

NUREG/CR-4708
ORNL/TM-10147/V3
Vol. 3

Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects

Report for October 1987 – June 1989

Prepared by R. E. Meyer, W. D. Arnold, G. D. O'Kelley,
F. I. Case, J. F. Land

Oak Ridge National Laboratory

Prepared for
U.S. Nuclear Regulatory Commission

HYDROLOGY DOCUMENT NUMBER 557

8969180318

AVAILABILITY NOTICE

Availability of Reference Materials Cited in NRC Publications

Most documents cited in NRC publications will be available from one of the following sources:

1. The NRC Public Document Room, 2120 L Street, NW, Lower Level, Washington, DC 20555
2. The Superintendent of Documents, U.S. Government Printing Office, P.O. Box 37082, Washington, DC 20013-7082
3. The National Technical Information Service, Springfield, VA 22161

Although the listing that follows represents the majority of documents cited in NRC publications, it is not intended to be exhaustive.

Referenced documents available for inspection and copying for a fee from the NRC Public Document Room include NRC correspondence and internal NRC memoranda; NRC Office of Inspection and Enforcement bulletins, circulars, information notices, inspection and investigation notices; Licensee Event Reports; vendor reports and correspondence; Commission papers; and applicant and licensee documents and correspondence.

The following documents in the NUREG series are available for purchase from the GPO Sales Program: formal NRC staff and contractor reports, NRC-sponsored conference proceedings, and NRC booklets and brochures. Also available are Regulatory Guides, NRC regulations in the *Code of Federal Regulations*, and *Nuclear Regulatory Commission Issuances*.

Documents available from the National Technical Information Service include NUREG series reports and technical reports prepared by other federal agencies and reports prepared by the Atomic Energy Commission, forerunner agency to the Nuclear Regulatory Commission.

Documents available from public and special technical libraries include all open literature items, such as books, journal and periodical articles, and transactions. *Federal Register* notices, federal and state legislation, and congressional reports can usually be obtained from these libraries.

Documents such as theses, dissertations, foreign reports and translations, and non-NRC conference proceedings are available for purchase from the organization sponsoring the publication cited.

Single copies of NRC draft reports are available free, to the extent of supply, upon written request to the Office of Information Resources Management, Distribution Section, U.S. Nuclear Regulatory Commission, Washington, DC 20555.

Copies of industry codes and standards used in a substantive manner in the NRC regulatory process are maintained at the NRC Library, 7920 Norfolk Avenue, Bethesda, Maryland, and are available there for reference use by the public. Codes and standards are usually copyrighted and may be purchased from the originating organization or, if they are American National Standards, from the American National Standards Institute, 1430 Broadway, New York, NY 10018.

DISCLAIMER NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability of responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects

Report for October 1987 – June 1989

Manuscript Completed: June 1989
Date Published: August 1989

Prepared by
R. E. Meyer, W. D. Arnold, G. D. O'Kelley,
F. I. Case, J. F. Land

Oak Ridge National Laboratory
Operated by Martin Marietta Energy Systems, Inc.

Oak Ridge National Laboratory
Oak Ridge, TN 37831

Prepared for
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555
NRC FIN B0290

Previous reports in this series:

October 1982 - September 1983	NUREG/CR-3730
October 1983 - December 1983	NUREG/CR-3851, Vol. 1
January 1984 - March 1984	NUREG/CR-3851, Vol. 2
April 1984 - June 1984	NUREG/CR-3851, Vol. 3
October 1983 - September 1984	NUREG/CR-3851, Vol. 4
October 1984 - December 1984	NUREG/CR-4236, Vol. 1
January 1985 - March 1985	NUREG/CR-4236, Vol. 2
April 1985 - June 1985	NUREG/CR-4236, Vol. 3
October 1984 - September 1985	NUREG/CR-4236, Vol. 4
October 1985 - March 1986	NUREG/CR-4708, Vol. 1, No. 1
April 1986 - September 1987	NUREG/CR-4708, Vol. 2

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. The principal emphasis in this report period was on column studies of migration of uranium and technetium in water from well J-13 at the Yucca Mountain site. Columns 1 cm in diameter and about 5 cm long were constructed and carefully packed with ground tuff. The characteristics of the columns were tested by determination of elution curves of tritium and TcO_4^- . Elution peaks obtained in past studies with uranium were asymmetrical and the shapes were often complex, observations that suggested irreversibilities in the sorption reaction. To try to understand these observations, the effects of flow rate and temperature on uranium migration were studied in detail. Sorption ratios calculated from the elution peaks became larger as the flow rate decreased and as the temperature increased. These observations support the conclusion that the sorption of uranium is kinetically hindered. To confirm this, batch sorption ratio experiments were completed for uranium as a function of time for a variety of conditions. These experiments confirmed that the reaction was slow because 20 to 30 days elapsed before sorption ratios reached steady-state values. A preliminary column experiment was completed under conditions simulating unsaturated flow in tuff for transport of Sr^{2+} , Cs^+ , and TcO_4^- . The technetium traveled the farthest and the cesium the least, observations which are consistent with their sorption ratios measured in saturated batch tests. The effect of particle size of tuff was determined for batch sorption studies of uranium, cesium, and strontium. The sorption ratio increased somewhat as the particle size decreased. The significance of these experiments with respect to data obtained by DOE investigators for evaluation of the suitability of the Yucca Mountain site is discussed. Our data for ions such as Cs^+ and Sr^{2+} , which have uncomplicated chemical behavior in aqueous solutions, are in approximate agreement with data from DOE. However, our results for elements that have more complicated behavior such as europium and uranium leave many questions about sorption data reported by DOE.

CONTENTS

	<u>Page</u>
ABSTRACT	iii
LIST OF FIGURES	vii
LIST OF TABLES	ix
1. EXECUTIVE SUMMARY	1
2. INTRODUCTION	3
3. MATERIALS AND METHODS	5
3.1 TUFF SAMPLES	5
3.2 GROUNDWATER	5
3.3 COLUMN CONTACT METHODOLOGY	6
3.4 BATCH CONTACT METHODOLOGY	8
4. PUBLISHED INFORMATION ON SORPTION ONTO YUCCA MOUNTAIN TUFF . .	10
5. EVALUATION OF SORPTION DATA	16
5.1 INTRODUCTION TO SORPTION EXPERIMENTS	16
5.2 COLUMN TESTS	16
5.2.1 <u>Effect of Flow Rate on Technetium Sorption</u>	16
5.2.2 <u>Effect of Flow Rate on Uranium Sorption</u>	16
5.2.3 <u>Effect of Temperature on Column Void Volume</u>	24
5.2.4 <u>Effect of Temperature on Technetium Sorption</u>	26
5.2.5 <u>Effect of Temperature on Uranium Sorption</u>	26
5.2.6 <u>Movement of Technetium, Strontium, and Cesium</u> <u>through Unsaturated Tuff</u>	28
5.2.7 <u>Movement of Europium through Unsaturated Tuff</u>	32
5.3 BATCH TESTS	32
5.3.1 <u>Effect of Contact Time on Uranium</u> <u>Sorption and Desorption</u>	32
5.3.2 <u>Sorption/Desorption Isotherms for Uranium</u> <u>on Tuff</u>	36
5.3.3 <u>Effect of Particle Size on Sorption of</u> <u>Strontium, Cesium, and Uranium onto Tuff</u>	40
6. COMPARISON OF RESULTS WITH DOE DATA	44
7. DISCUSSION	47
8. REFERENCES	49

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
3.3.1 Apparatus to measure the transport of radionuclides in tuff under partially saturated conditions.	9
5.2.1 Effect of flow rate on sorption of TcO_4^- onto Topopah Spring tuff. Column method, 24°C.	18
5.2.2 Elution curve of TcO_4^- in J-13 well water from a column of Topopah Spring tuff. 0.1 mL/min, 24°C. $R_s = -0.003$ L/kg.	19
5.2.3 Effect of flow rate on sorption of uranium onto Topopah Spring tuff. Column method, 24°C.	21
5.2.4 Elution curve of uranium in J-13 well water from a column of Topopah Spring tuff. 0.2 mL/min, 24°C. $R_s = 1.69$ L/kg.	22
5.2.5 Elution curve of uranium in J-13 well water from a column of Topopah Spring tuff. 0.2 mL/min, 24°C.	23
5.2.6 The effect of temperature on the measured void volume of a column of Topopah Spring tuff.	25
5.2.7 The effect of temperature on column measurements of the sorption of TcO_4^- onto Topopah Spring tuff.	27
5.2.8 The effect of temperature on column measurements of the sorption of uranium onto Topopah Spring tuff.	29
5.2.9 Elution curve of uranium in J-13 well water from a column of Topopah Spring tuff. 0.2 mL/min, 60°C.	30
5.2.10 Distributions of technetium (TcO_4^-), strontium, and cesium in J-13 well water in a column of Topopah Spring tuff after transport under unsaturated conditions.	31
5.2.11 Distribution of europium in J-13 well water in a column of Topopah Spring tuff after transport under unsaturated conditions. (a) Full range of distribution (b) Expanded range.	33
5.3.1 Effect of contact time on sorption and desorption ratios of uranium onto Topopah Spring tuff. Batch method, 24°C.	35
5.3.2 Sorption and desorption isotherms of uranium on Topopah Spring tuff.	37
5.3.3 Effect of sorption contact time on the desorption of uranium from Topopah Spring tuff.	39

5.3.4 Effect of particle size fraction on sorption and desorption ratios of strontium, cesium, and uranium on Topopah Spring tuff. 43

<u>Table</u>	<u>Page</u>
3.1 Composition of J-13 well water	6
4.1 Sorption data for Yucca Mountain Project sample G1-2901. . .	12
4.2 Sorption data for Yucca Mountain Project sample JA-32. . . .	13
4.3 Sorption data for Yucca Mountain Project sample YM-54. . . .	14
5.2.1 Effect of flow rate on technetium sorption onto Topopah Spring tuff.	17
5.2.2 Effect of flow rate on uranium sorption onto Topopah Spring tuff.	20
5.2.3 Effect of temperature on column void volume.	24
5.2.4 Effect of temperature on technetium sorption onto Topopah Spring tuff	26
5.2.5 Effect of temperature on uranium sorption onto Topopah Spring tuff	28
5.3.1 Effect of contact time on uranium sorption and desorption with Topopah Spring tuff.	34
5.3.2 Uranium sorption and desorption isotherms on Topopah Spring tuff.	36
5.3.3 Effect of sorption contact time on desorption of uranium from Topopah Spring tuff.	38
5.3.4 Effect of particle size fraction on sorption and desorption ratios of strontium, cesium, and uranium on Topopah Spring tuff	41
5.3.5 Ratios of R_s and R_d values for sorption and desorption of Sr, Cs, and U on Topopah Spring tuff for different particle size fractions	42

PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION
DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS:
REPORT FOR OCTOBER 1987 - JUNE 1989

R. E. Meyer
W. D. Arnold
G. D. O'Kelley
F. I. Case
J. F. Land

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 Yucca Mountain Project (formerly Nevada Nuclear Waste Storage Investigations) managed by the Nevada Operations Office of the DOE. This is the final report in this series because this NRC project was terminated effective June 30, 1989.

The rock samples used in these and the previous studies were prepared from a core sample of Topopah Spring tuff from well USW-G1 and a rock sample from the Busted Butte outcrop of the Topopah Spring tuff. 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.

The principal emphasis in this report period was on column studies of migration of uranium and technetium in water from well J-13 at the Yucca Mountain site. Columns 1 cm in diameter and about 5 cm long were constructed and carefully packed with ground tuff. The characteristics of the columns were tested by determination of elution curves in J-13 well water containing tritium (as HTO) or technetium as the TcO_4^- ion.

Elution peaks obtained previously with uranium were asymmetrical and the shapes were often complex, observations that suggested irreversibilities in the sorption reaction. To try to understand these observations, the effects of flow rate and temperature on uranium migration were studied in detail. Sorption ratios calculated from the elution peaks became larger as the flow rate was decreased and when the temperature was increased. These observations can be explained if the sorption of uranium is kinetically hindered. To confirm this, batch sorption ratio

experiments were completed for uranium as a function of time for a variety of conditions. These experiments confirmed that the reaction was slow because 20 to 30 days elapsed before sorption ratios reached steady-state values.

Preliminary column experiments were completed under conditions simulating unsaturated flow in tuff for transport of traced Sr^{2+} , Cs^+ , and TcO_4^- in one experiment and for transport of Eu(III) in a second experiment. A small volume of J-13 well water that contained these ions was introduced to the entry end of the column of tuff and periodically the end was wetted with J-13 well water. The distribution of strontium, cesium and technetium was determined by sectioning the column and determining the radioactivity in each section. The technetium traveled the farthest and the cesium the least, observations which are consistent with their sorption ratios measured in saturated batch tests. In the second experiment, most of the europium was found on the entry frit of the column but a small fairly uniform amount was found throughout the column.

The effect of particle size of tuff was determined for batch sorption studies of strontium, cesium, and uranium. The sorption ratios increased somewhat as the particle size decreased.

The significance of these experiments with respect to data obtained by DOE investigators for evaluation of the suitability of the Yucca Mountain site is discussed. Our data for strontium and cesium are in order of magnitude agreement with those of DOE for similar types of tuff. However, strontium and cesium have relatively simple aqueous chemistry. For those elements, such as europium and uranium, that have complicated behavior in aqueous solutions our data leave questions relative to the published DOE data on these elements. Data taken by DOE without pH control are suspect unless it can be proven that changes of pH do not significantly alter the sorption behavior of the elements tested.

2. INTRODUCTION

The Oak Ridge National Laboratory (ORNL) has been 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 that are 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 efforts and may be able to resolve important technical issues before the final licensing activities. This NRC project was terminated on June 30, 1989, and this report constitutes the final report of a series of reports on this project.

DOE characterization of the Yucca Mountain site is 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) has been closely integrated with another NRC project at ORNL (FIN B0287) which has been providing technical assistance to the NRC by reviewing and assessing available DOE information. NRC project B0287 was also terminated as of June 30, 1989. Through project B0287, key geochemical information has been identified and independent laboratory investigations were 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 had 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. 1988), batch studies of sorption onto tuff were described. Column methodology was studied, and column studies of sorption were begun. In the current report, effects of temperature and flow rate on column determinations of sorption ratios of uranium and technetium are described. The kinetics of sorption and desorption of uranium were investigated by batch methods. Because the proposed location of the repository at the Yucca Mountain site is in an unsaturated zone, a preliminary experiment was completed to measure transport in a column of unsaturated tuff, and the results were compared

to those obtained from saturated column experiments. The results of these studies are compared to information published by DOE concerning the Yucca Mountain, Nevada site for the proposed HLW repository. Information pertinent to this site is the responsibility of the Yucca Mountain Project (formerly Nevada Nuclear Waste Storage Investigations) managed by the Nevada Operations Office of the DOE.

3. MATERIALS AND METHODS

3.1 TUFF SAMPLES

The tuff samples used in the tests described in this report are core material from the Topopah Spring tuff, lithophysal zone, from the 1189.7 to 1190.3 ft level of well USW-G1. In previous studies, samples of Busted Butte outcrop of the Topopah Spring tuff were used. The core samples were characterized and ground to -70 mesh as described previously (Meyer et al. 1986, Meyer et al. 1987).

The tuff samples were characterized 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 to 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 core samples contain significant quantities of smectite (approximately 10% by weight), whereas the outcrop material from Busted Butte contains only trace amounts of smectite. In addition, the core samples were found to have lower quartz/cristobalite ratios.
2. No major differences in bulk or clay mineralogy were detected among five size fractions prepared from the Busted Butte material. The only minor mineralogic variation detected was an apparent decrease in quartz and a concomitant increase in alkali feldspar with decreasing grain size.

3.2 GROUNDWATER

Water from well J-13 at the Yucca Mountain site was used in all of the tests described in this report. The well water was obtained in completely filled 1-gallon amber polypropylene bottles sealed with tape. When the bottles were opened the water was transferred to smaller amber polypropylene bottles and stored in a controlled atmosphere glove box containing 1.5% CO₂ in air. The experiments were conducted in the controlled atmosphere glove box air to maintain the pH of the groundwater at 6.8 to 7.1. The controlled atmosphere box, the CO₂ monitor, and the control system were described previously (Meyer et al. 1986). The composition of the well water is given in Table 3.1.

Table 3.1 Composition of J-13 well water

Constituent	Concentration (mg/L)
Li	0.05
Na	51.0
K	4.9
Mg	2.1
Ca	14.0
Sr	0.05
Ba	0.003
Fe	0.04
Al	0.03
Si	61.0
F ⁻	2.2
Cl ⁻	7.5
HCO ₃ ⁻	120.0
SO ₄ ²⁻	22.0
NO ₃ ⁻	5.6
PO ₄ ³⁻	0.12
pH = 7.1	

3.3 COLUMN CONTACT METHODOLOGY

Column sorption tests under saturated conditions were made with a 1.0 cm diameter column of the crushed tuff core and 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 grams 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 through the tuff until the weight of water in the reservoir stabilized, which indicated that all the air had been displaced from the column. 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. With each column, the calculated void volume was checked by measuring the void volume of the system with tritiated water in J-13 well water. If the measured void volume was not within 15% of the calculated void volume, the column was abandoned and a new one was prepared.

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

The J-13 well water flow rate for most of our previous tests was 0.20 mL/min, equivalent to a velocity through the column of 4.2×10^{-3} cm/sec. In this report, we describe work with flow rates from 0.05 mL/min to 1.0 mL/min. The ratio of the column length to the column diameter was 5 and the ratio of the column diameter to the packing material maximum particle size 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 well water 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 well water upflow through the tuff. In most cases, 0.200 mL of the radionuclide spike solution was prepared and 0.100 mL was transferred to a separate tube for addition to the column; counting standards were prepared from the remaining 0.100 mL. For elements such as uranium with potential stability problems, the spike solutions were prepared as near as practical (usually within 30 minutes) 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 previously (Meyer et al., 1987) using both the top of the peak and the centroid as the elution volume. The centroid of the peak is the volume where 50% of the tracer has been eluted, and, according to Relyea (1982), the centroid is a better indication of the elution volume to be used in the calculation of the sorption ratio. In our experiments with uranium described below, it was generally observed that sorption ratios calculated from the centroid were closer to those measured by batch techniques than those calculated from the peak position. However, agreement between sorption ratios calculated from the peak or centroid of the elution curve is expected only under ideal conditions. If there are kinetic factors, or other complications, than a much more complicated relation between batch sorption ratios and peak or centroid positions would be expected. Most of the sorption ratios given in this report were calculated from both the centroid and the peak. If only one sorption ratio is given, it was calculated from the centroid.

