

**NUREG/CR-3851, Vol. 2**  
**ORNL/TM-9191/V2**

**Progress in Evaluation of  
Radionuclide Geochemical  
Information Developed by DOE  
High-Level Nuclear Waste Repository  
Site Projects: Report for  
January - March 1984**

A. D. Kelmers  
J. H. Kessler  
W. D. Arnold  
R. E. Meyer  
N. H. Cutshall  
G. K. Jacobs  
S. Y. Lee  
R. J. Clark

Prepared for the  
Division of Waste Management  
Office of Nuclear Material Safety and Safeguards  
U.S. Nuclear Regulatory Commission  
Washington, D.C. 20555

8412260116 841130  
PDR NUREG  
CR-3851 R PDR

## 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.

## 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, 1717 H Street, N.W.  
Washington, DC 20555
2. The NRC/GPO Sales Program, U.S. Nuclear Regulatory Commission,  
Washington, DC 20555
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 NRC/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 Division of Technical Information and Document Control, 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.

PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED  
BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS:  
REPORT FOR JANUARY - MARCH 1984

A. D. Kelmers  
J. H. Kessler\*  
Chemical Technology Division

W. D. Arnold  
R. E. Meyer  
Chemistry Division

N. H. Cutshall  
G. K. Jacobs  
S. Y. Lee  
Environmental Sciences Division

R. J. Clark  
Department of Chemistry  
Florida State University  
Tallahassee, Florida

\*Present address: Nutech Engineers, 145 Martinvale Lane,  
San Jose, CA 95119.

Manuscript Completed: July 1984  
Date of Issue: November 1984

**NOTICE** This document contains information of a preliminary nature.  
It is subject to revision or correction and therefore does not represent a  
final report.

Prepared for the  
Division of Waste Management  
Office of Nuclear Material Safety and Safeguards  
U. S. Nuclear Regulatory Commission  
Washington, D. C. 20555

NRC FIN No. B0290

Prepared by the  
OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
MARTIN MARIETTA ENERGY SYSTEMS, INC.

Previous reports in this series:

"Progress in Evaluation of Radionuclide  
Geochemical Information Developed by  
DOE High-Level Waste Repository Site  
Projects: Report for October -  
December 1983"

NUREG/CR-3851, Vol. 1  
ORNL/TM-9191/V1



## ABSTRACT

Geochemical information relevant to the retention of radionuclides by Department of Energy (DOE) candidate high-level waste repositories is being investigated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). The project has evaluated values that have been reported by the Basalt Waste Isolation Project (BWIP) and the methodologies used to develop those values. Neptunium(V) sorption was dependent upon the basalt flow used in the test. Increasing the test temperature from 24 to 60°C increased the neptunium sorption ratio. Hydrazine did not reduce neptunium(V) to neptunium(IV) in solution. The Amicon filters used to separate the basalt and groundwater after contact have been shown to adsorb a low but significant fraction of the neptunium(V) in solution. Technetium(VII) removal by basalt from groundwater solutions was shown to be independent of the contact methodology but was quite sensitive to the solution composition. Sorption of uranium(VI) by basalt has yielded sorption ratio values higher than those reported by BWIP. Column chromatographic experiments have confirmed the technetium(VII) sorption ratio of  $\sim 0$  L/kg. The McCoy Canyon basalt used in this experimental work was mineralogically characterized. Six phases were identified: plagioclase, mesostasis, pyroxene, magnetite, apatite, and pyrite. Geochemical modeling with PHREEQE and MINTEQ checked the calculated solubilities of 16 radionuclides reported by BWIP; the agreement was generally excellent.

## CONTENTS

	<u>Page</u>
ABSTRACT. . . . .	iii
PREFACE . . . . .	vii
1. EXECUTIVE SUMMARY . . . . .	i
2. INTRODUCTION . . . . .	5
3. NEPTUNIUM STUDIES . . . . .	7
3.1 BWIP SOLUBILITY AND SORPTION INFORMATION . . . . .	7
3.2 EXPERIMENTAL METHODS AND MATERIALS . . . . .	7
3.3 RESULTS . . . . .	8
3.4 CONCLUSIONS . . . . .	11
3.5 EVALUATION OF BWIP VALUES AND METHODS . . . . .	11
4. TECHNETIUM . . . . .	13
4.1 BWIP SOLUBILITY AND SORPTION INFORMATION . . . . .	13
4.2 EXPERIMENTAL METHODS AND MATERIALS . . . . .	13
4.3 RESULTS . . . . .	15
4.4 DISCUSSION AND CONCLUSIONS . . . . .	17
4.5 NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PERTECHNETATE-HYDRAZINE REACTION. . . . .	18
5. URANIUM . . . . .	21
5.1 BWIP SOLUBILITY AND RETARDATION INFORMATION . . . . .	21
5.2 EXPERIMENTAL METHODS AND MATERIALS . . . . .	22
5.3 RESULTS . . . . .	22
5.4 DISCUSSION AND CONCLUSIONS . . . . .	25
6. COLUMN CHROMATOGRAPHY . . . . .	26
7. GEOCHEMICAL MODELING . . . . .	29
7.1 BWIP INFORMATION . . . . .	29
7.2 EVALUATION METHODS . . . . .	29
7.2.1 Radionuclide Solubility Calculations . . . . .	29
7.2.2 Synthetic Groundwater Calculations . . . . .	31
7.3 RESULTS . . . . .	31
7.3.1 Radionuclide Solubility Calculations . . . . .	31
7.3.2 Synthetic Groundwater Calculations . . . . .	33
7.4 CONCLUSIONS . . . . .	35
7.4.1 Radionuclide Solubility Calculations . . . . .	35
7.4.2 Synthetic Groundwater Calculations . . . . .	35
7.5 EVALUATION OF BWIP VALUES AND METHODS . . . . .	36
8. SAMPLE CHARACTERIZATION . . . . .	37
9. ACKNOWLEDGEMENTS . . . . .	42
10. REFERENCES . . . . .	43
APPENDIX. . . . .	47

## PREFACE

This document is the second in a series of quarterly progress reports that are being issued by the Nuclear Regulatory Commission to describe the current status of an experimental program to evaluate the radionuclide geochemical information developed by the high-level nuclear waste repository site projects of the Department of Energy.

PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION  
DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY  
SITE PROJECTS: REPORT FOR JANUARY -- MARCH 1984

A. D. Kelmers  
W. D. Arnold  
R. J. Clark  
N. H. Cutshall  
G. K. Jacobs  
J. H. Kessler  
S. Y. Lee  
R. E. Meyer

1. EXECUTIVE SUMMARY

This project, supported by the Nuclear Regulatory Commission (NRC), is being conducted to evaluate radionuclide solubility and retardation values that may be employed by Department of Energy (DOE) site projects in performance assessment calculations to show reasonable assurance of expected repository compliance with regulatory requirements. Initial evaluation has been of information developed by the Basalt Waste Isolation Project (BWIP) for a candidate repository site on the DOE Hanford Reservation in the Columbia River basalts at Richland, Washington.

The sorption behavior of neptunium(V) in synthetic groundwater GR-2 shows a characteristic dependence on the basalt flow used in the test. In oxic redox condition (air present) experiments at 24°C, a fourfold increase in the sorption ratio ( $R_s$ ) was observed with Umtanum basalt, compared to the work reported last quarter with McCoy Canyon basalt; the average  $R_s$  value increased from 1.7 to 6.8 L/kg. BWIP has previously reported higher sorption of neptunium with Umtanum basalt than with Flow E basalt (the same as McCoy Canyon), although our  $R_s$  values are significantly lower than the BWIP values for both flows. Therefore, sorption data developed with basalt from one flow may not be valid for performance assessment modeling of neptunium retardation in other flows. This suggests that sorption information for neptunium may have to be experimentally established for each important basalt flow in the release pathway in order to support the performance assessment calculations.

The sorption of neptunium(V) by McCoy Canyon basalt under oxic redox conditions increased about threefold when the contact temperature was increased from 24 to 60°C; the average  $R_s$  value changed from 1.7 to 5.8 L/kg. Our  $R_s$  value at 60°C is close to the neptunium sorption value of  $8.3 \pm 0.5$  L/kg for Flow E basalt at 60°C reported by BWIP. Since neptunium sorption increases with temperature, data collected at room temperature may be conservative for performance assessment modeling of neptunium retardation at the repository temperature of 55-60°C.



BWIP expects the groundwater in the engineered facility (after repository closure) and the site far field to be strongly reducing; a calculated groundwater Eh value of  $-0.48$  V is often invoked. To simulate this redox condition in their laboratory experiments, BWIP added hydrazine hydrate to the synthetic groundwaters. While we believe that use of hydrazine hydrate for this purpose is highly questionable (KELMERS 1984b), we carried out a few neptunium sorption and desorption tests in the presence of hydrazine to evaluate the data reported by BWIP under reducing redox conditions. Neptunium sorption ratios were two to three orders of magnitude higher in these experiments ( $R_s$  values ranged from 101 to 18,100 L/kg) with McCoy Canyon basalt in parallel oxic condition tests; similar but smaller increases in  $R_s$  have been reported by BWIP. The hydrazine did not reduce neptunium(V) in synthetic groundwater GR-2 to neptunium(IV), as expected by BWIP from standard redox potentials.

The Amicon filters used in the neptunium sorption work to remove any colloiddally dispersed neptunium from the groundwater solution after contact with the basalt adsorbed a small but constant fraction ( $5 \pm 2\%$ ) of the neptunium(V) in solution in both oxic and reducing redox condition experiments. Amicon filters were similarly used by BWIP in all their sorption experiments. If the filters are not pretreated before use to neutralize this sorption capacity or if the data are not corrected for the loss of neptunium from solution, the solution concentrations measured yield nonconservative results (higher sorption ratios or lower solubility values than actual). It does not appear that BWIP has made such corrections in their neptunium data, so their reported neptunium values may have a small but significant nonconservative bias.

We believe that anoxic redox condition tests best simulate the actual repository condition, and we have been exploring various methods of rigorously eliminating air from the batch contact test environment. Experiments with pertechnetate solutions and McCoy Canyon basalt at  $27^\circ\text{C}$  in an argon-filled, controlled-atmosphere glove box have helped resolve differences reported last quarter between technetium sorption in batch tests and in recirculating column tests. Our recent results show that technetium behavior is independent of the contact methodology (batch vs column) but is strongly dependent upon the solution composition. Pertechnetate anion in an  $0.1$  M NaCl solution buffered at pH 9 showed substantial sorption onto McCoy Canyon basalt ( $R_s$  values of 31 to 66 L/kg in 50-d batch contact anoxic redox condition tests). On the other hand, pertechnetate anion in synthetic groundwater GR-2 under equivalent experimental conditions showed no technetium sorption ( $R_s$  of  $\sim 0$  L/kg). It seems likely that some solution component in GR-2 (or the absence of that component in the NaCl solution) has a major effect on the chemistry of the system. This suggests that selection of the synthetic groundwater formulation used in experiments with basalt may have a major effect on the technetium sorption behavior observed.

A study of the kinetics of the hydrazine/pertechnetate reduction reaction in various aqueous solutions was completed this quarter. Nuclear magnetic resonance (NMR) techniques were used to follow the concentration of pertechnetate in solution as a function of time. This technique



proved to be useful because of the very strong NMR signal for  $TcO_4^-$ ; pertechnetate could be detected down to a concentration level of about  $10^{-5}$  mol/L. The rates of reduction of Tc(VII) varied widely in different media, but appeared to be independent of pH. With sufficient excess hydrazine, the pertechnetate signal disappeared completely, suggesting that technetium was completely reduced (to unknown valence and species) in sorption experiments employing hydrazine to establish reducing redox conditions. Therefore, the high technetium apparent concentration limit we reported earlier (KELMERS 1984a), relative to the low-solubility value calculated by BWIP, may actually represent the solubility of an unidentified reduced-valence technetium solid phase rather than unreduced pertechnetate or colloiddally dispersed technetium.

Results describing the sorption of uranium(VI) are reported for the first time this quarter. In tests at  $27^\circ C$  under oxic or reducing redox conditions, the uranium  $R_s$  values measured with McCoy Canyon basalt and synthetic groundwater GR-2 were consistently higher than those reported by BWIP for Flow E basalt (the same as McCoy Canyon) under similar conditions ( $\sim 1.5$  vs  $0.2$  L/kg for oxic conditions,  $\sim 52$  vs  $17$  L/kg under reducing conditions). Linear sorption isotherms were obtained in both cases.

Column chromatographic experiments have confirmed the sorption ratio of  $\sim 0$  L/kg for pertechnetate anion measured in batch contact tests both in our work and at BWIP under oxic redox conditions. The retardation factor for pertechnetate was measured relative to tritium (as HTO) in synthetic groundwater GR-4 with McCoy Canyon basalt. The  $^3H$  and  $^{95m}Tc$  elution peaks were essentially identical and were symmetric. No evidence for technetium sorption, anion exclusion, or precipitation was observed. The results were independent of temperature ( $25$  or  $70^\circ C$ ) and eluant flow rate.

The solubilities of 16 radionuclides which had been calculated by BWIP (EARLY 1982, EARLY 1984) in synthetic groundwater GR-3 under an Eh of  $-0.3$  V were checked by comparison calculations using the computer codes PHREEQE and MINTEQ. The results obtained were compared to those of Early (1982, 1984) for limiting concentrations, limiting solid phases, and dominant aqueous species. The agreement was generally excellent. Calculations for uranium, nickel, and lead utilizing the data base of MINTEQ illustrated the importance of having a documented, verified, and internally consistent data base. Differences in the thermodynamic values for only one reaction can significantly affect the results, as shown for uranium and nickel. One implication from this comparison is that code-to-code evaluations for geochemical calculations may be less important than a detailed evaluation of the data bases during repository licensing activities.

The saturation indices for the latest BWIP synthetic groundwater formulations (GR-3 and GR-4) were calculated at  $25$  and  $60^\circ C$ . Both formulations were found to be oversaturated with respect to silica phases and

fluorite at 25°C, but at 60°C were calculated to be undersaturated with respect to these phases. Oversaturation with respect to calcite increased with temperature.

The McCoy Canyon basalt that is being used in this experimental work was mineralogically characterized by electron microprobe techniques. Six distinct phases were identified by energy dispersive x-ray spectroscopy (in order of decreasing abundance): plagioclase, mesostasis, pyroxene, magnetite, apatite, and pyrite. The magnetite had considerable amounts of titanium and should be considered as titaniferous magnetite. Pyrite was present as tiny (0.01-mm) grains. The fluorine content of the basalt was concentrated in the apatite phase. The estimated proportions of the mineral phases were generally within the compositional ranges reported by BWIP, although the mesostasis content was lower and pyroxene higher.

## 2. INTRODUCTION

Oak Ridge National Laboratory is conducting an analysis and evaluation of selected geochemical information for DOE high-level waste repository candidate sites for the Nuclear Regulatory Commission. The project is a laboratory-oriented effort to evaluate data for key radionuclides (radionuclides likely to be major contributors to any releases from a repository.) ORNL is determining radionuclide apparent concentration limit values and radionuclide retardation parameters, such as radionuclide sorption isotherms, under site-specific conditions. ORNL also is evaluating experimental strategies, laboratory techniques, and geochemical modeling efforts undertaken by DOE. The results of this project will help the NRC staff independently review and evaluate data employed by the DOE sites for performance assessment analyses, and the methods used to develop these values. The results will also help NRC (1) define the accuracy of or uncertainties in the DOE data and methods, and (2) identify technical areas that may require additional attention by the DOE site programs.

Several regulatory requirements will necessitate quantified knowledge of radionuclide behavior in order to show expected repository compliance. The draft EPA Standard (40 CFR 191) limits the cumulative release of radionuclides to the accessible environment over a 10,000-year period. The NRC Regulation (10 CFR 60) requires that the release rate of radionuclides from the engineered barrier system be no greater than  $10^{-5}$  per year of the inventory of each radionuclide present 1,000 years after repository closure. The NRC rule also requires that favorable and potentially adverse repository conditions be evaluated in providing reasonable assurance that the performance objectives will be met. Quantified knowledge of radionuclide behavior under site-specific conditions is needed as input to performance assessment calculations to demonstrate reasonable assurance of expected compliance with these regulatory requirements. Radionuclide solubility or limiting concentration values, as well as sorption data, will be important input for the performance assessment calculations.

