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

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# PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS: REPORT FOR OCTOBER-DECEMBER 1983

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ABSTRACT

Oak Ridge National Laboratory (ORNL) is conducting an experimental investigation of geochemical information for the Nuclear Regulatory Commission (NRC). During this quarter, the project has evaluated both radionuclide solubility data and retardation parameters reported by the Basalt Waste Isolation Project (BWIP) and the experimental and calculational methodologies used by BWIP to develop those values. Key radionuclides (i.e., those most likely to be major contributors to radioactivity release from emplaced waste to the accessible environment in groundwater-ingress—groundwater-migration release scenarios) are being investigated. All work during this report period involved neptunium and technetium behavior in basalt/synthetic groundwater systems. Under oxic redox conditions (air present), neptunium sorption can be represented by a sorption ratio of 1.7 L/kg for McCoy Canyon basalt and synthetic groundwater GR-2. This value is lower than the "conservative best estimate" value for neptunium sorption recommended by BWIP. Our results suggest that neptunium sorption may be characteristically different for different basalt flows. Thus, it may not be conservative to transfer neptunium sorption behavior obtained in tests with one basalt flow for use in predicting repository behavior for other basalt flows. Neptunium desorption ratios were higher than the sorption ratios, thus sorption/desorption equilibrium was not established in the tests. The fact that sorption/desorption equilibrium was not obtained indicates that the sorption values reported by BWIP as "distribution coefficients" should be considered as only sorption ratios. Under anoxic test conditions (isolation from air in a controlled-atmosphere glove box), McCoy Canyon basalt showed little or no ability to remove technetium(VII) from synthetic groundwater GR-2 by sorption or precipitation reactions. This finding is in contrast to the very low technetium solubility and moderate sorption described by BWIP as "conservative best estimate" values.

Serious concerns are expressed relative to the use of the addition of hydrazine to synthetic groundwaters, as was done by BWIP, to attempt to experimentally simulate the reducing redox condition expected in the repository. The more important concerns were: (1) the reaction between hydrazine and any reducible solute is undefined, (2) hydrazine dissociation to release hydroxide ions likely dominates the groundwater pH, (3) hydrazine could react with the bicarbonate in the groundwater to form the carbamate anion, (4) hydrazine is an aggressive chemical and attacked polycarbonate or polypropylene test tubes, (5) hydrazine may alter or disaggregate clay mineral structure, and, (6) considerable uncertainty exists as to the technetium solid phase or solution species formed from the pertechnetate anion by reaction with hydrazine. Thus, it may not be possible to assert that the addition of hydrazine is modeling the repository redox condition, as expected by BWIP, and their sorption and solubility information obtained in the presence of hydrazine may be nonconservative for use in performance assessment calculations.

# CONTENTS

## PREFACE

This document represents the first in a series of quarterly progress reports that will be 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.

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## 1. EXECUTIVE SUMMARY

This project, supported by the Nuclear Regulatory Commission (NRC), is being conducted to evaluate key radionuclide 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. This project is focused on parameters that are important to the mobility of radionuclides (namely, sorption and apparent concentration limit) under anticipated repository-relevant geochemical conditions. This work is in parallel with the schedule for the DOE repository projects; thus, initial emphasis is on the Basalt Waste Isolation Project (BWIP) information for a site on the DOE Hanford Reservation in the Columbia River basalts at Richland, Washington.

Results of the work on this project during the first year have been previously reported (KELMERS 1984).

### 1.1 NEPTUNIUM

Under oxic redox conditions (air present) at 24°C, sorption of neptunium(V) synthetic groundwater GR-2 onto McCoy Canyon basalt was nearly independent of neptunium concentration, contact time, or basalt pretreatment. A linear sorption isotherm was obtained which can be represented by a single-value sorption ratio (Rs) of ~1.7 L/kg. This value is significantly lower than the "conservative best estimate" value of 10 L/kg recommended by BWIP (SCR 1982) and, therefore, that BWIP value of 10 L/kg may not be defensible for conservative modeling purposes. Our results, as well as those reported by BWIP (SALTER 1981c), suggest that the neptunium sorption value may be different for different basalt flows. Thus, it may not be possible to transfer neptunium sorption information obtained in tests with one basalt to other basalt flows.

Desorption behavior of neptunium previously adsorbed onto McCoy Canyon basalt was complex. These experiments also were under oxic conditions at 24°C and employed synthetic groundwater GR-2. The desorption ratios (Rd) were almost all significantly higher than the sorption ratios (i.e., sorption/desorption equilibrium was not established), and the sorption values measured by BWIP, therefore, are not distribution coefficients. The Rd values ranged from 61 L/kg at $4.4 \times 10^{-8}$ mol/L Np to 0.5 L/kg at $4.0 \times 10^{-13}$ mol/L Np. Our desorption results are not compared to BWIP information, since BWIP has not published desorption ratio values for any radionuclide.

In these tests under oxic redox conditions, no apparent neptunium concentration limit was encountered in synthetic groundwater GR-2. Some solution values measured have slightly exceeded the solubility limit of $2 \times 10^{-7}$ mol/L expected by BWIP (SCR 1982).

## 1.2 TECHNETIUM

BWIP expects the repository redox condition to be strongly reducing. In order to measure radionuclide values in the laboratory under such conditions, BWIP added hydrazine to the synthetic groundwater solutions to attempt to simulate the expected reducing redox condition. We have strong reservations as to the applicability of hydrazine for this purpose (see below) and have been exploring a methodology that excludes air (i.e., anoxic redox conditions) in order to allow the basalt rock to establish a "natural" redox condition in the test. McCoy Canyon basalt rock has been crushed, technetium-traced synthetic groundwater GR-2 prepared, and the batch contact experiments conducted in an argon-filled, controlled-atmosphere glove box. Little or no sorption or removal of technetium from solution was observed in 14-d tests at 28°C. This result is in disagreement with anoxic redox condition recirculating column tests (MEYER 1984) that gave up to 70% technetium removal with McCoy Canyon basalt. The reason for this disagreement is not known at this time. The kinetics of the heterogeneous reaction of iron(II) in basalt solid phases (the probable reductant in basalt) and the pertechnetate anion in solution (or differences in the two test methodologies) may account for the apparent inconsistency. Work to explore reaction kinetics is continuing. This result helps to highlight the need to carefully establish laboratory experimental methodology in order to simulate radionuclide behavior in geologic environments.

## 1.3 COLUMN CHROMATOGRAPHY

A high-pressure chromatographic system, including an automated sample collector and gamma detector, was set up during this report period. Test columns of crushed McCoy Canyon basalt and synthetic groundwater GR-4 showed satisfactory flow, and chromatographic measurements with technetium are being initiated.

## 1.4  CONCERNS RELATIVE TO USE OF HYDRAZINE

The BWIP has conducted radionuclide sorption experimental work with 0.05 to 0.1 $\underline{M}$ hydrazine hydrate added to the synthetic groundwater in order to simulate the expected repository redox condition. They have identified these tests as "reducing condition" tests and reported results with basalt (SALTER 1981c), secondary minerals (SALTER 1981b), and interbed materials (BARNEY 1982a and BARNEY 1982b).

We have a number of fundamental concerns relative to the use of hydrazine in sorption experiments. We have identified both (1) general concerns that may be applicable to any radionuclide sorption experiment with hydrazine, and (2) specific concerns relative only to technetium and neptunium measurements. The major concerns are:

1.  Hydrazine can exhibit four different reduction reactions and two oxidation reactions that have widely different standard potentials. Without knowledge of the specific reaction occurring in solution between hydrazine and the solute of interest, it is not possible to estimate what Eh value or redox condition is effective in the tests.

2.  Hydrazine hydrate dissociates to release hydroxide ions, and these ions likely dominate the groundwater pH since hydrazine is present at 50 to 100 times the carbonate/bicarbonate concentration of the groundwaters. In our tests, addition of hydrazine raised the pH by nearly 0.5 to 1 pH unit. Synthetic groundwaters containing hydrazine probably are no longer representative of in situ pH conditions.

3.  Hydrazine can react with the bicarbonate anion to form the carbamate anion. This reaction could deplete the bicarbonate present because of the large excess of hydrazine and further affect the solution pH. Also, carbamate complexes of actinides or fission products (similar to the well-known amine complexes) could be formed.

4.  Hydrazine is a very aggressive chemical and reacts with plastics. In our work, we experienced a rapid reaction of hydrazine with polycarbonate test tubes and a slight reaction with polypropylene tubes. Similar reactions were observed by BWIP (BARNEY 1982b). We conclude that hydrazine should not be contacted with plastics. This practical experimental problem would seem to render all the BWIP sorption work under reducing conditions uncertain since all BWIP work was performed in polycarbonate tubes.

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5. Hydrazine has been reported to react with clay minerals and disaggregate the mineral structure. Also, hydrazine may also be preferentially ion exchanged onto clay surfaces and complete with other solutes.

6. The chemistry of basalt/groundwater systems seems to be primarily dominated by the rock components. Thus, reactions leading to radionuclide removal from solution by sorption or precipitation must involve heterogeneous reactions between basalt solid surfaces and radionuclide solutes in solution. The addition of hydrazine, or any reducing chemical, seems likely to result in rapid homogeneous solution reactions involving the radionuclides; such reactions may poorly model repository conditions.