Sorption ratios were calculated from the formula (Meyer et al. 1988)

$$R_S = \frac{V_r - V_p}{W} \quad (1)$$

where R_S = sorption ratio (L/kg)

V_r = elution volume, determined either from peak or centroid

V_p = void volume or pore volume

W = weight of tuff, g

Tests to measure transport of radionuclides under partially saturated conditions were made with the apparatus shown in Figure 3.3.1. A small

chamber, shown on the left in Fig. 3.3.1, was used for introduction of the well water to the column inlet. The teflon end fitting on the right was adjustable and was used to compress the tuff by applying pressure on it with a steel tube which fitted around the rod shown in Fig. 3.3.1. The 2.5-cm diameter column was loaded dry with 50 g of crushed Topopah Spring tuff, and the tuff bed was compressed to a length of about 8.2 cm. At the start of the sorption test, a 0.250-mL spike solution of the radionuclides was spread evenly on the tuff at the column inlet. Twice a week, the small chamber at the inlet was filled with J-13 well water; the J-13 was left in the compartment for 30 s and then removed. Throughout the test, the saturation level of the tuff was monitored by weighing the column and comparing the weight with that before any J-13 addition. The column was allowed to stand for 2 weeks after the tuff reached the desired level of saturation. The tuff was then carefully extruded into small sections by applying pressure on the teflon end fitting and cutting off the small sections with a thin sharp spatula. The radionuclide count rate was then measured for each section.

3.4 BATCH CONTACT METHODOLOGY

The batch contact experiments described in this report were made using the methods and techniques described previously for work with tuff (Meyer et al., 1987) and for similar work with basalt from the Hanford Site (Kelmers et al. 1985). In the tests, either 0.2 g or 0.4 g of crushed tuff was contacted with 2 mL or 4 mL respectively of traced well water under gentle agitation for the periods given. Before contact with the traced well water, the tuff was usually conditioned three times with untraced well water to assure that the well water composition did not change during contact with the traced well water. After the conditioned tuff samples were contacted with traced well water, the samples were centrifuged and aliquots of the solution were counted.

For desorption tests, as much of the solution from the sorption tests as possible was decanted without removing any of the tuff. Untraced well water was added to the tuff samples and desorption was measured as described above for measuring sorption.

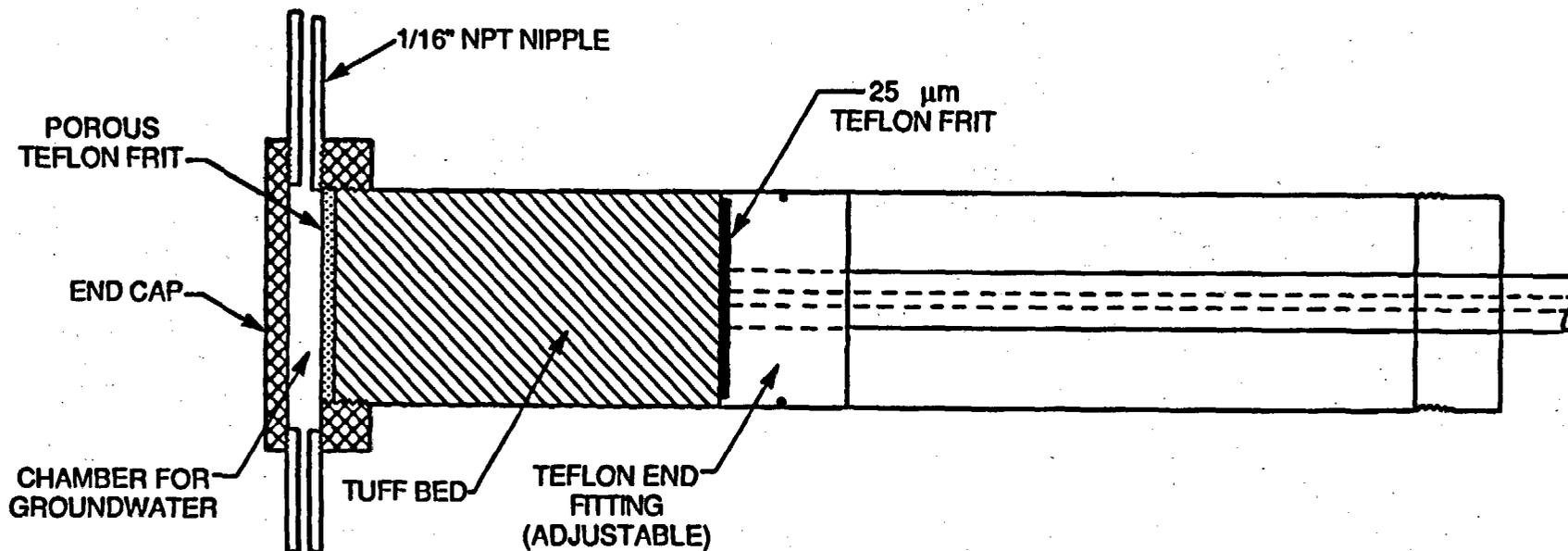


Fig. 3.3.1 Apparatus to measure the transport of radionuclides in tuff under partially saturated conditions.

4. PUBLISHED INFORMATION ON SORPTION ONTO YUCCA MOUNTAIN TUFF

A great deal of information has been obtained by the Yucca Mountain Project 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 our previous report (Meyer et al. 1988), we included a brief summary of sorption results obtained from these references. More recently, the sorption studies undertaken from 1977 to 1985 have been compiled and summarized by Thomas (1987). This is an excellent reference with a complete tabulation of batch sorption results in the Appendix. Our discussion below of Yucca Mountain Project results is based on this reference. However, it is stated in this report that it contains "an unrefined data set", i.e., some data are included that were obtained during the process of developing the methodology. A final refined Reference Data Base is being compiled at Sandia National Laboratory.

For purposes of comparison, Thomas (1987) divides the tuffs into 4 major rock groups; devitrified (composed primarily of quartz and alkali feldspar), zeolitized (dominated by an alteration assemblage of zeolites), glass (high percentage of original glass in sample which is not devitrified or altered to zeolites), and clays (clays being the major alteration assemblage). Except for the clay group, these groups are subdivided into 3 subgroups each, depending on the relative amounts of clays, zeolites, and glasses. The Topopah Spring core sample that we used (USW-G1, 1189.7 - 1190.3 ft) is in the second subgroup of the devitrified group, because it contains more than 10% clay (11%) and less than 10% zeolites (no zeolites were detected by X-ray analysis, Meyer et al. 1986). The sample of Topopah Spring tuff from the Busted Butte category is in the first subgroup of devitrified tuff, because it contains no detectable amounts of clays or zeolites.

Three of the Yucca Mountain Project tuff samples (G1-2901, JA-32, and YM-54) are listed as being in the same classification, the second subgroup of the devitrified group, as the Topopah Spring core that we used (Thomas, 1987, p 15). Their compositions (Daniels et al. 1982) and a selection of data compiled by Thomas are given in Tables 4.1 - 4.3. However, according to the compositions given by Daniels et al. (1982), sample G1-2901 has less than 10% clays, and this would put it into the first subgroup of the devitrified group. Perhaps, Thomas placed this particular sample into the second subgroup because it was re-examined and found to have more clay than indicated in Daniels et al. (1982). The tables in Thomas' report give the concentrations of the nuclides before the start of the sorption experiments. All data were taken with J-13 well water. The initial and final pH values of the solutions are not given. Duplicate runs are indicated by the numbers 1 and 2. All

determinations shown were performed at room temperature. Some experiments were done at 70°C, but they are not shown in Tables 4.1 - 4.3. The prefix G1 indicates that the sample was taken from drill hole USW-G1, the prefix JA indicates drill hole J-13, and YM indicates drill hole UE25a-1. The location of the drill holes are shown on a map given in Thomas (1987). The atmosphere designation "CO₂" indicates that a partial pressure on the order of 5% CO₂ was maintained over the sample to hold its pH constant at about 7.

Estimates of errors such as the standard deviations of the means are not given in the tables in the Appendix of Thomas (1987). However Thomas states that a "realistic" estimate of the magnitude of the sorption ratios is $\pm 50\%$. This is not a rigorously determined estimate but is apparently a judgmental estimate by the investigators involved in making the measurements.

Although no sorption or desorption ratios using the circulating column method are shown in Thomas (1987), a table is given (p. 24 in Thomas) with a comparison of sorption ratios obtained by the two different methods. The circulating column method is similar to the batch method in that the amount of fluid and rock are the same throughout the experiment and the calculation method is the same, but in the circulating column method the groundwater is continuously recirculated through a column of crushed rock. In general, sorption ratios obtained by the two different methods agree within a factor of two. For sample YM-54 (data in Table 4.3), the ratio of batch to circulating column sorption ratios is 1.3 for Sr, 1.3 for Cs, and 1.6 for Ba. Comparisons are not given for sample G1-2901 (Table 4.1) and sample JA-32 (Table 4.2).

A comparison is also given for sorption ratios determined by the batch method and the crushed-rock column method. In this case the column method refers to experiments in which the solution flows through the column once; usually fluid is passed through the column until the tracer has passed through the column. For strong sorption, breakthrough did not occur in a reasonable period of time; in this case the column was cut up into sections at the end of the experiment to determine the position of the tracer. For G1-2901 tuff, the column method consistently gave smaller values than the batch for Sr, Cs, and Ba; good agreement was obtained for JA-32 tuff with Sr, the only element compared, and good agreement is obtained for Sr, Cs, and Ba for YM-54 tuff.

Table 4.1 Sorption data for Yucca Mountain Project
sample G1-2901*

Elements	Atmos- sphere	Sorption		Desorption			
		Time (d)	Ratio (L/kg) 1	Ratio (L/kg) 2	Time (d)	Ratio (L/kg) 1	Ratio (L/kg) 2
Sr	air	21	68.0	66.0	42	67.0	66.0
	air	42	69.0	71.0	21	69.0	74.0
Cs	air	21	1400	950	42	1300	1400
	air	42	1400	1400	21	1400	1400
Eu	air	21	1.95x10 ⁵	2.30x10 ⁵	42	2.20x10 ⁵	2.00x10 ⁵
	air	42	2.10x10 ⁵	2.10x10 ⁵	21	2.10x10 ⁵	2.00x10 ⁵
U	CO ₂	42	4.75	4.03	-	-	-

*The particle size for the experiments with Sr, Cs, and Eu was ≤ 500 μm . For U, it was 75-500 μm . This sample was from the Tram Member of the Crater Flat Tuff. Its composition is (Daniels et al. 1982): trace smectite, 2-5% illite, 25-40% quartz, 5-10% cristobalite, 40-60% alkali feldspar, 2-5% calcite.

Table 4.2 Sorption data for Yucca Mountain Project sample JA-32*

Elements	Atmo- sphere	Sorption		Desorption		Particle Size (μm)
		Time (d)	Sorption Ratio (L/kg)	Time (d)	Desorption Ratio (L/kg)	
Sr	air	7	48.0	7	48.0	106-150
	air	7	50.0	14	55.0	355-500
	air	21	50.0	21	41.0	106-150
	air	21	52.0	28	52.0	355-500
	air	35	72.0	35	35.0	106-150
	air	35	56.0	35	50.0	355-500
	air	56	55.0	77	50.0	106-150
	air	56	71.0	84	72.0	355-500
Cs	air	7	120.0	7	170.0	106-150
	air	7	110.0	14	200.0	355-500
	air	21	120.0	21	230.0	106-500
	air	21	120.0	28	150.0	355-500
	air	35	130.0	35	130.0	106-500
	air	35	140.0	42	200.0	355-500
	air	56	140.0	77	150.0	106-500
	air	56	120.0	84	180.0	355-500
Eu	air	7	51.0	7	1600.0	106-150
	air	7	48.0	14	610.0	355-500
	air	21	69.0	21	600.0	106-150
	air	21	92.0	28	600.0	355-500
	air	35	73.0	35	740.0	106-500
	air	35	88.0	35	570.0	355-500
	air	56	190.0	77	1300.0	106-150
	air	56	120.0	84	780.0	355-500
U	air	7	3.5	21	15.0	106-150
	air	7	1.4	21	0.2	355-500
	air	14	2.9	14	12.0	106-150
	air	14	1.3	14	5.4	355-500
	air	21	2.5	7	9.6	106-150
	air	21	1.3	7	5.2	355-500

*This sample is from the Bullfrog Member of the Crater Flat Tuff. Its composition range is (Daniels et al. 1982): <5% smectite, 5-15% illite, 35-50% quartz, 40-60% alkali feldspar, trace analcime.

Table 4.3 Sorption data for Yucca Mountain Project sample YM-54*

Elements	Atmo- sphere	Sorption		Desorption		Particle Size (μ m)
		Time (d)	Sorption Ratio (L/kg)	Time (d)	Desorption Ratio (L/kg)	
Sr	air	21	280.0	-	-	≤ 38
	air	21	270.0	-	-	≤ 38
	air	21	95.0	42	120.0	≤ 106
	air	21	56.0	-	-	38-106
	air	21	57.0	-	-	39-106
	air	21	42.0	-	-	106-500
	air	21	88.0	42	80.0	106-150
	air	21	37.0	-	-	106500
	air	42	97.0	21	110.0	≤ 106
	air	42	80.0	21	84.0	106-500
	air	42	150.0	21	120.0	≤ 75
	air	42	130.0	21	120.0	75-500
	air	84	130.0	-	-	≤ 75
	air	84	70.0	-	-	75-500
Cs	air	21	890.0	-	-	≤ 38
	air	21	940.0	-	-	≤ 38
	air	21	270.0	42	270.0	≤ 106
	air	21	190.0	-	-	≤ 106
	air	21	190.0	-	-	38-106
	air	21	190.0	-	-	38-106
	air	21	130.0	-	-	106-500
	air	21	290.0	42	290.0	106-500
	air	21	110.0	-	-	106-500
	air	42	230.0	21	320.0	106-500
	air	42	200.0	21	350.0	106-500
Eu	air	21	1600.0	-	-	≤ 38
	air	21	1600.0	-	-	≤ 38
	air	21	390.0	42	1900.0	≤ 106
	air	21	420.0	-	-	≤ 106
	air	21	260.0	-	-	38-106
	air	21	440.0	-	-	106-500
	air	21	580.0	42	2100.0	106-500
	air	21	490.0	-	-	106-500
	air	42	700.0	21	1700.0	≤ 106
	air	42	370.0	21	1700.0	106-500
U	air	7	2.0	14	14.0	≤ 106
	air	7	1.0	14	4.0	106-500
	air	14	2.0	7	15.0	≤ 106
	air	14	2.0	7	19.0	106-500
	air	21	2.0	-	-	≤ 106
	air	21	1.0	-	-	106-500

Table 4.3 (continued)

*This sample is from the Bullfrog Member of the Crater Flat Tuff. Its composition range is (Daniels et al. 1982): 5-10% smectite, 2-5% illite, 35-50% quartz, 30-50% alkali feldspar.

Much of the Yucca Mountain Project 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 the Yucca Mountain Project. Rather, the objective is to evaluate data obtained by the Yucca Mountain Project concerning the tuffs through a careful selection of experiments designed to examine their key conclusions derived from sorption studies. So far, we have investigated two samples of Topopah Spring tuff, and we have investigated the elements strontium, cesium, europium, uranium, and technetium. Most of the experiments described in this report are column measurements concerned with the effects of flow rate and temperature. These experiments were designed to investigate the kinetics of sorption reactions, mainly the kinetics of uranium sorption. To investigate further the kinetics of uranium sorption, a series of batch sorption and desorption experiments with uranium at varying lengths of time were done. A problem with application of batch and column sorption experiments to understanding transport of elements is whether results from saturated conditions are applicable to unsaturated conditions. Therefore, experiments concerning transport under unsaturated conditions were begun and are reported below.

5.2 COLUMN TESTS

5.2.1 Effect of Flow Rate on Technetium Sorption

Because technetium is normally present as the anion TcO_4^- in air-saturated groundwaters, it is not expected to sorb significantly on tuff. Thus, sorption ratios should be almost zero. In fact, if anion exclusion occurs, negative sorption ratios could be observed. Column tests of the sorption of technetium on tuff were carried out as a function of flow rate, and the results are shown in Table 5.2.1 and in Fig. 5.2.1. Because the peak shapes were close to symmetrical, the centroid position is only slightly greater than the position of the top of the peak. An example of an elution curve for technetium is given in Fig. 5.2.2. Although the computed sorption ratios are close to zero, they are consistently negative. It is difficult to determine from Fig. 5.2.1 whether there is a trend with flow rate; it is possible that there is a slight decrease in sorption ratio with increasing flow rate. The slightly negative sorption ratios suggest anion exclusion.

5.2.2 Effect of Flow Rate on Uranium Sorption

The effect of flow rate on uranium sorption by the column method is shown in Table 5.2.2 and Figure 5.2.3. All of the peaks, as illustrated in Fig. 5.2.4, are asymmetrical, and sorption ratios computed from the centroid are roughly twice those computed from the positions of the top of the peak. The sorption ratio calculated from the centroid agrees better with batch sorption ratios than those calculated from the

position of the top of the peak (Section 3.3). However, the peaks appear at smaller volumes than those of the centroids, and this would mean that significant amounts of the radionuclide would arrive at a given point in the flow path earlier than what would be calculated using the sorption ratio calculated from the centroid.

