

# **Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects:**

## **Annual Progress Report for October 1983–September 1984**

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EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED  
BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS:  
ANNUAL PROGRESS REPORT FOR OCTOBER 1983-SEPTEMBER 1984

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## ABSTRACT

Geochemical information relevant to the retention of radionuclides by candidate high-level nuclear waste geologic repositories being characterized by Department of Energy (DOE) projects is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). During this report period, emphasis has been given to the experimental evaluation of published sorption and solubility information for key radionuclides which is relevant to the Hanford Site in the Columbia River basalts being characterized by the Basalt Waste Isolation Project (BWIP). In work by the BWIP, hydrazine was added to synthetic groundwater to simulate the reducing redox condition expected by the DOE in the repository. We believe such laboratory methodology may not adequately model in situ repository geochemical conditions and are concerned that the radionuclide sorption values measured by such methodology may be inappropriate for performance assessment modeling calculations. We have been employing anoxic redox conditions (established by use of argon-filled controlled-atmosphere glove boxes) to allow the basalt to establish the effective redox condition in batch contact sorption experiments. We believe that sorption of neptunium(V) or technetium(VII) by basalt from synthetic groundwaters under anoxic redox conditions involves chemisorption reduction reactions on the basalt surface. Our sorption ratio of 1.7 L/kg for neptunium under oxic redox conditions does not compare favorably with the value of 10 L/kg published by the BWIP. The published solubility of technetium under the reducing redox conditions expected by BWIP at the repository ( $10^{-14}$  mol/L) probably is based on calculations involving inadequate thermodynamic data. In our experimental work, apparent concentration limit values of  $10^{-5}$  or  $10^{-6}$  mol/L have been measured for technetium. Under oxic redox conditions, our uranium sorption ratio of 1 to 4 L/kg was much lower than values reported by the BWIP, that is, the published values may be nonconservative. A mineralogical and chemical characterization was completed for the three basalt samples used in our work. Significant differences were seen in both the quantity and composition of the mesostasis. Since iron(II) in the mesostasis may be the active reducing element in basalt, such sample differences in reducing element composition could be important in comparing experimental sorption results for different basalt samples. A potential deficiency in the information published by the BWIP is the absence of lithological information as well as mineralogical and chemical characterization for the basalt samples used in the experiments to measure sorption information. Our geochemical modeling work suggested that code-to-code evaluation for geochemical calculations may be less important than a detailed evaluation of the data bases. We calculated that the most recent Hanford Site synthetic groundwater formulations were oversaturated with silica phases and fluorite at 25°C, thus these groundwaters could be unstable in laboratory work at this temperature.

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## PREFACE

This document is the fifth in a series of 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.

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1. EXECUTIVE SUMMARY

This project, supported by the Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards (NMSS), is being conducted to evaluate the radionuclide geochemical information and data acquisition methodology that may be employed by Department of Energy (DOE) high-level nuclear waste repository site projects in performance assessment calculations to show reasonable assurance of expected compliance with regulatory requirements. The project is focused on parameters that are important to the mobility of radionuclides in geologic media (primarily, sorption behavior on host rock and apparent concentration limits in groundwater) under the anticipated geochemical conditions of the repository. Initial emphasis is on information applicable to the Hanford Site candidate repository in the Columbia River basalts on the DOE Hanford Reservation at Richland, Washington, being characterized by the Basalt Waste Isolation Project (BWIP).

Batch contact methodology was employed by the BWIP to develop the published radionuclide sorption information for the Hanford Site. Since the in situ host rock/groundwater system is expected by the DOE to be strongly reducing, hydrazine was added to the synthetic groundwater (in work published by BWIP) in order to simulate the expected repository redox condition in laboratory experiments exposed to air; this was identified as reducing redox conditions. We have expressed (KELMERS 1984a) concern as to the applicability of data developed by this methodology for performance assessment applications and believe that the radionuclide sorption ratios measured under reducing redox conditions may be non-conservative in some cases and inappropriate for performance assessment calculations. We have been measuring radionuclide sorption isotherms for basalt/groundwater systems under anoxic redox conditions established by the use of argon-filled controlled-atmosphere glove boxes. This anoxic condition methodology may permit the effective test redox condition to be established by the basalt. We have been constructing radionuclide sorption isotherms rather than reporting sorption information for one radionuclide concentration only, as was done for much of the Hanford Site

information published by the BWIP. Sorption isotherms reveal the dependence of the sorption ratio on radionuclide concentration as well as identifying the apparent concentration limit. Such information may be necessary to obtain accurate or conservative estimates of radionuclide release rates.