7. The literature suggests considerable uncertainty as to the reduced form of technetium to be expected from reaction with hydrazine. BWIP expects the product to be a hydrated form of $TcO_2$ (BARNEY 1982a, BARNEY 1982b). The literature suggests that other species or phases could be formed. The formation of metalo-organic technetium compounds has been reported to result from hydrazine-technetium reactions. Also, technetium(V) complexes and technetium(III) organic compounds are reported to be more stable in aqueous solution than previously suspected.

8. Hydrazine does not reduce neptunium(V) in solution to neptunium(IV), as expected by BWIP (BARNEY 1982b). The BWIP assumption probably was based on the formal redox potentials. Apparently, the reaction is kinetically blocked in these groundwater systems.

These concerns render questionable all the BWIP sorption results obtained under reducing test conditions (hydrazine added). It likely cannot be asserted that tests with hydrazine model or simulate repository redox conditions, and radionuclide sorption or solubility information obtained in the presence of hydrazine may be nonconservative for use in performance assessment calculations.

## 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 release calculations) that may be employed by DOE in performance assessment calculations. ORNL is determining limiting radionuclide concentration 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 define the accuracy of or uncertainties in the DOE data and methods, and will aid in identifying 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 first being directed toward values produced to quantify the behavior of radionuclides in basalt/groundwater systems. This work is relevant to the BWIP candidate site in the Columbia River basalts in eastern Washington in the DOE Hanford Reservation. In the 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

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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 (October through December 1983), all work involved basalt/synthetic groundwater systems. The sorption behavior and apparent concentration limit of two key radionuclides, technetium and neptunium, were evaluated under site-relevant test conditions. Alternative laboratory methods of simulating the expected geochemical conditions were explored. Serious concerns were developed relative to some of the BWIP experimental methodology for determining radionuclide sorption values under reducing redox conditions. The results of the work for FY 1983 (October 1982 through September 1983) have been published in an Annual Report (KELMERS 1984).

## 3. NEPTUNIUM STUDIES

### 3.1 BWIP SOLUBILITY AND RETARDATION INFORMATION

A summary of the neptunium information published by BWIP was given in
the Annual Report (KELMERS 1984). No additional BWIP reports describing
neptunium sorption or solubility data were received during this report
period. As shown in that summary, calculated neptunium solubilities of
$2.0 \times 10^{-7}$ and $1.0 \times 10^{-18}$ mol/L were given for oxidizing and reducing
conditions, respectively, in the Site Characterization Report (SCR
1982). Distribution coefficients (Kd) for $^{237}$Np of $30 \pm 13$, $4.1 \pm 0.9$,
and $9.8 \pm 0.5$ L/kg were reported for Umtanum, Flow E (the same as McCoy
Canyon), and Pomona basalts, respectively, under oxidizing conditions
(SALTER 1981c). Similar values were obtained in elevated temperature
tests at 60°C. Under reducing conditions (hydrazine added), a much
higher sorption distribution coefficient of 200 L/kg was reported. The
"conservative best estimate" values for the neptunium distribution coef-
ficient reported in the Site Characterization Report (SCR 1982) for
basalt were 10 and 200 L/kg for oxidizing and reducing conditions,
respectively.

### 3.2 EXPERIMENTAL METHODS AND MATERIALS

Preparation of the McCoy Canyon basalt sample and the synthetic ground-
water GR-2 used in these oxic redox condition experiments were described
previously in Sects. 3.2.1 and 3.2.2 of the Annual Report (KELMERS
1984). Details of the batch contact sorption method were described pre-
viously in Sect. 3.2.3 of the Annual Report (KELMERS 1984).

Several changes were made in the test methodology to prepare the basalt
for the two sets of sorption/desorption experiments described in this
report. The first set of experiments used the basalt "as is" with no
conditioning; the second set used "pre-equilibrated" basalt. The
"pre-equilibrated" basalt was prepared in the following manner: One
gram of the basalt was placed in a 12-mL polypropylene centrifuge tube.
(This same tube containing the pre-equilibrated basalt was later used in
the sorption/desorption experiments.) Ten milliliters of GR-2 ground-
water was added to the tube, and the mixture was contacted on a rocking
table under oxic conditions at room temperature ($24 \pm 2$°C) for 1 week.
At the end of the week, the tube was centrifuged at 4100 relative
centrifugal force (rcf) for 10 min, the bulk of the supernatant ground-
water was removed (>9.5 mL), and fresh GR-2 groundwater was added to
bring the liquid volume back up to 10 mL. The basalt/groundwater mix-
ture was contacted for another week. This process was repeated for a
total of four, 1-week time periods. Three additional samples were con-
tacted under the same conditions for a total of 28 d without groundwater
replacement.

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For the desorption experiments, most of the supernate (>9.5 mL) was removed from the centrifuge tubes containing the neptunium-loaded basalt after sorption. The tubes were then refilled with fresh GR-2 to bring the total groundwater volume back to 10 mL. The blank tubes (no basalt) were treated in a similar manner. The refilled tubes were then capped and contacted at $24 \pm 2°C$ for the same amount of time that they were contacted during the sorption portion of the test (7 or 28 d). At the end of the desorption period, the solution was recovered and counted.

## 3.3 RESULTS

Measurement of sorption ratios (Rs) and desorption ratios (Rd) for neptunium(V) with McCoy Canyon basalt at $24 \pm 2°C$ under oxic redox conditions were completed during this report period. The sorption and desorption data are given in Tables A.1 and A.2, respectively, of the Appendix. [A portion of the sorption data was reported in the FY 1983 Annual Report (KELMERS 1984).]

Sorption ratio values were similar in tests with initial neptunium(V) concentrations covering six orders-of-magnitude ($3.8 \times 10^{-12}$ to $1 \times 10^{-6}$ mol/L). No significant difference was observed for either a 1-week or 4-week contact time, with use of either pre-equilibrated or "as is" McCoy Canyon basalt, or for solutions centrifuged or filtered after contact. For the 48 Rs values at the lower neptunium concentrations in Table A.1, the mean value is 4.0 L/kg. This slightly higher sorption ratio at the highest neptunium concentration could be due to either (1) an approach to the apparent concentration limit of Np(V) in the GR-2 groundwater, or (2) the inadvertent presence of a small amount of Np(VI) in the concentrated stock solution used to prepare the traced groundwater at the highest neptunium concentrations. The sorption isotherm is shown in Fig. 1; a straight line is shown through the data at the lower concentrations, then rising slightly at the highest concentration investigated to date. As reported previously (KELMERS 1984), neptunium sorption under oxic conditions at 24°C displayed a nearly linear sorption isotherm and sorption can probably be adequately represented by a single-value sorption ratio. The experimental system apparently comes to a steady-state condition in 1 week or less, since little difference in Rs was observed with contact time. Since the Rs values for filtered and centrifuged samples were similar (the filtered samples being only slightly higher), there do not appear to be significant quantities of colloidally dispersed neptunium in these experiments. The sorption reaction also appeared to be independent of the basalt rock pretreatment used in these experiments; values with "as is" basalt were within the data spread for pre-equilibrated basalt samples. Neptunium was not significantly adsorbed by the test apparatus, since blank sample solution neptunium concentrations were near the initial solution neptunium concentrations.

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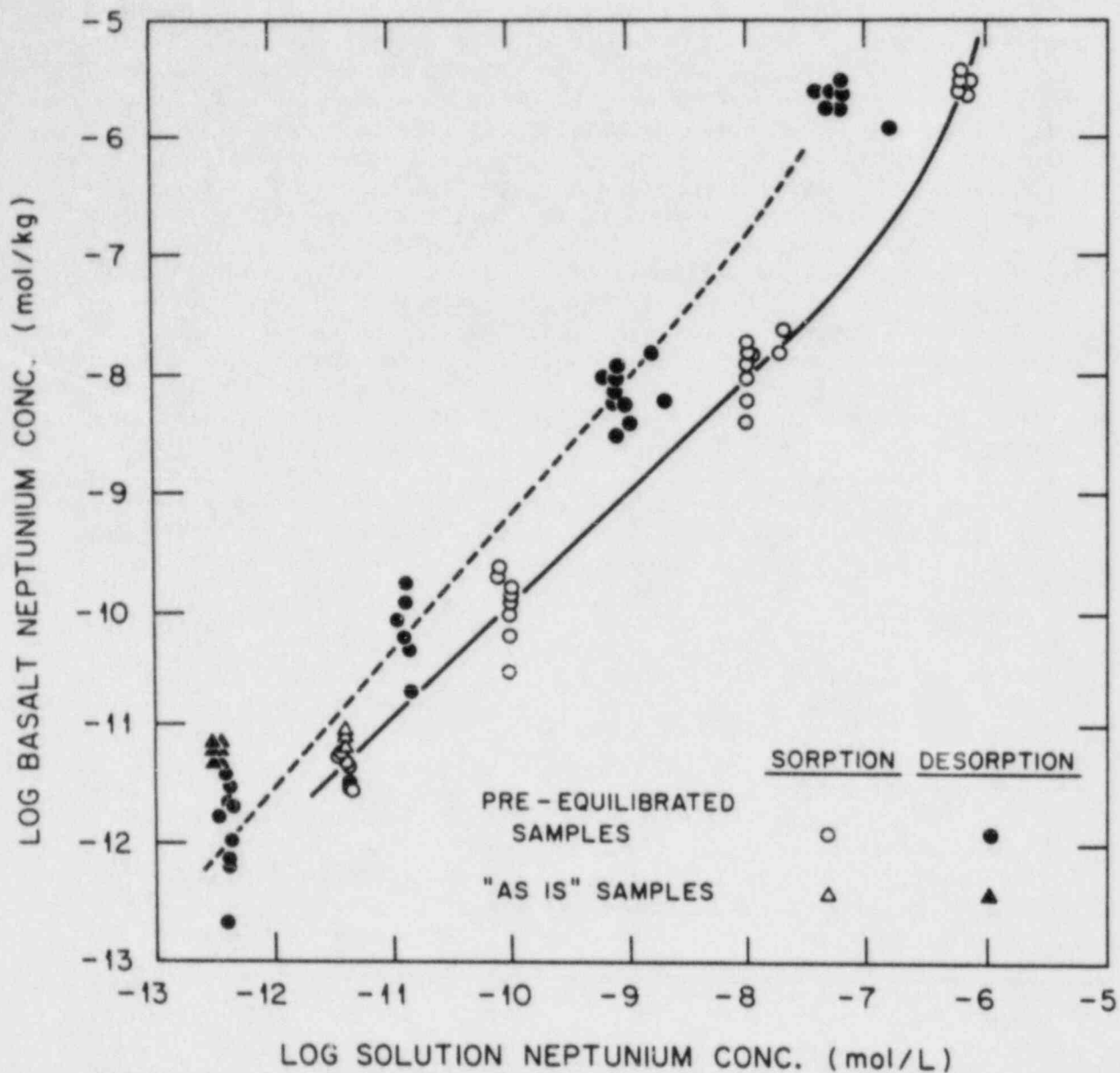