As shown in Fig. 5.2.3, the sorption ratios decrease as the flow rate increases, probably because of slow sorption kinetics.

Table 5.2.1 Effect of flow rate on technetium sorption onto Topopah Spring tuff

Test #	Volume (mL)		Tc Rs (L/kg)		Flow Rate (mL/min)
	Peak	Centroid	Peak	Centroid	
T-101	1.604	1.661	-0.010	-0.003	0.10
T-87	1.619	1.599	-0.031	-0.015	0.20
T-100	1.579	1.645	-0.019	-0.006	0.40
T-99	1.390	1.498	-0.057	-0.035	0.60

Test conditions: 0.100 mL of J-13 wellwater containing ca. 500 c/s of ^{99m}Tc was eluted from a 1.0 cm column of Topopah Spring core at flow rates from 0.10 to 0.60 mL/min. The column effluent was collected in 0.20-mL fractions, and each fraction was assayed for ^{99m}Tc . The temperature was 24°C.

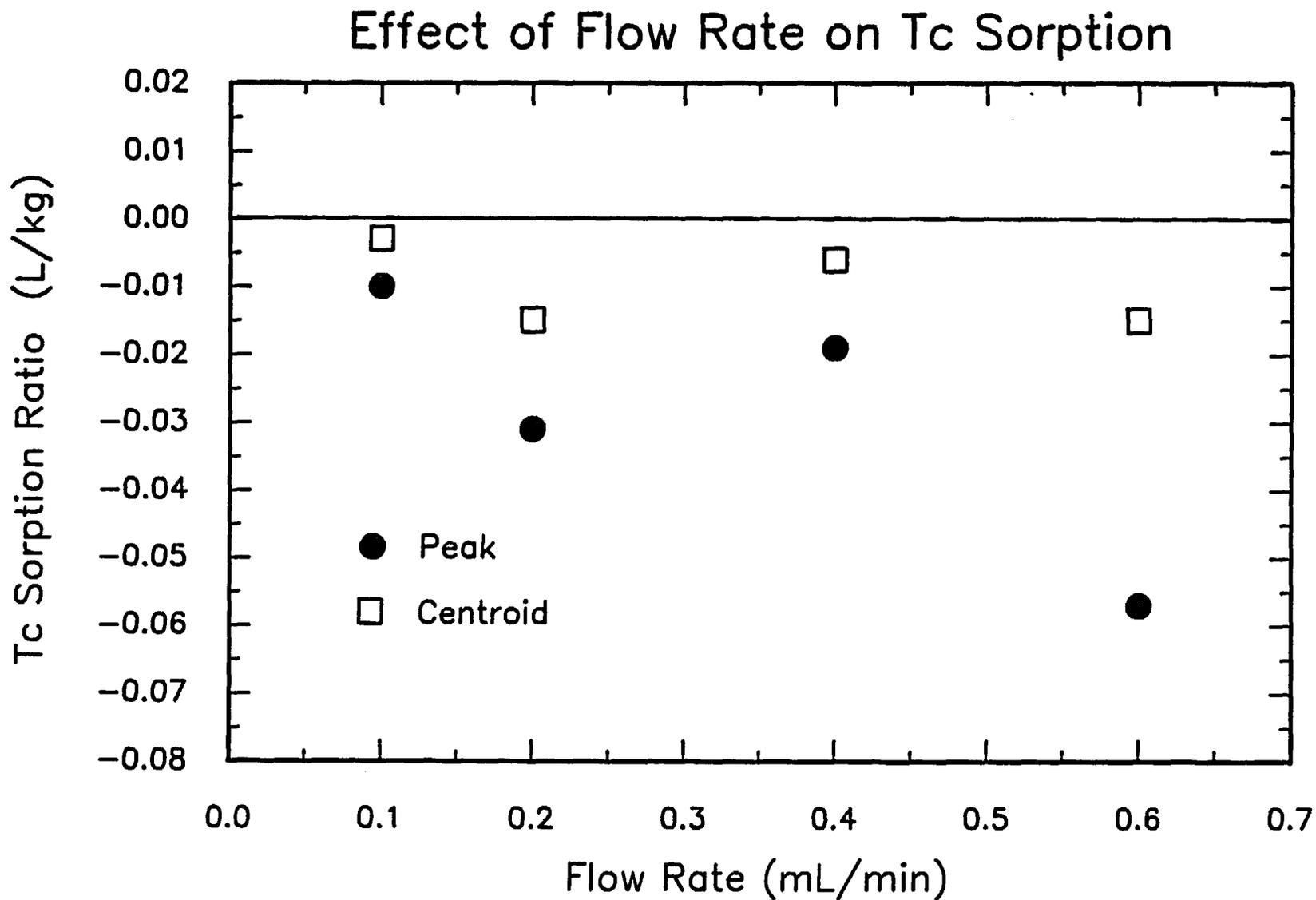


Fig. 5.2.1 Effect of flow rate on sorption of TcO_4^- onto Topopah Spring tuff. Column method, 24°C.

Technetium Sorption Topopah Spring Core Column

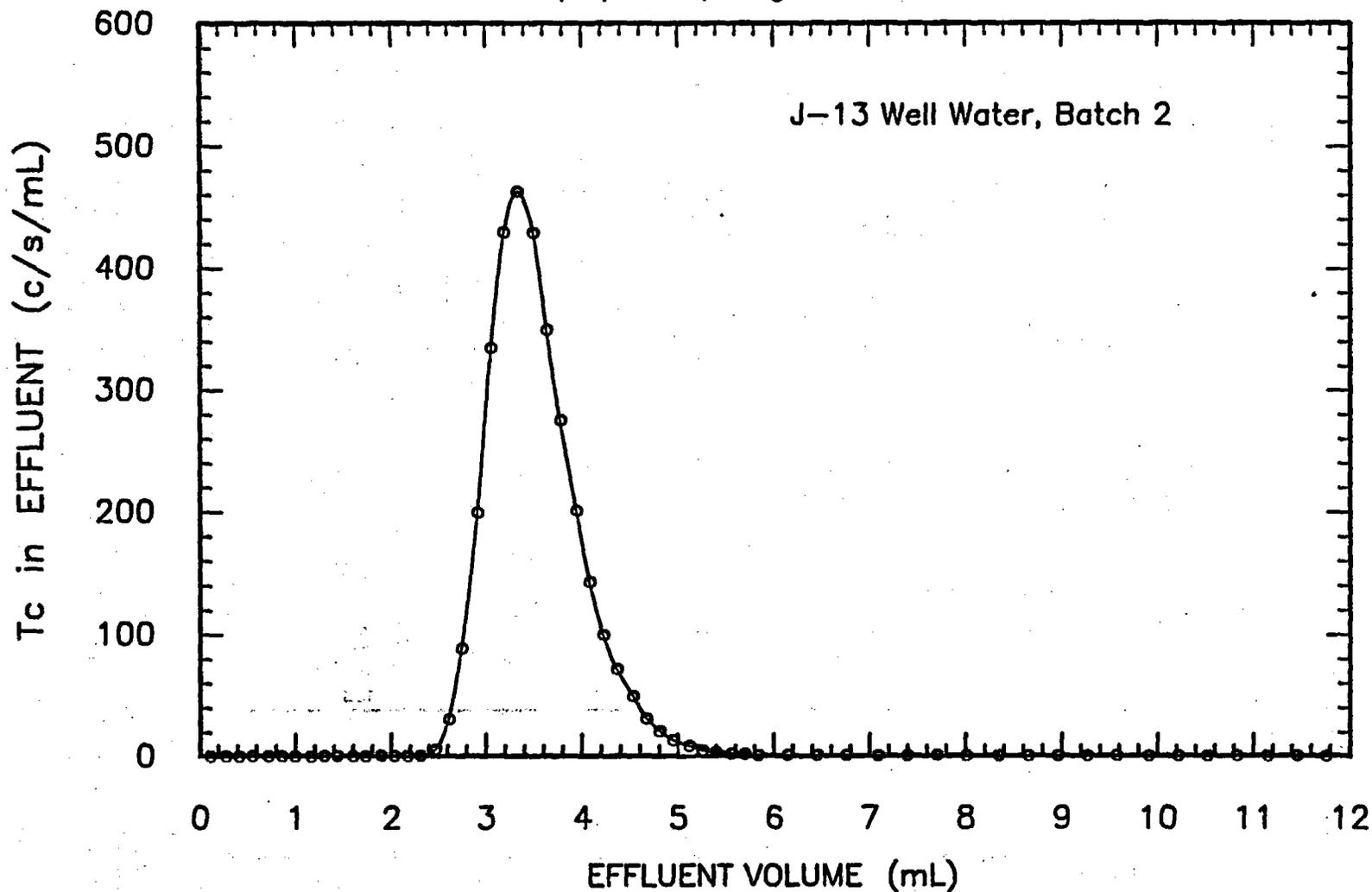


Fig. 5.2.2 Elution curve of TcO_4^- in J-13 well water from a column of Topopah Spring tuff. 0.1 mL/min, 24°C. $R_s = -0.003$ L/kg.

Table 5.2.2 Effect of flow rate on uranium sorption onto Topopah Spring tuff

Test #	Volume (mL)			U Rs (L/kg)			Flow Rate (mL/min)
	Peak I	Peak II	Centroid	Peak I	Peak II	Centroid	
T-105	--	12.2	25.9	--	2.10	4.83	0.05
T-97	--	19.9	34.2	--	3.64	6.49	0.05
T-85	--	6.14	11.5	--	0.89	1.95	0.10
T-88	--	5.47	9.79	--	0.76	1.62	0.20
T-80	--	5.77	10.2	--	0.82	1.69	0.20
T-102	--	7.25	14.9	--	1.13	2.64	0.20
T-104	--	8.89	18.9	--	1.44	3.43	0.20
T-90	--	6.33	12.8	--	0.93	2.22	0.20
T-83	--	6.08	10.8	--	0.88	1.82	0.20
T-81	1.80	5.93	9.69	0.03	0.85	1.59	0.20
T-95	--	5.70	10.2	--	0.80	1.69	0.30
T-89	1.80	4.77	7.81	0.03	0.62	1.22	0.40
T-91	1.68	7.55	12.7	0.00	1.17	2.20	0.60
T-98	1.20	4.77	8.99	-0.09	0.62	1.46	0.60
T-94	1.68	4.93	8.69	0.00	0.65	1.39	0.60
T-92	1.51	4.72	6.93	-0.03	0.61	1.05	0.80
T-96	1.35	3.98	7.75	-0.06	0.46	1.21	1.00

Test conditions: 0.100 mL of J-13 wellwater containing about 3000 c/s of ^{233}U were eluted from a 1.0 cm column containing 5.01 g of -70 mesh Topopah Spring core at flow rates of 0.05 mL/min to 1.00 mL/min. The column effluent was collected as twenty 0.6-mL fractions and forty 1.0-mL fractions; a 0.50-mL aliquot of each fraction was assayed for ^{233}U by liquid scintillation counting. The temperature was 24°C.

At the higher flow rates, there are two peaks in the elution curves as illustrated in Fig. 5.2.5, and the first peak occurs at a position corresponding to essentially zero sorption. The appearance of two peaks could be caused by uranium sorbed on colloidal material that is flushed through the column at higher flow rates or by two species not at equilibrium; the species corresponding to zero sorption would probably be a negative or neutral species, and the adsorbing species would be a positively charged species. Another possible explanation for the appearance of two peaks is that at higher flow rates, and hence at higher input pressures, uneven flow occurs, and part of the fluid passes through the column at a much faster rate; the uranium in that portion of the fluid may be in contact with the tuff only a relatively short period of time, and if the kinetics of sorption are sufficiently slow, little or no sorption would be observed. Because these observations suggested that the kinetics of sorption of uranium are slow, the kinetics were studied by batch sorption studies at varying periods of time (Section 5.3).

Effect of Flow Rate

U Sorption on Topopah Spring Core

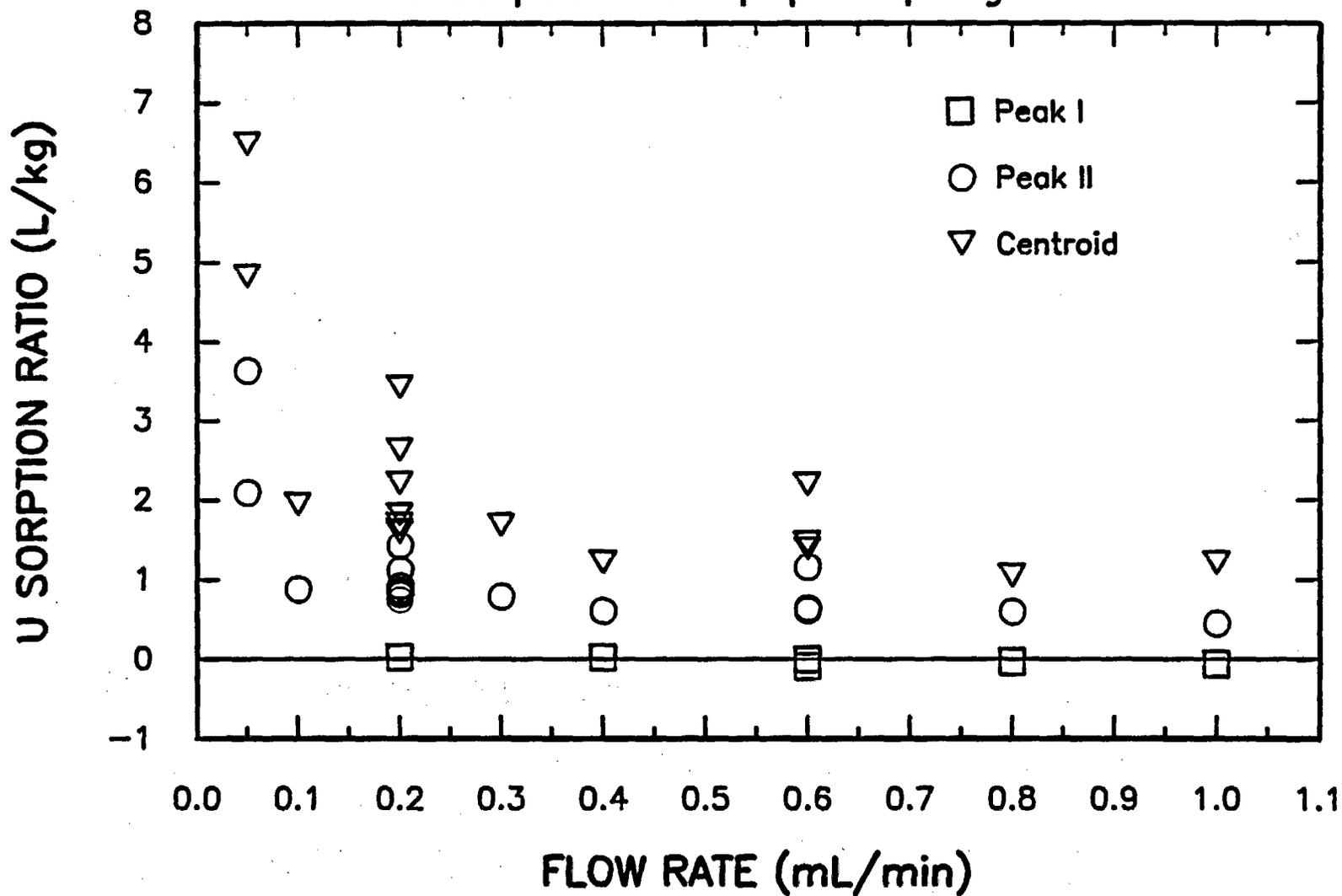


Fig. 5.2.3 Effect of flow rate on sorption of uranium onto Topopah Spring tuff. Column method, 24°C.

U Sorption on Topopah Spring Core Column

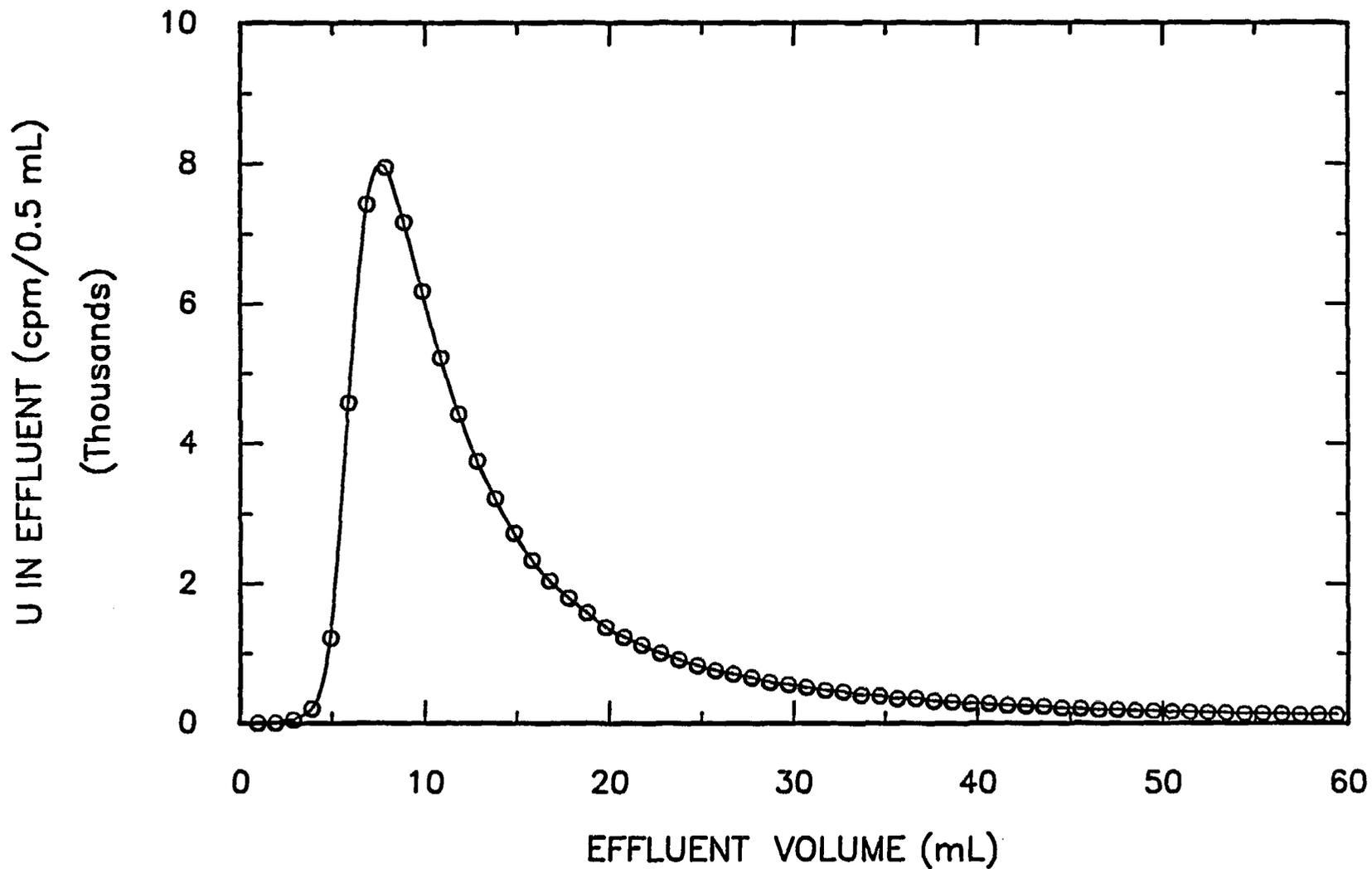


Fig. 5.2.4 Elution curve of uranium in J-13 well water from a column of Topopah Spring tuff. 0.2 mL/min, 24°C. $R_s = 1.69$ L/kg.