Much of our work this year has been with neptunium and technetium — two of the key radionuclides for the Hanford Site (i.e., those expected to be among the major contributors to radioactivity release rates). We now believe that both neptunium(V) (added in tests to the synthetic groundwater as  $\text{NpO}_2^+$  possibly hydrolyzed or complexed in groundwater to anionic species) and technetium(VII) (present in groundwater as  $\text{TcO}_4^-$ ) are removed from solution by chemisorption reactions on the basalt surface which involve reduction to neptunium(IV) and technetium(IV) species or compounds. The reduction may involve reaction with iron(II) in a basalt phase. In our oxic redox condition experiments (both batch contact and column chromatographic tests) with neptunium(V), we measured a lower sorption ratio value (1.7 L/kg) with McCoy canyon basalt than the most recently reported (SALTER 1983) value of 10 L/kg (measured with Umtanum basalt) expected under repository conditions. Since the Umtanum is only one of four candidate repository horizons, differences in neptunium sorption between different basalt flows could be important to performance assessment modeling. We have shown that the neptunium sorption ratio value obtained is sensitive to many experimental parameters, including: the specific basalt and synthetic groundwater used, radionuclide concentration, temperature, and time. It is difficult to rigorously compare our neptunium results with the summary of published expected and conservative information (SALTER 1983) since the report does not identify important test parameters.

In our oxic redox condition tests, technetium showed no sorption or apparent concentration limit. These results are in agreement with information published by the BWIP. Under anoxic redox conditions, we obtained significant removal-from-solution of technetium; sorption ratio values as high as 53 L/kg were measured in some cases. Steady-state conditions were not established in tests with technetium lasting up to 50 d; a continuing removal from solution seems to be occurring. We believe that the published (SALTER 1983) low solubility value expected for technetium under repository conditions ( $\sim 10^{-14}$  mol/L) probably was calculated based on inadequate thermodynamic data and may not be defensible.

Our preliminary calculations based on the only data available for technetium(IV) solution species, as well as preliminary laboratory measurements, suggest that an apparent concentration limit of  $10^{-5}$  or  $10^{-6}$  mol/L may be more representative of the solubility under repository conditions. Additional anoxic redox condition work is under way to complete sorption isotherms and determine apparent concentration limit values for neptunium and technetium with Cohasset basalt and synthetic groundwater GR-4, since the Cohasset formation is now considered to be the leading candidate horizon.



If spent fuel is the waste form, uranium will likely be a key radionuclide. We have completed some oxic redox condition work with uranium this year. Sorption isotherms with McCoy Canyon basalt gave low sorption ratio values of 1 to 4 L/kg. This value is much lower than the reported (SALTER 1983) value of 20 L/kg expected under repository conditions. That report also gave an oxic redox condition value for Umtanum basalt of 6 L/kg. In our tests, a uranium(VI) precipitate formed in groundwater solutions that were initially  $10^{-4}$  mol/L in uranium. Additional work is under way to identify the nature of this precipitate and to prepare uranium sorption isotherms for Cohasset basalt and synthetic groundwater GR-4 under anoxic redox conditions.

A limited amount of work was done with strontium. Strontium is not a key radionuclide, but considerable strontium sorption information has been published by the BWIP for the Hanford Site. Under oxic redox conditions in tests with McCoy Canyon basalt, we obtained an average sorption ratio value of 208 L/kg, which was close to the value of 170 L/kg reported for Umtanum basalt under oxic conditions (SALTER 1983).