Fig. 1. Sorption and desorption isotherms for neptunium with McCoy Canyon basalt and synthetic groundwater GR-2.

The desorption isotherm is shown in Fig. 1. All desorption ratios were considerably larger than the corresponding sorption ratios. As for sorption, no significant difference was observed for 1 week compared to 4-week contact times, nor were significant differences noticed between centrifuged vs filtered samples. The desorption reaction(s) also apparently reach a steady-state condition in 1 week or less. Again, as in sorption, the desorption ratios for the highest neptunium concentration were slightly higher, possibly indicating the effect of the Np(VI) content of these most concentrated solutions. The "as is" basalt samples give higher desorption ratios than the pre-equilibrated basalt at a neptunium concentration of $4 \times 10^{-13}$ mol/L. Vandegrift et al. (1983) have noted a decrease in the fraction of neptunium, plutonium, and uranium adsorbed on basalt fissure surfaces that have undergone hydrothermal "aging" compared to fresh basalt surfaces. In their studies, basalt fissures were exposed to a simulated groundwater under hydrothermal conditions of 320°C for 30 to 60 d previous to the sorption experiment; this method is a much more severe pretreatment than used in our experiments. Their work also showed that hydrothermally altered basalt did not significantly change the initial groundwater composition, although significant changes were noted with fresh basalt. These observations point out the possible experimental difference between using a freshly crushed basalt surface vs a basalt surface previously exposed to groundwater, or otherwise pretreated.

## 3.4 CONCLUSIONS

The following conclusions were reached:

1. Under oxic redox conditions at 24°C, sorption of neptunium(V) from synthetic groundwater GR-2 onto McCoy Canyon basalt was nearly independent of the neptunium concentration, contact time, or basalt pretreatment used in these tests. A linear sorption isotherm was obtained which could be represented by a single-value sorption ratio of ~1.7 L/kg. Little evidence for colloidally dispersed neptunium or for neptunium sorption by the test apparatus was observed. The neptunium adsorbed onto the basalt has been reported to be reduced to the tetravalent state (MEYER 1984).

2. Slightly higher sorption ratios (4.0 L/kg) were obtained for the most concentrated neptunium solution. This solution contained some Np(VI), and the greater Rs values may indicate a preferential adsorption of Np(VI), compared with Np(V), rather than an approach to an apparent concentration limit for Np(V).

3. Desorption behavior into synthetic groundwater GR-2 of neptunium previously adsorbed onto McCoy Canyon basalt was more complex. The desorption ratios were all significantly higher than the measured sorption ratio. The Rd values ranged from 61 L/kg at $4.4 \times 10^{-8}$ mol/L Np to

0.5 L/kg at $4.0 \times 10^{-13}$ mol/L Np. These Rd values may represent reoxidation of adsorbed Np(IV) or desorption reactions involving reduced neptunium species (MEYER 1984). Pre-equilibration of the basalt appeared to decrease the measured desorption ratio values. The desorption ratios measured appeared to be independent of contact time.

4. No apparent concentration limit for neptunium was encountered in these oxic redox condition tests at 24°C. Some solution concentrations have slightly exceeded the solubility limit of $2 \times 10^{-7}$ mol/L Np expected by BWIP (SCR 1982).

## 3.5 EVALUATION OF BWIP VALUES AND METHODS

Our oxic redox condition tests have consistently yielded neptunium sorption ratios lower than the BWIP "conservative best estimate" Kd of 10 L/kg (SCR 1982). A likely explanation for this difference [discussed in the Annual Report (KELMERS 1984)] can be seen by comparing results for the McCoy Canyon basalt used in these experiments with those for the Umtanum, Pomona, and Flow E basalts used in the BWIP work (SALTER 1981c). The sorption Kds reported for the Pomona, Umtanum, and Flow E basalts under oxic conditions at 23°C with GR-2 groundwater were 52 ± 16, 7 ± 3, and 0.5 ± 0.1 L/kg, respectively. McCoy Canyon is the same as Flow E, and our Rs value of ~1.7 L/kg compares favorably with the Flow E value of 0.5 L/Kg. It seems possible that the "conservative best estimate" Kd value given by BWIP in the SCR may be based upon results with Umtanum basalt only. These findings suggest that neptunium sorption behavior could be different for different basalt flows, that it may not be possible to generalize neptunium sorption for the site, and that the BWIP "conservative best estimate" value may not be valid for modeling purposes.

Since no desorption ratios have been reported by BWIP, no comparison of our desorption data can be made.

# 4. TECHNETIUM STUDIES

## 4.1 BWIP SOLUBILITY AND RETARDATION INFORMATION

A review and summary of the information published by the BWIP project describing technetium limiting solubility or sorption distribution coefficient values were given in Sect. 4.1 of the Annual Report (KELMERS 1984). No new BWIP reports with additional technetium information have been received during this report period. Under oxic conditions, technetium exists in solution as the pertechnetate anion. BWIP has not identified a solubility limit and has reported low to no sorption with basalt for pertechnetate under oxic conditions. Under reducing conditions, however, they report very low calculated solubility limits of $10^{-12}$ or $10^{-14}$ mol/L. A "conservative best estimate" sorption distribution coefficient of 29 L/kg was obtained by BWIP under reducing conditions (hydrazine added) (SRC 1982).

## 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 geochemical parameters in laboratory experiments. We have reported values for technetium apparent concentration limits and described sorption behavior under both oxic (air present) and reducing (hydrazine added) redox conditions in batch contact tests (KELMERS 1984). 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 perhaps also for other elements (see Sect. 5).

In order to attempt to more closely simulate the actual redox conditions that would exist in a basalt repository, anoxic condition tests have been initiated in which as much oxygen as possible (from air) 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 were carried out in a controlled atmosphere glove box. The box atmosphere was argon, which contained about 0.3 to 0.4 ppm of oxygen. Since air contains 200,000 ppm of oxygen, these values represent a reduction in oxygen concentration of the test environment of about $2 \times 10^6$. 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 $1.6 \times 10^-$ ppm oxygen, equivalent to $5 \times 10^{-10}$ mol/L of oxygen. (It is possible that the oxygen content might initially be slightly greater than $1.6 \times 10^{-5}$ ppm 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 ($1 \times 10^{-12}$ mol/L), but is much less than the technetium in the more concentrated solutions (as high as $1 \times 10^{-3}$ mol/L Tc). The presence of these low oxygen concentrations does not generate a reducing redox condition, but it does help permit the basalt to establish a reducing condition if basalt is capable of doing so.

The batch contact experimental methodology and the basalt and synthetic groundwaters used in the tests were previously described in detail in Sect. 4.2 of the Annual Report (KELMERS 1984). For the anoxic condition tests described in this Quarterly Progress Report, several steps were taken to exclude air. The McCoy Canyon basalt was crushed, screened to $-70/+325$ mesh size, and stored under argon in the glove box. The solution was synthetic groundwater GR-2 that was traced with $^{99}$Tc and/or $^{95m}$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 $1 \times 10^{-12}$ to $1 \times 10^{-3}$ mol/L Tc. Three replicate tests were run at each technetium concentration. In these experiments, 0.4 g of basalt and 4 mL of traced groundwater were contacted for 14 d at 28°C in the controlled-atmosphere glove box. After the contact, the samples were centrifuged for 30 min at 2300 relative centrifugal force (rcf) using a small centrifuge inside the controlled-atmosphere glove box. Aliquots of the supernate were then taken for counting to measure the technetium concentration in solution, and for solvent extraction tests to analyze the valence of the technetium in solution. In the solvent extraction valence analysis, the basalt-contacted solutions were extracted with 0.05 $\underline{M}$ tetraphenylarsonium chloride (TPAC) in chloroform (TRIBALAT 1953). The technetium counted in the extracted organic phase is reported as Tc(VII), and that remaining in the aqueous phase is reported as reduced Tc of unknown valence or solution species.