U Sorption on Topopah Spring Core Column

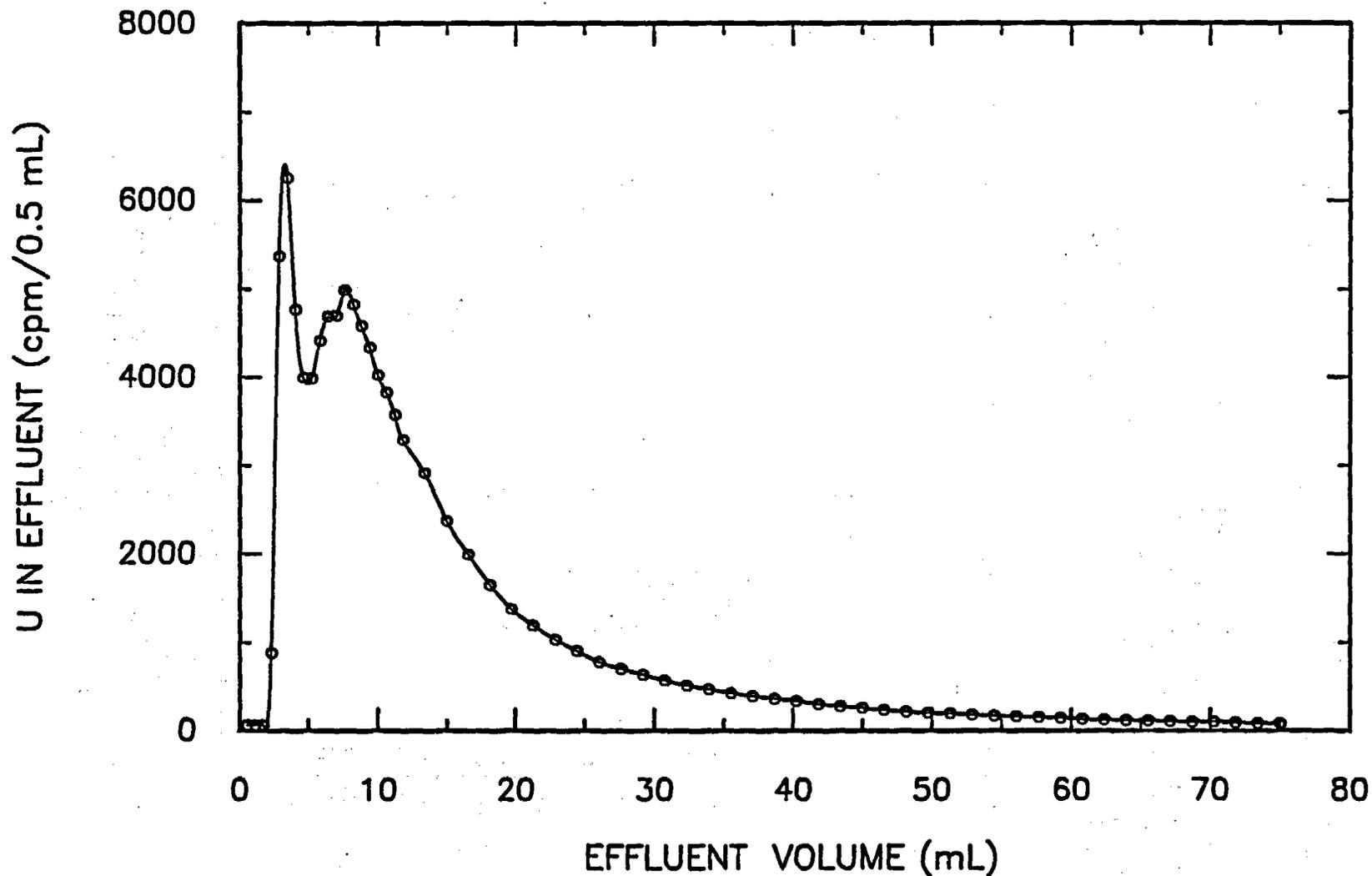


Fig. 5.2.5 Elution curve of uranium in J-13 well water from a column of Topopah Spring tuff. 0.2 mL/min, 24°C.

5.2.3 Effect of Temperature on Column Void Volume

In the calculation of the values of the sorption ratio at various temperatures, the void volume at that temperature must first be known. To determine the void volume, tritium peaks were determined immediately before the sorption determination. Because the tritiated water is not sorbed, the position of the peak indicates the void volume. The void volumes used in the calculation of the sorption ratios were taken from the volume at the centroid of the peak. These measurements are summarized in Table 5.2.3 and in Fig. 5.2.6. Both the centroid and peak volumes are shown; they generally agree within a few tenths of a milliliter. As shown in Table 5.2.3 and in Fig. 5.2.6, the column void volumes do not change greatly with temperature.

Table 5.2.3 Effect of temperature on column void volume

Test #	Void volume (mL)				Temp (°C)
	Incr. Temp.		Decr. Temp.		
	Peak	Cent-roid	Peak	Cent-roid	
T-106	2.346	2.201	--	--	24
T-109	2.268	2.135	--	--	30
T-113	2.569	2.153	--	--	40
T-113R	2.501	2.085	--	--	40
T-113R2	1.866	2.007	--	--	40
T-113R3	1.741	2.020	--	--	40
T-116	1.905	2.035	--	--	40
T-116R	1.738	1.915	--	--	40
T-1162	1.800	2.018	--	--	40
T-117	1.679	2.029	--	--	50
T-120	1.859	2.029	--	--	60
T-127	--	--	2.102	1.934	50
T-127R	--	--	1.843	1.803	50
T-131	--	--	2.040	1.829	40
T-134	--	--	2.211	1.933	30
T-137	--	--	2.066	1.948	24
T-137R	--	--	2.046	1.978	24
T-141	--	--	2.069	2.045	24
T-143	--	--	2.357	2.091	24

Test conditions: 0.100 mL of J-13 wellwater containing about 1,000 c/s tritiated water was eluted from a 1.0 cm column containing 5.01 g of -70 mesh Topopah Spring core at a flow rate of 0.20 mL/min. The column effluent was collected in 0.20-ml increments and 0.10 mL of each fraction was assayed for tritium by liquid scintillation counting.

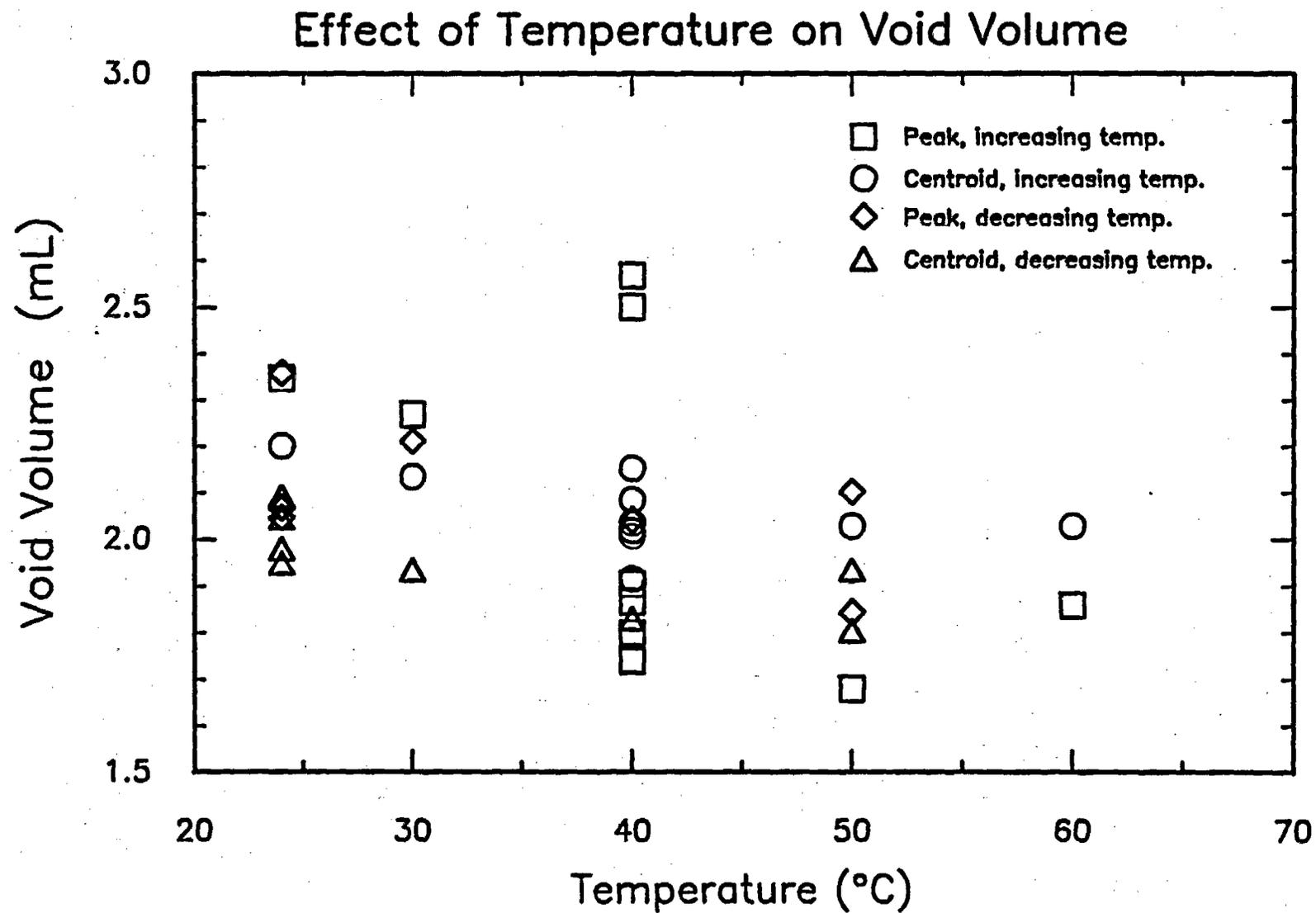


Fig. 5.2.6 The effect of temperature on the measured void volume of a column of Topopah Spring tuff.

5.2.4 Effect of Temperature on Technetium Sorption

The effect of temperature on sorption of technetium is shown in Table 5.2.4 and in Fig 5.2.7. As shown, all values of R_s are very close to zero, and there appears to be no effect of temperature on sorption of technetium. Except for one determination, all values of R_s were negative.

Table 5.2.4 Effect of temperature on technetium sorption onto Topopah Spring tuff

Test #	Volume (mL)		Void Volume (mL)		Tc Sorption Ratio (L/kg)				Temp. (°C)
	Peak	Cent-roid	Peak	Cent-roid	Incr. Temp.		Decr. Temp.		
					Peak	Cent-roid	Peak	Cent-roid	
T-107	2.143	2.008	2.346	2.201	-0.040	-0.038	--	--	24
T-110	2.249	2.044	2.268	2.135	-0.004	-0.018	--	--	30
T-114	1.886	1.856	2.017	2.031	-0.026	-0.035	--	--	40
T-118	1.753	1.800	1.679	2.029	0.015	-0.046	--	--	50
T-121	1.593	1.665	1.859	2.029	-0.053	-0.073	--	--	60
T-121R	1.813	1.640	1.859	2.029	-0.009	-0.078	--	--	60
T-128	1.676	1.755	1.843	1.803	--	--	-0.033	-0.009	50
T-132	1.849	1.788	2.040	1.830	--	--	-0.038	-0.008	40
T-135	1.947	1.817	2.211	1.933	--	--	-0.053	-0.023	30
T-138	1.694	1.811	2.056	1.963	--	--	-0.072	-0.030	24
T-142	1.927	1.876	2.277	2.035	--	--	-0.070	-0.032	24

Test conditions: 0.100 mL of J-13 wellwater containing about 500 c/s of ^{99m}Tc was eluted from a 1.0 cm column containing 5.01 g of -70 mesh Topopah Spring core at a flow rate of 0.20 mL/min. The column effluent was collected in 0.20-mL fractions and each fraction was counted for ^{99m}Tc .

5.2.5 Effect of Temperature on Uranium Sorption

The effect of temperature on sorption of uranium is shown in Table 5.2.5 and in Fig. 5.2.8. The peaks are asymmetrical as illustrated by Fig. 5.2.9, an experiment at 60°C. The values of R_s computed from the centroids are approximately twice those computed from the positions of the peaks. The two experiments at 30°C do not agree; we have no explanation for this. As shown in Fig. 5.2.8, the sorption ratios computed from either the peak or the centroid increase with temperature. However, the values of R_s computed from the centroid are in general higher at increasing temperatures compared to those at decreasing temperatures. The increased values of the sorption ratios suggest that the sorption of uranium is kinetically hindered; increasing the temperature increases the amount of uranium sorbed during its transit through the column.

Effect of Temperature on Tc Sorption

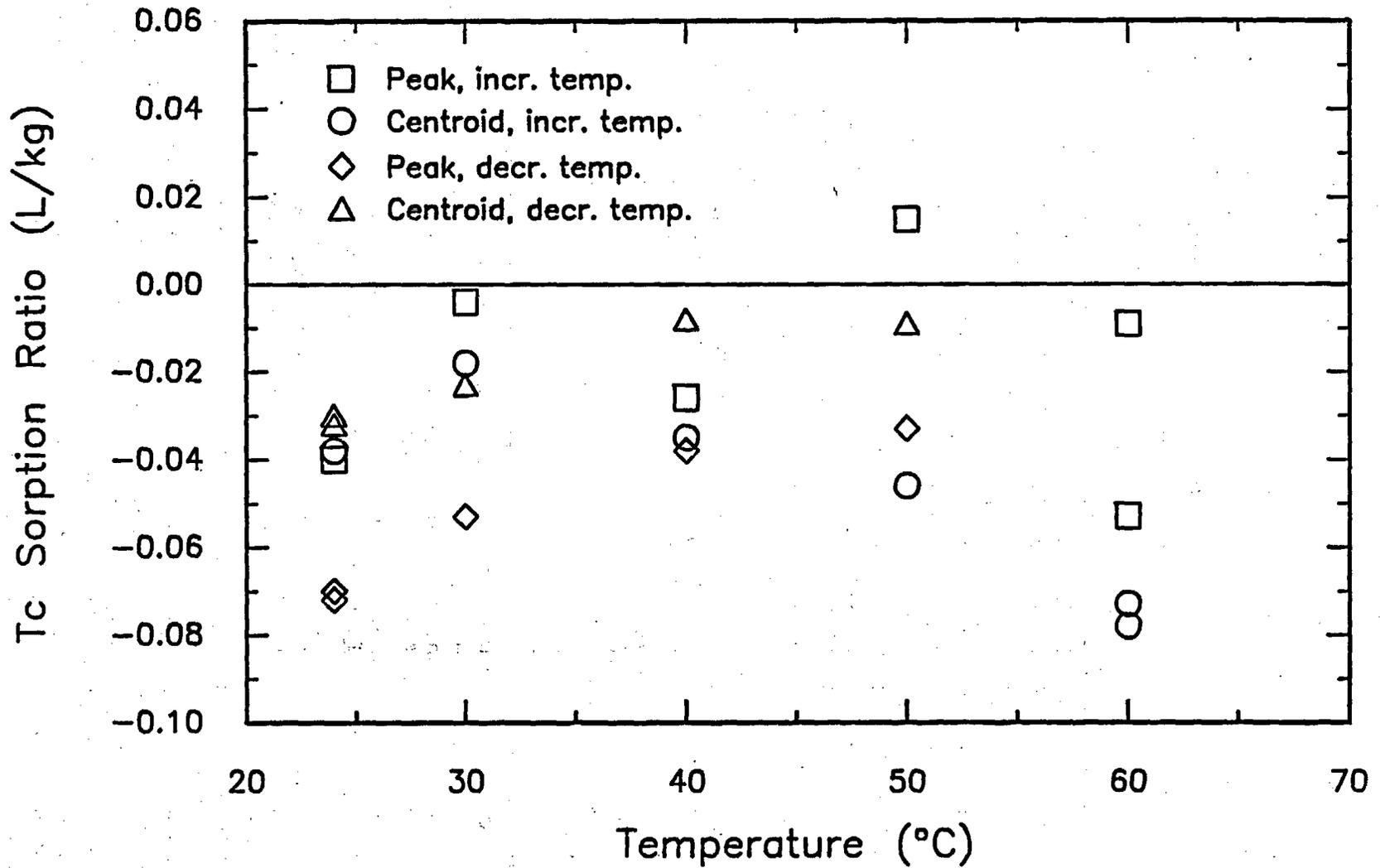


Fig. 5.2.7 The effect of temperature on column measurements of the sorption of TcO_4^- onto Topopah Spring tuff.