The ORNL experimental work is closely tied to the DOE site development activities. Attention is being directed initially toward values produced to quantify the behavior of radionuclides in basalt/groundwater systems relevant to the BWIP candidate site in the Columbia River basalts in eastern Washington in the DOE Hanford Reservation. In the near future, work will include quantifying radionuclide behavior in (1) tuff/groundwater systems relevant to the Nevada Nuclear Waste Storage Investigations (NNWSI) candidate site in volcanic tuff beds at Yucca Mountain in the DOE Nevada Test Site (NTS), and (2) salt/groundwater systems relevant to several bedded and domal salt sites being developed by the DOE Office of Nuclear Waste Isolation (ONWI). Other media (e.g., crystalline rock or shales) may be added. Data and data-gathering techniques to be investigated will emphasize site- and media-specific problem areas.

During the current report quarter (January through March 1984), all work involved basalt/synthetic groundwater systems. The sorption behavior and apparent concentration limit of the key radionuclides technetium, neptunium, and uranium were evaluated under site-relevant test conditions. Computational methods of estimating radionuclide solubility limits were evaluated, and the mineralogy of basalt samples was characterized. The results of the work for FY 1983 (October 1982-September 1983) have been published in an Annual Report (KELMERS 1984a) and for the first quarter of FY 1984 (October-December 1983) in the preceding Progress Report (KELMERS 1984b).



### 3. NEPTUNIUM STUDIES

#### 3.1 BWIP SOLUBILITY AND SORPTION INFORMATION

A review and summary of the information published by the BWIP project describing neptunium solubility or sorption distribution coefficient values have been presented (KELMERS 1984a). No new BWIP reports with additional neptunium information have been received since that time. Calculated neptunium solubilities of  $2.0 \times 10^{-7}$  mol/L for oxic redox conditions and  $1.0 \times 10^{-10}$  mol/L for reducing redox conditions were given in the Site Characterization Report (SCR 1982). A solubility of  $1.1 \times 10^{-10}$  mol/L for reducing conditions was calculated by Early (1982). "Conservative best estimate" sorption distribution coefficients for basalt of 10 L/kg for oxic conditions and 200 L/kg for reducing conditions were given in the Site Characterization Report (SCR 1982). Prior BWIP data (SALTER 1981) gave distribution coefficient values of  $30 \pm 13$ ,  $4.1 \pm 0.9$ , and  $9.8 \pm 0.5$  L/kg for Umtanum, Flow E (the same as McCoy Canyon), and Pomona basalt, respectively, under oxic conditions. The BWIP sorption information has been separately reviewed (KELMERS 1984d).

#### 3.2 EXPERIMENTAL METHODS AND MATERIALS

Preparation of the McCoy Canyon basalt sample and the neptunium(V)-traced synthetic groundwater (GR-2 formulation) used in the oxic redox condition experiments was described previously (KELMERS 1984a). Work in this report period also included the use of Umtanum basalt and synthetic GR-2 groundwater containing 0.07 M hydrazine hydrate to establish reducing redox conditions. The Umtanum basalt sample was prepared in a manner similar to that for the McCoy Canyon basalt. Details of the batch contact sorption and desorption methods have been described previously (KELMERS 1984a, KELMERS 1984b). Sorption/desorption experiments at  $60 \pm 1^\circ\text{C}$  were also conducted this report period using the batch contact method. An air thermostat was employed to establish the elevated temperature. Contact times of 7 to 14 d were used.

A series of double and triple filtrations, using a new Amicon filter cone for each successive filtering, were performed with GR-2 groundwater solutions containing  $3 \times 10^{-12}$  mol/L and  $1 \times 10^{-6}$  mol/L neptunium(V). These experiments were designed to check for the possibility that the Amicon filters being used to detect the presence of colloidal dispersed neptunium after contact with basalt may be adsorbing neptunium and thus introducing a data bias. Experiments at both neptunium concentrations were performed under oxic conditions; experiments at the low neptunium concentration were also conducted under reducing redox conditions (0.07 M hydrazine hydrate). Each of the Amicon filter cones used was initially soaked in deionized water for at least 1 h, following the standard Amicon specifications, prior to being used to filter the GR-2 solutions containing the neptunium. In one set of tests, the surfaces of the filters were rinsed with 2 mL of the Np-traced GR-2 solution in an attempt to passivate the filters against sorption, and the



solution was poured out without allowing it to pass through the filter. In some of the oxic condition tests, the filtrate was passed through the same filter a second time to determine the effect of refiltering on the sorptive capacity of the filters.

### 3.3 RESULTS

Measurement of sorption ratios ( $R_s$ ) and desorption ratios ( $R_d$ ) for neptunium(V) with McCoy Canyon basalt at  $24 \pm 2^\circ\text{C}$  and  $60 \pm 1^\circ\text{C}$  under reducing redox conditions were completed during this report period. A few sorption tests were also performed using Umtanum basalt at  $24 \pm 2^\circ\text{C}$  under oxic redox conditions. The sorption and desorption data are given in Tables A.1 and A.2, respectively, of the Appendix.

The basalt flow sample used in the experiment was observed to have a strong effect on the sorption ratios measured under oxic redox conditions. Changing from McCoy Canyon basalt to Umtanum basalt resulted in an approximately fourfold increase in the sorption ratios (from 1.7 L/kg, as reported in KELMERS 1984b, to 6.8 L/kg). The higher sorption seen with Umtanum relative to McCoy Canyon basalt is similar to the trend reported by BWIP, although our values are lower. No reason for this difference in sorption behavior, which is apparently related to the basalt flow used in the test, has been suggested by BWIP or is obvious from our experiments.

Increasing the contact temperature from 24 to  $60^\circ\text{C}$  increased the average sorption ratio from 1.7 to 5.8 L/kg with McCoy Canyon basalt. This suggests that under oxic conditions, test results obtained with McCoy Canyon basalt at room temperature may be conservative relative to the behavior to be expected in the repository at approximately  $55\text{--}60^\circ\text{C}$ .

Neptunium sorption ratios measured under reducing redox conditions (hydrazine added) were two to three orders of magnitude higher than the corresponding oxic condition values. Sorption ratios observed ranged from 101 L/kg to as high as 18,100 L/kg.

Substantial removal of neptunium from solution was observed with blank samples in the absence of basalt (21 to 26% removal at  $24^\circ\text{C}$  and 3 to 11% removal at  $60^\circ\text{C}$ ). Loss of neptunium from solution in the blanks may result from sorption by the test apparatus, or possibly precipitation of a fraction of the neptunium as an insoluble reduced phase. The change in fraction removed as a function of temperature may be a result of differences in the initial neptunium concentration of the test solution. The room temperature tests were conducted nearly five orders of magnitude higher neptunium concentration than the  $60^\circ\text{C}$  tests.

The maximum neptunium concentration measured in the hydrazine-containing solutions was approximately  $9 \times 10^{-7}$  mol/L  $M$ , the highest concentration tested. The limiting neptunium(V) concentration value must lie above this concentration.

Hydrazine was not found to reduce the neptunium(V) that remained in solution after contact to neptunium(IV). A valence check for neptunium(IV/V/VI) was performed by solvent extraction techniques (KELMERS 1984a) on the hydrazine-containing solutions before and after contact. All of the neptunium remaining in solution after contact with basalt was in the +5 valence. Since one of the neptunium(V) stock solutions used contained some neptunium(VI), this shows that hydrazine does reduce neptunium(VI) to neptunium(V), but it clearly does not reduce neptunium(V) to neptunium(IV). Based on standard redox potentials, reduction would be expected (BURNEY 1974). This lack of reactivity may indicate some kinetic block for the reduction reaction involving hydrazine. Slow or blocked reduction kinetics have been observed for the reaction of hydrazine with neptunium(V) in acidic solutions (KOLTONOV 1975; KARRAKER 1981; EL-NAGGAR 1982).

Some aspects of the reducing condition test results were surprising. The 11-d sorption tests at 60°C yielded lower sorption ratios than the 7-d tests. Furthermore, the desorption ratios at 24 and 60°C were higher and lower, respectively, than their corresponding sorption ratios. It seems plausible that the decrease in the sorption and desorption ratios at 60°C, compared to 24°C, could be due to hydrazine instability and decomposition during the test, resulting in a partial loss of the reducing state of the test solution. This observation was not explored further, but it suggests that hydrazine may not be suitable for simulation of repository reducing conditions in long-term laboratory tests. Concerns as to the applicability of hydrazine for this purpose were previously expressed (KELMERS 1984b).

The results of the Amicon filter studies show that fresh filters adsorb a small but consistent fraction of the neptunium(V) from synthetic groundwater GR-2 solutions. The removal process appears to be sorption, with a low but constant sorption ratio. No difference was seen between oxic and reducing redox condition tests. None would be expected, however, since hydrazine did not change the valence of the neptunium in solution. For all filtrations that used a fresh filter (Table 1), approximately  $5 \pm 2\%$  of the neptunium(V) was adsorbed from solution. Additional removal was not observed for repetitive filtrations using the same filter. Since essentially no neptunium was removed from a fresh solution by a used filter, there did not seem to be a significant amount of colloiddally dispersed neptunium in these solutions, and the removal from solution by the filters was not a result of the filtration process.

Sorption of neptunium onto the filters may present an additional complicating effect in the reporting of neptunium(V) sorption ratios and apparent solubility limits if the filters are not first preconditioned with some of the solution containing the neptunium. This implies that much of the sorption data collected using Amicon filtration for colloidal particulate removal may have a systematic bias if the filters were not preconditioned. If the sorption effect of the filters is not taken into account, (1) the sorption ratios reported without preconditioning will be higher, and (2) the apparent solubility values limit will be lower than is actually the case.

Table 1. Neptunium(V) removed from GR-2 groundwater solutions by amicon filters

	Np removed by filter (%)	
	Series 1	Series 2
Fresh filters used for each successive filtering:		
Each filter rinsed on the surface with 2 mL of Np(V)/GR-2 solution; oxic redox conditions; neptunium concentration: $3 \times 10^{-12}$ mol/L		
1st Filter:	6.5	3.0
2nd Filter:	5.6	5.3
3rd Filter:	5.0	5.4
Each filter used "as-is"; oxic redox conditions neptunium concentration: $3 \times 10^{-12}$ mol/L		
1st Filter:	3.2	3.6
2nd Filter:	6.3	6.7
3rd Filter:	6.3	5.4
Replicate tests:		
1st Filter:	5.0	3.5
2nd Filter:	6.7	7.8
Each filter rinsed on the surface with 2 mL of the Np(V)/GR-2 solution; reducing redox conditions (hydrazine); neptunium concentration: $3 \times 10^{-12}$ mol/L		
1st Filter:	4.8	6.4
2nd Filter:	7.6	4.7
3rd Filter:	11.4	1.4
Each filter used "as-is"; oxic redox conditions; neptunium concentration: $1 \times 10^{-6}$ mol/L		
1st Filter:	4.3	5.0
2nd Filter:	6.4	6.3
Second filtering using the same filter used for the first filtering; oxic redox conditions:		
Neptunium concentration: $3 \times 10^{-12}$ mol/L		
1st Filtering:	5.4	6.7
2nd Filtering:	-0.8 <sup>a</sup>	-1.1 <sup>a</sup>
Neptunium concentration: $1 \times 10^{-6}$ mol/L		
1st Filtering:	7.5	2.2
2nd Filtering:	1.2	0.6

<sup>a</sup>Negative values are due to randomness in the number of disintegrations per unit time.

### 3.4 CONCLUSIONS

1. Umtanum basalt gives an approximately fourfold increase in the neptunium(V) sorption ratios (from 1.7 to 6.8 L/kg), compared to McCoy Canyon basalt, under oxic redox conditions with synthetic groundwater GR-2 at 24°C.
2. Increasing the temperature from 24 to 60°C increased the sorption ratios approximately threefold for McCoy Canyon basalt under oxic conditions with synthetic groundwater GR-2 (from 1.7 to 5.8 L/kg).
3. Neptunium sorption ratios were two to three orders of magnitude higher under reducing redox conditions in synthetic groundwater GR-2 containing hydrazine at 24 or 60°C than the corresponding oxic condition values. Sorption ratios observed at 60°C ranged from 101 to 18,100 L/kg.
4. The maximum neptunium concentration in solution measured to date under reducing redox conditions was approximately  $9 \times 10^{-7}$  mol/L. The apparent concentration limit must lie above this value.
5. Hydrazine was found to be unsuitable for simulating repository reducing conditions in laboratory experiments because of an apparent instability at 60°C, as well as failing to achieve the expected reduction of neptunium(V) to neptunium(IV) in solution.
6. The Amicon filters used to test neptunium(V) groundwater solutions for the presence of colloiddally dispersed neptunium were found to adsorb a small but constant fraction ( $5 \pm 2\%$ ) of the neptunium in solution. It is necessary to precondition the filters before use in order to prevent this sorption. Data obtained with fresh (not preconditioned) filters have a consistent bias and yield nonconservative values (higher sorption ratios and lower solubility limit values).

### 3.5 EVALUATION OF BWIP VALUES AND METHODS

The BWIP Site Characterization Report (SCR 1982) reported a neptunium sorption ratio "conservative best estimate" of 10 L/kg. This value is probably based on their work with Umtanum basalt. Our work yielded an average sorption value for neptunium(V) onto Umtanum basalt of 6.8 L/kg, which is fairly close to the BWIP "conservative best estimate" value. We seem to be observing greater neptunium sorption with Umtanum basalt relative to McCoy Canyon basalt, as was reported by BWIP. No reason for this apparent basalt-flow specificity of neptunium sorption has been suggested.

Under reducing redox conditions (0.1 mol/L hydrazine in the groundwater), a neptunium sorption ratio of  $1015 \pm 164$  L/kg was reported (SALTER 1981) for Umtanum basalt, and Barney (1981) reports a sorption ratio of  $159 \pm 47$  L/kg under similar conditions. The BWIP Site Characterization Report gives a "conservative best estimate" of 200 L/kg



for "basalt" under reducing conditions. Our work under reducing redox conditions at 24°C with synthetic groundwater GR-2 and McCoy Canyon basalt resulted in an average neptunium(V) sorption ratio of about 150 L/kg for 7-d contact times. At 60°C for similar conditions, the average sorption ratio increased to about 5000 L/kg. Thus, the BWIP "conservative best estimate" value seems to be conservative for these conditions (i.e., it is lower than the value we obtained in the presence of hydrazine). However, the relevance of such information for repository evaluation seems questionable due to concerns relative to the use of hydrazine (KELMERS 1984b).

The maximum neptunium concentration measured in the hydrazine-containing solutions was approximately  $9 \times 10^{-7}$  mol/L. Since these neptunium tests stopped at  $9 \times 10^{-7}$  mol/L, the limiting neptunium(V) concentration must lie above this value. This value is as much as two orders of magnitude higher than the solubility values of  $1.0 \times 10^{-10}$  mol/L calculated by BWIP for reducing conditions, and is also above the  $2 \times 10^{-7}$  mol/L limiting concentration value given in the BWIP Site Characterization Report (SCR 1982) for oxic conditions. The calculated values probably assume crystalline  $\text{NpO}_2$  as the stable solid phase, but in our experiments no solid neptunium-containing phase has been observed.

The batch contact methodology employed by BWIP has utilized filtration through Amicon filters for the liquid/solid separation after contact (SALTER 1981, BARNEY 1982). Our work has shown that these filters have a small but significant sorption capability for neptunium(V). The BWIP reports do not discuss this effect, thus it seems unlikely that the BWIP data have been corrected for sorption by the filter. The BWIP sorption values therefore are likely nonconservative (i.e., higher than actual due to lack of correction for sorption by the filter).