## 4.3 RESULTS

The first set of anoxic redox condition experiments was designed to measure technetium sorption onto McCoy Canyon basalt from GR-2 synthetic groundwater. Little or no sorption or removal of technetium from solution was observed in 14 d (Table 4.1). Sorption ratios were less than or equal to 1 L/kg at all Tc concentrations. Also, no significant quantity of reduced-valence technetium was observed in the solutions after contact with basalt. The small amounts (2 to 4%) of reduced Tc present in some of the solutions was probably not due to reduction by basalt since parallel control samples (traced groundwater with no basalt present) contained higher reduced Tc concentrations than the samples with basalt. The data are given in Table 4.2.

Table 4.1. Technetium sorption under anoxic conditions[a]

| Initial concentration ($\underline{M}$) | pH | Rs (L/kg) | Valence in solution (%) Tc(VII) | Reduced Tc |
|---|---|---|---|---|
| $1 \times 10^{-12}$ | 9.6 | $0.42 \pm 0.11$ | 96.5 | 3.5 |
| $1 \times 10^{-8}$ | 9.6 | $1.10 \pm 1.40$ | 99.7 | 0.3 |
| $1 \times 10^{-6}$ | 9.6 | $0.13 \pm 0.06$ | 98.1 | 1.9 |
| $1 \times 10^{-4}$ | 9.6 | $<0.1$ | 99.3 | 0.7 |
| $1 \times 10^{-3}$ | 9.3 | $<0.1$ | 99.2 | 0.8 |

[a]Test Conditions:
  Rs value - errors are ± 1 standard deviation for triplicate samples.
  Basalt - McCoy Canyon crushed, screened to -70/+325 mesh size, and stored under argon.
  Groundwater - GR-2 traced with $^{95m}$Tc and $^{99}$Tc.
  Contact - basalt/groundwater ratio of 0.1, contacted for 14 d at 28°C under argon.

Table 4.2. Comparison of technetium valence with and without basalt present[a]

| Initial concentration ($\underline{M}$) | Valence in solution (%) Basalt present | | Basalt absent | |
|---|---|---|---|---|
| | Tc(VII) | Reduced Tc | Tc(VII) | Reduced Tc |
| $1 \times 10^{-12}$ | 96.5 | 3.5 | 96.2 | 3.8 |
| $1 \times 10^{-8}$ | 99.7 | 0.3 | 95.9 | 4.1 |
| $1 \times 10^{-6}$ | 98.1 | 1.9 | 98.0 | 2.0 |
| $1 \times 10^{-4}$ | 99.3 | 0.7 | 98.9 | 1.1 |
| $1 \times 10^{-3}$ | 99.2 | 0.8 | 99.1 | 0.9 |

[a]Test Conditions: same as given in Table 4.1, except parallel blank tests added.

No technetium sorption onto the polypropylene test tubes was observed in the blank experiments (no basalt present), as shown in Table 4.3. Previously (KELMERS 1984), reducing condition tests (hydrazine added) with glass tubes and screw caps with polyvinyl chloride (PVC) liners had shown substantial technetium sorption by the glass and PVC.

In some earlier experiments (KELMERS 1984), technetium balances in the solvent extraction valence measurement tests were low. Much of the technetium was found in a layer of material that collected at the interface between the organic and aqueous phases during the extraction with TPAC, and possible precipitation or presence of colloidal material was suspected. Technetium balances in the current tests were excellent (90 to 110% of the initial Tc quantity), except for the highest Tc concentration where they were about 70%. Technetium balances of 95 to 100% were obtained for the samples at the highest concentration of Tc when these tests were repeated with larger amounts of the extractant; apparently the solubility of the Tc-TPAC complex in chloroform was exceeded in the first tests.

Table 4.3. Data for blank technetium experiments[a]

| Initial concentration ($\underline{M}$) | $^{95m}Tc$ (counts/10,000 s/mL) | |
|---|---|---|
| | Standards | Controls |
| $1 \times 10^{-12}$ | 69,455 | 69,841 |
| $1 \times 10^{-8}$ | 69,538 | 70,841 |
| $1 \times 10^{-6}$ | 66,756 | 66,973 |
| $1 \times 10^{-4}$ | 69,193 | 69,647 |
| $1 \times 10^{-3}$ | 71,612 | 71,716 |

[a]Data obtained under the following specifications:

Test conditions - same as given in Table 4.1, except no basalt present.

Standards - 2 mL aliquots of solution taken at the start of the test.

Controls - 2 mL aliquots taken from test tube after blank contact.

## 4.4 DISCUSSION AND CONCLUSIONS

These anoxic redox condition test results are similar to earlier oxic redox condition results (KELMERS 1984) which showed no sorption and no apparent concentration limit for technetium(VII) $\underline{M}$, the technetium valence state which is stable in the presence of air. Apparently, in these anoxic condition tests with McCoy Canyon basalt and synthetic groundwater GR-2, the basalt was unable to reduce the technetium and, therefore, no removal of technetium from solution was observed. These tests were conducted for only 14 d at 28°C, so it is difficult to extrapolate these results to geologic time scales in a repository.

The findings that technetium was not adsorbed by the McCoy Canyon basalt and that the valence of the technetium in the groundwater solutions was not reduced by the basalt are in contrast with results obtained previously under NRC/RES project BO462 (MEYER 1984). In that work in recirculating columns under anoxic redox conditions, up to 70% of the technetium was removed from 0.1 $\underline{M}$ NaCl solution by McCoy Canyon basalt. The technetium was present on the basalt in a relatively insoluble form of reduced valence technetium. At the present time, the reason(s) for this difference in the technetium removal from solution for the two different experiments is not known. The understanding of technetium removal is important to resolve, since it deals with the ability of the basalt site to retard release of technetium to the environment.

In order for the basalt to reduce the technetium, initially present as $TcO_4^-$, the technetium must interact with a reducing species. Basalt contains ferrous iron in several of its phases (MYERS 1981), and the $Fe(II)$ may be the reducing agent in basalt responsible for technetium reduction. The reduction process may require that either (1) ferrous ions are leached out of the basalt and react with the pertechnetate ion in solution, or (2) the pertechnetate ion is adsorbed onto the basalt surface and subsequently reduced after sorption. Neither the leaching of $Fe(II)$ ions from basalt phases nor the surface chemisorption reduction would necessarily be expected to be a rapid reaction at low temperatures, since they could involve solid-state diffusion of the $Fe(II)$ in a basalt phase to the surface or to the reaction site.

One possible explanation for the marked difference in technetium behavior between the groundwater batch experiments and the NaCl solution recirculating column experiments may be that the relatively high chloride content of the 0.1 mol/L NaCl solution or the absence of some soluble species present in the synthetic groundwater could accelerate solution attack or surface dissolution of the reactive iron-containing phase(s) of basalts relative to synthetic groundwater GR-2. This attack could either increase the ferrous ion concentration in the test solution or expose $Fe(II)$-containing surfaces of the basalt; either of these effects could result in greatly accelerated technetium reduction/removal from solution.

## 4.5  EVALUATION OF BWIP VALUES AND METHODS

No BWIP information derived from tests under anoxic redox conditions has been identified in the published reports; all BWIP technetium sorption information was reported as oxic condition (air present) or reducing condition (hydrazine added).  Based on our investigations, we have strong concerns as to the validity of the technetium information obtained by BWIP using hydrazine to attempt to simulate expected repository redox conditions (see below and Sect. 5), and have discontinued use of hydrazine in our technetium experiments.

In our earlier technetium experiments (KELMERS 1984) with hydrazine-containing synthetic groundwaters in either polycarbonate or polypropylene tubes, we noticed that these solutions attacked the container.  When concentrated hydrazine (85% hydrazine hydrate) was put into contact with polycarbonate tubes, they immediately cracked.  At room temperature over periods of weeks, synthetic groundwater containing 0.1 mol/L hydrazine also visibly attacked the polycarbonate tube, either causing them to crack with resulting loss of solution, or causing etching of the tube and a brown discoloration of the groundwater solution.  At 60°C these effects were more pronounced and occurred in a few days.  A similar effect was noted in a BWIP report (BARNEY 1982b, p. 4).  In that BWIP report, the attack was described only for solutions at 85°C; however, it was suggested that their 85°C experiments should be repeated.  Our current position is that polycarbonate tubes should never be used with hydrazine-containing solutions, and that experimental results obtained in such a system are highly suspect.

We also observed a much slower attack of 0.1 mol/L hydrazine in synthetic groundwater GR-2 on polypropylene test tubes.  The solutions became cloudy, and the polypropylene tube was slightly attacked after a period of 2 months at 60°C.  Polypropylene also seems inadvisable for use with hydrazine-containing solutions.  It should be noted that our previous (KELMERS 1984) technetium apparent concentration limit values under reducing conditions (hydrazine added) were measured in polypropylene.  Higher technetium apparent concentration limit values were obtained in polypropylene, compared to glass.  This could be explained by:  (1) the reaction of hydrazine with the polypropylene and resulting loss of hydrazine from solution (less reducing test condition) or (2) possible formation of soluble reduced technetium-organic complexes.