A mineralogical and chemical characterization of the three basalt samples used in our work (McCoy Canyon, Cohasset, and Umtanum) was completed. Emphasis was given to quantifying differences between the samples; this information is useful in interpreting differences in radionuclide sorption behavior with the three basalts. The proportion of primary phases was similar for the three basalts, with the exception of the interstitial or glassy mesostasis; the Umtanum and Cohasset samples had nearly twice the mesostasis content of the McCoy Canyon. In addition, the total iron content of the Umtanum and Cohasset mesostasis was 3 to 4 times that of the McCoy Canyon mesostasis. These values are potentially significant differences for sorption of radionuclides such as technetium(VII) or neptunium(V), which are believed to be removed from solution by reduction reactions involving the basalt surface, since the iron(II) content of the mesostasis may be the source of reducing capability of the basalts. Lithologic information to identify the source as colonnade or entablature, as well as mineralogical and chemical characterization, has not been published by the BWIP for the basalt samples used in the Hanford Site sorption work. This deficiency may be important for performance assessment considerations since it makes difficult a rational consideration of differences in radionuclide sorption behavior between various candidate basalt flows, or between our results and those published by the BWIP for the Hanford Site.

Geochemical modeling work this year addressed interpretation of Hanford Site groundwater chemistry and estimation of solubility-controlled concentrations of radionuclides in groundwater. The reported solubilities (EARLY 1983) of 16 radionuclides in synthetic groundwater GR-3 at an Eh of -0.3 V were checked by comparison calculations using the computer codes PHREEQE and MINTEQ. Generally excellent agreement was obtained for limiting concentrations, limiting solid phases, and dominant aqueous species. Calculations using the data base of MINTEQ for uranium, nickel, and lead illustrated the importance of having a documented, verified, and

internally consistent data base. Code-to-code evaluations for geochemical calculations may be less important than a detailed evaluation of the data bases during the analysis of radionuclide release calculations for performance assessment modeling. The most recent Hanford Site synthetic groundwater formulations (GR-3 and GR-4) were calculated to be oversaturated with respect to silica phases and fluorite at 25°C but were calculated to be undersaturated at 60°C (the in situ temperature). Thus, these synthetic groundwaters may model in situ groundwaters but may be unstable and precipitate in laboratory experiments at 25°C.

## 2. INTRODUCTION

### 2.1 PROJECT OBJECTIVE AND RELATIONSHIP TO REPOSITORY ANALYSIS

The objective of this project is to support the NRC staff analysis of geochemical information used by the DOE to predict the performance of candidate high-level waste geologic repository sites. Under this project, both experimental and calculational activities are undertaken to evaluate pertinent geochemical values and the methodology used in the development of these values. The results of the work conducted under this project are compared with published information reported by the DOE site projects or others, and, where appropriate, concerns are expressed relative to the accuracy, conservatism, or relevance of the information for the prediction of repository performance.

One of the more credible scenarios that could result in the release of radioactivity from emplaced waste in a high-level waste repository to the accessible environment involves groundwater-intrusion-groundwater-migration events. Multiple barriers (both natural and engineered) may exist at a geologic repository which can retard or limit the rate of release of radionuclides to the biosphere in such events. These potential barriers include, in sequence of operation:

1. radionuclide inventory in the waste,
2. isolation of the waste form from intruding groundwater by the waste package,
3. waste form dissolution rate in intruding groundwater,
4. radionuclide apparent concentration limit (radionuclide species solubility plus concentration of suspended particulate and colloid forms) in the migrating groundwater,
5. groundwater flux (groundwater volume times flow rate),
6. groundwater travel time to the accessible environment,
7. dilution of the radionuclide concentration in migrating groundwater by uncontaminated groundwater in the site during travel to the accessible environment,
8. matrix diffusion of radionuclides in migrating groundwater into static pore water in the repository host rocks,
9. sorption of radionuclide solution species in migrating groundwater onto repository host rocks, and
10. filtration of radionuclide particulate and colloidal forms in migrating groundwater by repository host rocks.

