% of the technetium in the effluent, and considerable technetium remained on the column. These low values are consistent with the data in Tables 4.1 and 4.3.

The data for europium are difficult to interpret in terms of conventional sorption ratios. Our experiments indicate that europium is readily removed from solutions with or without sorbents present. Therefore, it is difficult to compare our data with those of NNWSI.

In general, our data taken from column experiments are in agreement with comparable experiments performed by NNWSI. Our results for column experiments with strontium, cesium and technetium agreed with those of our batch experiments; similar agreement with these elements was reported by NNWSI (Treher and Raybold, 1982). In the europium column experiment described above we observed no europium at all passing through our column. This contrasts with the work of Treher and Raybold (1982) who reported that in their column experiments a small percent of europium passed through with little or no retention. Possibly, differences in the preparation techniques of the europium spikes caused the difference between their and our results. Additional experiments are required to understand the behavior of europium experiments.

Rundberg, Ogard, and Vaniman (1985) reported that for plutonium, americium, and neptunium, column R_s values were considerably lower than those determined by the batch contact method. We observed similar

behavior with our column experiments with uranium and neptunium, and we are doing experiments to see whether kinetic effects, as postulated by Rundberg, Ogard, and Vaniman, can explain the results.

8. DISCUSSION

The experiments and data reported here are only a very small fraction of the experiments that have been reported by NNWSI with tuff. Our first experiments were designed primarily to evaluate methods of collecting data and to determine the effects of preequilibration, CO₂ control, solution concentration, and any other factors that may be important for the collection of sorption data. The data that we have collected so far with strontium and cesium in batch contact experiments agree approximately with the data given by NNWSI for conditions which, as far as we can tell, are similar to the conditions used by NNWSI. Unfortunately, much of the data given by NNWSI is in tabular form without reference to much of the information that is essential for the evaluation of the data. To evaluate data, it is essential that a detailed presentation of the experimental conditions be given. Details such as solution composition, pH, and concentrations of the element studied should be either stated or referenced. Often, it is not clear which data were taken with CO₂ control and which without, and whether J-13 well water was used. In addition, the solution concentrations are usually not given. A complete summary of recent data with reference to all of the pertinent experimental details is badly needed.

A concern that we mentioned in our last report is still valid; a great amount of data was apparently obtained without CO₂ control and hence pH control. Sorption ratios of uranium determined without control of CO₂ were from 3 to 8 times smaller than sorption ratios of uranium determined with CO₂ control (Ogard and Vaniman, 1985). In this case the change was in a direction such that the original data were conservative; but this may not necessarily be true for all nuclides. We therefore believe that the effects of CO₂ control should be determined for all nuclides to assure that: (1) there are no effects of speciation that may lead to non-conservative results or (2) conservative results are obtained because, as is often observed with natural materials, sorption increases markedly with pH.

Our experience with europium leads us to believe that sorption ratios reported for europium cannot be considered to be sorption ratios in the usual sense of the word. With or without sorbent present, large losses of europium were observed, and it was therefore very difficult to prepare initial solutions; in fact we did not succeed in preparing a standard or control solution that remained stable over the course of a sorption experiment. This was observed for solutions which contained enough europium to make initial solutions of 10⁻⁴, 10⁻⁷, and 10⁻¹⁰ mol/L. In all cases, the concentration of europium decreased with time, and the decreases were considerably enhanced by centrifugation. Values of the sorption ratio given in Table 4.1 vary considerably for the various samples; values in Table 4.3 are 100 ± 14 and 68 ± 14 L/kg. However, we have not been able to duplicate these results for lack of preparation of suitable stable standards and controls. We suspect that much of the losses are due to pseudocolloid formation. If that is so, then an important factor in the transport of europium (and similar

elements like americium) is the possible transport.

In the current report period, most of the emphasis was given to obtaining elution curves of elements through columns of crushed samples of both Busted Butte outcrop and Topopah Spring core. The objectives were to evaluate whether small columns could be used to obtain data consistent with the data obtained from batch sorption experiments, and to determine whether column experiments of this type are useful methods for evaluating radionuclide transport. The columns that we used are carefully packed to provide as homogeneous a column as possible, a situation that is not likely to occur in natural settings. However, on a large enough scale in natural settings it may be that tuff could be considered as fairly uniform. Another factor is that the flow rates through the column, usually 0.2 mL/min, translate to a linear flow of 1340 meters/year for our columns, and this flow is far larger than the expected flow rates in the vicinity of the repository (Sinnock et al. 1987). This relatively large flow rate may therefore not allow sufficient time for a nuclide with slow sorption kinetics to interact. On the other hand, studies at these high flow rates, particularly if they are varied, may help clarify some of the kinetic problems of sorption. For that reason we have begun experiments at other flow rates and also at elevated temperatures.

For strontium, we found that even at this relatively high flow rate there was good agreement between values of R_s measured by column and batch contact tests. For cesium, which was present at very low concentrations in the column, the value for Busted Butte outcrop tuff (Fig. 5.7) was 159 L/kg; this value is somewhat lower than the values 308 and 252 L/kg at initial concentrations of 2×10^{-12} and 10^{-8} mol/L respectively for washed Busted Butte tuff (Meyer et al. 1987). However, values of R_s for cesium vary widely among different samples, and this difference is probably not significant. Furthermore, there is a long tail in the cesium experiment that suggests some of the cesium was held tightly.

For uranium and neptunium, the elution curves consistently gave sorption ratios that were lower than those obtained using batch methodology. However, we have not yet completed many batch experiments for either element. More batch experiments with these elements should help clarify the relatively low values of R_s obtained from the column experiments.

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