## 5.  CONCERNS RELATIVE TO THE USE OF HYDRAZINE IN BWIP RADIONUCLIDE SORPTION EXPERIMENTS

The BWIP expects the in situ redox condition to be highly reducing.  A calculated or proposed groundwater Eh of −0.48 V is frequently cited (SALTER 1981a).  This value seems to be derived from unpublished information on the secondary minerals present and equilibrium thermodynamic reasoning.  After identifying this Eh value as the expected condition, the BWIP was then faced with the problem of reproducing this solution redox condition in their laboratory experiments in order to measure radionuclide sorption behavior that would be relevant to the basalt geochemical environment.  The presence of air, containing 20% oxygen, in the test apparatus would preclude attaining such a reducing redox condition without the addition of a chemical reductant to the synthetic groundwater.  The BWIP chose to add 0.05 to 0.1 $\underline{M}$ hydrazine (as hydrazine hydrate, $N_2H_4 \cdot H_2O$) to the synthetic groundwater solutions to attempt to duplicate the expected redox condition.  The justification for the use of hydrazine was never well developed in the BWIP reports that described its application in sorption tests (BARNEY 1982a, BARNEY 1982b, SALTER 1981b, SALTER 1981c, SCR 1982).

As a result of our laboratory work with technetium and neptunium, we have developed a number of fundamental concerns about the use of hydrazine for this application; these concerns are detailed in the following paragraphs.  The use of hydrazine seems unacceptable, and defensible (i.e., reasonably assured of being accurate or conservative) sorption distribution coefficients or isotherms and/or apparent concentration limit values cannot be shown to be obtained in the presence of hydrazine.  We have discontinued the addition of hydrazine to groundwater solutions to establish reducing redox conditions, except for occasional tests designed to directly duplicate BWIP experimental conditions.  At the present time, we consider all radionuclide information obtained in the presence of hydrazine to be suspect and potentially invalid for site performance assessment modeling calculations.  These concerns call into question all the BWIP radionuclide sorption distribution coefficients measured in the presence of hydrazine, which are all BWIP values reported for reducing conditions.

### 5.1  GENERAL CONCERNS

The following sections detail a number of general concerns relative to the use of hydrazine in groundwaters which are applicable to experiments involving any radionuclide.

## 5.1.1 Reactions with Hydrazine

The effective solution redox condition generated by hydrazine is strongly dependent upon the specific reduction reaction involved. The following four completely different reactions with widely varying standard potentials are commonly cited (KIRK-OTHMER 1980) for hydrazine reduction reactions:

$$N_2H_4 + 4OH^- = N_2 + 4H_2O + 4e \qquad -1.16 \text{ V}$$

$$N_2H_5^+ = N_2 + 5H^+ + 4e \qquad -0.23 \text{ V}$$

$$2OH^- + N_2H_4 = 2NH_2OH + 2e \qquad +0.73 \text{ V}$$

$$2H_2O + N_2H_5^+ = 2NH_3OH^+ + H^+ + 2e \qquad +1.42 \text{ V}$$
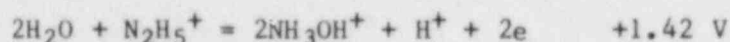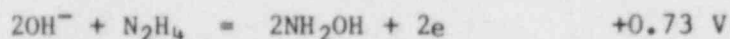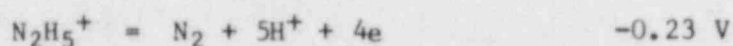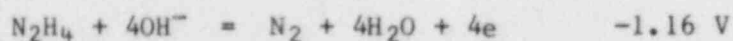
Hydrazine can also act as an oxidant in the same Eh potential range.

$$2e + N_2H_5^+ + 3H^+ = 2NH_4^+ \qquad -1.275 \text{ V}$$

$$2e + N_2H_4 + 2H_2O = 2NH_3 + 2OH^- \qquad -0.1 \text{ V}$$
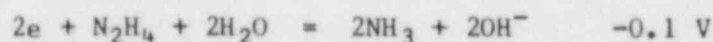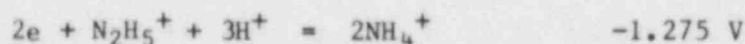
It would seem that without knowledge of the specific reaction occurring between hydrazine and the solute of interest, it may not be possible to estimate what Eh value or redox condition is effective in the experimental solutions. Clearly, more information concerning the solution chemistry of hydrazine is required than has been reported by BWIP before the use of hydrazine can be accepted as simulating the basalt redox condition.

## 5.1.2 Hydrazine Dissociation

Hydrazine hydrate dissociation likely dominates the synthetic groundwater pH. Hydrazine in aqueous solution is present as the hydrate, which dissociates to generate hydroxide ions.

$$N_2H_4 \cdot H_2O = N_2H_5^+ + OH^-$$

The dissociation constant is $1.7 \times 10^{-6}$ (AUDRIETH 1951). Since the hydrazine was added to the groundwater at 0.05 to 0.1 $\underline{M}$ concentration, while the carbonate/bicarbonate concentration in the synthetic groundwater was only about 0.001 $\underline{M}$, it seems probable that all the synthetic groundwater samples containing hydrazine were buffered by the hydrazine rather than by the synthetic groundwater carbonate/bicarbonate components, or by the basalt rock phases. In our tests, the addition of hydrazine was observed to raise the groundwater pH by about 0.5 to 1 pH unit. It can only be concluded that synthetic groundwaters containing hydrazine are no longer representative of in situ pH conditions.

### 5.1.3 Carbamate Formation

Hydrazine can react with the bicarbonate anion to form the carbamate anion (STAAL 1951):

$$N_2H_4 + HCO_3^- = H_2NNHCOO^- + H_2O$$

This reaction could deplete the bicarbonate concentration present because of the large excess of hydrazine relative to bicarbonate in the synthetic groundwaters. This depletion of bicarbonate could further affect the solution pH, in addition to hydrazine hydrate dissociation. In any case, the solution would no longer be representative of in situ groundwater conditions. Also, the carbamate anion could form complexes with transition elements or actinides similar to the well-known amine complexes; little information is available in the literature concerning hydrazine carbamate chemistry.

### 5.1.4 Hydrazine Reactions With Plastics

Hydrazine is a very aggressive chemical and reacts with plastics. Our experience with the rapid reaction of hydrazine with polycarbonate test tubes was discussed in Sect. 4.6. We have also noticed a slight reaction with polypropylene. All the radionuclide sorption work reported to date by BWIP was conducted in polycarbonate tubes, and, as noted in Sect. 4.6, one of their own reports described this reaction and recommended that their work at 85°C be repeated (BARNEY 1982b). While the details of the hydrazine-polycarbonate reaction are not known, it clearly represents a loss of hydrazine from solution. In addition, the formation of brown-colored groundwater solutions strongly suggests the presence of organic degradation products in the radionuclide sorption tests. Our present position is that use of any type of plastic tube with hydrazine-containing solutions is unacceptable. This practical experimental problem would seem to render uncertain all the BWIP sorption work for all radionuclides under reducing conditions.

### 5.1.5 Hydrazine Reactions With Clays

Hydrazine has been reported to interact with clay minerals in a number of ways (HAYES 1982). It may be preferentially adsorbed onto surface exchange sites and compete with ion exchange sorption processes. This potential problem has been recognized by BWIP (AMES 1982). Irreversible chemisorption also has been reported (HAYES 1982). Hydrazine attacks clay mineral structures, such as kaolinite, and can completely disrupt the silicate layering and lead to mineral disaggregation (BLAKELEY 1968; EL-MESSIDI 1977). The use of hydrazine hydrate solutions for chemical disaggregation of rock has been patented (HUFF 1971). Such reactions

between hydrazine in the synthetic groundwaters and basalt secondary
minerals could lead to significant alteration of the secondary minerals
in the reducing condition tests, as well as alter the apparent
radionuclide sorption behavior through sorption competition. The possi-
bility of significant chemical reactions between hydrazine and basalt
components with alteration of the phases and/or surface would seem to
contribute serious uncertainties and raise significant concerns relative
to the use of hydrazine in sorption experiments.

## 5.1.6 Heterogeneous vs Homogeneous Reactions

The chemistry of the basalt/groundwater systems seems to be primarily
dominated by the rock components. Thus, reactions leading to
radionuclide removal from solution by sorption or precipitation must
involve heterogeneous reactions between basalt solid phases and
radionuclide solute species in solution. Such reactions could be kinet-
ically hindered or slow. The addition of hydrazine, or any reducing
chemical, seems likely to result in rapid homogeneous solution reac-
tions. These reactions may model (very poorly, if at all) the heteroge-
neous in situ radionuclide reactions, and it seems unlikely that such
test systems could be shown to be accurately measuring the expected
radionuclide sorption or apparent concentration limit behavior. At the
present time, we are giving emphasis to anoxic redox condition tests
(see Sect. 4.2) and consider the addition of any strong reducing agent
open to serious questions.

## 5.2 SPECIFIC CONCERNS

A number of concerns specific to hydrazine reactions involving tech-
netium or neptunium were developed during our laboratory work and are
detailed in the following paragraphs.

## 5.2.1 Reduced Technetium Chemistry

The rate of reaction between hydrazine and technetium(VII) has only been
studied at pH 11, and the reaction was reported to go more slowly or not
at all at higher or lower pH values (GALATEANU 1977). The reaction prod-
ucts were not identified, but were assumed to be Tc(IV) compounds. No
BWIP reports identifying the products formed from the reaction of hydra-
zine with technetium (or any other radionuclide) have been identified.
Without characterising the reaction product and establishing that it is
identical to that expected to be formed in situ by the basalt/technetium
reaction, it can not be stated with reasonable assurance that the
laboratory test models the in situ system.