Table 5.2.5 Effect of temperature on uranium sorption onto Topopah Spring tuff

Test #	Volume (mL)		Void Volume (mL)		U Sorption Ratio (L/kg)				Temp (°C)
	Peak	Cent-roid	Peak	Cent-roid	Incr. Temp.		Decr. Temp.		
					Peak	Cent-roid	Peak	Cent-roid	
T-108	7.851	12.776	2.346	2.201	1.098	2.110	--	--	24
T-111	11.117	17.683	2.268	2.135	1.765	3.102	--	--	30
T-112	7.843	11.604	2.268	2.135	1.112	1.889	--	--	30
T-115	8.994	19.507	2.017	2.031	1.392	3.486	--	--	40
T-119	12.183	24.187	1.679	2.029	2.095	4.420	--	--	50
T-122	16.783	29.597	1.859	2.029	2.977	5.499	--	--	60
T-129	10.973	20.931	1.972	1.868	--	--	1.796	3.803	50
T-133	10.318	16.458	2.040	1.829	--	--	1.651	2.918	40
T-136	7.759	12.933	2.211	1.933	--	--	1.107	2.194	30
T-139	7.856	12.189	2.277	2.035	--	--	1.113	2.026	24

Test conditions: 0.100 mL of J-13 wellwater containing about 3000 c/s of ^{233}U was eluted from a 1.0 cm column containing 5.01 g of -70 mesh Topopah Spring core at a flow rate of 0.20 mL/min. The column effluent was collected as twenty 0.6-mL fractions and forty 1.6-ml fractions; a 0.50-mL aliquot of each fraction was assayed for ^{233}U by liquid scintillation counting.

5.2.6 Movement of Technetium, Strontium, and Cesium through Unsaturated Tuff

The movement of technetium, strontium, and cesium through unsaturated tuff was studied with the column shown in Fig. 3.3.1. A traced solution was uniformly spread on the tuff at the entry of the column, and then periodically the end of the column was wetted with J-13 well water. The amount of water in the column and the progress of the wetting front were followed with time. The last addition of J-13 was made at 30.9 d, and the saturation was then 40.1%. The column was then left for about 10 d to help promote uniform water distribution in the column. At the end of the experiment at 41 d, saturation was 39.1%, indicating a slight loss of water due to evaporation. It was then cut into sections, and each section was counted to determine the distribution of the elements in the column; results are shown in Fig. 5.2.10. As expected, most of the technetium appeared to move with the water; its profile is largely the result of water movement and diffusion. The small peak at the entry end of the column probably is a result of sorption of technetium, perhaps by reduction of TcO_4^- . Cesium, which is sorbed more than strontium and technetium onto tuff (Meyer et al. 1987, Meyer et al. 1988) moved the least, and strontium moved somewhat more. For this experiment, the driving force for the water movement is the suction potential of the tuff.

Effect of Temperature

U Sorption on Topopah Spring Core

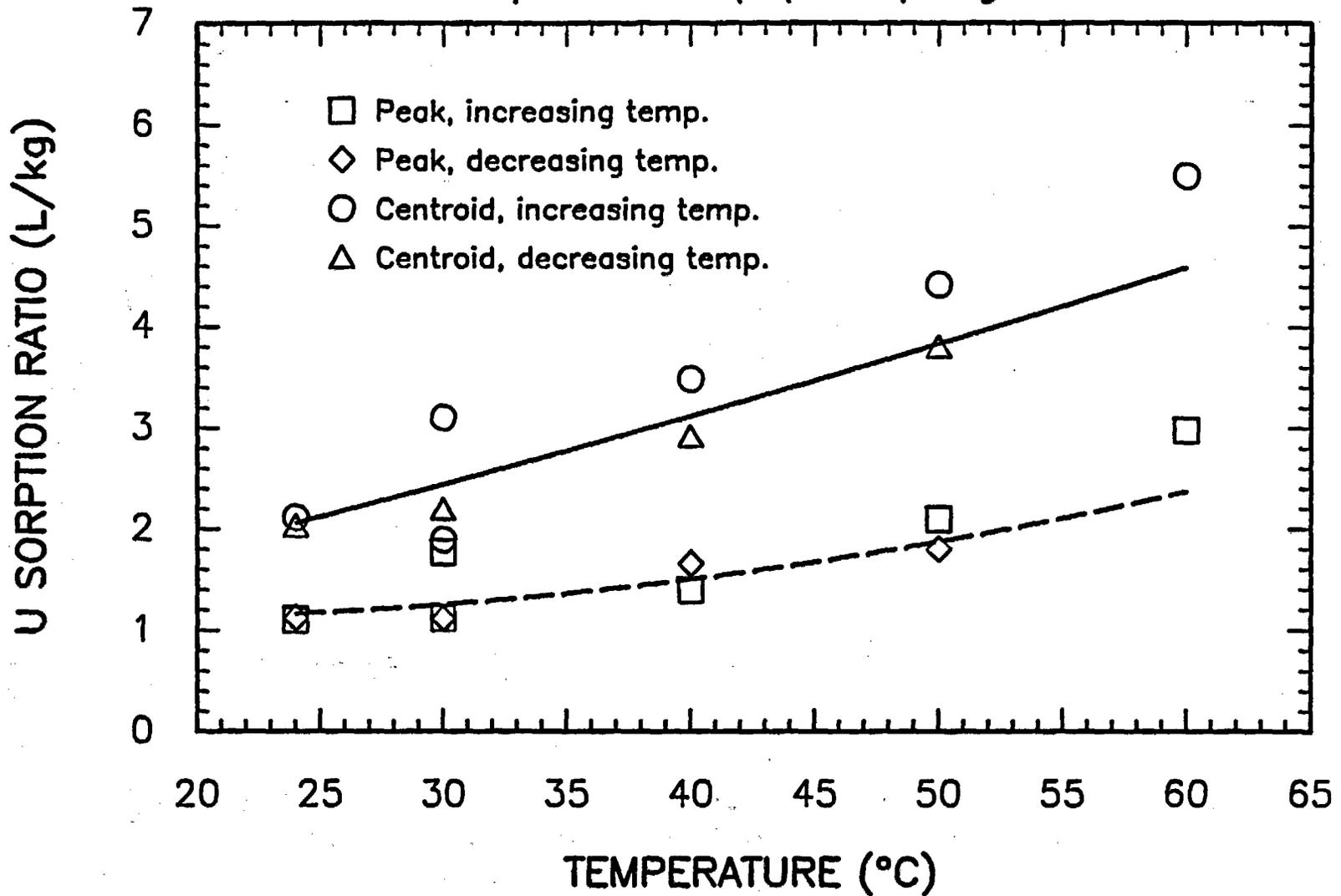


Fig. 5.2.8 The effect of temperature on column measurements of the sorption of uranium onto Topopah Spring tuff.

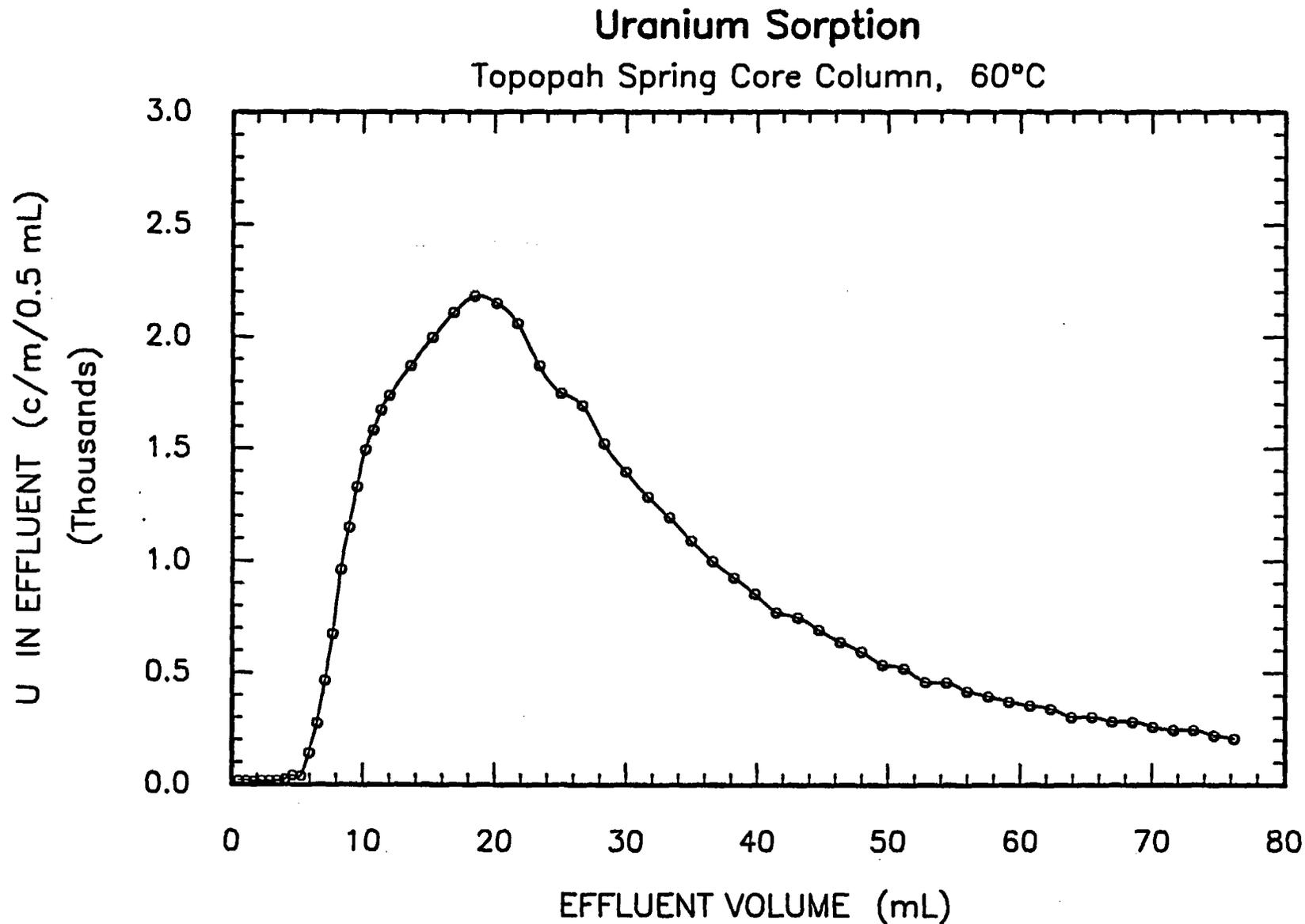


Fig. 5.2.9 Elution curve of uranium in J-13 well water from a column of Topopah Spring tuff. 0.2 mL/min, 60°C.

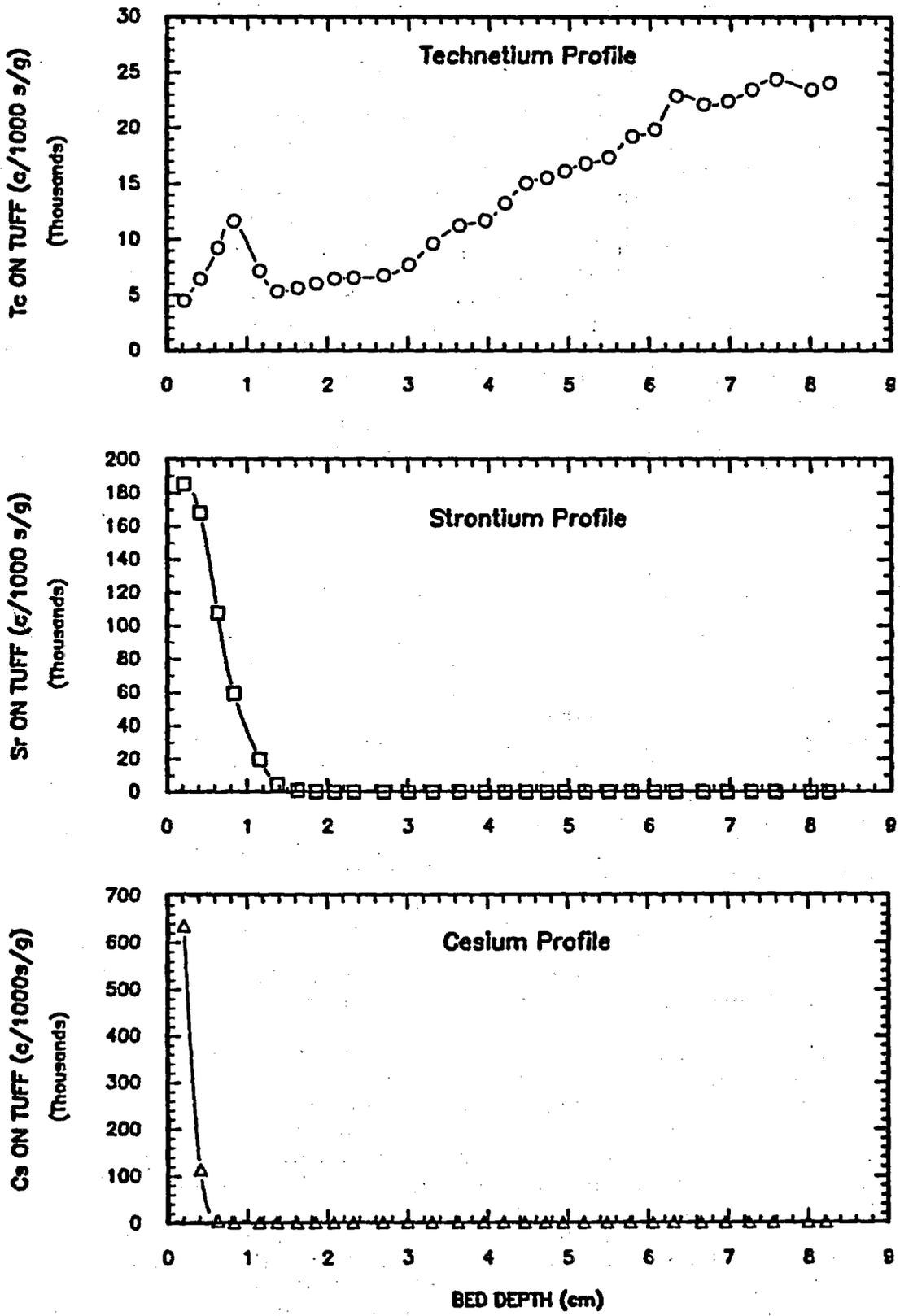


Fig. 5.2.10 Distributions of technetium (TcO_4^-), strontium, and cesium in J-13 well water in a column of Topopah Spring tuff after transport under unsaturated conditions.

5.2.7 Movement of Europium through Unsaturated Tuff

The transport of europium through an unsaturated column was done with the same procedure used in Section 5.2.6 for the movement of technetium, strontium, and cesium. The last addition of J-13 was made at 32.8 days, and it was then allowed to stand 14 d. Results are shown in Fig. 5.2.11. Although there was no difference in procedure, saturation reached only 23.2% after 32.8 d, and at the end of the experiment, the saturation was 21.8%, a little more than half that reached after the previous experiment with technetium, strontium, and cesium. As shown in Fig. 5.2.11, essentially all of the europium remained in the first section. However, the lower graph, which has a greatly expanded ordinate scale, shows that there was a small and fairly uniform distribution of europium in the column, amounting to about 1% of that originally put into the column. Thus, some of the europium was in a form that moved with the water. The material balance for europium was 86%. This does not necessarily indicate loss of europium but may reflect difficulties in estimating the efficiency of counting europium in the tuff.

5.3 BATCH TESTS

5.3.1 Effect of Contact Time on Uranium Sorption and Desorption

The column measurements with uranium indicated that the kinetics of sorption of uranium on tuff may be slow. Decreasing the flow rate allowed more time for contact with the tuff, and the resulting increase in sorption ratios indicates that the kinetics are slow. Also, increasing the temperature, which increases the reaction rate, resulted in increases in sorption ratio. The time of contact of the uranium with tuff in the column experiments was only a few hours; the column water/rock ratio of ~0.4 (void vol./wt. tuff) is much smaller than the usual 10 mL/g in the batch tests, but this does not appear to make up for the difference in contact time. Therefore, a series of batch tests were performed to measure uranium sorption on tuff as a function of time. After each sorption experiment, a desorption experiment was conducted for the same length of time as the corresponding sorption experiment. Results are shown in Table 5.3.1 and Fig. 5.3.1. The lines in Fig. 5.3.1 are polynomial fits and have no theoretical significance.

The results show that the sorption ratios increase with time up to about 14 to 21 d; they appear to be reaching a steady state after 21 d although there are some variations. Desorption ratios appear to be increasing with time up to 30 to 40 d, and, especially for the 10^{-6} mol/L solution, the 70 d points show increases. For the 10^{-6} mol/L solutions, desorption ratios are roughly twice the sorption ratios; for the 10^{-4} mol/L solutions, desorption ratios are about 50% greater than the sorption ratios, and both sorption and desorption ratios are considerably smaller than for the 10^{-6} mol/L uranium solution. These studies indicate a significant kinetic effect, and because of the considerable time necessary to reach a steady state, it is not surprising that the column studies result in much lower sorption ratio.