While the DOE site projects have not reported detailed performance

assessment strategies at this time, it is anticipated that these strategies may be partly based on the assumption that the apparent concentration limit in groundwater and sorption retardation by site host rocks will be important natural barriers to radionuclide migration, in addition to the engineered barriers. Thus, calculation of radionuclide release rates for indicating the effectiveness of these barriers will require, along with other information, values for the radionuclide apparent concentration limits and sorption retardation factors. A considerable body of information has been published by the DOE site projects for both the Hanford Site and the Yucca Mountain site, and in ongoing programs the projects are determining additional experimentally measured and calculated values for radionuclide solubility and sorption distribution coefficients. The NRC staff will need to evaluate these values in order to assess the DOE Site Characterization Plans and, in the future, the applications for Construction Authorization. Thus, under this project we are attempting to evaluate the methodologies employed in the determination of these values and the accuracy, conservatism, or relevance of the values reported by the DOE site projects.

This project is primarily a laboratory activity because it is expected that the DOE will rely principally on experimentally measured radionuclide apparent concentration limits and sorption distribution coefficients. The experimental methodologies used by the DOE site projects, the selection and characterization of site materials used in the DOE experiments, and the DOE test results are being evaluated. The appropriateness of the materials selected and the methodology employed to simulate repository geochemical conditions are considered. The conservatism inherent in the laboratory approach is being evaluated. In addition, attention is directed toward geochemical modeling efforts both to support our laboratory work and to evaluate the data bases and calculational methodologies employed in the geochemical modeling used by the DOE. For example, the DOE site projects may elect to calculate some geochemical values, such as radionuclide solubility, without supporting laboratory measurements. The DOE site projects may also use modeling methodology to extrapolate laboratory information to conditions of temperature and chemistry that are unexplored experimentally. These and other aspects of the DOE site project geochemical methodology and values will be examined in light of the reasonable assurance criteria of the NRC regulation 10 CFR Part 60.

## 2.2 APPROACH TO HANFORD SITE INFORMATION EVALUATION

### 2.2.1 Site Description

The Hanford Site candidate repository, being characterized by the Basalt Waste Isolation Project, is in the Pasco Basin of the Columbia River basalt formation. The Reference Repository Location (RRL) is on the DOE Hanford Reservation at Richland, Washington. The Columbia River basalts were formed by repeated eruptions of magma over millions of years and cover an extensive area of western Washington, eastern Idaho, northern Nevada, and eastern Oregon with multiple layers of basalt. In the Pasco Basin, the basalt depth exceeds 1000 m. Each flow formed a discrete horizon in the rock stratigraphy and is characterized by a brecciated

flow bottom and flow top that are more permeable and porous to groundwater than the dense colonnade and entablature center regions of the basalt flow. In addition, several periods of magmatic inactivity occurred and a weathered surface developed and extraneous (nonbasaltic) materials accumulated. These materials were subsequently buried under later basalt flows. These nonbasaltic strata have been identified as "interbed" regions, and some now contain major fresh water aquifers.

The candidate horizon for the location of a mined repository is in the Grande Ronde Basalt sequence. While a final selection of the repository horizon has not been identified, it appears that the Cohasset flow now may be the leading candidate. The Cohasset flow is at a depth of about 850 to 900 m at the RRL. Other Grande Ronde Basalt flows considered for the repository includes the McCoy Canyon, the Umtanum, and the Rocky Coulee. Much of the geochemical information published by the BWIP is descriptive of the Umtanum flow (the earlier leading candidate horizon); a summary of this information is given in the Site Characterization Report (SCR 1982).

The geochemical parameters in the Umtanum flow that are identified in BWIP publications (SALTER 1981c, SCR 1982) are: temperature, 59°C; pressure, 114 bars; groundwater composition,  $\text{Na}^+$ ,  $\text{HCO}_3^- \gg \text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^- > \text{Fe}^{2+}$ ,  $\text{SO}_4^{2-} > \text{F}^-$ , saturated with  $\text{SiO}_2$ ; pH, 9.6; and, Eh -0.48 V. With the exception of Eh, these are measured values. The low Eh value was inferred from knowledge of the minor mineral assemblage. Measured groundwater Eh values using inert indicating electrode ranged from -0.2 to +0.35 V. The major basalt primary mineral phases are laboradorite and augite with lesser amounts of titaniferous magnetite (SALTER 1981b). The major basalt secondary minerals are smectite clays, zeolites, and silica phases (SALTER 1981a). A significant portion of the basalt mesostasis exists as a silica-rich glass. Clays, silica, and tuff are present in interbed materials (BARNEY 1982).