Considerable uncertainty exists as to the reduced form of technetium produced by hydrazine. It has been reported (BALDAS 1982) that metalo-organic compounds containing a Tc-N bond are formed; the formal valence of the technetium was not established. The possible formation of at least transiently stable Tc(V) complexes can not be ruled out (DAVISON 1982). Recent work has shown that a number of what were believed to be Tc(VI) organic compounds are actually Tc(III) compounds, and that Tc(III) is generally more stable in aqueous solutions that had been generally believed (JONES 1982). Two different BWIP reports have suggested that the solid phase formed by the reaction of hydrazine with the pertechnetate anion are $TcO_2 \cdot xH_2O$ (BARNEY 1982b) or $TcO_2 \cdot 2H_2O$ (BARNEY 1981). In our work, a black solid was formed, presumably a hydrated Tc(IV) oxide, when hydrazine was added to pertechnetate solutions. The technetium solution species in equilibrium with this solid is undefined.

## 5.2.2 Neptunium(V) Reduction

In recent experiments (to be described in the next quarterly progress report), hydrazine did not reduce neptunium(V) in synthetic groundwater GR-2 solutions to neptunium(IV), as expected by BWIP (BARNEY 1982b). Reduction would be expected from the formal redox potentials, but it has been previously reported that the reaction is slow or does not proceed at all in the absence of a catalyst in nitric acid media (KOLTUNOV 1975, KARRAKER 1981, EL-NAGGAR 1982). No references describing carbonate solutions were identified. Apparently, the reduction reaction is kinetically blocked in these synthetic groundwater systems. No BWIP reports describing the reaction between hydrazine and Np(V) species have been identified.

# 6. COLUMN CHROMATOGRAPHIC STUDIES

Column chromatographic methodology has been used for the direct measurement of retardation factors ($R_f$) which predict the mobility of trace elements in geomedia. The experimental $R_f$ value is controlled by the groundwater chemical composition (concentration of ionic and complexed ions and redox potential), geomedia characteristics (mineralogy, chemical composition, surface area, and exchange properties), and aqueous chemistry of the radionuclides. The purpose of this column chromatographic study is to investigate the migration behavior of the radionuclides that may form multiple species in the site-specific geologic media. The study will first explore experimental $R_f$ values of selected radionuclides ($^{95m}Tc$, $^{239}Np$, $^{237}U$) at different temperatures for basalt/groundwater systems relevant to the BWIP candidate repository site.

During this reporting period, a column chromatographic system consisting of a high-pressure pump, injector, temperature-controlled column oven, fraction collector, ultra violet (UV) detector, and high-resolution germanium gamma detector with an automatic sample changer was assembled (Fig. 2). Relatively unaltered parts of a large piece (about 1 kg) of McCoy Canyon basalt were crushed and a 2- to 45-μm size-fraction of the ground material was separated for the column experiments. Other size fractions and small pieces of the basalt were stored for mineralogical characterization.

Glass columns (3-mm ID and 250 mm long) packed with the selected size fraction of the ground basalt, were prepared. Pretests of the packed columns indicate that they are in operable condition with a 1-mL/min flow rate and less than 10 MPa back pressure at 25°C. We are now ready to inject $^3H_2O$ and $^{95m}TcO_4^-$ tracers to the column for the measurement of $^{99}Tc$ $R_f$ under oxic conditions. GR-4 synthetic groundwater has been selected as an eluent since the BWIP project is now using that formulation.

ORNL/DWG 83-18219
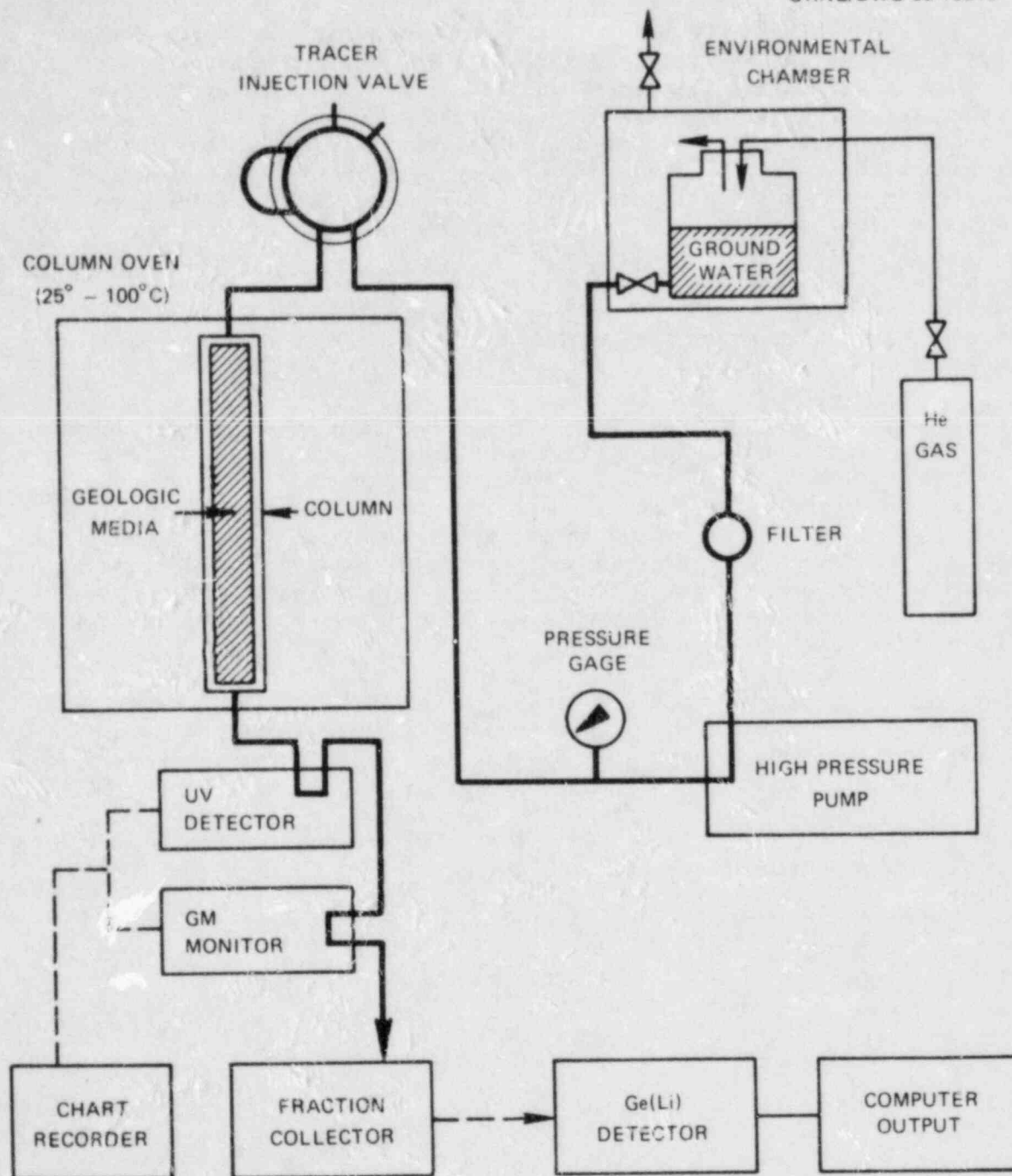


Fig. 2. Schematic diagram of high-performance liquid chromotography system.

# 7. GEOCHEMICAL MODELING

Geochemical modeling activities underway during this report period
involved: (1) checking the radionuclide solubility calculations
published by BWIP using the code MINTEQ, (2) modeling the saturation
indices and speciation for BWIP synthetic groundwater formulations at 25
and 60°C, and (3) modeling the actinide speciation reported by Cleveland
and coworkers (CLEVELAND 1983a, CLEVELAND 1983b). These activities will
be described in future progress reports.