## 4. TECHNETIUM

### 4.1 BWIP SOLUBILITY AND SORPTION INFORMATION

A review and summary of the information published by the BWIP project describing technetium limiting solubility or sorption distribution coefficient values have been presented (KELMERS 1984a). No new BWIP reports with additional technetium information have been received since that time. Under oxic conditions, technetium exists in solution as the pertechnetate anion. BWIP has not identified a solubility limit and has reported low to zero sorption with basalt for pertechnetate under oxic conditions. Under reducing conditions, very low solubility limits of  $10^{-12}$  or  $10^{-14}$  mol/L were calculated by BWIP. As discussed previously (KELMERS 1984a), our laboratory tests with hydrazine suggest an apparent concentration limit of  $10^{-5}$  to  $10^{-6}$  mol/L. A "conservative best estimate" sorption distribution coefficient of 29 L/kg was reported by BWIP under reducing conditions (SCR 1982). The BWIP sorption information has been separately reviewed (KELMERS 1984d).

### 4.2 EXPERIMENTAL METHODS AND MATERIALS

Anoxic redox condition (air excluded) batch contact tests are being evaluated as a test methodology to permit simulating the basalt far-field geochemical parameters in laboratory experiments. Previously (KELMERS 1984a) we reported values for technetium apparent concentration limits describing sorption behavior under both oxic (air present) and reducing (hydrazine added) redox conditions in batch contact tests. Hydrazine was added in our work, as was done by BWIP, to evaluate the BWIP methodology and the values obtained by BWIP under their experimental conditions. The BWIP tests were designed to simulate the calculated redox condition expected in the basalt repository far field through the addition of hydrazine to establish a low solution Eh, or reducing redox condition. However, the use of hydrazine to simulate repository redox conditions now seems highly questionable in the case of technetium and also for other elements (KELMERS 1984b). In order to attempt to more closely simulate the actual far-field redox conditions that would exist in a basalt repository, anoxic condition tests have been initiated in which as much oxygen from air as possible is excluded from the test solutions and solids in order to allow the host rock/groundwater system to establish a "natural" redox condition in the test.

These anoxic condition tests are carried out in a controlled-atmosphere glove box. The box atmosphere is argon that contains about 0.3 to 0.4 ppm of oxygen,  $2 \times 10^{-6}$  times the oxygen concentration in air. Air saturation of aqueous solutions corresponds to about 8 ppm oxygen; thus, assuming Henry's Law to be valid, the groundwaters in the controlled atmosphere box should contain about  $1.6 \times 10^{-5}$  ppm oxygen (equivalent to  $5 \times 10^{-10}$  mol/L). It is possible that the oxygen content might initially be slightly greater than this because of oxygen adsorbed on the surface of the test tubes. This concentration of oxygen is greater than that of the technetium in the most dilute solutions used ( $10^{-12}$  mol/L), but is

much less than the technetium in the more concentrated solutions (as high as  $10^{-3}$  mol/L Tc). These low oxygen concentrations do not generate a reducing redox condition, but they do help permit the basalt to establish a reducing condition if it is capable of doing so.

The batch contact experimental methodology and the basalt and synthetic groundwaters used in the tests were described in detail in the preceding Annual Report (KELMERS 1984a). For the anoxic condition tests described in this report, several steps were taken to exclude air. The McCoy Canyon basalt was crushed, screened to -70/+325 mesh, and stored under argon. The solution was synthetic groundwater GR-2 traced with  $^{99}\text{Tc}$  and/or  $^{95\text{m}}\text{Tc}$  added as the pertechnetate anion from sodium or ammonium pertechnetate solutions. The groundwater and technetium tracer solutions were sparged with argon before introduction into the glove box. The test solution technetium concentrations ranged from  $10^{-12}$  mol/L to  $10^{-3}$  mol/L. Three replicate tests were run at each technetium concentration. The basalt (0.4 g) and traced groundwater (4 mL) were contacted for 14 d and 50 d at about  $27^\circ\text{C}$  (the ambient temperature inside the glove box) in the controlled-atmosphere glove box. After the contact, the samples were centrifuged for 30 min at 4000 relative centrifugal force (rcf) using a small centrifuge inside the controlled-atmosphere glove box. Aliquots of the supernate were taken (1) to measure the technetium concentration in solution, and (2) for solvent extraction tests to determine the valence of the technetium in solution. Three control samples containing traced solution but no basalt were run at each technetium concentration to measure technetium loss onto the polypropylene tubes. In the solvent extraction valence analysis, the basalt-contacted solutions were extracted with 0.05 M tetraphenylarsonium chloride (TPAC) in chloroform (TRIBALAT 1953). The technetium counted in the organic phase is reported as Tc(VII), and that remaining in the aqueous phase is reported as reduced technetium of unknown valence or solution species.

At the present time, we do not have elevated temperature apparatus inside a controlled-atmosphere glove box to permit carrying out the batch contact tests within the glove box, as was done at  $27^\circ\text{C}$ . Therefore, some anoxic experiments at  $60^\circ\text{C}$  were carried out by adapting a procedure that is used to transfer materials from one controlled-atmosphere glove box to another. In this transfer procedure, Mason jars are filled inside a glove box with the materials and then sealed with the rubber-gasketed lids before transfer. For our sorption experiments, we prepared the samples inside a glove box. The test samples were placed into Mason jars along with several tubes that contained 5%  $\text{Na}_2\text{SO}_3$  solution. The purpose of these tubes, which had caps with permeable membranes, was to attempt to chemically scavenge any oxygen that might enter the jars during the contact period outside the glove box. The jars were then taken outside the controlled-atmosphere glove box, and the samples were contacted by shaking in an air thermostat at  $60^\circ\text{C}$ . After contacting, the jars were cooled in a vessel that was continuously flushed with argon. The jars were then taken back inside a glove box and opened for weighing, pH measurement, centrifugation to recover the solution, and sampling for  $^{95\text{m}}\text{Tc}$  gamma counting.

Because the Mason jars were outside the glove box for long periods of time, there was some uncertainty if the rubber seal of the jar lid and the  $\text{Na}_2\text{SO}_3$  scavenger had adequately protected the basalt/groundwater samples from oxygen resulting from air inleakage. We attempted to determine whether there was any significant amount of oxygen in the jars after the contact period by the following technique: A suction device was fitted to a Mason jar lid and connected directly to the glove box oxygen analyzer. Several Mason jars were prepared inside the glove box, brought outside for contacting, and then transferred back to the glove box to be opened. When the jars were opened, they were capped with the suction lid as quickly as possible, and the oxygen concentration was monitored. Two initial tests indicated that some oxygen was present in jars that had been outside the glove box for 14 h. The first of these two jars was empty, and the second contained four tubes filled with  $\text{Na}_2\text{SO}_3$  oxygen scavenger solution. In both cases, the oxygen concentration indicated by the analyzer peaked in 1 to 1.5 min after the jars were opened. The peak concentrations were 17 ppm oxygen for the empty jar and 15 ppm for the jar with the oxygen scavenger tubes. The baseline oxygen concentration in the chamber at the time of these tests was 2.5 ppm oxygen. It appears that some air inleakage had occurred.

#### 4.3 RESULTS

Batch contact tests under anoxic redox conditions did not show any significant removal of technetium from GR-2 by McCoy Canyon basalt (Table 2). In 14-d and 50-d anoxic tests, sorption ratios were less than 1 L/kg at initial pertechnetate concentrations from  $10^{-12}$  mol/L to  $10^{-3}$  mol/L. No significant valence reduction of the technetium in solution was observed, as measured by extraction of the basalt-contacted solutions with 0.05 M TPAC in chloroform. Little or no sorption was noted in anoxic tests with McCoy Canyon basalt that had been crushed and stored in air. Air-crushed basalt may be representative of material that could be used for engineered facility backfill. It would be exposed to air during mining, surface storage, and emplacement in the engineered facility on repository closure. Sorption ratios with this material were also 1 L/kg or less, except for the tests at a technetium concentration of  $10^{-8}$  mol/L, where the measured sorption ratios were about 2. The valence determination tests also indicated slightly higher concentrations of reduced technetium in the  $10^{-8}$  mol/L Tc solutions. The reasons for the different behavior with this solution are not known at this time, since all the solutions were treated the same. In any case, the results indicate much less technetium sorption from GR-2 groundwater than was measured from 0.1 M NaCl solutions in recirculating column tests conducted under NRC/RES Project B0462 (MEYER 1984).

Table 2. Technetium sorption under anoxic conditions from synthetic groundwater GR-2 onto McCoy Canyon basalt<sup>a</sup>

Initial Tc concn (mol/L)	14-d contact			50-d contact		
	pH	Rs (L/kg)	Reduced Tc in soln. (% of total)	pH	Rs (L/kg)	Reduced Tc in soln. (% of total)
Argon-crushed basalt:						
10 <sup>-12</sup>	9.6	0.4 ± 0.1	3.5	9.8	0.4 ± 0.2	1.4
10 <sup>-8</sup>	9.6	1.1 ± 1.4	0.3	9.8	0.6 ± 0.1	1.8
10 <sup>-6</sup>	9.6	0.1 ± 0.1	1.9	9.8	0.1 ± 0.1	0.1
10 <sup>-4</sup>	9.6	0.0 ± 0.1	0.7	9.8	0.0 ± 0.1	0.2
10 <sup>-3</sup>	9.3	0.0 ± 0.1	0.8	9.5	0.0 ± 0.1	0.2
Air-crushed basalt:						
10 <sup>-12</sup>	9.7	0.5 ± 0.4	2.7	9.6	0.8 ± 0.5	1.5
10 <sup>-8</sup>	9.7	2.1 ± 0.2	3.8	9.6	1.8 ± 0.1	6.2
10 <sup>-4</sup>	9.7	-0.1 ± 0.1	2.0	9.5	-0.1 ± 0.1	3.0

<sup>a</sup>Conditions: 27°C; 0.4 g -70/+325 mesh McCoy Canyon basalt; 4 ml GR-2 traced with <sup>95m</sup>Tc and made up to concentration with <sup>99</sup>Tc; 14-d and 50-d contact time; centrifuged at 4000 rcf for 30 min; errors in sorption ratio values are one standard deviation for triplicate samples; negative sorption ratios are due to counting errors.

Anoxic condition sorption tests were conducted at 60°C to measure technetium sorption onto -70/+325 mesh McCoy Canyon basalt. The Mason jar technique (described in Sect. 4.2) was used with synthetic GR-2 groundwater and basalt that had been crushed, sized, and stored in an argon atmosphere. The groundwater contained 10<sup>-8</sup> mol/L <sup>99</sup>Tc and tracer <sup>95m</sup>Tc, and the contact times were 14 d and 50 d. As in the anoxic condition tests at 27°C, essentially no technetium was sorbed from the groundwater. The sorption ratios were 0.2 ± 0.2 L/kg after 14 d and 0.0 ± 0.3 L/kg after the 50-d contact.

Anoxic condition batch tests at 27°C using 0.1 M NaCl as the solution instead of groundwater GR-2 were also carried out. These tests were made to test the Mason jar procedure by comparing the results of experiments done inside a controlled-atmosphere glove box and in Mason jars done outside the glove box. We selected 0.1 M NaCl as the solution because previous recirculating column experiments (MEYER 1984) had shown that there should be substantial sorption of technetium onto basalt from 0.1 M NaCl under anoxic conditions but not under oxic conditions. In the current tests, all of the pertechnetate-traced solutions and McCoy Canyon basalt samples were prepared inside the controlled-atmosphere glove box, and the Mason jars were loaded with three test samples, three control samples (no basalt), and four Na<sub>2</sub>SO<sub>3</sub> scavenger tubes inside the glove box. The jar was taken outside the chamber for the contact period



in a 60°C air thermostat and then returned to the chamber for centrifugation and sampling as described above. The tests inside the glove box were made by the usual procedure for anoxic condition tests.

The results (Table 3) show considerable technetium sorption for both the glove box tests and the Mason jar tests. After 14 d, the sorption rates averaged 71.9 L/kg for two of the three Mason jar samples (sorption was much lower in the third sample), nearly identical to the sorption ratio of  $69.2 \pm 3.9$  L/kg for the triplicate samples inside the glove box. This similarity in sorption rates indicates that not enough oxygen entered the Mason jars to affect technetium sorption for two of the three samples. Technetium sorption was lower after 50 d in both sets of tests. The sorption ratio decreased to  $57.1 \pm 9.5$  L/kg in the glove box tests and to  $36.2 \pm 6.1$  L/kg in the Mason jar tests. These results suggest a slow leakage of air into the tubes in the Mason jars.

Table 3. Technetium sorption under anoxic conditions onto McCoy Canyon basalt from 0.1 mol/L NaCl solution<sup>a</sup>

Sample tubes	14-day contact		50-day contact	
	pH	Rs (L/kg)	pH	Rs (L/kg)
Inside glove box	8.9	69.6	8.6	47.2
	8.9	72.9	8.6	57.8
	8.9	65.2	8.7	66.2
In Mason jars outside glove box	9.0	28.7	8.5	34.6
	9.1	67.2	8.5	31.1
	9.1	76.5	8.5	43.0

<sup>a</sup> Conditions: 27°C; 0.4 g McCoy Canyon basalt, -70/+325 mesh, ground, sized and stored in argon atmosphere; 4 mL 0.1 mol/L NaCl containing  $10^{-8}$  mol/L <sup>99</sup>Tc and tracer <sup>95m</sup>Tc.

#### 4.4 DISCUSSION AND CONCLUSIONS

We have observed different technetium sorption behavior with basalt in anoxic condition experiments conducted in different ways. In the tests described in this report, essentially no sorption of technetium onto McCoy Canyon basalt from pertechnetate-traced groundwater GR-2 was observed after a 14-d or 50-d contact at 27°C in experiments conducted in a controlled-atmosphere glove box with an argon atmosphere containing only 0.3 to 0.5 ppm oxygen. The results were the same with McCoy Canyon basalt crushed, sized, and stored in either air or argon. However, considerable sorption of technetium onto the same sample of McCoy Canyon basalt was observed earlier in a recirculating column experiment (MEYER 1984) under similar anoxic conditions when the pertechnetate-traced



solution was 0.1 M NaCl adjusted to pH 9. In experiments done last summer (KELMERS 1984c), some technetium sorption was measured on <325 mesh McCoy Canyon basalt from GR-2 groundwater at 60°C in tests lasting for 99 d. These earlier experiments were done in sealed glass containers with the fine fractions of basalt crushed in air, and a freeze-thaw technique was used to deaerate the GR-2 solution. The batch contact tests described in this report were carried out in polypropylene test tubes with a larger sized fraction of the basalt. The moderately high technetium sorption from 0.1 M NaCl by McCoy Canyon basalt in the batch anoxic condition tests tend to confirm the earlier recirculating column test results with 0.1 M NaCl and indicate that technetium sorption from 0.1 M NaCl is not dependent on the contact method used. The results suggest that differences in the solution compositions may be in some way responsible for the differences observed in technetium sorption behavior. It is possible that some technetium sorption from GR-2 groundwater might be observed with McCoy Canyon basalt if the temperature was increased to 60°C, the oxygen was more completely excluded from the system, and/or longer contact times were used.

We believe that anoxic condition test methodology simulates actual BWIP repository conditions more realistically than the reducing redox condition experiments in an air environment with hydrazine added to the simulated groundwater. The test procedure involving the use of Mason jars for anoxic condition tests at elevated temperature outside the controlled atmosphere glove box has several disadvantages. Our results so far indicate a slow leakage of air into the jars, which cannot be detected until the end of the test. In addition, the transfer of the samples in and out of the glove box is tedious and time consuming. A more useful approach to conducting anoxic condition batch contact experiments at elevated temperatures may be to heat and contact the samples inside the controlled-atmosphere glove box, where the oxygen concentration is continuously monitored. We are exploring this procedure by constructing a thermostat inside one of the glove boxes.

#### 4.5 NUCLEAR MAGNETIC RESONANCE STUDIES OF THE PERTECHNETATE--HYDRAZINE REACTION

This section describes some nuclear magnetic resonance (NMR) studies of the reduction of pertechnetate ion by hydrazine solutions performed under subcontract by Prof. R. L. Clark at Florida State University. The study centered on the question of whether pertechnetate ion in various aqueous solutions is fully reduced to a lower valence by hydrazine. The summary below was prepared by Dr. Clark. A full report will be published separately.