The probable release pathway for groundwater migration from emplaced waste to the biosphere may be primarily horizontally along the repository level flowtop, or may follow a stair-step vertical path and transect multiple basalt flows and interbed strata until reaching a fresh water aquifer. Thus, a quantified description of radionuclide behavior along the release pathway may require knowledge of radionuclide geochemical reactions with basalt primary and secondary minerals, basalt mesostasis, and interbed materials in groundwater compositions representative of migration events under relevant geochemical conditions. This comprises a relatively complex system to be treated in the performance assessment analysis.

#### 2.2.2 Information to be Evaluated

The Site Characterization Report (SCR 1982) indicates (Chap. 6) that concentration limits imposed on all dissolved radionuclides by solubility constraint and radionuclide precipitation and/or sorption reactions, in both the near-field and far-field environments, will be important geochemical interactions for a repository in basalt. A considerable body of

information describing radionuclide sorption has been published by the BWIP (SALTER 1981a, SALTER 1981b, BARNEY 1982, SCR 1982) as well as calculated radionuclide solubility limits (EARLY 1982, SCR 1982). A data package compiling solubility and distribution coefficient values to be used for modeling calculations has been issued (SALTER 1983). The published Hanford Site information on sorption, solubility, and geochemical conditions has been reviewed and assessed in separate reports prepared by ORNL under another project supported by NRC/NMSS (KELMERS 1984d, BLENCOE 1985a, BLENCOE 1985b).

Under this project, we are giving emphasis to experimental evaluation of the radionuclide solubility and sorption information reported for the Hanford Site. Attention has been directed primarily to three of the "key" radionuclides, that is, those likely to dominate release calculations: neptunium, technetium, and uranium. The appropriateness of laboratory methods of simulating repository geochemical conditions was considered. Geochemical modeling activities addressed groundwater composition and radionuclide solubility limits. Progress during the preceding year has been reported (KELMERS 1984c). Some of the information contained in this annual progress report for FY 1984 has been described previously in published quarterly progress reports (KELMERS 1984a, KELMERS 1984b, KELMERS 1984c).



### 3. EXPERIMENTAL MATERIALS AND METHODS

#### 3.1 MATERIALS

##### 3.1.1 Basalt Samples

McCoy Canyon basalt was obtained from an outcrop at the same location as that for the Waste Isolation Safety Analysis Project (WISAP) studies (SERNE 1982). In the past, basalt from this outcrop has been designated as Flow E or Sentinel Gap basalt; it is currently identified as McCoy Canyon basalt.

Large chunks of the basalt were broken with a hammer into ~2-cm pieces. Contact of the basalt with the steel hammer was avoided by wrapping the basalt in canvas. The 2-cm pieces were hand picked to remove any pieces with weathered surfaces and also to remove canvas particles. Fines (<0.5 cm) were discarded. The hammer was used again, and the 2-cm pieces were reduced further to ~0.5 to 1 cm. The broken pieces were hand picked to remove canvas particles, and the fines (<2 mm) were discarded. The basalt was reduced to ~2 mm to 6 mm with a porcelain mortar and pestle. Final size reduction was made in a Siebtechnik crusher (an agate-lined vessel containing two concentric agate rings). The crusher agitates the vessel so as to sling the agate rings against the sides of the vessel and crush the basalt. The final fraction, 210 to 45  $\mu\text{m}$  (-70/+325 mesh), was screened thoroughly to remove <45 $\mu\text{m}$  fines.

For two different batches of McCoy Canyon basalt, the final size reduction to 210 to 45  $\mu\text{m}$  was made in an argon atmosphere. The crusher vessel was loaded with basalt inside a controlled-atmosphere glove box (argon containing <1 ppm  $\text{O}_2$ ), brought outside for crushing, and returned to the box to open the vessel and screen the crushed basalt. The basalt was protected from oxygen while it was outside the box by the weight of the vessel lid pressing on a tightly fitting gasket.