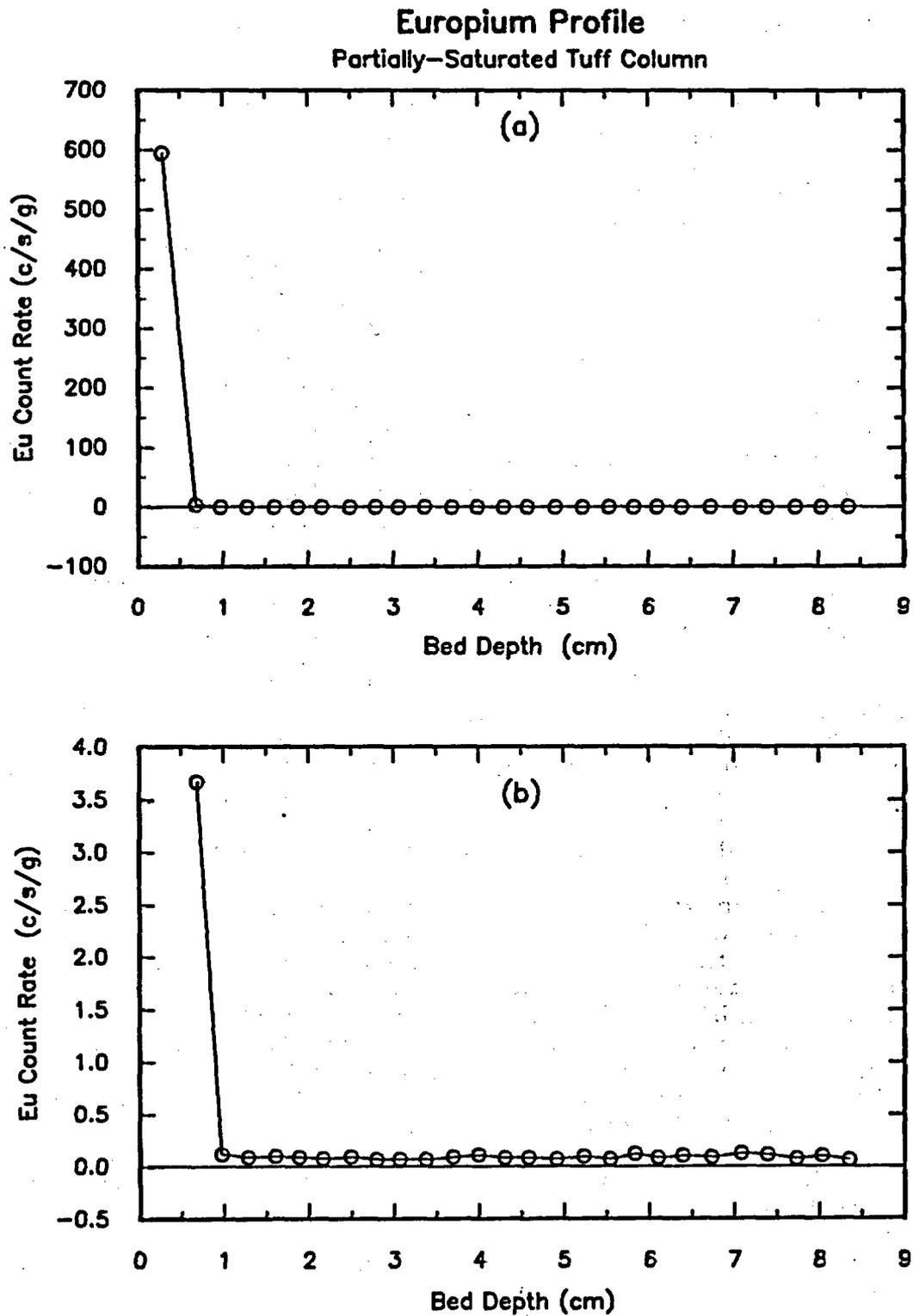


Fig. 5.2.11 Distribution of europium in J-13 well water in a column of Topopah Spring tuff after transport under unsaturated conditions. (a) Full range of distribution (b) Expanded range.

Table 5.3.1 Effect of contact time on uranium sorption and desorption with Topopah Spring tuff

Test No.	Initial U Conc. (mol/L)	Contact Time (d)	Rs (L/kg)		Rd (L/kg)		Avg. pH	
			Avg.	Std. Dev.	Avg.	Std. Dev.	Sorp.	De-sorp.
T-124	10 ⁻⁶	0.25	3.83	0.16	9.39	0.66	6.73	6.63
T-124	"	1	4.55	0.19	8.44	0.31	6.77	6.74
T-124	"	3	4.94	0.27	9.12	0.48	6.79	6.73
T-124	"	7	6.01	0.42	13.13	0.35	6.72	6.73
T-124	"	14	8.10	0.70	14.92	0.46	6.76	6.77
T-125	"	14	8.59	0.27	14.15	0.46	6.70	6.66
T-125	"	21	10.30	1.92	16.68	3.32	6.73	6.74
T-124	"	28	8.95	0.45	17.89	1.77	6.75	6.69
T-125	"	42	10.28	0.20	17.99	1.38	6.72	6.70
T-125	"	56	9.45	0.89	17.44	1.82	6.69	6.69
T-125	"	70	9.68	0.21	19.93	1.22	6.76	6.74
T-124	10 ⁻⁴	0.25	1.66	0.07	2.81	0.10	6.75	6.66
T-124	"	1	2.04	0.23	2.88	0.38	6.77	6.72
T-124	"	3	2.55	0.07	3.34	0.12	6.74	6.71
T-124	"	7	2.77	0.07	4.40	0.30	6.71	6.76
T-124	"	14	3.55	0.19	4.00	0.58	6.74	6.78
T-125	"	14	3.54	0.06	4.38	0.37	6.66	6.66
T-125	"	21	3.75	0.24	5.09	0.27	6.69	6.75
T-124	"	28	3.81	0.31	5.61	0.61	6.71	6.69
T-125	"	42	4.39	0.08	5.37	0.47	6.70	6.71
T-125	"	56	3.90	0.18	5.13	0.16	6.64	6.69
T-125	"	70	3.86	0.15	5.86	0.84	6.70	6.79

Test conditions: Triplicate 0.20-g samples of -70 mesh Topopah Spring core were conditioned three times with 2.0 mL of J-13 well water; the samples were centrifuged and the solution was decanted after each conditioning contact. Uranium sorption from 2.0 mL of J-13 that contained 10⁻⁶ or 10⁻⁴ mol/L U was measured with the conditioned tuff samples for the indicated contact times. After the sorption measurements, the traced J-13 was decanted and untraced J-13 was added to a total volume of 2.0 mL; uranium desorption was then measured for the same contact times that were used for each corresponding set of sorption measurements. Centrifugations after each contact were for 30 minutes at 25000 rcf.

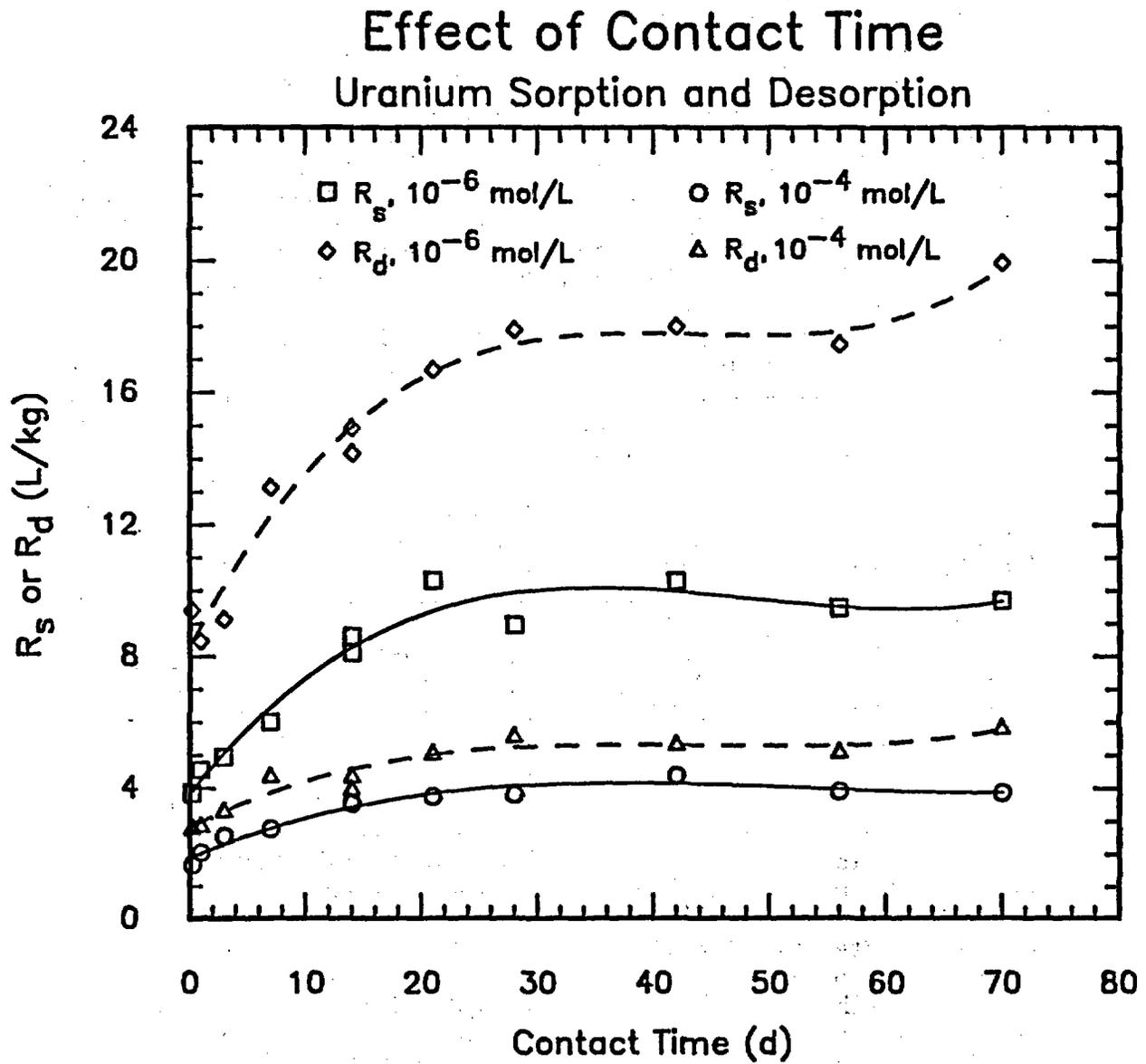


Fig. 5.3.1 Effect of contact time on sorption and desorption ratios of uranium onto Topopah Spring tuff. Batch method, 24°C.

5.3.2 Sorption/Desorption Isotherms for Uranium on Tuff

According to Fig. 5.3.1, the sorption ratio appears to have reached steady state at 28 d; desorption ratios appeared to reach a plateau at 42 days. A sorption/desorption isotherm was completed by the batch method for four initial concentrations of uranium. The duration of the sorption experiments was 28 d and that of the desorption experiments was 42 days. The data are shown in Table 5.3.2 and Fig. 5.3.2. Initial uranium concentrations were 10^{-7} , 10^{-6} , 10^{-5} , and 10^{-4} mol/L. The sorption isotherm plotted as log concentration in the solid vs log concentration in the liquid was linear with a slope of 0.75 ± 0.015 . The desorption isotherm was not linear, and the desorption ratio for the 10^{-4} mol/L solution was smaller than the corresponding sorption ratio.

Table 5.3.2 Uranium sorption and desorption isotherms on Topopah Spring tuff

Sorption				
Initial U Conc. (mol/L)	Contact Time (d)	Sorption Ratio (L/kg)	Final Uranium Concentration	
			Solution mol/L	Tuff mol/kg
10^{-7}	28	15.9	3.52×10^{-8}	6.08×10^{-7}
10^{-6}	28	8.01	5.52×10^{-7}	4.41×10^{-6}
10^{-5}	28	3.73	7.26×10^{-6}	2.71×10^{-5}
10^{-4}	28	2.38	8.06×10^{-5}	1.92×10^{-4}

Desorption				
Initial U Conc. (mol/L)	Contact Time (d)	Desorption Ratio (L/kg)	Final Uranium Concentration	
			Solution mol/L	Tuff mol/kg
10^{-7}	42	18.7	2.24×10^{-8}	4.18×10^{-7}
10^{-6}	42	10.6	2.40×10^{-7}	2.55×10^{-6}
10^{-5}	42	4.53	2.29×10^{-6}	1.04×10^{-5}
10^{-4}	42	0.81	2.44×10^{-5}	1.97×10^{-5}

Test conditions: Triplicate 0.40-g samples of -70 mesh Topopah Spring core were conditioned three times with 4.0 mL of J-13 well water; the samples were centrifuged and the solution was decanted after each conditioning contact. Uranium sorption from 4.0 mL of J-13 that contained uranium was measured with the conditioned tuff samples for 28 days. After the sorption measurements, the traced J-13 was decanted and untraced J-13 was added to a total volume of 4.0 mL; uranium desorption was then measured for 42 days. Centrifugations after each contact were for 30 minutes at 25000 rcf.

Uranium Sorption/Desorption Isotherm

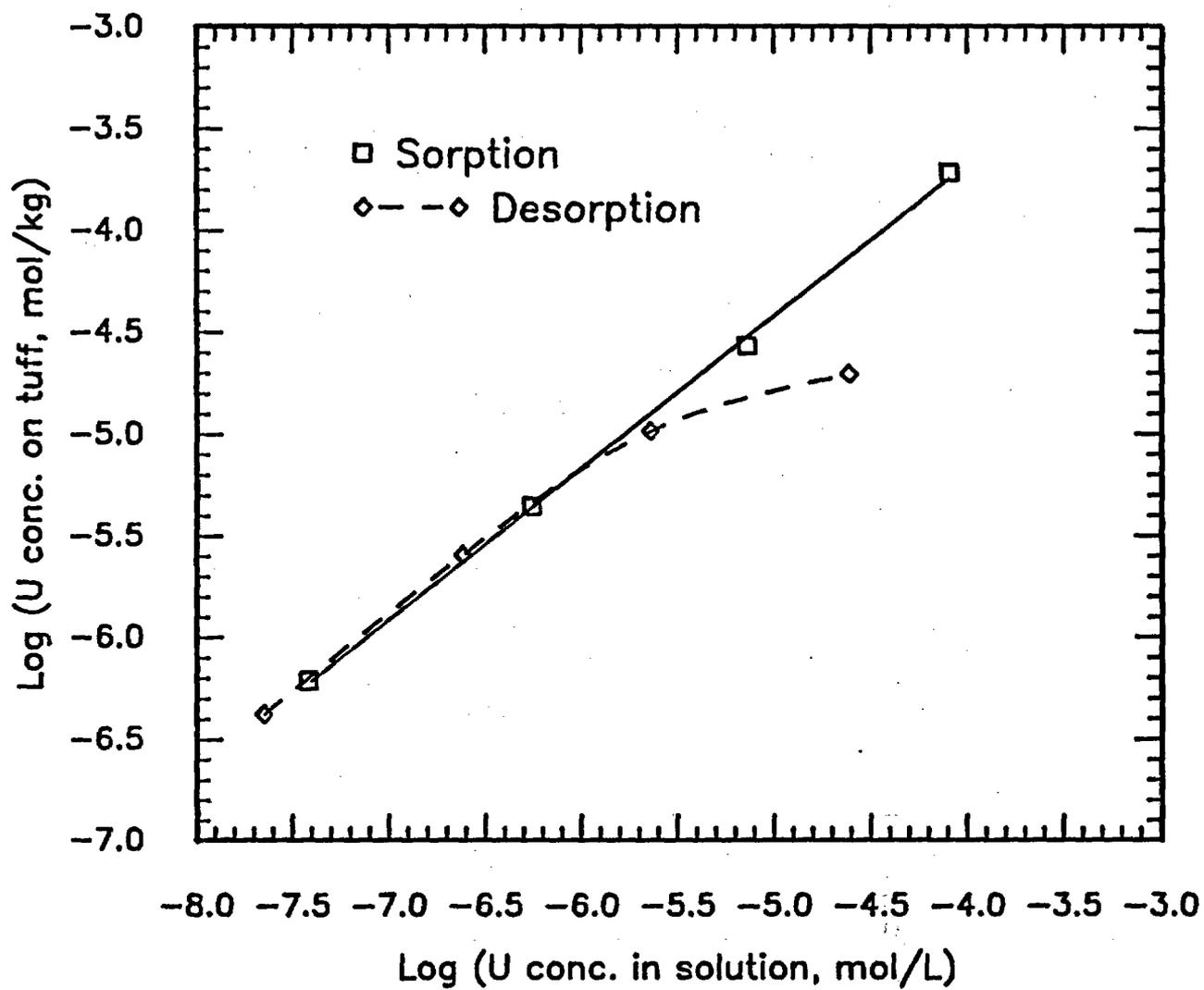


Fig. 5.3.2 Sorption and desorption isotherms of uranium on Topopah Spring tuff.

Finally, experiments were done to explore the effects of sorption contact time on the desorption ratio of uranium. A series of samples were prepared for batch sorption determinations. One set was contacted with the traced solution for 1 day and a second set for 28 days. Immediately after the sorption contact the desorption experiments were started, and they were done as a function of contact time. Results are shown in Table 5.3.3 and Fig. 5.3.3.

As shown in Table 5.3.3 and Fig. 5.3.3, there are considerable differences between the values of Rd for the first 28 days, but afterwards the differences are probably not significant. The samples that had sorption contact times of 28 days had considerably higher desorption ratios for the first 28 d of desorption. Apparently, more uranium became fixed in the tuff in the 28 d sorption.