The study centered on the question of whether technetium in the form of the pertechnetate ion is fully reduced by hydrazine in various aqueous solutions. This is an important subject in nuclear waste management since one is questioning whether the reduction of technetium by basalt can be modeled by the use of hydrazine.

The technetium NMR signal of the  $\text{TcO}_4^-$  ion can be detected at fairly low levels by our modern equipment. Solutions of 0.01 M concentration were used for routine work. The signal can be seen with good sensitivity from a single pulse. It is likely that one could study solutions having concentrations of  $10^{-5}$  M with little difficulty. The line is sharp, having a width of about 3 Hz at half-height. It is not altered by the presence of the reaction products.

The pertechnetate ion is reduced, at least to some degree, by hydrazine in all types of solutions used thus far. The solutions ranged from 0.1 M HCl to 0.1 M NaOH and included a wide variety of other salts or buffers. The rates of reduction vary quite widely, but they do not appear to depend in a direct way on the pH. Sodium hydroxide solutions react quite rapidly (a minute or two), carbonates and silicates react at intermediate rates and a phosphate buffer reacts at rates measured in hours. Other solutions fall in between these extremes. No explanation for the variation in rate among the various types of solution has become obvious. The rate of reaction is also dependent upon the concentration of hydrazine. In most cases, when a large excess of hydrazine is used, the reaction is too fast to be followed conveniently by our NMR method.

The degree of completeness of the reduction depends upon the relative concentrations of hydrazine and technetium. When the hydrazine is present to no more than a 50% excess, the pertechnetate signal often never totally disappears. However, with a large excess of hydrazine, the signal will generally disappear and not be seen even on runs in which a large number of pulses are taken to enhance the sensitivity.

Although the reductions can be complete with an adequate excess of hydrazine, the process is complicated by several competing reactions. Based upon the potentials of the pertechnetate/technetium dioxide and the hydrazine/nitrogen half reactions, there should be no need for a significant excess of hydrazine. However, we have clearly demonstrated that oxygen will slowly reoxidize the reduced technetium back to the  $\text{TcO}_4^-$  ion. Reduction rates are measured in minutes and hours and the reoxidation in days. Samples which have had their  $\text{TcO}_4^-$  signal reduced to 2 to 4% of the original value can have it return to 50% of the initial quantity within a week if the oxygen above the solution is renewed. In addition, a survey of the literature makes it seem quite certain that hydrazine undergoes disproportionation.

It is my conclusion that in order for hydrazine to act as a good reducing agent for pertechnetate, several conditions must be fulfilled. Enough hydrazine is needed to reduce the

technetium, and to react with the oxygen present in both the dead space and dissolved in the solution (if the solutions had not been previously purged). Since the reaction with oxygen will almost always be slow, then the hydrazine disproportionation will probably be complete before the oxygen is totally removed. Thus, unless special experimental precautions are taken, hydrazine is needed for both technetium reduction and oxygen removal while it itself is steadily disappearing through disproportionation. If the oxygen removal is not rapid enough, then the disproportionation will be complete while oxygen is still present for reoxidation. Further hydrazine additions of sampling operations will admit more oxygen unless this is done in an inert atmosphere. Another question concerns whether plastic tubes or plastic caps provide an adequate oxygen barrier.

Experiments have shown that the technetium signal totally disappears in samples that have been carefully degassed. It does not reappear with time as it does in samples containing oxygen. (A significant excess of hydrazine appears necessary to overcome the disproportionation problem.)

The reduction reactions are mechanistically quite complicated. They appear to be catalytic (probably autocatalytic) in some way. Also, the reduction products do not always have the same appearance. In some cases black precipitates are present and in other cases various deep colored solutions or colloids are formed. It is not clear whether the products are chemically different or only superficially different.

The reader should be reminded that these studies were done at technetium concentration orders of magnitude above those used in the  $^{95m}\text{Tc}$  tracer studies of sorption on basalt.

The results are basically repeatable. However, there is often an induction period before onset of the reaction that varies somewhat among presumably identical samples. Impurities in the ammonium pertechnetate solutions are possibly responsible.

## 5. URANIUM

### 5.1 BWIP SOLUBILITY AND RETARDATION INFORMATION

Uranium has been identified as one of the key radionuclides for a repository in basalt (BARNEY 1980). The information published by BWIP on uranium solubility in synthetic groundwaters and sorption from these groundwaters onto basalt, secondary minerals, and interbed materials is summarized in Table 4. Generally, low solubilities and low-to-moderate sorption ratios are reported. Lower solubilities and higher sorption ratio values are reported for reducing redox conditions maintained by the addition of hydrazine to the test solutions than under air-saturated oxic conditions.

Although not explicitly stated in the Site Characterization Report (SCR 1982), uranium migration to the accessible environment in a groundwater-intrusion-groundwater-migration event involving emplaced waste may be controlled by a combination of the low solubility under the reducing conditions expected by BWIP for the basalt geochemical environment (EARLY 1982, EARLY 1983, SALTER 1981a, SCR 1982) and from the moderate sorption onto basalt, secondary minerals, or interbed materials under either oxic or reducing conditions (AMES 1982, SALTER 1981c, SCR 1982, SALTER 1981b, BARNEY 1982). The BWIP sorption information has been separately reviewed (KELMERS 1984d). Information on both uranium solubility and uranium sorption is important for the NRC BWIP-analysis effort.

Table 4. Summary of BWIP values for uranium

	Redox conditions		Reference	
	Oxidizing	Reducing		
Solubility (mol/L)	$10^{-4}$	$10^{-8}$	SCR 1982	
	a	$2.1 \times 10^{-10}$	EARLY 1982	
	a	$2.0 \times 10^{-10}$	EARLY 1984	
	a	$10^{-8}$	SALTER 1981a	
Sorption ratio (L/kg)				
	Basalt (Flow E)	$0.2 \pm 0.5$	$17 \pm 2$	SALTER 1981c
	(Flow E)	0.19 to 0.78	a	AMES 1982
	(Umtanum)	2.4 to 2.9	a	AMES 1982
	(Umtanum)	6	40	SCR 1982
Secondary minerals	76 to 1450	a	SALTER 1981b	
	70	a	SCP 1982	
Interbed materials	a	30-40	BARNEY 1982	

<sup>a</sup>No data given.



## 5.2 EXPERIMENTAL METHODS AND MATERIALS

Uranium sorption isotherms were completed at 27°C for oxic, anoxic, and reducing (hydrazine added) redox conditions with McCoy Canyon basalt and groundwater GR-2. The oxic tests were made at air saturation and ambient laboratory temperature. Anoxic condition (air excluded) tests were carried out in an argon atmosphere (0.2 to 0.4 ppm oxygen) in a controlled-atmosphere glove box. Reducing conditions were maintained by the addition of hydrazine to the test solutions (0.1 mol/L), the same procedure used at BWIP. Although we consider the use of hydrazine to be highly questionable (KELMERS 1984b), a few tests were made with this reagent to evaluate BWIP methodology and the values obtained by BWIP under their experimental conditions.

The batch contact experimental methodology and the basalt and synthetic groundwaters used in the tests were described in detail in Kelmers (1984a), and the precautions taken to exclude air from the anoxic condition tests were described in Sect. 3.2 of this report. The groundwater used in the tests was traced with  $^{238}\text{U}$  and/or  $^{233}\text{U}$  added as the uranyl chloride at concentrations from  $10^{-12}$  to  $10^{-4}$  mol/L.

## 5.3 RESULTS

The results of the sorption tests are shown in Table 5. The sorption ratios measured under anoxic conditions were slightly higher than those under oxic conditions, especially at the lowest uranium concentrations. For the reducing condition tests with hydrazine, the sorption ratios were much higher than those obtained under oxic conditions. We measured  $R_s$  values of 1.2 to 2.0 L/kg under oxic conditions, 2.0 to 4.8 L/kg under anoxic conditions, and 15 to 88 L/kg under reducing conditions. These values were adjusted for uranium loss onto the polypropylene tubes, which ranged from 3 to 10% of the uranium present except for a 45% loss from the  $10^{-4}$  mol/L uranium solution under reducing conditions. Sorption was higher under anoxic conditions than under oxic conditions over the uranium concentration range tested.

Table 5. Uranium sorption onto McCoy Canyon basalt from groundwater GR-2<sup>a</sup>

Basalt crushing atmosphere	Initial uranium (mol/L)	14-d contact		50-d contact	
		pH	Rs (L/kg)	pH	Rs (L/kg)
<u>Oxic conditions (air atmosphere)</u>					
Argon	10 <sup>-7</sup>	9.0	1.6 ± 0.2	8.9	1.7 ± 0.3
	10 <sup>-6</sup>	9.0	2.0 ± 0.3	8.9	1.7 ± 0.2
	10 <sup>-5</sup>	9.0	1.3 ± 0.1	8.9	1.2 ± 0.1
	10 <sup>-4</sup>	9.0	1.8 ± 0.1	8.9	1.4 ± 0.1
Air	10 <sup>-6</sup>	9.1	2.0 ± 0.2	9.1	1.8 ± 0.1
	10 <sup>-4</sup>	9.0	1.6 ± 0.2	9.0	1.4 ± 0.1
<u>Anoxic conditions (argon atmosphere)</u>					
Argon	10 <sup>-7</sup>	9.7	4.0 ± 0.1	9.5	4.8 ± 0.8
	10 <sup>-6</sup>	9.6	3.8 ± 0.1	9.6	3.4 ± 0.1
	10 <sup>-5</sup>	9.6	2.3 ± 0.3	9.5	2.5 ± 0.3
	10 <sup>-4</sup>	9.6	2.0 ± 0.2	9.5	2.4 ± 0.2
Air	10 <sup>-6</sup>	9.6	2.0 ± 0.2	9.5	2.4 ± 0.2
	10 <sup>-4</sup>	9.6	1.8 ± 0.1	9.4	1.9 ± 0.6
<u>Reducing conditions (hydrazine added to groundwater)</u>					
Argon	10 <sup>-6</sup>	9.5	61.5 ± 4.4	9.5	88.5 ± 8.6
	10 <sup>-4</sup>	9.5	17.4 ± 0.5	9.4	29.2 ± 2.6
Air	10 <sup>-6</sup>	9.5	46.4 ± 6.3	9.5	68.2 ± 5.7
	10 <sup>-4</sup>	9.5	15.0 ± 1.4	9.5	24.2 ± 2.4

<sup>a</sup>Experimental parameters: contact conditions - 27°C, 0.4 g -70/+325 mesh size McCoy Canyon basalt, 4 mL GR-2; solution recovery - centrifuged 30 min at 5000 rcf; Rs values - mean ± one standard deviation for triplicate samples.

ORNL DWG 84-672

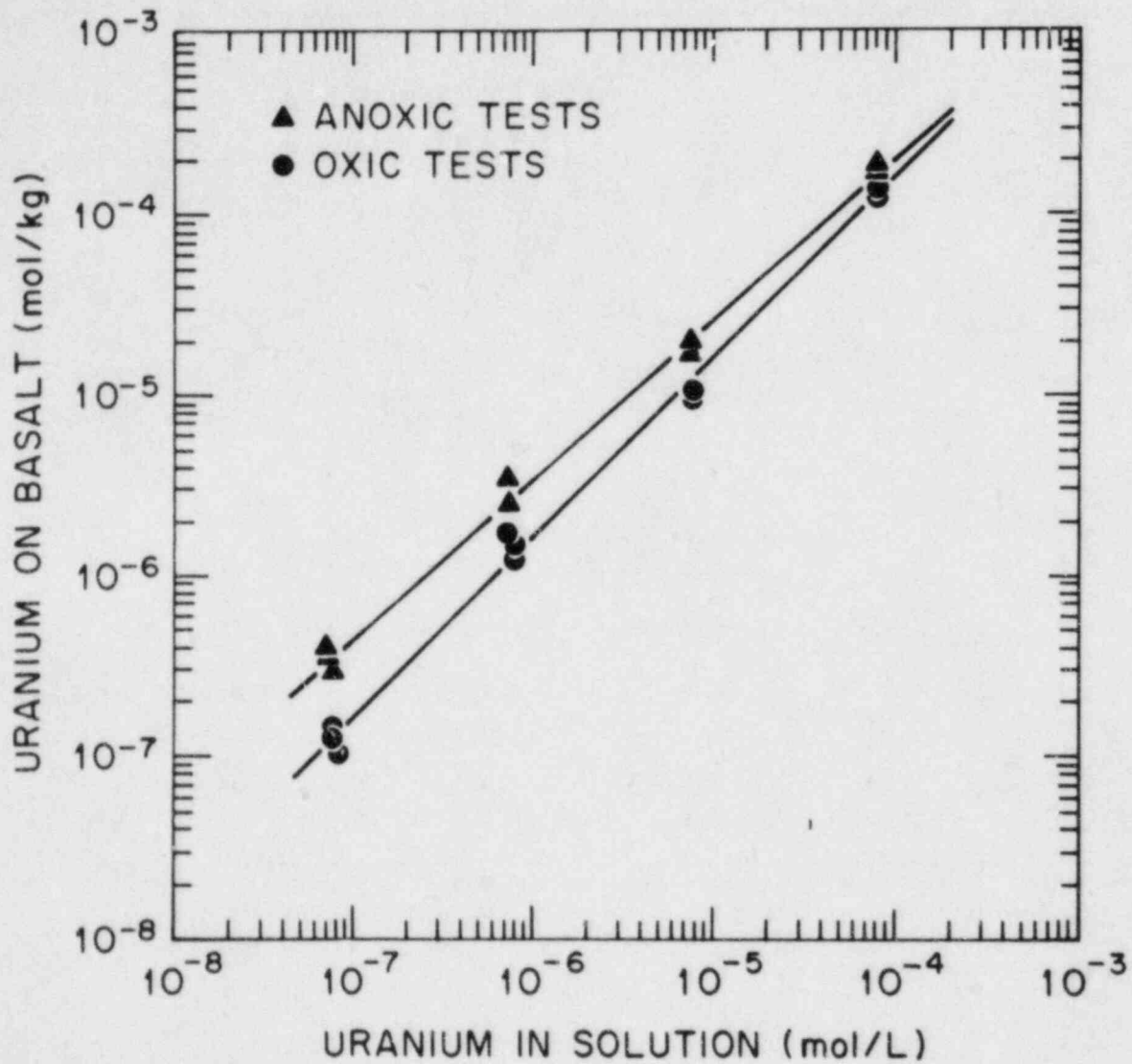


Fig. 1. Sorption isotherms for uranium(VI) onto McCoy Canyon basalt from groundwater GR-2. Conditions: 50-d contact at 27°C; basalt crushed under argon.

Uranium sorption under oxic redox conditions was essentially the same with basalt crushed in air and with basalt crushed in argon and stored in the controlled-atmosphere chamber. However, sorption was significantly lower with the air-crushed basalt under anoxic or reducing conditions. The argon atmosphere evidently preserved the reactivity of the fresh basalt surfaces generated during crushing.

Under oxic or anoxic conditions, uranium sorption was almost the same after 50-d contact of the basalt and groundwater as after 14 d. Apparently these tests reached steady state in 14 d or less. In the presence of hydrazine, however, larger  $R_s$  values were measured at 50 d.

Solutions from the oxic condition tests were tested for the presence of colloiddally dispersed uranium with negative results. The solutions were centrifuged for 30 min at 5000 rcf before removal of aliquots for counting. The count rates were not changed significantly by centrifuging a second time for 30 min at 5000 rcf, or by centrifuging for 30 min at 20,000 rcf after the second centrifugation at 5000 rcf.

#### 5.4 DISCUSSION AND CONCLUSIONS

The sorption ratios measured in these tests are significantly higher than the published BWIP values of  $0.2 \pm 0.5$  L/kg for oxic conditions and  $17 \pm 2$  L/kg for reducing conditions (SALTER 1981c). Another BWIP publication (AMES 1982) gives uranium  $R_s$  values from groundwater GR-2 at 23°C under oxic conditions of 2.4 to 2.9 L/kg for Umtanum basalt and 0.19 to 0.78 L/kg for Flow E basalt (the same as McCoy Canyon). The "conservative best estimate" values given in the SCR (1982) were 6 L/kg for oxidizing conditions and 40 L/kg for reducing conditions. These higher sorption ratios were probably derived from BWIP tests with Umtanum basalt. Our sorption ratio values are consistently higher than the BWIP values for Flow E basalt, and our McCoy Canyon basalt appears to be behaving more like BWIP Umtanum basalt than Flow E (i.e., giving higher uranium sorption).