One ~3-kg piece of Cohasset basalt was obtained from Brookhaven National Laboratory. It was reduced to a 210- to 45- $\mu\text{m}$  particle size by the same procedure used for the McCoy Canyon basalt samples, except that the reduction of pieces 0.5 to 1 cm to 2 to 6 mm was made with a laboratory hydraulic press instead of a mortar and pestle. The basalt was wrapped in canvas when it was pressed to avoid contact with the steel platens. The final size reduction of the Cohasset basalt to 210- to 45- $\mu\text{m}$  particles was made in an argon atmosphere.

A sample of basalt from an outcrop of the Umtanum flow was also obtained. It was crushed to 0.5 to 2 cm as described above for McCoy Canyon basalt. Reduction to smaller sizes was made in the air in a porcelain mortar and pestle and then in an electrically driven agate mortar and pestle.

For column chromatographic investigations, the <45- $\mu\text{m}$ -sized fractions of both McCoy Canyon and Cohasset basalts were dispersed in demineralized

water, and the <2- $\mu$ m particles were removed by centrifugation. The 45- to 2- $\mu$ m fractions were washed with 100% ethanol and dried in an oven at 105°C.

Several 2-cm pieces of McCoy Canyon, Cohasset, and Umtanum basalt were embedded in plastic and polished for electron microprobe and scanning electron microscope examination.

### 3.1.2 Synthetic Groundwaters

Synthetic groundwaters GR-2 and GR-4 were prepared as described by SALTER (1981a; 1984). The compositions are given in Table 1. The groundwater compositions were varied in a few tests which were made to determine the effect of groundwater constituents on sorption behavior. The synthetic groundwaters were prepared by diluting concentrates of the components with freshly boiled double-distilled water. For use in anoxic redox condition tests, the groundwaters were prepared outside the controlled-atmosphere box and sparged with argon before being put into the box. Groundwaters were prepared separately for most tests and were not stored for more than a few days. The appropriate radioactive tracers were added to the groundwaters just before the start of the equilibration tests.

Table 1. Composition of synthetic groundwaters

Constituent	Concentration (mg/L)	
	GR-2	GR-4
Na <sup>+</sup>	225	334
K <sup>+</sup>	2.5	13.8
Ca <sup>2+</sup>	1.06	2.2
Mg <sup>2+</sup>	0.07	-
Cl <sup>-</sup>	131	405
CO <sub>3</sub> <sup>2-</sup>	59	
HCO <sub>3</sub> <sup>-</sup>	75	
Inorganic carbon		18.1
F <sup>-</sup>	29	19.9
SO <sub>4</sub> <sup>2-</sup>	72	4.0
SiO <sub>2</sub>	108	96.3
pH <sup>a</sup>	Reference <sup>b</sup> 10.0	9.7
	Measured <sup>c</sup> 9.7 to 9.9	9.1 to 9.3

<sup>a</sup>In pH units.

<sup>b</sup>Value for expected pH given in 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, Wash., 1981; P. F. Salter, Rockwell Hanford Operations, Richland, Wash., personal communication, 1984.

<sup>c</sup>Value measured in our solutions.

## 3.2 METHODS

### 3.2.1 Batch Contact

#### 3.2.1.1 Oxic Redox Condition

Batch contact tests were conducted in polypropylene tubes at a solution/solids ratio of 10. Control samples (solution but no basalt) were included in each series to determine radionuclide sorption by the tubes (if any). Triplicate test and control samples were run in most cases. The samples were agitated on an Eberbach shaker at about 65 cycles/min for the technetium, uranium, and strontium experiments, or on a rocking table at about 30 cycles/min for the neptunium experiments. Tests were made at room temperature (24 to 25°C) or in an air thermostat at 60°C. At the end of the equilibration period, the samples were centrifuged between 4100 to 5000 rcf for 10 to 30 min, and aliquots of the supernatant solutions were taken for counting. In some cases, portions of the aliquots were filtered through a 25,000 mol. wt cutoff Amicon filter to test for the presence of colloidal forms of the radionuclides.