Table 5.3.3 Effect of sorption contact time on desorption of uranium from Topopah Spring tuff

Sple. No.	Time (d)		Rs (L/kg)	Std. Dev.	Rd (L/kg)	Std. Dev.
	Sorp.	Desorp.				
A1-A3	1	1	5.52	0.31	10.54	0.40
A4-A6	1	3	5.56	0.06	11.81	1.38
A7-A9	1	7	5.03	0.19	10.87	1.03
A10-A12	1	14	5.08	0.20	12.14	0.73
A13-A15	1	28	5.43	0.18	13.17	0.17
A16-A18	1	70	5.34	0.05	12.22	0.20
A19-A21	1	85	5.22	0.05	11.92	0.29
A22-A24	1	107	5.00	0.07	10.53	0.17
B1-B3	28	1	9.25	0.29	18.45	1.64
B4-B6	28	3	9.07	0.12	17.14	0.25
B7-B9	28	7	8.64	0.30	14.89	0.50
B10-B12	28	14	9.21	0.41	14.30	0.17
B13-B15	28	28	8.74	0.28	12.94	0.28
B16-B18	28	45	8.99	0.25	13.42	0.28
B19-B21	28	60	9.09	0.23	12.96	0.95
B22-B24	28	80	9.01	0.21	10.52	0.32

Test conditions: Triplicate 0.40-g samples of -70 mesh Topopah Spring core were conditioned three times with 4.0 mL of J-13 well water; the samples were centrifuged and the solution was decanted after each conditioning contact. Uranium sorption from 4.0 mL of J-13 that contained uranium was measured with the conditioned tuff samples for the indicated contact times. After the sorption measurements, the traced J-13 was decanted and untraced J-13 was added to a total volume of 4.0 mL; uranium desorption was then measured for the indicated contact times. Centrifugations after each contact were for 30 minutes at 25000 rcf.

Effect of Sorption Contact Time Uranium Desorption from Tuff

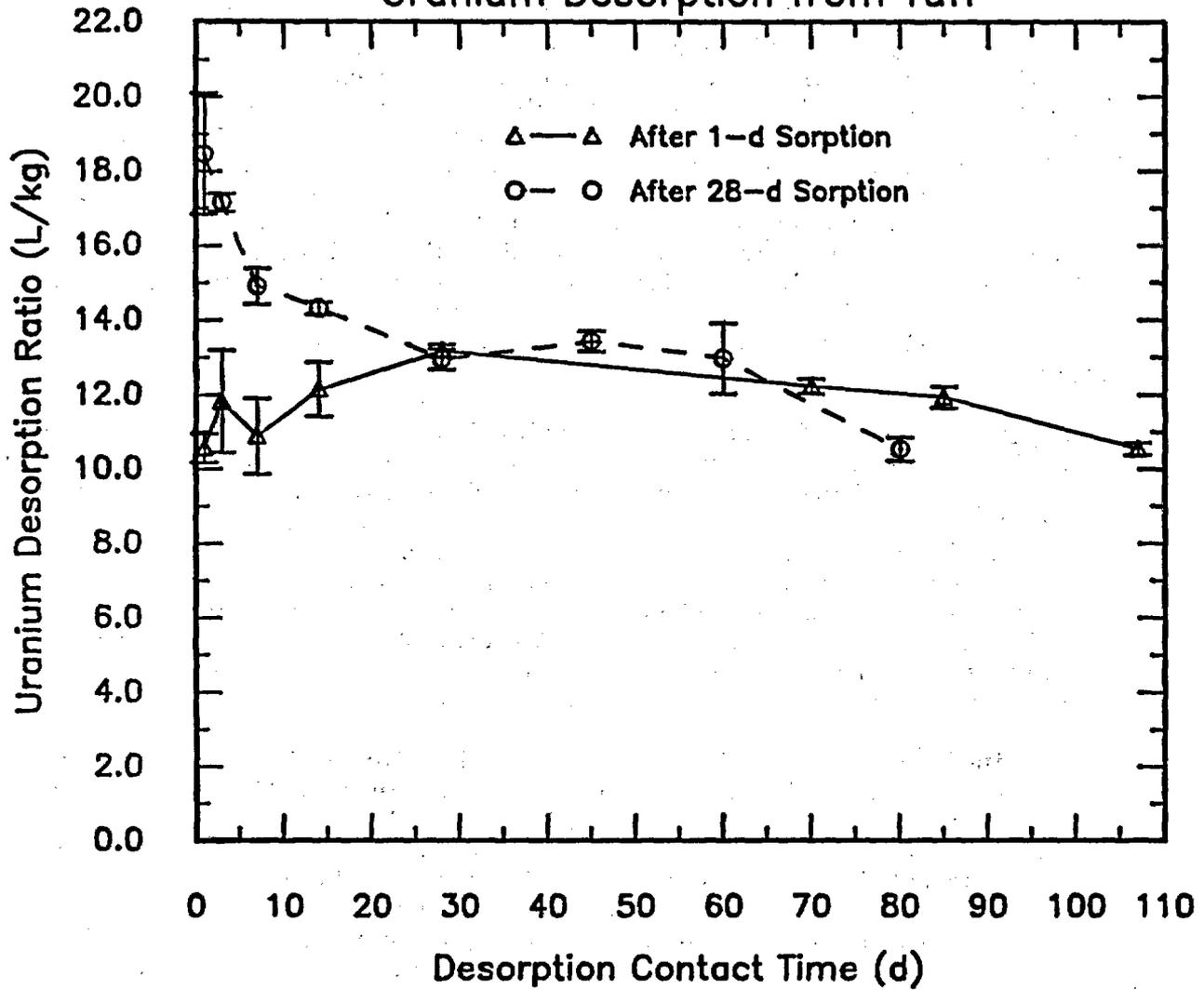


Fig. 5.3.3 Effect of sorption contact time on the desorption of uranium from Topopah Spring tuff.

5.3.3 Effects of Particle Size on Sorption of Strontium, Cesium, and Uranium on Topopah Spring tuff

The effects of particle size of Topopah Spring tuff upon sorption of strontium, cesium, and uranium were investigated with batch sorption tests using varying particle size ranges. As shown in Table 5.3.4 and Fig. 5.3.4, the sorption and desorption ratios increased as the particle size decreased. For the various particle size ranges, the ratio of the desorption ratio to the sorption ratio varied randomly from 1.65 to 1.69 for strontium and from 1.09 to 1.20 for cesium; i. e. these ratios did not change significantly as the particle size was changed. For uranium, however, there was a consistent decreasing trend from 1.80 to 1.32 in R_d/R_s as the particle size was decreased. These observations suggest that sorption/desorption equilibrium was not attained for all three elements tested, but cesium most nearly reached equilibrium. For uranium, equilibrium was most nearly approached for the smallest particle size range.

To analyze these differences it is helpful to look at the factors by which the sorption and desorption ratios are increased as the particle size fraction is decreased. As shown in Table 5.3.5, these factors are different for the three elements. The smallest increases in sorption ratios as the particle size is decreased are observed with strontium. For strontium and cesium, the increases of the sorption ratios and the increases of desorption ratios were approximately the same as the particle size range was decreased. However, for uranium there was a significant difference in the ratios for sorption and desorption; the increases were smaller for the desorption ratios.

As explained in Section 3.1, there was no significant difference in the mineralogy of the different particle sizes for the different size fractions of the ground Topopah Spring Busted Butte outcrop tuff. However, the mineralogy of the different particle sizes for the core material was not investigated because of the termination of the project. The main difference between the Busted Butte outcrop and the core sample is that the core sample contains about 10% smectites; these clay minerals could have segregated somewhat to the smallest size fraction.

Table 5.3.4 Effect of particle size fraction on sorption and desorption ratios of strontium, cesium, and uranium on Topopah Spring tuff.

(a) Strontium (Initial concentration 10^{-6} mol/L)

Tuff Particle Size (um)	Sorption			Desorption			
	Rs (L/kg)	Std. Dev.	pH	Rd (L/kg)	Std. Dev.	pH	Rd/Rs
149-210	89.4	3.6	6.56	147.6	3.4	6.71	1.65
88-149	96.0	0.8	6.65	160.0	4.4	6.70	1.67
74-88	102.0	1.3	6.66	171.2	6.0	6.68	1.68
44-74	104.3	1.6	6.68	173.9	0.9	6.68	1.67
<44	135.3	3.0	6.71	229.1	5.6	6.70	1.69

(b) Cesium (Initial concentration 10^{-6} mol/L)

Tuff Particle Size (um)	Sorption			Desorption			
	Rs (L/kg)	Std. Dev.	pH	Rd (L/kg)	Std. Dev.	pH	Rd/Rs
149-210	236.8	10.1	6.64	280.0	15.1	6.70	1.18
88-149	264.1	12.4	6.68	299.3	10.0	6.72	1.13
74-88	290.3	5.7	6.70	338.5	15.7	6.74	1.17
44-74	335.5	5.8	6.71	402.3	2.9	6.73	1.20
<44	632.1	30.8	6.75	689.2	45.0	6.70	1.09

(c) Uranium (Initial concentration 10^{-6} mol/L)

Tuff Particle Size (um)	Sorption			Desorption			
	Rs (L/kg)	Std. Dev.	pH	Rd (L/kg)	Std. Dev.	pH	Rd/Rs
149-210	4.78	0.09	6.58	8.60	0.25	6.59	1.80
88-149	5.38	0.18	6.61	9.35	0.60	6.60	1.74
74-88	6.33	0.31	6.57	10.56	0.49	6.61	1.67
44-74	8.85	0.38	6.59	14.25	0.72	6.57	1.61
<44	13.40	0.14	6.58	17.65	0.73	6.58	1.32

Test conditions: Triplicate 0.20-g samples of -70 mesh Topopah Spring core were conditioned three times with 2.0 mL of J-13 well water; the samples were centrifuged, and the solution was decanted after each conditioning contact. Sorption from 2.0 mL of J-13 that contained strontium, cesium, or uranium was measured with the conditioned tuff samples for a contact time of 28 days. After the sorption

Table 5.3.4 (continued)
 measurements, the traced J-13 was decanted and untraced J-13 was added to a total volume of 2.0 mL; desorption was then measured for 42 days. Centrifugations after each contact were for 30 minutes at 25000 rcf.

Table 5.3.5 Ratios of Rs and Rd values for sorption and desorption of Sr, Cs, and U on Topopah Spring tuff for different particle size fractions.

Tuff Particle Size (um)	Strontium Ratios		Cesium Ratios		Uranium Ratios	
	Rs	Rd	Rs	Rd	Rs	Rd
149-210	1.00	1.00	1.00	1.00	1.00	1.00
88-149	1.07	1.08	1.12	1.07	1.13	1.09
74-88	1.14	1.16	1.23	1.21	1.33	1.23
44-74	1.17	1.18	1.42	1.44	1.85	1.66
<44	1.51	1.55	2.67	2.46	2.80	2.05

Test Conditions: Same as Fig. 5.3.4. Ratios calculated from values in Table 5.3.4 by dividing each value of Rs and Rd by the value for the largest particle size fraction.

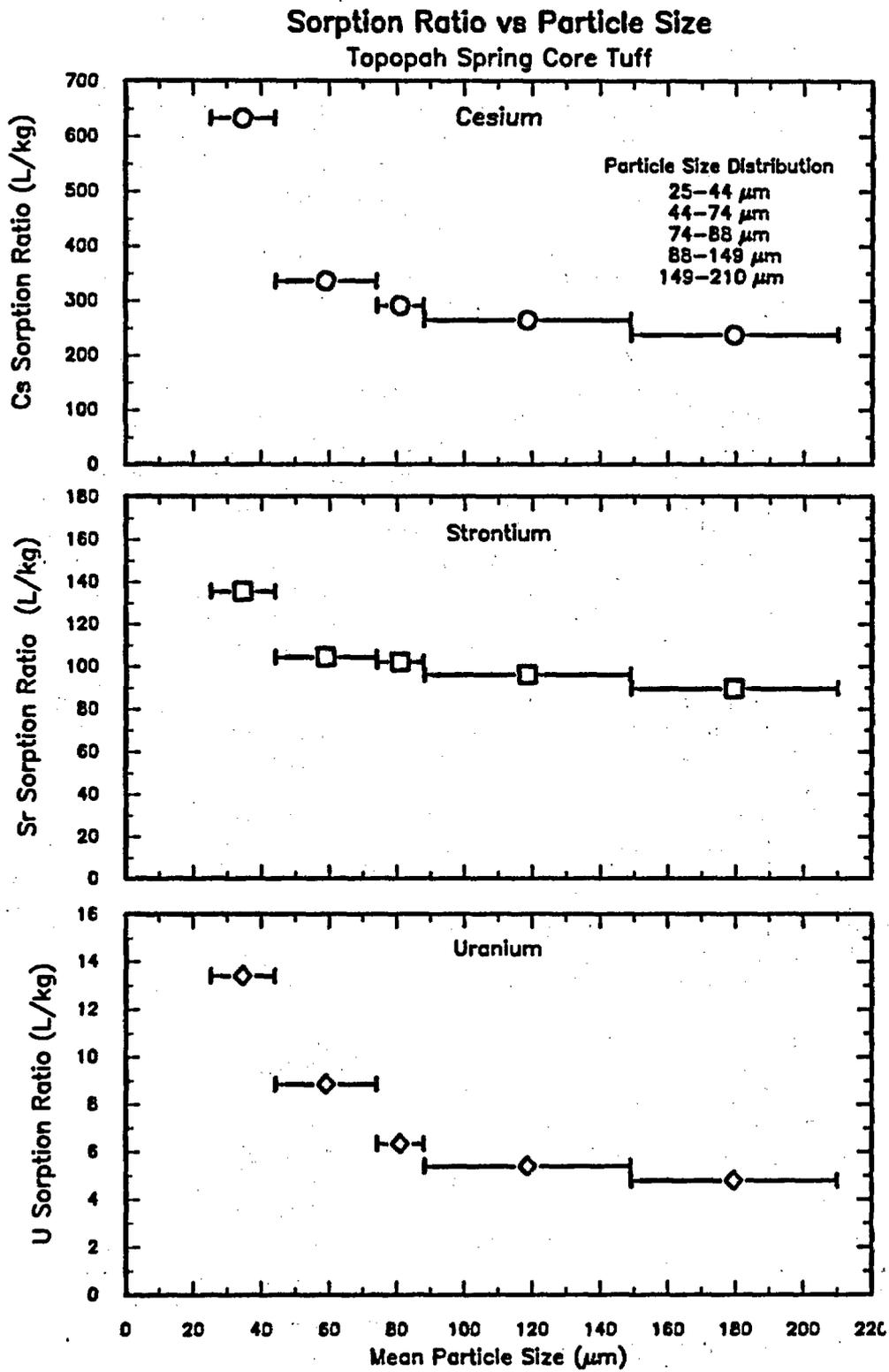


Fig. 5.3.4 Effect of particle size fraction on sorption and desorption ratios of strontium, cesium, and uranium on Topopah Spring tuff.

6. COMPARISON OF RESULTS WITH DOE DATA

In our report for the period April 1986 - September 1987 (Meyer et al. 1988), we cited the need for a summary of DOE sorption data for the Yucca Mountain site. Such a report has now appeared (Thomas 1987), and the task of assessing the data is now much easier. However, it should be noted that Thomas presents a qualifying statement that the data set presented in the report is "an unrefined data set" (p. 12 in Thomas 1987), i.e., some of the data were obtained while the methods were still under development.

The pH values of the groundwaters after each experiment are not given in Thomas (1987). This omission concerns us because sorption often is dependent on pH, in some cases strongly. In our experience, J-13 well water, when left in air, changes from its initial pH of about 7 to values between 8 and 9. It will remain at 7 if an appropriate partial pressure of CO₂ is maintained over the groundwater. We have found that air containing 1.5% CO₂ will maintain the pH at 7. Because many sorption reactions are dependent on pH, this omission makes it difficult to compare results. Further, for cases where sorption increases as the pH increases, the sorption ratios determined in air will be too high, and in these cases the results will be non-conservative.

Strictly speaking, there are no experiments reported by DOE directly comparable to ours because each section of tuff is unique. However, the classification offered by Thomas (1987), which is described above in Section 3, helps comparison of data. The DOE data given above in Tables 4.1 - 4.3 are for tuffs in the same general classification as the Topopah Spring core with which we did most of our work (devitrified tuff with >10% clays and <10% zeolites). Because clays and zeolites may constitute the principal sorbing minerals in the tuffs for some elements, there may be differences within these classifications depending upon the composition of the tuffs. However, there should at least be order of magnitude agreement within a general classification.

For strontium, the sorption ratios listed in Tables 4.1 - 4.3 range from 37 L/kg to 280 L/kg. The data listed in Table 4.3 for sample YM-54, which has 5-10% smectite and 2 - 5% illite, show an increase in sorption ratio with decrease in particle size as we have observed (Table 5.3.4). The two samples that had the highest sorption ratios are for particle sizes \leq 38 microns, the finest fraction that was generally used. Our data from Table 5.3.4 range from 89.4 to 135.3 L/kg. In most of our previous experiments, -70 mesh size (<210 microns) was used, and for these experiments, results fall in the range 100 ± 15 L/kg for 14 d contact times (Meyer et al., 1988). Thus, there is order of magnitude agreement between their and our data for strontium sorption on the same general classification of tuff. However, our data were taken using gaseous CO₂ to maintain the pH near 7; the pH of the data given in Tables 4.1 - 4.3 is not given in the reference and is probably higher than 7. Our data also show that the desorption ratio is roughly 50 to 75% higher than the corresponding sorption ratio whereas the DOE data in Tables 4.1 - 4.3

indicate that most of the sorption and desorption ratios are almost equal.

The DOE data for cesium in Tables 4.1 - 4.3 are more varied than those of strontium, and for many of their measurements the desorption ratios were higher than the corresponding sorption ratios as we have found. For sample YM-54 in Table 4.3, sorption ratios increase significantly as the particle size is decreased as we have observed. In Table 4.1 for sample G1-2901, sorption ratios range from 950 to 1400 L/kg. In Table 4.2 for sample JA-32, sorption ratios range from 110 to 140 L/kg, and in Table 4.3 for sample YM-54, sorption ratios range from 110 to 940 L/kg, depending on the particle size range. According to the compositions given by Daniels et al. (1982), sample JA-32 has the highest clay content, but it also has the lowest sorption ratios of the three samples. Our data fall in this general range; our values range from 191.7 to 626 L/kg for cesium concentration $\leq 10^{-6}$ mol/L (Meyer et al. 1988).