# 8. ACKNOWLEDGMENTS

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APPENDIX A

NEPTUNIUM SORPTION/DESORPTION DATA

Table A.1. Neptunium(V) Sorption on McCoy Canyon Basalt
under oxic conditions

| Starting Np conc. ($\underline{M}$) | Contact time (weeks) | Sample | Centrif.(C) or filtered(F) | Np in solution ($\underline{M}$) | Np on rock (mol/kg) | Rs (L/kg) |
|---|---|---|---|---|---|---|
| Pre-equilibrated samples: | | | | | | |
| $1.0 \times 10^{-6}$ | 1 | Rock | C | $7.6 \times 10^{-7}$ | $2.4 \times 10^{-6}$ | 3.2 |
| | | | F | $7.1 \times 10^{-7}$ | $2.9 \times 10^{-6}$ | 4.0 |
| | | | C | $7.4 \times 10^{-7}$ | $2.6 \times 10^{-6}$ | 3.6 |
| | | | F | $7.1 \times 10^{-7}$ | $2.9 \times 10^{-6}$ | 4.1 |
| | | | C | $7.4 \times 10^{-7}$ | $2.6 \times 10^{-6}$ | 3.5 |
| | | | F | $7.2 \times 10^{-7}$ | $2.8 \times 10^{-6}$ | 4.0 |
| $1.0 \times 10^{-6}$ | | Blank | C | $8.9 \times 10^{-7}$ | | |
| | | | F | $8.8 \times 10^{-7}$ | | |
| | | | C | $8.8 \times 10^{-7}$ | | |
| | | | F | $8.7 \times 10^{-7}$ | | |
| $1.1 \times 10^{-8}$ | 1 | Rock | C | $1.0 \times 10^{-8}$ | $7.0 \times 10^{-9}$ | 0.7 |
| | | | F | $1.1 \times 10^{-8}$ | $4.5 \times 10^{-9}$ | 0.4 |
| | | | C | $1.0 \times 10^{-8}$ | $1.4 \times 10^{-8}$ | 1.4 |
| | | | F | $1.0 \times 10^{-8}$ | $1.3 \times 10^{-8}$ | 1.3 |
| $2 \times 10^{-8}$ | 1 | Rock | C | $2.0 \times 10^{-8}$ | $1.7 \times 10^{-8}$ | 0.8 |
| | | | F | $2.0 \times 10^{-8}$ | $2.3 \times 10^{-8}$ | 1.2 |
| $1.1 \times 10^{-8}$ | 1 | Blank | C | $1.1 \times 10^{-8}$ | | |
| | | | F | $1.1 \times 10^{-8}$ | | |
| | | | C | $1.1 \times 10^{-8}$ | | |
| | | | F | $1.1 \times 10^{-8}$ | | |
| $1.1 \times 10^{-10}$ | 1 | Rock | C | $9.7 \times 10^{-11}$ | $1.4 \times 10^{-10}$ | 1.5 |
| | | | F | $1.1 \times 10^{-10}$ | $5.7 \times 10^{-11}$ | 0.5 |
| | | | C | $9.9 \times 10^{-11}$ | $1.1 \times 10^{-10}$ | 1.1 |
| | | | F | $9.7 \times 10^{-11}$ | $1.3 \times 10^{-10}$ | 1.4 |
| | | | C | $1.1 \times 10^{-10}$ | $3.4 \times 10^{-11}$ | 0.3 |
| | | | F | $1.1 \times 10^{-10}$ | $3.4 \times 10^{-11}$ | 0.3 |
| | | Blank | C | $1.1 \times 10^{-10}$ | | |
| | | | F | $1.1 \times 10^{-10}$ | | |
| | | | C | $1.1 \times 10^{-10}$ | | |
| | | | F | $1.1 \times 10^{-10}$ | | |
| $3.7 \times 10^{-12}$ | 1 | Rock | C | $3.3 \times 10^{-12}$ | $4.8 \times 10^{-12}$ | 1.5 |
| | | | F | $3.2 \times 10^{-12}$ | $5.0 \times 10^{-12}$ | 1.5 |
| | | | C | $3.6 \times 10^{-12}$ | $1.5 \times 10^{-12}$ | 0.4 |
| | | | F | $3.6 \times 10^{-12}$ | $1.5 \times 10^{-12}$ | 0.4 |

Table A.1. (continued)

| Starting Np conc. ($\underline{M}$) | Contact time (weeks) | Sample | Centrif.(C) or filtered(F) | Np in solution ($\underline{M}$) | Np on rock (mol/kg) | Rs (L/kg) |
|---|---|---|---|---|---|---|
| | | | C | $3.4 \times 10^{-12}$ | $3.8 \times 10^{-12}$ | 1.1 |
| | | | F | $3.4 \times 10^{-12}$ | $3.5 \times 10^{-12}$ | 1.0 |
| | | Blank | C | $3.7 \times 10^{-12}$ | | |
| | | | F | $3.7 \times 10^{-12}$ | | |
| | | | C | $3.6 \times 10^{-12}$ | | |
| | | | F | $3.7 \times 10^{-12}$ | | |
| $1.0 \times 10^{-6}$ | 4 | Rock | C | $7.9 \times 10^{-7}$ | $3.0 \times 10^{-6}$ | 3.8 |
| | | | F | $7.0 \times 10^{-7}$ | $3.8 \times 10^{-6}$ | 5.3 |
| | | | C | $7.5 \times 10^{-7}$ | $2.6 \times 10^{-6}$ | 3.4 |
| | | | F | $6.9 \times 10^{-7}$ | $3.2 \times 10^{-6}$ | 4.7 |
| | | | C | $7.4 \times 10^{-7}$ | $2.6 \times 10^{-6}$ | 3.5 |
| | | | F | $6.9 \times 10^{-7}$ | $3.2 \times 10^{-6}$ | 4.6 |
| | | Blank | C | $9.8 \times 10^{-7}$ | | |
| | | | F | $9.1 \times 10^{-7}$ | | |
| | | | C | $9.7 \times 10^{-7}$ | | |
| | | | F | $8.8 \times 10^{-7}$ | | |
| $1.1 \times 10^{-8}$ | 4 | Rock | C | $1.0 \times 10^{-8}$ | $1.0 \times 10^{-8}$ | 1.0 |
| | | | F | $9.5 \times 10^{-9}$ | $1.7 \times 10^{-8}$ | 1.8 |
| | | | C | $1.0 \times 10^{-8}$ | $1.2 \times 10^{-8}$ | 1.2 |
| | | | F | $9.4 \times 10^{-9}$ | $1.9 \times 10^{-8}$ | 2.0 |
| | | | C | $1.0 \times 10^{-8}$ | $1.3 \times 10^{-8}$ | 1.3 |
| | | | F | $9.5 \times 10^{-9}$ | $1.9 \times 10^{-8}$ | 2.0 |
| | | Blank | C | $1.1 \times 10^{-8}$ | | |
| | | | F | $1.1 \times 10^{-8}$ | | |
| | | | C | $1.1 \times 10^{-8}$ | | |
| | | | F | $1.1 \times 10^{-8}$ | | |
| $1.1 \times 10^{-10}$ | 4 | Rock | C | $9.4 \times 10^{-11}$ | $1.5 \times 10^{-10}$ | 1.6 |
| | | | F | $8.4 \times 10^{-11}$ | $2.5 \times 10^{-10}$ | 3.0 |
| | | | C | $9.4 \times 10^{-11}$ | $1.6 \times 10^{-10}$ | 1.7 |
| | | | F | $9.0 \times 10^{-11}$ | $2.0 \times 10^{-10}$ | 2.2 |
| | | | C | $9.2 \times 10^{-11}$ | $1.7 \times 10^{-10}$ | 1.9 |
| | | | F | $9.0 \times 10^{-11}$ | $2.0 \times 10^{-10}$ | 2.2 |
| | | Blank | C | $1.1 \times 10^{-10}$ | | |
| | | | F | $1.1 \times 10^{-10}$ | | |
| | | | C | $1.1 \times 10^{-10}$ | | |
| | | | F | $1.1 \times 10^{-10}$ | | |

Table A.1. (continued)

| Starting Np conc. $(\underline{M})$ | Contact time (weeks) | Sample | Centrif.(C) or filtered(F) | Np in solution $(\underline{M})$ | Np on rock (mol/kg) | Rs (L/kg) |
|---|---|---|---|---|---|---|
| $3.7 \times 10^{-12}$ | 4 | Rock | C | $3.4 \times 10^{-12}$ | $3.8 \times 10^{-12}$ | 1.1 |
| | | | F | $3.1 \times 10^{-12}$ | $6.2 \times 10^{-12}$ | 2.0 |
| | | | C | $3.5 \times 10^{-12}$ | $3.0 \times 10^{-12}$ | 0.9 |
| | | | F | $3.2 \times 10^{-12}$ | $6.2 \times 10^{-12}$ | 2.0 |
| | | | C | $3.5 \times 10^{-12}$ | $3.2 \times 10^{-12}$ | 0.9 |
| | | | F | $3.2 \times 10^{-12}$ | $6.2 \times 10^{-12}$ | 2.0 |
| | | Blank | C | $3.7 \times 10^{-12}$ | | |
| | | | F | $3.7 \times 10^{-12}$ | | |
| | | | C | $3.7 \times 10^{-12}$ | | |
| | | | F | $3.7 \times 10^{-12}$ | | |

"As-Is" samples:

| Starting Np conc. $(\underline{M})$ | Contact time (weeks) | Sample | Centrif.(C) or filtered(F) | Np in solution $(\underline{M})$ | Np on rock (mol/kg) | Rs (L/kg) |
|---|---|---|---|---|---|---|
| $3.8 \times 10^{-12}$ | 1 | Rock | C | $3.0 \times 10^{-12}$ | $8.2 \times 10^{-12}$ | 2.7 |
| | | | F | $2.9 \times 10^{-12}$ | $9.0 \times 10^{-12}$ | 3.1 |
| | | | C | $2.9 \times 10^{-12}$ | $9.3 \times 10^{-12}$ | 3.2 |
| | | | F | $3.1 \times 10^{-12}$ | $7.9 \times 10^{-12}$ | 2.6 |
| | | | C | $3.0 \times 10^{-12}$ | $8.4 \times 10^{-12}$ | 2.8 |
| | | | F | $3.0 \times 10^{-12}$ | $8.5 \times 10^{-12}$ | 2.8 |
| | | Blank | C | $3.8 \times 10^{-12}$ | | |
| | | | F | $3.8 \times 10^{-12}$ | | |
| | | | C | $3.7 \times 10^{-12}$ | | |
| | | | F | $3.8 \times 10^{-12}$ | | |
| $3.6 \times 10^{-12}$ | 4 | Rock | C | $2.9 \times 10^{-12}$ | $7.8 \times 10^{-12}$ | 2.7 |
| | | | F | $2.8 \times 10^{-12}$ | $9.2 \times 10^{-12}$ | 3.3 |
| | | | C | $2.9 \times 10^{-12}$ | $7.2 \times 10^{-12}$ | 2.5 |
| | | | F | $2.7 \times 10^{-12}$ | $9.4 \times 10^{-12}$ | 3.4 |
| | | | C | $3.0 \times 10^{-12}$ | $6.7 \times 10^{-12}$ | 2.2 |
| | | | F | $2.9 \times 10^{-12}$ | $8.0 \times 10^{-12}$ | 2.8 |
| | | Blank | C | $3.6 \times 10^{-12}$ | | |
| | | | F | $3.6 \times 10^{-12}$ | | |
| | | | C | $3.6 \times 10^{-12}$ | | |
| | | | F | $3.5 \times 10^{-12}$ | | |