Solvent extraction tests were made with neptunium and technetium to determine the valence state of the radionuclide remaining in the test solutions after contact or in the control samples. In the case of neptunium, the solutions were adjusted to 1 mol/L in HCl, and the neptunium(IV) was extracted with 1 mol/L thenoyltrifluoroacetone (TTA) in xylene. The aqueous phase was adjusted to 4 mol/L HCl, and neptunium(VI) was extracted with 10 vol % tri-*n*-octyl amine (TOA) in xylene; the unextracted neptunium was reported as neptunium(V) (MOORE 1957, KEDER 1960, KEDER 1962). For technetium valence analysis, the samples were extracted without pH adjustment with 0.05 mol/L tetraphenylarsonium chloride in CHCl<sub>3</sub>. The extracted technetium was reported as technetium(VII) and the technetium remaining in the aqueous phase was reported as reduced technetium of unknown valence (TRIBALAT 1953). For the oxic redox condition tests, the valence measurements were usually also made under oxic redox conditions.

#### 3.2.1.2 Reducing Redox Condition

A few reducing redox condition tests were made in which the test solutions were made 0.1 mol/L in hydrazine by the addition of hydrazine hydrate. These tests were conducted in the presence of air. Although we consider the use of hydrazine to be unsuitable for simulating low Eh repository redox conditions (KELMERS 1984a), these tests were made to evaluate the published methodology, which included the addition of hydrazine and the results obtained under these reducing conditions (SALTER 1981a, SALTER 1981b, BARNEY 1982). Other than the addition of hydrazine, the procedures for the reducing condition tests were the same as those for the oxic condition tests.

### 3.2.1.3 Anoxic Redox Condition

In an effort to more closely simulate the actual redox conditions that would exist in a basalt repository, we are conducting "anoxic" redox condition tests in which air is excluded as thoroughly as possible from the basalt, the groundwater, and all apparatus used in the experiments. The purpose is to allow the basalt and the radionuclide species in the synthetic groundwater to react without interference from added chemical reagents such as hydrazine or from oxygen introduced from air. Absence of oxygen does not constitute a reducing condition, but it does permit the basalt to act as a reductant if basalt is capable of doing so. If technetium(VII) or neptunium(V) are reduced to lower valences by basalt in experimental time periods of months or less, then these anoxic redox condition tests should show some valence reduction and concomitant removal-from-solution by sorption and/or precipitation processes involving the reduced species.

Our anoxic condition tests are carried out in an argon atmosphere in controlled-atmosphere glove boxes. Oxygen concentration levels of about 0.3 to 1 ppm in the argon are maintained by continuous circulation of the argon through an oxygen getter that is periodically regenerated by reduction with hydrogen. The oxygen level in the argon is monitored with a gas-phase oxygen analyzer. As discussed previously (KELMERS 1984b), this level of oxygen in the argon would correspond to an oxygen concentration level of about  $5 \times 10^{-10}$  mol/L in the groundwater solution at equilibrium.

Recently, we have also found that it is necessary to evacuate the plastic test tubes prior to their use in the anoxic batch contact experiments. To varying degrees, plastics are permeable to oxygen and therefore contain small amounts of oxygen from air. Removal of this air probably involves a diffusion process and could take considerable time, depending on the thickness and oxygen diffusion coefficient of the plastic. In experiments done under NRC/RESEARCH Project FIN No. B0462 (MEYER 1985b), we determined that the polypropylene tubes used in the batch contact experiments must be evacuated for at least 3 d before use in order to observe reduction of technetium(VII) by basalt. We now routinely evacuate all plastic equipment (equilibration tubes, centrifuge tubes, pipette tips, and counting tubes) before they are used in anoxic redox condition tests with any radionuclide.