Sorption of uranium can often be highly dependent on pH. For solutions that contain carbonate ion, it is important that an overpressure of CO_2 be used so that the solution composition and the pH remain constant. At higher pH values in solutions containing bicarbonate and carbonate ions, the formation of negatively charged uranium-carbonate complexes is expected (Langmuir 1978, Paquette and Lemire 1981), and these negatively charged complexes would not be expected to sorb strongly. Therefore, the sorption ratios listed in Tables 4.2 and 4.3 that were done in an air atmosphere and hence at a pH higher than 7 are quite low. The uranium sorption ratios listed in Table 4.1 were obtained from experiments done under a CO_2 pressure sufficient to maintain the pH at 7. These data can be compared to our data, which were also obtained under a partial pressure of CO_2 . The DOE sorption ratios of 4.75 and 4.03 L/kg for uranium at 42 d listed in Table 4.1 are higher than those in Tables 4.2 and 4.3 and more nearly approach the value of 10.28 L/kg which we observed at 42 d (Table 5.3.1).

In our description of the uranium column experiments as a function of flow rate (Section 5.2.2), we noted that at higher flow rates a double peak was observed. Further, the first peak corresponds to a sorption ratio of about 0 L/kg, indicating that some of the uranium traversed the column unretarded. Similar observations were noted by Thomas (1987) for column experiments with neptunium, plutonium, and americium, for which it was noted that from 10-50% of the activity arrived virtually unretarded. Checks of the columns were made to insure their proper operation. Several explanations were proposed to explain this effect. Slow and complicated kinetics is one of the proposed explanations. Another is that some of the activity was sorbed on colloidal material, which may have washed through the column unretarded. Thomas suggested that sorption of actinides may involve one or more steps that have slow kinetics and that further experimentation is needed to clarify the kinetics of sorption processes of actinides.

Our uranium batch experiments as a function of contact time (Section

5.3) were designed to clarify some of the questions regarding the column determinations of sorption of uranium. It is clear from these results that considerable time is necessary, at least 21 d, before sorption ratios reach what appears to be a steady state. Desorption ratios were always considerably higher than the corresponding sorption ratios. It is therefore not surprising that equilibrium is not achieved in column experiments in which the flow rates are such that the uranium contacts the tuff for only hours or a few days. It would be of considerable interest to determine the kinetics of sorption on the different particle size fractions to determine whether diffusion or transport within the particles affects the kinetics.

We have been unable to determine meaningful data on europium because we have been unable to prepare stable solutions of europium in real J-13 at pH 7. Thus we cannot compare our data to the DOE data in Table 4.1 - 4.3. For sample G1-2901 (Table 4.1) the values of the sorption and desorption ratios are so high that for all practical purposes all europium has been removed from solution. For sample JA-32 (Table 4.2), the sorption ratios are much smaller, but the desorption ratios are much larger than corresponding sorption ratios. The same is true for sample YM-54 (Table 4.3). The sorption process in contact with tuff is not at all clear i.e. it is not clear whether europium is sorbing on the tuff, aggregating into colloidal forms, or sorbing onto the tube walls or colloidal material in the groundwater.

In our experience, stable solutions of europium can be prepared only in low pH solutions. Solutions of Eu(III) in J-13 at pH 7 will slowly decrease in Eu(III) concentration, and centrifugation results in large losses of Eu(III) (Meyer et al. 1988), possibly by formation of colloids or sorption on colloidal material in J-13. It may be that hydrolyzed forms of Eu(III) sorb much more readily than the non-hydrolyzed form, Eu^{3+} . Europium does not hydrolyze significantly below pH 8 (Schmidt et al. 1978, Baes and Mesmer 1976); however, if the hydrolyzed form sorbs significantly more than the non-hydrolyzed form, then the removal of the hydrolyzed form from the solution can cause the equilibrium to shift so that most of the europium is sorbed even when the hydrolysis equilibrium shows that only a small percentage of europium is hydrolyzed. Thus, at pH 7, the pH of J-13 well water, it would be possible for essentially all of europium to be removed from solution if the hydrolyzed form sorbs strongly on colloids or the container walls. If the kinetics of either hydrolysis and/or sorption are slow, then the overall removal from solution will be slow as we have observed (Meyer et al. 1988).

For technetium in the form of the pertechnetate ion, TcO_4^- , it is clear both from our data and DOE data that very little sorption is to be expected.

In summary, comparison between DOE data and ours for similar tuff types shows that there is confirmation of the low sorption of technetium, order of magnitude agreement for strontium and cesium, and considerable problems with europium and uranium.

7. DISCUSSION

The main purpose of our experiments is to help the NRC determine whether DOE methods and data concerning sorption are suitable for inclusion in transport modeling. There are a number of significant problems to be resolved. Certainly one of the principal problems is the extreme variability of the mineral components of the tuffs at the Yucca Mountain Site and the consequent large variability of sorption ratios. The question is what method should be used to select sorption ratios to use in modeling; a conservative approach might be to select the lowest sorption ratios encountered in any of the tuffs. However, this would assume that accurate sorption data have been collected for all possible tuffs for the groundwater path under study. (Selecting the proper groundwater flowpath is itself a major problem but outside the scope of the discussion here.)

Any technique or method for simplifying the selection of data for inclusion into modeling of transport would be helpful. We believe that understanding the type of sorption process is the most important factor in this simplification. For example, if it is known that a given element sorbs mainly by ion exchange, then knowledge of the amount and nature of the minerals that are ion exchangers in the tuffs in the flowpath could be used to predict with confidence the sorption of the element. In our NRC program B0462, we are attempting to correlate the sorption of Cs^+ and Sr^{2+} with the zeolite content of tuffs. The data obtained so far are not complete, but they do support the idea that the zeolites are the principal sorbing minerals for Cs^+ and Sr^{2+} . Applying this to $Eu(III)$ would be difficult because the sorption process of $Eu(III)$ is not known. It makes little sense to determine ever larger quantities of batch sorption data unless an understanding of the sorption process is obtained. It is likely that the chemistry of some of the elements, particularly those of higher oxidation state such as uranium, neptunium, and plutonium, is by far the most important area of study. It may not matter what the minerals are if the chemistry of the element determines its removal. Therefore, speciation, solubility, and the trace chemistry of elements should be understood before massive numbers of sorption studies are carried out.

If the sorption process is not known, then systematic experiments should be performed to determine the process. The best way to attempt this is to study sorption with simple aqueous solutions at controlled pH rather than with the complex groundwaters used so far. The dependence on solution variables should be determined, and single mineral components of tuff should be selected for study. To the best of our knowledge these type of studies have not been done by DOE.

Our sorption studies of $Eu(III)$ and $U(VI)$ point out some of the difficulties of understanding sorption processes. We have been unable to prepare solutions of $Eu(III)$ in J-13 well water that remain stable. Our general experience with $Eu(III)$ suggests that only solutions considerably more acidic than pH 7 will remain stable. Our column work

described in this report on uranium suggests that a kinetic problem exists with uranium in J-13 well water. This could involve slow solution equilibrium between multiple species in J-13 well water, slow sorption/desorption kinetics, and/or slow transport within the particles of tuff. There is some evidence that diffusion of uranium species in the particles may partially control equilibrium since the desorption and sorption ratios were most nearly equal in the smallest particle size range Table 5.3.4. Thus, there may be both the problem of determining the speciation of these elements and the problem of slow sorption kinetics of any of the multiple species. For these elements the sorption process may be extremely complex and difficult to predict. What is especially disturbing is that in both the DOE experiments (Thomas 1988) and ours reported here a portion of these elements is carried along with the water in column experiments. If this behavior is general and occurs in the field, then there will be serious problems in the prediction of transport of these elements.

Thus, further sorption experiments with tuffs in groundwaters which are not designed to lead to an understanding of the sorption process are not needed and would add little to the needs of transport modeling. It is especially important that the solution chemistry of elements whose chemistry in the groundwaters is not understood (e.g. Eu, Am and Pu) be studied and understood before additional sorption experiments on tuff are undertaken.

8. REFERENCES

- Baes, C. F. Jr., and R. E. Mesmer, The Hydrolysis of Cations, Wiley-Interscience, N. Y., 1976.
- Daniels, W. R., K. Wolfsberg, R. S. Rundberg, A. E. Ogard, J. F. Kerrisk, C. J. Duffy, T. W. Newton, S. D. Knight, F. O. Lawrence, V. L. Rundberg, M. Skyes, G. Thompson, B. Travis, E. Treher, R. Vidale, G. Walter, R. Aguilar, M. Cisneros, S. Maestas, A. Mitchell, P. Oliver, N. Raybold, and P. Wanek, 1982. Summary Report on the Geochemistry of Yucca Mountain and Environs, LA-9328-MS, Los Alamos National Laboratory, Los Alamos, NM.
- DOE 1986. Nuclear Waste Policy Act (Section 112), Environmental Assessment, Yucca Mountain Site, Nevada Research and Development Area, Nevada, DOE/RW-0073, (Vol. 2), U. S. Department of Energy, Office of Civilian Radioactive Waste Management, Washington, DC.
- Kelmers, A. D., J. H. Kessler, F. G. Seeley, W. D. Arnold, R. E. Meyer, F. J. Smith, N. H. Cutshall, G. K. Jacobs, and S. Y. Lee, 1985a. Evaluation of Radionuclide Information Developed by DOE High Level Radioactive Waste Repository Site Projects: Annual Progress Report for October 1983-September 1984, NUREG/CR-3851, (Vol. 4), ORNL/TM 9191, Oak Ridge National Laboratory, Oak Ridge, TN.
- Langmuir, D, 1978. "Uranium Solution-Mineral Equilibria at Low Temperatures with Application to Sedimentary Ore Deposits," Cosmochimica Acta, Vol. 42, 547-569.
- Meyer, R. E., W. D. Arnold, J. G. Blencoe, G. K. Jacobs, A. D. Kelmers, F. G. Seeley, and S. K. Whatley, 1986. Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Annual Report for October 1984-September 1985, NUREG/CR-4236, Vol. 4, ORNL/TM 9614, Oak Ridge National Laboratory, Oak Ridge, TN.
- Meyer, R. E., W. D. Arnold, J. G. Blencoe, G. D. O'Kelley, F. I. Case, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Semiannual Report for October 1985-March 1986, NUREG/CR-4708, ORNL/TM-10147, Vol. 1, No. 1, Oak Ridge National Laboratory, Oak Ridge, TN.
- Meyer, R. E., W. D. Arnold, J. G. Blencoe, G. D. O'Kelley, and J. F. Land, 1988. Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Report for April 1986-September 1987, NUREG/CR-4708, ORNL/TM-10147, Vol. 2, Oak Ridge National Laboratory, Oak Ridge, TN.

- Ogard, A. E. and D. T. Vaniman, Compilers, 1985. Research and Development Activities Related to the Nevada Waste Storage Investigations, July 1-September 30, 1984, LA-10299-PR, Los Alamos National Laboratory, Los Alamos, NM.
- Paquette, J and Lemire, R. J., 1981. "A Description of the Chemistry of Aqueous Solutions of Uranium and Plutonium to 200°C Using Potential-pH Diagrams," Nuclear Science and Engineering, 79, 26-48.
- Relyea, J. F., 1982. "Theoretical and Experimental Considerations for the Use of the Column Method for Determining Retardation Factors", Radioactive Waste Management and the Nuclear Fuel Cycle 3(2), 151-156.
- Rundberg, R. S., A. E. Ogard, and D. T. Vaniman, Compilers, 1985. Research and Development Activities Related to the Nevada Waste Storage Investigations, April 1-June 30, 1984, LA-10297-PR, Los Alamos National Laboratory, Los Alamos, NM.
- Schmidt, K. H., J. C. Sullivan, S. Gordon, and R. C. Thompson, 1978. "Determination of Hydrolysis Constants of Metal Cations by a Transient Conductivity Method," Inorg. Nucl. Chem. Letters, Vol. 14, 429-434.
- Thomas, K. W., 1987. Summary of Sorption Measurements Performed with Yucca Mountain, Nevada, Tuff Samples and Water from Well J-13, LA-10960-MS, Los Alamos National Laboratory, Los Alamos, NM.
- Tien, P. L, M. D. Siegel, C. D. Updegraff, K. K. Wahl, and R. V. Guzowski, 1985. Repository Site Data Report for Unsaturated Tuff, Yucca Mountain, Nevada, NUREG/CR-4110, SAND84-2668, Sandia National Laboratories, Albuquerque, NM.
- Treher, E. N. and N. A. Raybold, 1982, The Elution of Radionuclides through Columns of Crushed Rock from the Nevada Test Site, LA-9329-MS, Los Alamos National Laboratory, Los Alamos, NM.

NUREG/CR-5236
ORNL/TM-10934
Dist. Category-RW

INTERNAL DISTRIBUTION

W. D. Arnold
J. G. Blencoe
F. I. Case
A. G. Croff
N. H. Cutshall
L. M. Ferris
G. K. Jacobs
A. D. Kelmers
A. P. Malinauskas
S. Y. Lee
J. D. Marsh
R. E. Meyer(8)
G. D. O'Kelley
M. L. Poutsma
S. H. Stow
V. J. Tripathi
K. L. Von Damm
Central Research Library(2)
ESD Library(2)
Laboratory Records Dept.(2)
Laboratory Records ORNL-RC
ORNL Patent Section
ORNL Y-12 Technical Library

Battelle Pacific Northwest Laboratory, PO Box 999, Richland, WA 99352

L. L. Ames	D. Rai
M. J. Apted	P. F. Salter
D. G. Coles	J. Serne
E. A. Jenne	D. M. Strachan
K. M. Krupka	

Brookhaven National Laboratory, Upton, NY 11973

D. G. Schweitzer	P. Soo
------------------	--------

Center for Nuclear Waste Analysis, 6220 Colebra Road,
San Antonio, Texas 78284

W. Murphy	J. Russel
R. Pabalan	

Desert Research Institute, 2505 Chandler Ave., Las Vegas, NV 89120

J. W. Hess

Lawrence Berkeley Laboratory, University of California, Berkeley, CA
94720

C. L. Carnahan	S. L. Phillips
S. C. Lee	A. F. White
H. Nitché	

Lawrence Livermore National Laboratory, PO Box 808, L-204,
Livermore, CA 94550

D. Isherwood	R. J. Silva
W. F. McKenzie	T. J. Wolery
V. M. Oversby	

Los Alamos National Laboratory, PO Box 1663, Los Alamos, NM 87545

D. L. Bish	A. E. Ogard
W. R. Daniels	K. W. Thomas
G. L. DePoorter	D. T. Vaniman
J. F. Kerrisk	K. Wolfsberg
A. Meijer	

Sandia National Laboratory, PO Box 5800, Albuquerque, NM 87185

M. D. Siegel

Office of Scientific and Technical Information, PO Box 62, Oak Ridge,
TN 37831

Savannah River Laboratory, Chemical Technology Division, Aiken, SC
29808

C. M. Jantzen

University of California, Berkeley, CA 94720

T. H. Pigford

U.S. Department of Energy, Office of Assistant Manager for Energy
Research and Development, DOE-ORO, PO Box 2001, Oak Ridge, TN 37831

U.S. Department of Energy, Waste Management Project Office, Nevada
Operations Office, Las Vegas, NV 89104

J. S. Szymanski

U.S. Nuclear Regulatory Commission, Geotechnical Branch, Office of
Nuclear Material Safety and Safeguards, MS 4H3, Washington, DC 20555

R. L. Ballard

J. W. Bradbury(10)

D. J. Brooks

D. Chery

P. S. Justus

T. Mo

R. J. Starmer

U.S. Nuclear Regulatory Commission, MS 260, Washington, DC 20555

G. F. Birchard

L. A. Kovach

U.S. Nuclear Regulatory Commission, 1050 E. Flamingo Road, Suite 319,
Las Vegas, NV 89109

P. T. Presthold

Given distribution as shown in Category RW

BIBLIOGRAPHIC DATA SHEET

(See instructions on the reverse)

1. REPORT NUMBER
(Assigned by NRC, Add Vol., Supp., Rev.,
and Addendum Numbers, if any.)

NUREG/CR-4708
ORNL/TM-10147/V3
Vol. 3

2. TITLE AND SUBTITLE

Progress in Evaluation of Radionuclide Geochemical Information
Developed by DOE High-Level Nuclear Waste Repository Site Projects

Report for October 1987 - June 1989

3. DATE REPORT PUBLISHED

MONTH YEAR
August 1989

4. FIN OR GRANT NUMBER

B0290

5. AUTHOR(S)

R. E. Meyer, W. D. Arnold, G. D. O'Kelley,

F. I. Case, J. F. Land

6. TYPE OF REPORT

Technical

7. PERIOD COVERED (Inclusive Dates)

Oct. 1987 - June 1989

8. PERFORMING ORGANIZATION - NAME AND ADDRESS (If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6201

9. SPONSORING ORGANIZATION - NAME AND ADDRESS (If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)

Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

10. SUPPLEMENTARY NOTES

11. ABSTRACT (200 words or less)

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). All experiments were conducted with tuff from the proposed high-level nuclear waste site at Yucca Mountain, Nevada. The principal emphasis was on column studies of migration of uranium and technetium in water from well J-13 at the Yucca Mountain site. The effects of flow rate and temperature on uranium migration were studied. Sorption ratios calculated from the elution peaks became larger as the flow rate decreased and as the temperature increased. These observations support the conclusion that the sorption of uranium is kinetically hindered. Batch sorption ratio experiments as a function of time confirmed that the reaction was slow because 20 to 30 days elapsed before sorption ratios reached steady-state values. A preliminary column experiment was completed under conditions simulating unsaturated flow in tuff for transport of Sr^{2+} , Cs^+ , and TcO_4^- . The significance of these experiments with respect to data obtained by DOE investigators for evaluation of the suitability of the Yucca Mountain site is discussed.

12. KEY WORDS/DESCRIPTORS (List words or phrases that will assist researchers in locating the report.)

Radionuclide sorption
Geochemical conditions
High-level waste repositories
Tuff
Strontium

Cesium
Europium
Uranium
Technetium
Columns

13. AVAILABILITY STATEMENT

unlimited

14. SECURITY CLASSIFICATION

(This Page)

unclassified

(This Report)

unclassified

15. NUMBER OF PAGES

16. PRICE