Table A.2. Neptunium desorption from McCoy Canyon Basalt
under oxic conditions

| Contact time (weeks) | Sample | Centrif.(C) or filtered(F) | Np in solution (M) | Np on rock (mol/kg) | Rd (L/kg) |
|---|---|---|---|---|---|
| Pre-equilibrated samples: | | | | | |
| 1 | Rock | C | $4.8 \times 10^{-8}$ | $2.2 \times 10^{-6}$ | 45 |
| | | F | $4.4 \times 10^{-8}$ | $2.7 \times 10^{-6}$ | 61 |
| | | C | $1.6 \times 10^{-7}$ | $1.2 \times 10^{-6}$ | 7.4 |
| | | F | $5.0 \times 10^{-8}$ | $2.7 \times 10^{-6}$ | 53 |
| | | C | $5.3 \times 10^{-8}$ | $2.3 \times 10^{-6}$ | 44 |
| | | F | $4.5 \times 10^{-8}$ | $2.6 \times 10^{-6}$ | 59 |
| | Blank | C | $1.7 \times 10^{-9}$ | | |
| 1 | Rock | C | $7.7 \times 10^{-10}$ | $3.2 \times 10^{-9}$ | 4.2 |
| | | C | $1.1 \times 10^{-9}$ | $7.0 \times 10^{-9}$ | 7.0 |
| | | F | $6.9 \times 10^{-10}$ | $1.0 \times 10^{-8}$ | 15 |
| | | C | $1.8 \times 10^{-9}$ | $6.1 \times 10^{-9}$ | 3.3 |
| | | F | $1.6 \times 10^{-9}$ | $1.4 \times 10^{-8}$ | 8.3 |
| 1 | Rock | C | $1.3 \times 10^{-11}$ | $4.5 \times 10^{-11}$ | 3.5 |
| | | C | $1.2 \times 10^{-11}$ | $1.9 \times 10^{-11}$ | 1.5 |
| | | F | $1.3 \times 10^{-11}$ | $3.7 \times 10^{-11}$ | 2.9 |
| 1 | Rock | C | $4.0 \times 10^{-13}$ | $1.9 \times 10^{-12}$ | 4.7 |
| | | F | $3.8 \times 10^{-13}$ | $2.2 \times 10^{-12}$ | 5.8 |
| | | C | $3.4 \times 10^{-13}$ | $1.4 \times 10^{-12}$ | 4.2 |
| | | F | $3.6 \times 10^{-13}$ | $7.6 \times 10^{-13}$ | 2.1 |
| 4 | Rock | C | $6.3 \times 10^{-8}$ | $2.6 \times 10^{-6}$ | 41 |
| | | F | $6.0 \times 10^{-8}$ | $3.4 \times 10^{-6}$ | 56 |
| | | C | $5.7 \times 10^{-8}$ | $2.2 \times 10^{-6}$ | 38 |
| | | F | $5.4 \times 10^{-8}$ | $2.8 \times 10^{-6}$ | 52 |
| | | C | $5.8 \times 10^{-8}$ | $2.3 \times 10^{-6}$ | 40 |
| | | F | $5.5 \times 10^{-8}$ | $2.8 \times 10^{-6}$ | 52 |
| | Blank | C | $9.4 \times 10^{-10}$ | | |
| | | F | $2.5 \times 10^{-9}$ | | |
| | | C | $7.9 \times 10^{-10}$ | | |
| | | F | $2.0 \times 10^{-9}$ | | |
| 4 | Rock | C | $9.8 \times 10^{-10}$ | $4.0 \times 10^{-9}$ | 4.0 |
| | | F | $8.4 \times 10^{-10}$ | $1.1 \times 10^{-8}$ | 14 |
| | | C | $8.8 \times 10^{-10}$ | $5.6 \times 10^{-9}$ | 6.4 |
| | | F | $8.7 \times 10^{-10}$ | $1.3 \times 10^{-8}$ | 15 |
| | | C | $8.6 \times 10^{-10}$ | $7.8 \times 10^{-9}$ | 9.0 |
| | | F | $9.5 \times 10^{-10}$ | $1.3 \times 10^{-8}$ | 13 |

Table A.2. (continued)

| Contact time (weeks) | Sample | Centrif.(C) or filtered(F) | Np in solution ($\underline{M}$) | Np on rock (mol/kg) | Rd (L/kg) |
|---|---|---|---|---|---|
| | Blank | C | $1.2 \times 10^{-10}$ | | |
| | | F | $1.1 \times 10^{-10}$ | | |
| 4 | Rock | C | $1.0 \times 10^{-11}$ | $7.4 \times 10^{-11}$ | 7.1 |
| | | F | $1.2 \times 10^{-11}$ | $1.6 \times 10^{-10}$ | 14 |
| | | C | $1.3 \times 10^{-11}$ | $5.3 \times 10^{-11}$ | 4.0 |
| | | F | $1.3 \times 10^{-11}$ | $1.0 \times 10^{-10}$ | 8.0 |
| | | F | $1.2 \times 10^{-11}$ | $1.1 \times 10^{-10}$ | 9.8 |
| | Blank | F | $1.5 \times 10^{-12}$ | | |
| 4 | Rock | C | $4.2 \times 10^{-13}$ | $7.1 \times 10^{-13}$ | 1.7 |
| | | F | $4.0 \times 10^{-13}$ | $3.2 \times 10^{-12}$ | 8.2 |
| | | C | $4.0 \times 10^{-13}$ | $2.2 \times 10^{-13}$ | 0.5 |
| | | F | $3.8 \times 10^{-13}$ | $3.4 \times 10^{-12}$ | 8.9 |
| | | C | $3.7 \times 10^{-13}$ | $7.0 \times 10^{-13}$ | 1.9 |
| | | F | $3.5 \times 10^{-13}$ | $3.9 \times 10^{-12}$ | 11 |
| ".s-Is" samples: | | | | | |
| 1 | Rock | C | $3.9 \times 10^{-13}$ | $5.4 \times 10^{-12}$ | 14 |
| | | F | $3.5 \times 10^{-13}$ | $6.7 \times 10^{-12}$ | 19 |
| | | C | $3.7 \times 10^{-13}$ | $7.1 \times 10^{-12}$ | 19 |
| | | F | $3.7 \times 10^{-13}$ | $5.7 \times 10^{-12}$ | 15 |
| | | C | $3.4 \times 10^{-13}$ | $5.9 \times 10^{-12}$ | 17 |
| | | F | $3.2 \times 10^{-13}$ | $6.3 \times 10^{-12}$ | 20 |
| 4 | Rock | C | $4.1 \times 10^{-13}$ | $4.8 \times 10^{-12}$ | 12 |
| | | F | $3.4 \times 10^{-13}$ | $6.7 \times 10^{-12}$ | 20 |
| | | C | $3.7 \times 10^{-13}$ | $4.6 \times 10^{-12}$ | 12 |
| | | F | $3.9 \times 10^{-13}$ | $6.5 \times 10^{-12}$ | 17 |
| | | C | $3.7 \times 10^{-13}$ | $4.1 \times 10^{-12}$ | 11 |
| | | F | $3.4 \times 10^{-13}$ | $5.6 \times 10^{-12}$ | 16 |

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16. ABSTRACT (200 words or less)   Oak Ridge National Laboratory (ORNL) is conducting an experimental investigation of geochemical information for the Nuclear Regulatory Commission (NRC). During this quarter, the project evaluated both radionuclide solubility data and retardation parameters reported by the Basalt Waste Isolation Project (BWIP), and the methodologies used to develop those values. Under oxic conditions, neptunium had a sorption ratio of 1.7 L/kg for McCoy Canyon basalt and synthetic groundwater GR-2, which is lower than the "conservative best estimate" value recommended by BWIP. Under anoxic conditions, the basalt showed little or no ability to remove technetium(VII) from GR-2 by sorption or precipitation. Several important concerns may make it impossible to assert that the addition of hydrazine to groundwater is modeling the repository redox condition. These are: (1) its reaction with any reducible solute is undefined, (2) its dissociation to release hydroxide ions probably dominates the groundwater pH, (3) it could react with bicarbonate to form the carbamate ion, (4) it is corrosive to polycarbonate or polypropylene test tubes, (5) it may alter or disaggregate clay mineral structure, and (6) uncertainty exists as to the solid phase or solution species formed by reaction with pertechnetate ion. Thus, BWIP data obtained in the presence of hydrazine may be nonconservative for use in assessment studies.

| 17. KEY WORDS AND DOCUMENT ANALYSIS | 17a. DESCRIPTORS |
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| Radionuclide sorption Radionuclide solubility Geochemical conditions High-level waste repositories Basalt   Neptunium   Technetium | Basalt Waste Isolation Project (BWIP) |

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ADM-DIV JF TIDC
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