## 6. COLUMN CHROMATOGRAPHY

The BWIP has conducted much of their radionuclide sorption experimental work using batch contact methodology, and the sorption information developed was applied to calculate the retardation factor ( $R_f$ ) used in modeling radionuclide transport (SCR 1982). In the work reported here, the  $R_f$  has been measured directly using column chromatographic methodology. Experimental setup of the chromatographic system and preparation of the McCoy Canyon basalt samples have been previously described (KELMERS 1984b).

During the current report period, the  $R_f$  values for technetium (as  $^{95m}\text{TcO}_4^-$ ) were measured for McCoy Canyon basalt under oxic redox conditions at 25 and 70°C. Glass columns (3 mm ID by 250 mm long) were prepared by pouring 2.75 g of oven-dried -2/+45 mm-sized basalt through a funnel into the columns. The porosity was 0.41, with a bulk density of 1.56 g/cm<sup>3</sup>. Each column was then connected to the chromatographic system and flushed with the elution solution (groundwater GR-4) for 3 h. The GR-4 formulation was selected since it is the most recent groundwater composition established by BWIP (SALTER 1984). The tracer solutions,  $1 \times 10^{-12}$  mol/L of  $^3\text{H}$  (HTO) and  $^{95m}\text{TcO}_4^-$  in GR-4 groundwater, were loaded onto the columns through a 20-ml injection loop. The column was eluted with GR-4 at either 0.48 or 0.96 mL/min flow rate, and the eluate was automatically collected in liquid scintillation vials. The samples were counted for  $^3\text{H}$  beta activity using liquid scintillation techniques and for  $^{95m}\text{Tc}$  gamma activity with a Ge(Li) gamma detector. The eluate activity data were plotted as C/At and A/At vs elution volume, where

C/At = cumulated sample activity/total activity,

A/At = sample activity/total activity.

The column chromatographic results confirm the BWIP "conservative best estimate" technetium sorption ratio of ~0 L/kg, which was determined by batch contact method under oxic conditions (SCR 1982). Both the  $^3\text{H}$  and  $^{95m}\text{Tc}$  activities had essentially identical breakthrough curves [Fig. 2(b)] and no detectable amount of  $^{95m}\text{Tc}$  remained on the column. The result indicates that the  $R_f$  value for the  $\text{TcO}_4^-$  species was close to 1 (Table 6). There was no evidence of technetium sorption, anion exclusion ( $R_f < 1$ ), or precipitation onto the McCoy Canyon basalt column. Increased flow rate and elevated temperature did not influence the retardation value of technetium. The high symmetry of the elution curves showed that experimental parameters such as the eluant flow rate, column dimensions (the ratio of ID to length), and particle size of basalt did not contribute to peak skewing or broadening.

Table 6. Technetium (VII) retardation in column experiments

Flow rate (mL/min)	Temp. (°C)	Volume eluted <sup>a</sup> (mL)	Peak vol. <sup>b</sup> (mL)	Retardation factor, Rf <sup>c</sup> (dimensionless)	Sorption ratio, Rs <sup>d</sup> (L/kg)
0.96	25	0.73	2.16	1	0
0.96	70	0.73	2.16	1	0
0.48	25	0.73	2.16	1	0
0.48	70	0.73	2.16	1	0

<sup>a</sup>Total volume eluted before the eluate activity reached 50% of the total spike activity, corrected for void volumes of the column, fittings, and tubing.

<sup>b</sup>Total volume where the activity of the eluate was between 0.01 and 0.99 of the total activity eluted.

<sup>c</sup>The Rf was calculated from the total volume eluted for radionuclides vs the total volume eluted for HTO.

<sup>d</sup>The Rs was calculated from the equation  $R_s = (R_f - 1)P/BD$ , where P = porosity (0.412) and BD = bulk density (1.56 g/cm<sup>3</sup>).

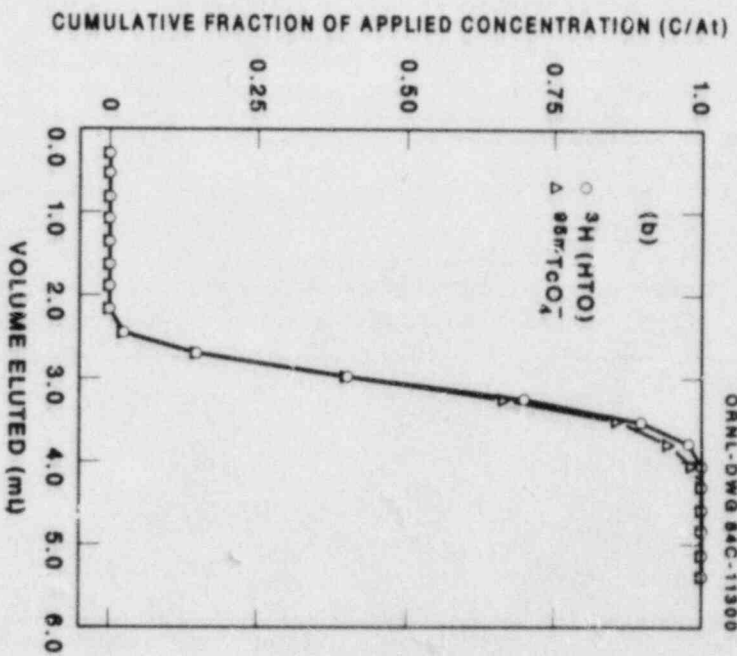
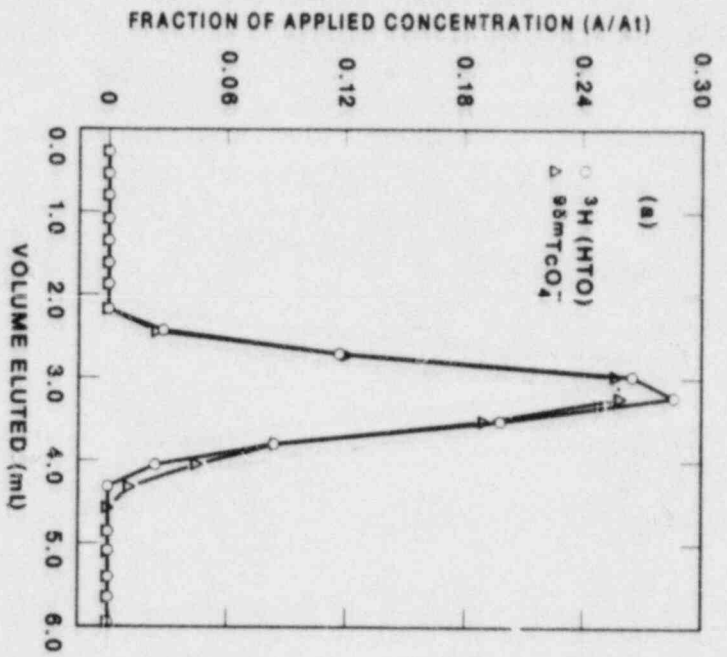


Fig. 2. Elution of technetium from McCoy Canyon basalt columns indicating (a) the elution curves and (b) the breakthrough curves of HTO and TcO<sub>4</sub><sup>-</sup> at 25°C.

## 7. GEOCHEMICAL MODELING

### 7.1 BWIP INFORMATION

Efforts in geochemical modeling during this quarter emphasized two areas: (1) comparative solubility calculations, and (2) calculation of saturation indices for synthetic groundwater formulations. The solubilities of selected elements important for nuclear waste isolation in BWIP groundwaters were calculated by Early (1982) and Early (1984)\*. Calculations using the geochemical codes PHREEQE (PARKHURST 1980) and MINTEQ (FELMY 1983) were conducted to verify the calculations of Early. A new synthetic groundwater formulation (GR-4) has been released by BWIP (SALTER 1984). The solution is intended to be a simulation of groundwater for the testing of engineered components and radionuclide solubility and sorption controls appropriate for the Cohasset candidate horizon. This formulation (GR-4) and previous groundwater formulations (GR-1, GR-2, and GR-3) were modeled to evaluate the saturation state of the solutions at 25°C. Solutions GR-3 and GR-4 were also modeled for 60°C in order to investigate possible effects of temperature on the saturation state of the solutions and, thus, the stability of the groundwater formulations during experimentation.

### 7.2 EVALUATION METHODS

#### 7.2.1 Radionuclide Solubility Calculations

The synthetic groundwater composition GR-3 (JONES 1982) which was used in calculations by Early was also used in this study. The composition of the solution is given in Table 7. Early calculated solubilities for a range of Eh values, illustrating the importance of this variable. This sensitivity analysis is not reported here, rather an Eh of -0.3 V, specified, by Early as a reference value, was used in the calculations.

No attempt was made to evaluate the reliability or correctness of the thermodynamic data used by Early. Rather, the same data base was used with PHREEQE to calculate limiting solid phases, dominant aqueous species, and concentrations for each element calculated by Early. Two typographical errors in the data base were corrected prior to use: (1) 16 electrons rather than 15 are required in the reaction for the aqueous species  $\text{Sb}_2\text{S}_4^{2-}$ , and (2) the sign on the log K for the technetium reaction was reversed (calculations by Early apparently used the correct log K).

Calculations of two types were performed using MINTEQ. First, the data of Early for Pu, Am, and Np were used for a comparison of the calculations of both Early and PHREEQE because the MINTEQ data base does not contain data for these elements and time constraints precluded compiling an independent, internally consistent, and critically evaluated thermodynamic data base. Second, solubility controls for U, Ni, and Pb were calculated using the thermodynamic data base of MINTEQ in order to illustrate the effect which different thermodynamic data can have on calculated results.

\*In this section, these publications are referred to simply as Early.



Table 7. BWIP synthetic groundwater formulations

Species	Composition (mg/L)			
	GR-1 <sup>a</sup>	GR-2 <sup>b</sup>	GR-3 <sup>c</sup>	GR-4 <sup>d</sup>
Na <sup>+</sup>	30.7	225	358	334
K <sup>+</sup>	9.0	2.5	3.4	13.8
Ca <sup>2+</sup>	6.5	1.06	2.8	2.2
Mg <sup>2+</sup>	1.0	0.07	0.03	0
Cl <sup>-</sup>	14.4	331	312	405
CO <sub>3</sub> <sup>2-</sup>	0	59	[54.7] <sup>e</sup>	[92.0] <sup>e</sup>
HCO <sub>3</sub> <sup>-</sup>	81.5	75		
F <sup>-</sup>	0	29	33.4	19.9
SO <sub>4</sub> <sup>2-</sup>	11.1	72	173	4.0
SiO <sub>2</sub> (aq)	25	108	76.2	96.3
pH	8.0	10.0	9.77	9.7

<sup>a</sup>SALTER 1981; SCR 1982.

<sup>b</sup>SALTER 1982; SCR 1982.

<sup>c</sup>JONES 1982.

<sup>d</sup>SALTER 1984.

<sup>e</sup>Total inorganic carbon, as bicarbonate.

### 7.2.2 Synthetic Groundwater Calculations

Computations were made using MINTEQ for all four groundwater formulations at 25°C for comparison to previous results obtained with PHREEQE. This approach provides an evaluation of the calculational methodologies of the codes as well as their data bases.

To evaluate potential effects of elevated temperature on the GR-3 and GR-4 solutions, calculations for 60°C were also made with MINTEQ.

## 7.3 RESULTS

### 7.3.1 Radionuclide Solubility Calculations

The results obtained with PHREEQE are compared to those of Early (1982) for limiting solution concentrations, limiting solid phases, and dominant aqueous species in Table 8. Agreement is generally excellent, although some minor numerical differences are present. These differences may be the result of: (1) rounding errors, (2) the fact that activity coefficient corrections were neglected by Early, or (3) differences in the thermodynamic data for the reference groundwater components in PHREEQE vs Early (1983). The small differences should not significantly affect assessments of repository performance based on solubility controls.

Results from MINTEQ calculations for plutonium, neptunium, and americium using the thermodynamic data of Early were in excellent agreement with those of PHREEQE and Early. Limiting solid phases and dominant aqueous species were identical. Calculated concentrations for Pu, Np, and Am (-log concentration, mol/L) were 9.26, 9.89, and 7.95, respectively.

Results using MINTEQ and its accompanying data base for uranium were not in close agreement to those of Early. With the MINTEQ data base,  $UO_2$  is calculated to be the limiting solid phase with a solubility of  $1 \times 10^{-8}$  mol/L. Early concludes that  $USiO_4$  is the most stable solid and has a calculated solubility of  $2.1 \times 10^{-10}$  mol/L. This inconsistency appears to be the result of different log K values for the formation of  $USiO_4$  in the data bases of Early and MINTEQ. Early used a value of 9.07, whereas the MINTEQ data base contains a value of 7.62. A calculation with MINTEQ using a log K for  $USiO_4$  adjusted to be the same as that used by Early provided excellent agreement with the result obtained by Early. The results utilizing the MINTEQ data base are probably more reliable, as the data for uranium in MINTEQ are part of a "partial validation of the WATEQ4 geochemical model" (KRUPKA 1983). The dominant aqueous complex is calculated to be  $U(OH)_5^-$  in both cases.

Results for lead using MINTEQ with its accompanying data base were in close agreement to those of Early. The limiting solid phases and dominant aqueous species were identical and the calculated solubilities obtained were  $1.8 \times 10^{-10}$  mol/L and  $2.4 \times 10^{-10}$  mol/L for MINTEQ and

Table 8. Comparison of our calculated solubility relationships using PHREEQE with BWIP calculations

Element	Early (1982); Early (1984)			PHREEQE		
	$-\log M$	Dominant aqueous complex	Limiting solid	$-\log M$	Dominant aqueous complex	Limiting solid
Ni	3.74	$\text{NiCO}_3^0$	$\text{NiO}$	4.01	$\text{NiCO}_3^0$	$\text{NiO}$
Se	7.29	$\text{HSe}^-$	$\text{Se}$	7.25	$\text{HSe}^-$	$\text{Se}$
Zr	8.70	$\text{Zr(OH)}_5^-$	$\text{ZrSiO}_4$	8.56	$\text{Zr(OH)}_5^-$	$\text{ZrSiO}_4$
Tc	> ~14	a	a	13.65	$\text{TcO}_4^-$	$\text{TcO}_2$
Pd	9.80	$\text{Pd(OH)}_2^0$	$\text{Pd}$	9.79	$\text{Pd(OH)}_2^0$	$\text{Pd}$
Sn	17.72	$\text{SnO(OH)}^+$	$\text{SnO}_2$	17.66	$\text{SnO(OH)}^+$	$\text{SnO}_2$
Sb	6.82	$\text{Sb(OH)}_3^0$	$\text{Sb(OH)}_3$	6.83	$\text{Sb(OH)}_3^0$	$\text{Sb(OH)}_3$
Sm	9.10	$\text{Sm(OH)}_3^0$	$\text{Sm(OH)}_3$	8.88	$\text{Sm(OH)}_3^0$	$\text{Sm(OH)}_3$
Eu	9.03	$\text{Eu(OH)}_4^-$	$\text{Eu(OH)}_3$	8.79	$\text{Eu(OH)}_4^-$	$\text{Eu(OH)}_3$
Pb	7.62	$\text{PbCO}_3^0$	$\text{Pb(OH)}_2$	7.70	$\text{PbCO}_3^0$	$\text{Pb(OH)}_2$
Ra	~ 8	a	a	7.21	$\text{Ra}^{2+}$	$\text{RaSO}_4$
Th	14.08	$\text{Th(OH)}_4^0$	$\text{ThO}_2$	14.08	$\text{Th(OH)}_4^0$	$\text{ThO}_2$
U	9.68	$\text{U(OH)}_5^-$	$\text{USiO}_4$	9.53	$\text{U(OH)}_5^-$	$\text{USiO}_4$
Np	9.96	$\text{Np(OH)}_5^-$	$\text{NpO}_2$	9.87	$\text{Np(OH)}_5^-$	$\text{NpO}_2$
Pu	9.35	$\text{PuCO}_3^{2+}$	$\text{PuO}_2$	9.15	$\text{PuCO}_3^{2+}$	$\text{PuO}_2$
Am	7.85	$\text{Am(CO}_3)_2^-$	$\text{Am(OH)}_3$	7.87	$\text{Am(CO}_3)_2^-$	$\text{Am(OH)}_3$

<sup>a</sup>No data available.

Early, respectively. The small differences in the computed values can be attributed to the reasons discussed above for PHREEQE calculations and to possible small differences in the thermodynamic data of MINTEQ and that used by Early.

Results for nickel were not in close agreement to those of Early. Again, the reason can be traced back to differences in the thermodynamic data. For the case where sulfur was not allowed to speciate into sulfate and sulfide complexes (see EARLY),  $\text{Ni}(\text{OH})_2$  was calculated to be the limiting solid phase using MINTEQ. Early calculates  $\text{NiO}$  to be most stable. The log K for the formation of  $\text{Ni}(\text{OH})_2$  in the data base of Early is approximately 100 times lower [i.e.,  $\text{Ni}(\text{OH})_2$  less stable] than the value contained in the MINTEQ data base. Therefore,  $\text{Ni}(\text{OH})_2$  would not be predicted to be the limiting solid phase in the calculations of Early (1982). The resultant solubilities were calculated to be  $2.8 \times 10^{-6}$  mol/L and  $1.8 \times 10^{-4}$  mol/L for MINTEQ and Early, respectively. For the case where sulfur was allowed to speciate into sulfate and sulfide complexes at  $E_h = -0.3$  V,  $\text{Ni}(\text{OH})_2$  was again calculated to be most stable using MINTEQ. Early, however, calculated  $\text{NiS}$  to be the limiting solid phase. The formation constant for  $\text{NiS}$  in MINTEQ is approximately  $1 \times 10^6$  times lower (i.e.,  $\text{NiS}$  less stable) than that used by Early. Therefore, because of the differences in log K values for  $\text{NiS}$  and  $\text{Ni}(\text{OH})_2$  in MINTEQ vs Early,  $\text{NiS}$  would not be calculated to be more stable than  $\text{Ni}(\text{OH})_2$  when the MINTEQ data base is utilized. For the selected Eh-pH conditions, solubilities calculated for the sulfur speciation case were identical to those for the case with no sulfur speciation (see Fig. 1 of EARLY 1982). For both cases, the codominant aqueous species of  $\text{NiCO}_3^0$  and  $\text{Ni}(\text{CO}_3)_2^{2-}$  were calculated by both MINTEQ and Early.

### 7.3.2 Synthetic Groundwater Calculations

Table 7 lists the four different BWIP synthetic groundwater compositions. GR-3 and GR-4 are the most recent and represent solutions designed to simulate groundwaters from the Umtanum and Cohasset candidate repository horizons, respectively. All of the groundwaters were modeled with MINTEQ for a temperature of 25°C. GR-3 and GR-4 were also modeled for 60°C because of the elevated temperatures encountered at the depths for these horizons at the BWIP site.

Saturation indices ( $\log \text{AP/K}$ )\* at 25°C for the solutions are listed in Table 9. A value of zero represents saturated conditions, while values greater than zero represent oversaturation, and values less than zero undersaturation. Saturation indices were calculated using both PHREEQE and MINTEQ in order to compare the codes and their data bases. As seen in Table 9, the agreement is excellent. At 25°C, the solutions are apparently oversaturated with respect to silica phases, fluorite, and calcite (except GR-1).

---

\*AP = ion activity product

K = equilibrium solubility product



Table 9. Saturation indices (log AP/K) at 25°C for synthetic groundwaters calculated with PHREEQE and MINTEQ

Mineral	GR-1		GR-2		GR-3		GR-4	
	PHREEQE	MINTEQ	PHREEQE	MINTEQ	PHREEQE	MINTEQ	PHREEQE	MINTEQ
Calcite	-0.70	-0.67	0.24	0.25	0.14	0.12	0.27	0.28
Fluorite	a	a	0.27	0.26	0.86	0.85	0.34	0.33
Chalcedony	0.14	0.14	0.41	0.41	0.38	0.38	0.47	0.51
Quartz	0.62	0.62	0.89	0.89	0.87	0.86	0.95	0.99

<sup>a</sup>No fluoride present in GR-1 formulation.

Table 10 illustrates the effect of temperature for solutions GR-3 and GR-4. At the higher temperature, which should more closely represent actual in situ conditions, the solutions are calculated to be more oversaturated with respect to calcite and less oversaturated with respect to the silica phases and fluorite.

Table 10. Saturation indices (log AP/K) for synthetic groundwaters GR-3 and GR-4 at 25 and 60°C calculated with MINTEQ

Mineral	GR-3		GR-4	
	25°C	60°C	25°C	60°C
Calcite	0.14	0.38	0.27	0.49
Flourite	0.86	0.43	0.34	-0.15
Chalcedony	0.38	-0.48	0.47	-0.33
Quartz	0.87	-0.12	0.95	0.03

## 7.4 CONCLUSIONS

### 7.4.1 Radionuclide Solubility Calculations

Comparison calculations have shown that when the same thermodynamic data are used, limiting solids, dominant aqueous species, and limiting concentrations calculated with PHREEQE and MINTEQ are virtually identical to those calculated by Early for selected elements in BWIP synthetic groundwater GR-3. No critical evaluation of the thermodynamic data has been attempted at this time. Calculations for uranium, nickel, and lead utilizing the data base of MINTEQ illustrate the importance of having a documented, verified, and internally consistent data base. Differences in the thermodynamic values for only one reaction can significantly affect the results, as shown for uranium and nickel. One implication from this comparison is that, during repository licensing activities, code-to-code evaluations for geochemical calculations may be less important than a detailed evaluation of the data bases, assumptions, and conceptual models.

### 7.4.2 Synthetic Groundwater Calculations

Calculations for BWIP synthetic groundwaters for 25°C using MINTEQ compare favorably with calculations using PHREEQE (see Table 9). This agreement suggests that the algorithms and data bases of the two codes are consistent for this simple system.

During sorption/apparent concentration limit experiments at 25°C, problems with instability of the solution GR-2 have been encountered (KELMERS 1984a). Precipitation of some unidentified phase(s) occurred. The GR-2 solution was formulated to simulate the chemistry of BWIP groundwaters which occur at depths where the temperature is approximately 55 to 60°C (SALTER 1981). As seen in Table 9, GR-2 is calculated to be oversaturated with respect to silica phases and fluorite at 25°C. It is possible that the instability problems encountered during experiments at 25°C are related to the precipitation of silica phases and/or fluorite. Silica is notorious for forming amorphous suspensions from supersaturated solutions. Instability problems might not be encountered in experiments at temperatures more closely approximating actual in situ conditions.

Modeling synthetic groundwaters GR-3 and GR-4 for 25 and 60°C suggests that care should be taken when designing solubility and/or sorption tests with these solutions. As seen in Table 10, the solutions are calculated to be oversaturated with respect to silica phases and fluorite at 25°C. However, at 60°C the solutions are calculated to be less oversaturated, or even undersaturated, for these phases. Therefore, experiments conducted at inappropriate temperatures (other than at 55 to 60°C) could lead to results that might not be representative of the actual repository system because of solution instability.

## 7.5 EVALUATION OF BWIP VALUES AND METHODS

The limiting solubilities of selected elements calculated by Early (1982) are apparently correct for the thermodynamic data used. Calculations with PHREEQE and MINTEQ have confirmed the values using the data of Early. However, until the thermodynamic data can be shown to be valid, the calculated solubilities must be considered as rough approximations and the conservative or nonconservative nature of the results unresolved. In addition, the basic assumption that equilibrium controls will predominate in the complex geochemical system of the disturbed zone has not yet been demonstrated. As discussed in Kelmers (1984a), true equilibrium controls on the groundwater chemistry have not even been established in the natural geologic setting. Therefore, establishing values for limiting concentrations of radionuclides with reasonable confidence that they are conservative must be supported by a complementary program of experimentation and calculation. As seen by the modeling analysis of BWIP synthetic groundwater solutions for 25 and 60°C, calculations can provide insight to possible mechanisms controlling experimental results and to help focus and guide experimental evaluations. For some geochemical parameters and processes, some degree of this type of qualitative understanding will help to provide reasonable assurance that extrapolations and predictions of performance based on simplified laboratory tests will not be nonconservative.

## 8. SAMPLE CHARACTERIZATION

Host rock geochemistry is an important aspect of the information required for understanding and predicting radionuclide retardation during migration through geologic media. The BWIP has, therefore, conducted an extensive investigation and characterization of the mineralogy and chemical composition of the Grande Ronde and other basalt flows, as well as the basalt interbed regions. The results were summarized in the Site Characterization Report (SCR 1982).

The purpose of sample characterization is to provide a mineralogical description of the basalt samples acquired for the experimental work on the ORNL project. The scope of this characterization work is twofold: (1) to establish whether or not our samples have features similar to those described by BWIP, and (2) to attempt to help identify chemically reactive basalt components that could be involved in radionuclide sorption or reduction reactions.

The McCoy Canyon basalt used in our experimental work (KELMERS 1984a, KELMERS 1984b, and this report) was mineralogically characterized. Small basalt chips, 2 x 2 x 0.5 cm, were cut from a large piece and polished for electron microprobe examination. Each mineral phase was identified from its chemical composition as determined by energy dispersive x-ray spectroscopy. The relative amounts of each phase were estimated from the relative areas of each phase present in a given surface area of back scattered electron micrographs.

Six distinct phases were identified (in order of decreasing abundance in the sample): plagioclase, mesostasis, pyroxene, magnetite, apatite, and pyrite. The texture of the basalt is dominated by large tabular or lath-shaped plagioclase crystals and prismatic or granular pyroxene crystals locked together by an interstitial glassy mesostasis matrix. Varying sizes and shapes of pores and microscopic cooling-fractures are common in the specimen [Fig. 3(A)]. Plagioclase  $(Ca,Na)(Al,Si)AlSi_2O_8$  is the most abundant phase (marked p in Fig. 3A) and is distinguished as the Ca-, Na-, and Al-rich phase [Figs. 3(B), 3(C), and 3(F), respectively] from other minerals in the elemental distribution (dot mapping mode) micrographs. The crystal sizes varied, ranging from 0.5 to 0.05 mm in length and 0.1 to 0.02 mm in width. No preferred orientation of the crystals was noted.

Pyroxene  $(Ca,Mg,Fe)_2Si_2O_6$ , consisting of Ca-rich augite [marked "a", top and bottom of left of Fig. 3(A)] and Mg-rich pigeonite [marked "a", center of Fig. 3(A)] was the other major mineral component in the samples. Both augite and pigeonite are Fe-rich minerals [Fig. 3(D)] and are often associated with magnetite in the sample. Pigeonite was less abundant than augite and occurred as groundmass or grains.

Interstitial glassy mesostasis is the other major phase [Fig. 3(A), marked "m"]. The mesostasis appears as groundmass, has a higher potassium content relative to other major phases [Fig. 3(E)], and has inclusions of tiny



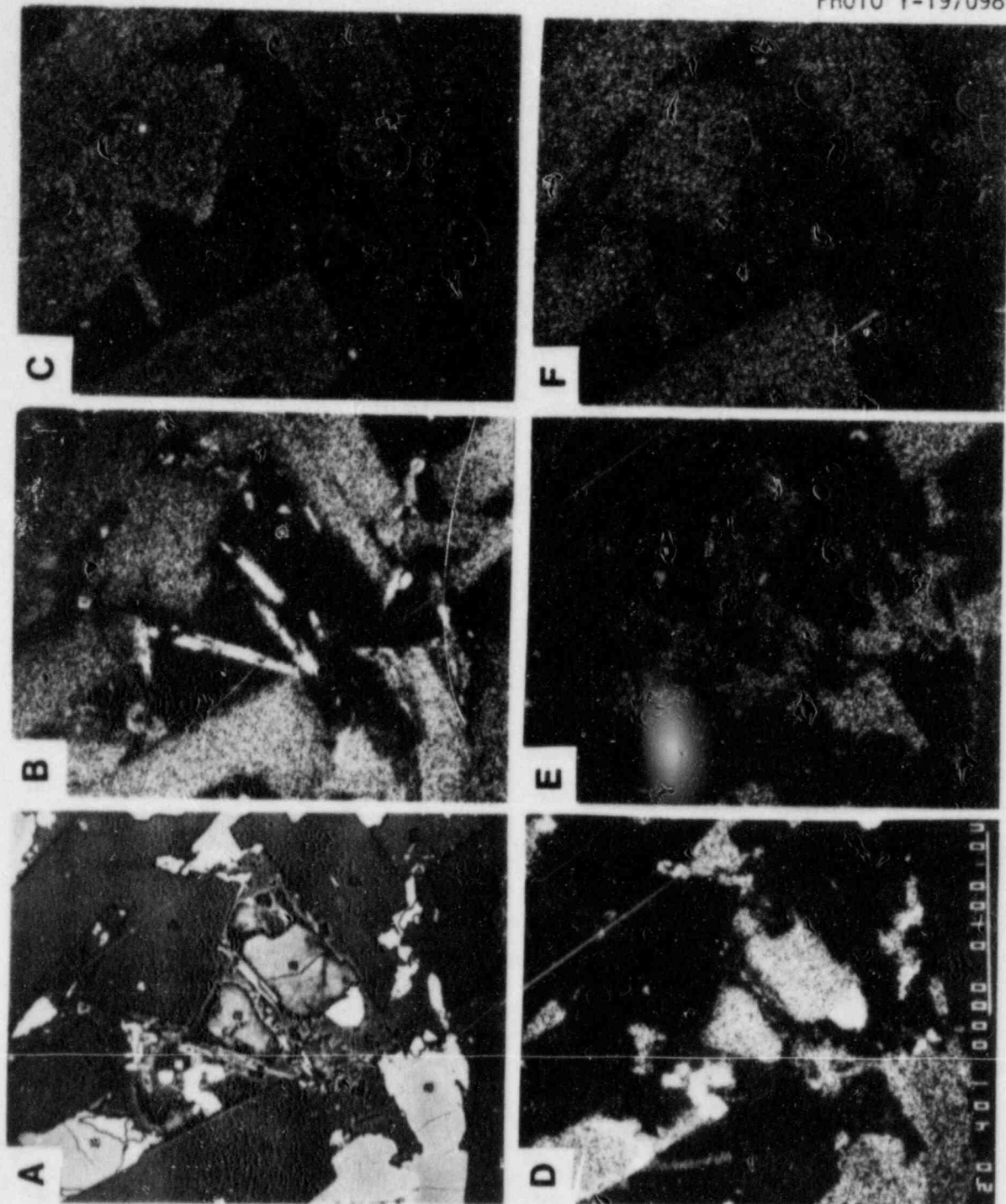


Fig. 3. Electron micrographs showing mineral phases in McCoy Canyon basalt sample (bar = 0.1 mm): (A) back scattering mode where "a" represents pyroxene, "p" represents plagioclase, and "m" represents mesostasis; (B) calcium distribution; (C) sodium distribution; (D) iron distribution; (E) potassium distribution; and (F) aluminum distribution.

pyroxene, magnetite, apatite, and pyrite grains. Mesostasis is thought to be the most reactive phase in the basalt with groundwater, and may act to buffer the pH and Eh of the groundwater through dissolution and hydrolysis reactions (BARNES 1979).

Magnetite occurs as small (0.05 mm) cubic, octahedral, or dendritic grains, and commonly associates with mesostasis and pyroxene phases [Figs. 4(A) and 4(B)]. The magnetite has considerable amounts of titanium [Fig. 4(C)] and has been referred to as titaniferous magnetite (SCR 1982). Another Fe-rich phase present is composed of tiny (0.01 mm) pyrite grains that can be identified from an S distribution micrograph [Fig. 4(D)]. Apatite occurs as an acicular (hollow) form with random orientation in glassy mesostasis [Fig. 5(A)]. The elongate crystals are less than 0.1 mm long and 0.01 mm wide. Microprobe analysis indicated that fluorine was concentrated in the apatite phase, but other major phases (including mesostasis) had only background levels [Fig. 5(D)].

Proportional distribution of the mineral phases in the McCoy Canyon basalt chip examined was: plagioclase, 40%; pyroxene, 25%; mesostasis, 25%; magnetite, 4%; apatite, 2%; and pyrite, <1%. These estimates are within the ranges reported in the SCR (1982), but the estimated mesostasis content was lower, while pyroxene content was higher than the values reported by Long (1983).

Characterization of an Umtanum basalt sample is under way and a similar characterization of Cohasset basalt samples is planned.

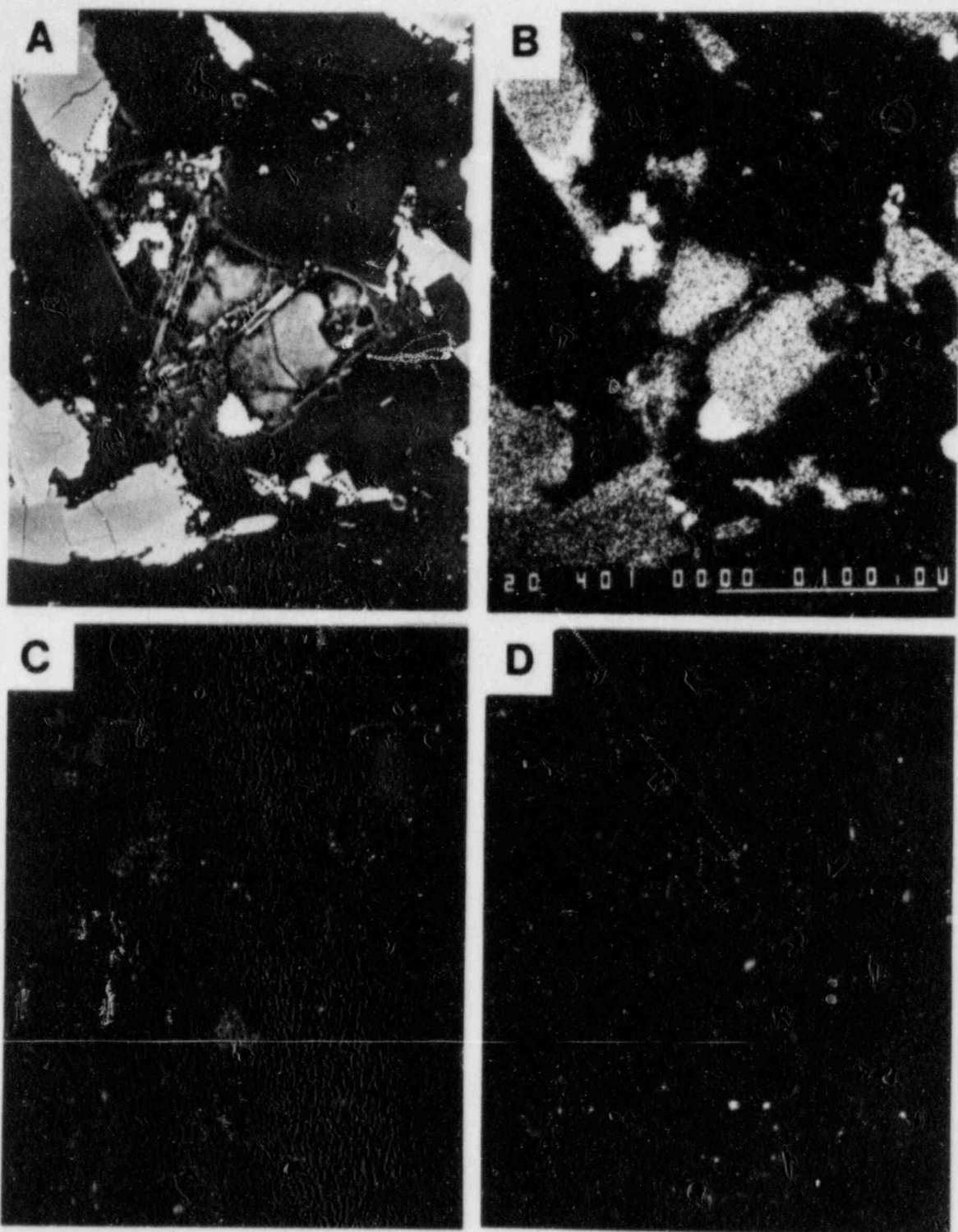


Fig. 4. Electron micrographs showing titaniferous magnetite and pyrite phases in McCoy Canyon basalt sample (bar = 0.1 mm): (A) back scattering mode; (B) iron distribution; (C) titanium distribution; (D) sulfur distribution.



PHOTO Y-197096

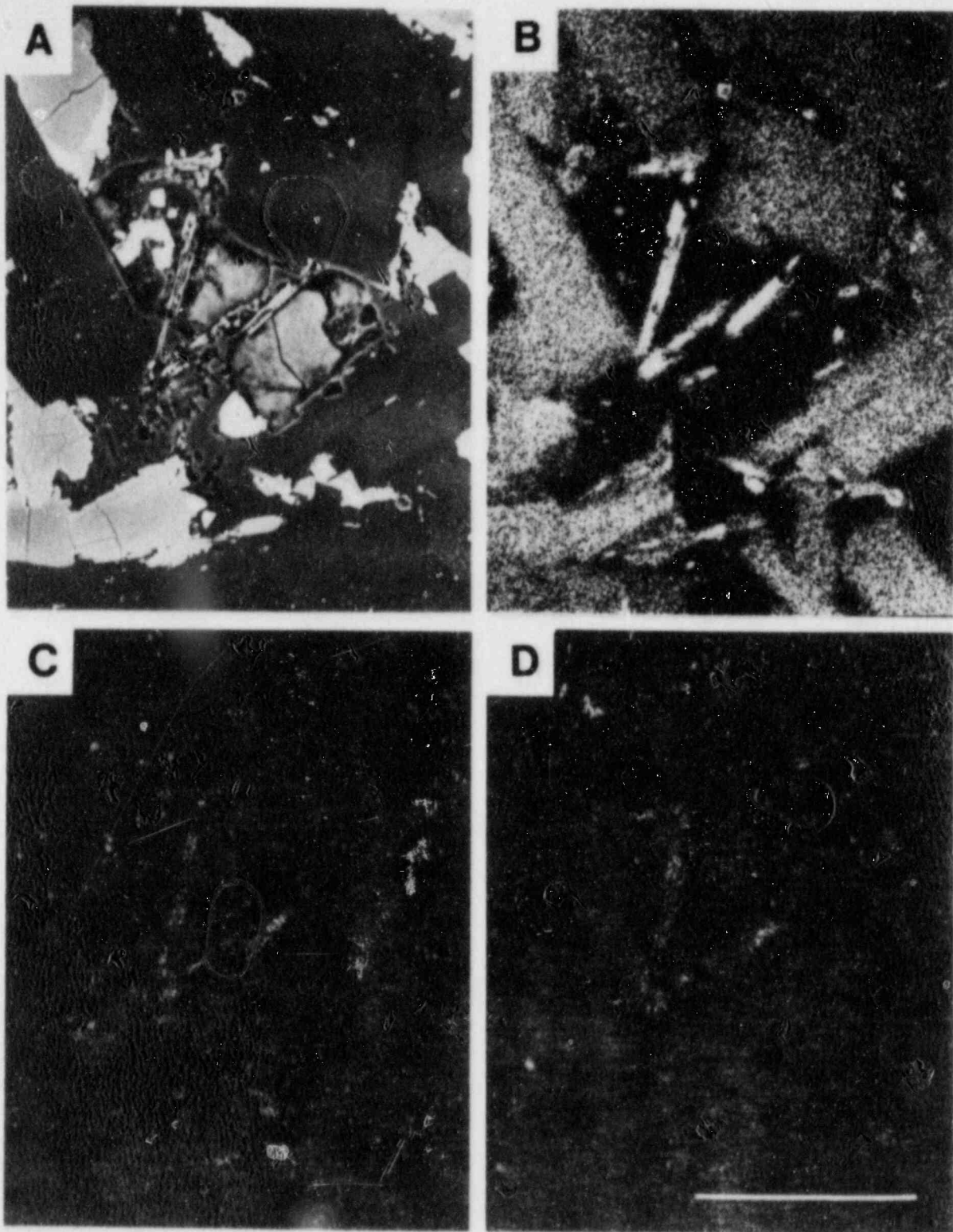


Fig. 5. Electron micrographs showing fluorapatite phase in McCoy Canyon basalt sample (Bar = 0.1 mm): (A) back scattering mode; (B) calcium distribution; (C) phosphorous distribution; and (D) fluorine distribution.



## 9. ACKNOWLEDGEMENTS

The authors wish to acknowledge the excellent laboratory technical work performed by C. P. Allen, F. I. Case, C. G. Westmoreland, and G. C. Young, and the secretarial effort of K. J. Kitts and editorial assistance of C. H. Shappert in the preparation of this document.

## 10. REFERENCES

- AMES 1982. L. L. Ames, J. E. McGarrah, B. A. Walker, and P. F. Salter, "Sorption of Uranium and Cesium by Hanford Basalts and Associated Secondary Smectite," Chem. Geol. **35**, 205-25, 1982.
- BARNES 1979. M. W. Barnes and B. E. Scheetz, Laboratory Alteration of a Columbia River Basalt by Hot Groundwater, RHO-BWI-ST-15, Rockwell Hanford Operations, Richland, Washington, 1981.
- BARNEY 1980. G. S. Barney and B. J. Wood, Identification of Key Radionuclides in a Waste Repository in Basalt, RHO-BWI-ST-9, Rockwell Hanford Operations, Richland, Washington, 1980.
- BARNEY 1981. G. S. Barney, Radionuclide Reactions with Groundwater and Basalts from Columbia River Basalt Formations, RHO-SA-217, Rockwell Hanford Operations, Richland, Washington, 1981.
- BARNEY 1982. G. S. Barney, Radionuclide Sorption of Columbia River Basalt Interbed Materials, RHO-BW-SA-198 P, Rockwell Hanford Operations, Richland, Washington, 1982.
- BURNEY 1974. G. A. Burney and R. M. Harbour, Radiochemistry of Neptunium, NAS-NS-3060, Subcommittee on Radiochemistry, National Academy of Sciences - National Research Council, 1974.
- EARLY 1982. T. O. Early, D. R. Drewes, G. K. Jacobs, and R. C. Routson, Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt: Estimated Solubilities for Selected Elements, RHO-BW-ST-39 P, Rockwell Hanford Operations, Richland, Washington, 1982.
- EARLY 1984. T. O. Early, G. K. Jacobs, and D. R. Drewes, "Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt: Estimated Solubilities for Selected Elements," in Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navrtil, and W. W. Schults, eds., ACS Symposium Series 246, 1984.
- FELMY 1982. A. R. Felmy, D. C. Girvin, and E. A. Jenne, MINTEQ - A Computer Program for Calculating Aqueous Geochemical Equilibria, Draft Pacific Northwest Laboratory Report, prepared for the U.S. Environmental Protection Agency, 1982.
- JONES 1982. T. E. Jones, Reference Material Chemistry - Synthetic Groundwater Formulation, RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Washington, 1982.
- KELMERS 1984a. A. D. Kelmers, R. J. Clark, N. H. Cutshall, G. K. Jacobs, J. S. Johnson, J. H. Kessler, and R. E. Meyer, Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects, NUREG/CR-3730, ORNL/TM-9109, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1984.

KELMERS 1984b. A. D. Kelmers, J. H. Kessler, W. D. Arnold, R. E. Meyer, N. H. Cutshall, G. K. Jacobs, and S. Y. Lee, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Volume 1, Report for October-December 1983, NUREG/CR-3851 (Vol. 1), ORNL/TM-9191/V1, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1984.

KELMERS 1984c. A. D. Kelmers, R. J. Clark, N. H. Cutshall, J. S. Johnson, and J. H. Kessler, "Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters: Description of Calculational and Experimental Activities", in NRC Nuclear Waste Geochemistry '83, D. H. Alexander and G. F. Birchard, eds., NUREG/CP-0052, pp. 151-167, 1984.

KELMERS 1984d. A. D. Kelmers, Review and Assessment of Radionuclide Sorption Information for the Basalt Waste Isolation Project Site, NUREG/CR-3763, ORNL/TM-9157, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1984.

KRUPKA 1983. K. M. Krupka, E. A. Jenne, and W. J. Deutsch, Validation of the WATEQ4 Geochemical Model for Uranium, PNL-4333, Pacific Northwest Laboratory, Richland, Washington, 1983.

LONG 1983. P. E. Long, R. D. Landon, R. W. Cross, K. R. Fairchild, and M. A. Chamness, Comparative Evaluation of Candidate Repository Horizons Within the Reference Repository Location, RHO-BW-ST-28 P, Rockwell Hanford Operations, Richland, Washington, 1983.

MEYER 1984. R. E. Meyer, W. D. Arnold, and F. I. Case, Valence Effects on the Sorption of Nuclides on Rocks and Minerals, NUREG/CR-3389, ORNL-5978, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1984.

PARKHURST 1980. D. L. Parkhurst, D. C. Thorstenson, and L. N. Plummer, PHREEQE -- A Computer Program for Geochemical Calculations, Water Resources Investigations Report 80-96, U.S. Geological Survey, 1980.

SALTER 1981a. P. F. Salter and G. K. Jacobs, Evaluation of Radionuclide Transport: Effect of Radionuclide Sorption and Solubility, RHO-BW-SA-192 A, Rockwell Hanford Operations, Richland, Washington, 1981.

SALTER 1981b. P. F. Salter, L. L. Ames, and J. E. McGarrah, Sorption of Selected Radionuclides on Secondary Minerals Associated with the Columbia River Basalts, RHO-BWI-LD-43, Rockwell Hanford Operations, Richland, Washington, 1981.

SALTER 1981c. P. F. Salter, L. L. Ames, and J. E. McGarrah, The Sorption Behavior of Selected Radionuclides on Columbia River Basalts, RHO-BWI-LD-48, Rockwell Hanford Operations, Richland, Washington, 1981.

SALTER 1984. Personal communication, P. F. Salter, Rockwell Hanford Operations, Richland, Washington, January 1984.

SCR 1982. Site Characterization Report for the Basalt Waste Isolation Project, DOE/RL 82-3, Department of Energy, Nevada Operations Office, Las Vegas, Nevada, 1982.

TRIBALAT 1953. S. Tribalat and H. Beydon, "Isolement du Technetium," Anal. Chim. Acta. 8, 22-28, 1953.



APPENDIX

NEPTUNIUM SORPTION/DESORPTION DATA

Table A.1. Neptunium sorption on McCoy Canyon and Umtanum basalt under oxic or reducing redox conditions

Starting Np conc. (M)	Contact time (d)	Rock or blank	Centri. or filtered (C or F)	Np in solution (mol/L)	Np on rock (mol/kg)	Sorption ratio (L/kg)		
<u>Umtanum basalt, oxic redox conditions, 24 ± 2°C:</u>								
3.2 × 10 <sup>-12</sup>	7	Rock	C	2.0 × 10 <sup>-12</sup>	1.3 × 10 <sup>-11</sup>	6.7		
			F	1.9 × 10 <sup>-12</sup>	1.3 × 10 <sup>-11</sup>	7.0		
			C	2.0 × 10 <sup>-12</sup>	1.3 × 10 <sup>-11</sup>	6.6		
			F	1.9 × 10 <sup>-12</sup>	1.4 × 10 <sup>-11</sup>	7.1		
			C	2.0 × 10 <sup>-12</sup>	1.3 × 10 <sup>-11</sup>	6.5		
			F	2.0 × 10 <sup>-12</sup>	1.3 × 10 <sup>-11</sup>	6.8		
		Blank	C	3.2 × 10 <sup>-12</sup>				
			F	3.2 × 10 <sup>-12</sup>				
			C	3.2 × 10 <sup>-12</sup>				
			F	3.2 × 10 <sup>-12</sup>				
			C	3.2 × 10 <sup>-12</sup>				
			F	3.2 × 10 <sup>-12</sup>				
		<u>McCoy Canyon basalt, oxic redox conditions, 60 ± 1°C:</u>						
		3.2 × 10 <sup>-12</sup>	7	Rock	C	2.2 × 10 <sup>-12</sup>	1.1 × 10 <sup>-11</sup>	5.0
F	2.0 × 10 <sup>-12</sup>				1.2 × 10 <sup>-11</sup>	5.8		
C	2.2 × 10 <sup>-12</sup>				1.0 × 10 <sup>-11</sup>	4.6		
F	2.1 × 10 <sup>-12</sup>				1.1 × 10 <sup>-11</sup>	5.3		
C	2.2 × 10 <sup>-12</sup>				1.0 × 10 <sup>-11</sup>	4.8		
F	1.7 × 10 <sup>-12</sup>				1.5 × 10 <sup>-11</sup>	9.0		
Blank	C			3.2 × 10 <sup>-12</sup>				
	F			3.2 × 10 <sup>-12</sup>				
	C			3.2 × 10 <sup>-12</sup>				
	F			3.2 × 10 <sup>-12</sup>				
	C			3.2 × 10 <sup>-12</sup>				
	F			3.2 × 10 <sup>-12</sup>				
<u>McCoy Canyon basalt, reducing redox conditions (hydrazine added), 24 ± 2°C:</u>								
1.0 × 10 <sup>-6</sup>	7			Rock	C	8.5 × 10 <sup>-8</sup>	9.1 × 10 <sup>-6</sup>	107
		F	3.8 × 10 <sup>-8</sup>		9.6 × 10 <sup>-6</sup>	250		
		C	8.1 × 10 <sup>-8</sup>		9.1 × 10 <sup>-6</sup>	113		
		F	4.7 × 10 <sup>-8</sup>		9.4 × 10 <sup>-6</sup>	201		
		C	8.9 × 10 <sup>-8</sup>		9.0 × 10 <sup>-6</sup>	101		
		F	6.9 × 10 <sup>-8</sup>		9.2 × 10 <sup>-6</sup>	135		
		Blank	C	9.3 × 10 <sup>-7</sup>				
			F	8.8 × 10 <sup>-7</sup>				
			C	9.2 × 10 <sup>-7</sup>				
			F	8.9 × 10 <sup>-7</sup>				
			C	9.2 × 10 <sup>-7</sup>				
			F	8.9 × 10 <sup>-7</sup>				

Table A.1 (continued)

Starting Np conc. (M)	Contact time (d)	Rock or blank	Centri.(C) or filtered(F)	Np in solution (mol/L)	Np on rock (mol/kg)	Sorption ratio (L/kg)			
<u>McCoy Canyon basalt, reducing redox conditions</u> (hydrazine added), 60 ± 1°C:									
3.2 x 10 <sup>-12</sup>	7	Rock	C	2.4 x 10 <sup>-14</sup>	3.2 x 10 <sup>-11</sup>	1330			
			F	7.4 x 10 <sup>-15</sup>	3.2 x 10 <sup>-11</sup>	4300			
			C	2.4 x 10 <sup>-14</sup>	3.2 x 10 <sup>-11</sup>	1330			
			F	1.8 x 10 <sup>-15</sup>	3.2 x 10 <sup>-11</sup>	18100			
			C	3.0 x 10 <sup>-14</sup>	3.1 x 10 <sup>-11</sup>	1030			
			F	7.4 x 10 <sup>-15</sup>	3.2 x 10 <sup>-11</sup>	4240			
		Blank	C	3.2 x 10 <sup>-12</sup>					
			F	3.2 x 10 <sup>-12</sup>					
			C	3.2 x 10 <sup>-12</sup>					
			F	3.2 x 10 <sup>-12</sup>					
			2.8 x 10 <sup>-12</sup>	11	Rock	C	5.3 x 10 <sup>-14</sup>	2.7 x 10 <sup>-11</sup>	510
						F	7.0 x 10 <sup>-15</sup>	2.8 x 10 <sup>-11</sup>	3940
						C	6.9 x 10 <sup>-14</sup>	2.7 x 10 <sup>-11</sup>	394
F	2.9 x 10 <sup>-15</sup>	2.8 x 10 <sup>-11</sup>				9690			
C	9.6 x 10 <sup>-14</sup>	2.7 x 10 <sup>-11</sup>				280			
F	7.6 x 10 <sup>-15</sup>	2.8 x 10 <sup>-11</sup>				3680			
C	8.6 x 10 <sup>-14</sup>	2.7 x 10 <sup>-11</sup>				314			
F	1.2 x 10 <sup>-14</sup>	2.8 x 10 <sup>-11</sup>				2250			
C	7.1 x 10 <sup>-14</sup>	2.7 x 10 <sup>-11</sup>				384			
F	8.2 x 10 <sup>-15</sup>	2.8 x 10 <sup>-11</sup>				3380			
C	6.7 x 10 <sup>-14</sup>	2.7 x 10 <sup>-11</sup>				410			
F	9.0 x 10 <sup>-15</sup>	2.8 x 10 <sup>-11</sup>				3110			
Blank	C	8.5 x 10 <sup>-13</sup>							
	F	6.7 x 10 <sup>-13</sup>							
	C	1.2 x 10 <sup>-12</sup>							
	F	9.2 x 10 <sup>-13</sup>							
	C	2.8 x 10 <sup>-12</sup>							
	F	2.8 x 10 <sup>-12</sup>							

Table A.2. Neptunium desorption from McCoy Canyon basalt under reducing (hydrazine) redox conditions

Contact time (d)	Rock or blank	Centri. (C) or filtered (F)	Np in solution (mol/L)	Np on rock (mol/kg)	Sorption ratio (L/kg)		
<u>Tests at 24 2°C:</u>							
7	Rock	C	$1.4 \times 10^{-8}$	$9.0 \times 10^{-6}$	640		
		F	$7.4 \times 10^{-9}$	$9.5 \times 10^{-6}$	1300		
		C	$1.6 \times 10^{-8}$	$9.0 \times 10^{-6}$	560		
		F	$9.2 \times 10^{-9}$	$9.4 \times 10^{-6}$	1000		
		C	$5.7 \times 10^{-8}$	$8.6 \times 10^{-6}$	150		
		F	$7.6 \times 10^{-8}$	$8.7 \times 10^{-6}$	120		
	Blank	C	$3.8 \times 10^{-8}$				
		F	$3.4 \times 10^{-9}$				
		C	$4.6 \times 10^{-9}$				
		F	$3.2 \times 10^{-9}$				
		<u>Tests at 60 ± 1°C:</u>					
		14	Rock	C	$7.1 \times 10^{-13}$	$2.0 \times 10^{-11}$	29
F	$6.7 \times 10^{-13}$			$2.1 \times 10^{-11}$	32		
C	$7.9 \times 10^{-13}$			$2.0 \times 10^{-11}$	25		
F	$7.4 \times 10^{-13}$			$2.1 \times 10^{-11}$	28		
C	$9.8 \times 10^{-13}$			$1.8 \times 10^{-11}$	18		
F	$9.4 \times 10^{-13}$			$2.1 \times 10^{-11}$	22		
Blank	C		$4.8 \times 10^{-12}$				
	F		$1.4 \times 10^{-12}$				
	C		$9.7 \times 10^{-13}$				
	F		$9.7 \times 10^{-13}$				
	Rock		C	$6.9 \times 10^{-13}$	$2.1 \times 10^{-11}$	30	
			F	$6.9 \times 10^{-13}$	$2.2 \times 10^{-11}$	32	
C			$5.7 \times 10^{-13}$	$2.2 \times 10^{-11}$	38		
F			$5.4 \times 10^{-13}$	$2.2 \times 10^{-11}$	41		
C			$5.7 \times 10^{-13}$	$2.2 \times 10^{-11}$	38		
F			$5.5 \times 10^{-13}$	$2.3 \times 10^{-11}$	41		
Blank	C		$5.0 \times 10^{-14}$				
	F		$5.1 \times 10^{-14}$				



INTERNAL DISTRIBUTION

- |                      |                                 |
|----------------------|---------------------------------|
| 1. W. D. Arnold      | 18. S. Y. Lee                   |
| 2. J. T. Bell        | 19. A. P. Malinauskas           |
| 3. J. G. Blencoe     | 20. R. E. Meyer                 |
| 4. R. O. Chester     | 21. F. G. Seeley                |
| 5. A. G. Croff       | 22. F. J. Smith                 |
| 6. N. H. Cutshall    | 23-25. C. H. Shappert           |
| 7. L. M. Ferris      | 26-30. S. K. Whatley            |
| 8. R. K. Genung      | 31. K. G. Wymer                 |
| 9. J. R. Hightower   | 32-33. Central Research Library |
| 10. G. K. Jacobs     | 34. ORNL Technical Library      |
| 11. E. K. Johnson    | 35-36. Laboratory Records       |
| 12-16. A. D. Kelmers | 37. Laboratory Records, RC      |
| 17. D. C. Kocher     | 38. ORNL Patent Section         |

EXTERNAL DISTRIBUTION

39. Office of Assistant Manager for Energy Research and Development,  
DOE-ORO, Oak Ridge, TN 37831.

Rockwell Hanford Operations, P. O. Box 800, Richland, WA 99352

- |                  |                  |
|------------------|------------------|
| 40. S. M. Baker  | 44. J. Myers     |
| 41. G. S. Barney | 45. P. F. Salter |
| 42. T. O. Early  | 46. R. M. Smith  |
| 43. J. H. LaRue  | 47. M. I. Wood   |

Battelle Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352

- |                 |                 |
|-----------------|-----------------|
| 48. L. L. Ames  | 52. E. A. Jenne |
| 49. M. J. Apted | 53. G. L. McVay |
| 50. D. G. Coles | 54. D. Rai      |
| 51. W. J. Gray  | 55. J. Serne    |

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

56. J. S. Szymanski  
57. D. L. Vieth

Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, NM 87545

- |                     |                   |
|---------------------|-------------------|
| 58. D. L. Bish      | 62. J. F. Kerrisk |
| 59. W. R. Daniels   | 63. A. E. Orgard  |
| 60. G. L. DePoorter | 64. D. T. Vaniman |
| 61. B. R. Erdal     | 65. K. Wolfsberg  |

Lawrence Livermore National Laboratory, P. O. Box 808, L-204,  
Livermore, CA 94550

66. D. Isherwood  
67. V. M. Owersby  
68. T. J. Wolery

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

69. C. M. Jantzen

U.S. Nuclear Regulatory Commission, Geotechnical Branch, Office of Nuclear  
Materials Safety and Safeguards, Rm. 623-SS, Washington, DC 20555

- |                    |                      |
|--------------------|----------------------|
| 70. G. F. Birchard | 75. M. R. Knapp      |
| 71. J. W. Bradbury | 76. L. A. Kovach     |
| 72. D. J. Brooks   | 77-86. R. J. Starmer |
| 73. S. M. Copley   | 87. R. W. Wright     |
| 74. P. S. Justus   |                      |

U.S. Nuclear Regulatory Commission, P. O. Box 1186, Richland, WA 99352

88. F. R. Cook

Sandia National Laboratories, P. O. Box 5800, Albuquerque, NM 87185

89. M. D. Siegel

Brookhaven National Laboratory, Nuclear Waste Management Division,  
Upton, New York 11973

- |                      |            |
|----------------------|------------|
| 90. E. P. Gause      | 92. P. Soo |
| 91. D. G. Schweitzer |            |

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

93. C. L. Carmahan  
94. R. J. Silva

Department of Chemistry, Florida State University, Tallahassee, FL 32306

95. R. J. Clark

Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Avenue, Argonne, IL 60439

96. M. G. Seitz

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

97. S. G. Bilhorn

98. P. T. Prestholt

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

99. J. W. Hess

Nutech Engineers, 145 Martinvale Lane, San Jose, CA 95119

100. J. H. Kessler

101-102. Technical Information Center, Oak Ridge, TN 37830

103-407. Given distribution as shown in Category RW

NRC FORM 335 12-84 NRCM 1102 3201, 3702		U.S. NUCLEAR REGULATORY COMMISSION		1. REPORT NUMBER (Assigned by TDC, add Vol. No., if any) NUREG/CR-3851, Vol. 2 ORNL/TM-9191/V2	
<b>BIBLIOGRAPHIC DATA SHEET</b>					
2. TITLE AND SUBTITLE PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS: REPORT FOR JANUARY-MARCH 1984				3. LEAVE BLANK	
5. AUTHOR(S) A. D. Kelmers, J. H. Kessler, W. D. Arnold, R. E. Meyer, N. H. Cutshall, G. K. Jacobs, S. Y. Lee, and R. J. Clark				4. DATE REPORT COMPLETED MONTH: July      YEAR: 1984	
				6. DATE REPORT ISSUED MONTH: November      YEAR: 1984	
7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Oak Ridge National Laboratory P.O. Box X Oak Ridge, TN 3781				8. PROJECT/TASK/WORK UNIT NUMBER	
10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Division of Waste Management Office of Nuclear Material Safety and Safeguards U. S. Nuclear Regulatory Commission Washington, D. C. 20555				9. FIN OR GRANT NUMBER B0290	
				11a. TYPE OF REPORT Quarterly Progress Report	
12. SUPPLEMENTARY NOTES WM-10, 11, 16				11b. PERIOD COVERED (inclusive dates) January-March 1984	
13. ABSTRACT (200 words or less) Geochemical information relevant to the retention of radionuclides by Department of Energy (DOE) candidate high-level waste repositories is being investigated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). The project has evaluated values that have been reported by the Basalt Waste Isolation Project (BWIP) and the methodologies used to develop those values. Neptunium(V) sorption was dependent upon the basalt flow used in the test. Increasing the test temperature from 24 to 60 C increased the neptunium sorption ratio. Hydrazine did not reduce neptunium(V) to neptunium(IV) in solution. The Amicon filters used to separate the basalt and groundwater after contact have been shown to adsorb a low but significant fraction of the neptunium(V) in solution. Technetium(VII) removal by basalt from groundwater solutions was shown to be independent of the contact methodology but was quite sensitive to the solution composition. Sorption of uranium(VI) by basalt has yielded sorption ratio values higher than those reported by BWIP. Column chromatographic experiments have confirmed the technetium(VII) sorption ratio of about 0 L/kg. The McCoy Canyon basalt used in this experimental work was mineralogically characterized. Six phases were identified: plagioclase, mesostasis, pyroxene, magnetite, apatite, and pyrite. Geochemical modeling with PHREEQE and MINTEQ checked the calculated solubilities of 16 radionuclides reported by BWIP; the agreement was generally excellent.					
14. DOCUMENT ANALYSIS - KEYWORDS DESCRIPTORS Radionuclide sorption Radionuclide solubility Geochemical conditions High-level waste repositories Basalt, Neptunium, Technetium				15. AVAILABILITY STATEMENT Unlimited	
16. IDENTIFIERS OF RELATED TERMS Basalt Waste Isolation Project (BWIP) Uranium Hydrazine Mineralogical characterization PHREEQE MINTEQ				16. SECURITY CLASSIFICATION (This page) Unclassified (This report) Unclassified	
				17. NUMBER OF PAGES	
				18. PRICE	



UNITED STATES  
NUCLEAR REGULATORY COMMISSION  
WASHINGTON, D.C. 20555

OFFICIAL BUSINESS  
PENALTY FOR PRIVATE USE, \$300

FOURTH CLASS MAIL  
POSTAGE & FEES PAID  
USNRC  
WASH. D.C.  
PERMIT No. G-87

NUREG/CR-3851, Vol. 2

PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL  
INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY  
SITE PROJECTS: REPORT FOR JANUARY-MARCH 1984

12055078877 L IANICHRWLD  
US NRC  
ADM DIV OF TDC  
POLICY & PUB MGT BR-PDR NUREG  
W-501  
WASHINGTON DC 20555

NOVEMBER 1984