Most of the experimental operations are carried out inside one of three controlled-atmosphere glove boxes. As described above, final grinding, sizing, and storage of the basalt samples are also done in the boxes. Groundwater solutions are prepared outside the boxes by dilution of concentrates of the groundwater components with freshly boiled double distilled water. The groundwater solutions are then sparged with argon and placed inside a glove box before being traced with the appropriate radionuclides. All weighing, solution pipetting, equilibration, centrifuging, valence distribution measurement, and sampling for counting is done inside a controlled-atmosphere box. Transfers of samples between boxes are made in sealed Mason jars.

The temperature inside the controlled-atmosphere boxes is usually about 27°C, and most of the anoxic tests have been made at this temperature. A constant temperature chamber has been installed in one of the controlled-atmosphere boxes for batch contact experiments at elevated temperatures. The plastic chamber encloses the top of a shaker and is equipped with a heater and thermistor probe that are controlled outside the box. The batch contact tests at elevated temperatures (~60°C) are made inside the plastic chamber, while other operations such as weighing, pH measurement, centrifugation, and sampling are conducted at the ambient temperature of the controlled-atmosphere boxes.

### 3.2.2 Counting Techniques

The concentrations of  $^{89}\text{Sr}$ ,  $^{95}\text{Tc}$ , and  $^{235}\text{Np}$  were measured by gamma-counting techniques; the  $^{89}\text{Sr}$  peak at 0.909 MeV, the  $^{95}\text{Tc}$  peak at 0.204 MeV, and the three  $^{235}\text{Np}$  peaks near 100 keV were counted. Uranium concentrations were measured by liquid scintillation counting of the  $^{233}\text{U}$  alpha peaks at 4.82 and 4.78 MeV.

### 3.2.3 Column Chromatography

A column chromatographic system consisting of a high-pressure pump, injector, temperature adjustable column oven, fraction collector, UV detector, and high-resolution germanium gamma detector with an automatic sample changer was established. Glass columns, 3 mm ID and 250 mm long, were packed by pouring the oven-dried 45- to 2- $\mu\text{m}$ -sized McCoy Canyon basalt through a small polypropylene funnel attached to the top of the column. The weight of the basalt in the column was 2.75 g; the porosity was 0.41, with a bulk density 1.56 g/cm<sup>3</sup>.

Each column was connected to the chromatographic system and flushed with eluting solution for 3 h. The eluting solution was synthetic groundwater water GR-4 (see Sect. 3.1.2) preequilibrated with mass-spectrographic-grade helium gas. Preliminary tests with acetone, which does not absorb, indicated that the packed columns are in operable condition with a flow rate of 1 mL/min and a back pressure of <10 MPa at 25°C. Radioactive tracers were not used in these tests.

The groundwater, traced with tritiated water and  $^{95}\text{Tc}(\text{VII})$  or  $^{239}\text{Np}(\text{V})$ , was loaded through an injection loop above the column and then eluted with the GR-4 solution. The column experiments were conducted at temperatures of 25, 45, 60, and 80°C to measure thermal effects under repository conditions. The solution eluted was collected at a flow rate of 0.96 mL/min (equivalent to 72 km/year) in liquid scintillation vials with a fraction collector. After counting the activity of each fraction using a liquid scintillation spectrometer for  $^3\text{H}$  and  $^{233}\text{U}$  and a Ge(Li) detector for  $^{95}\text{Tc}$  and  $^{239}\text{Np}$ , the elution curves were constructed by plotting "Fraction of Applied Activity (A/At) vs Volume Eluted" and a breakthrough curve "Cumulated Fraction of Activity Applied (C/At) vs Volume Eluted", where A = activities of each fraction, C = cumulated fraction activity, At = total activity of spike loaded on the column.

After elution, the column was marked at 10-mm intervals, and each section was removed and counted to determine the amount of radioactivity remaining on the column.



#### 4. CHARACTERIZATION OF BASALT SAMPLES

##### 4.1 MINERALOGICAL AND CHEMICAL ANALYSES

A mineralogical and chemical characterization of the three basalt samples that have been used in the radionuclide geochemical evaluation studies at ORNL was completed. These samples were from three candidate repository horizons: the Cohasset, McCoy Canyon, and Umtanum flows. Emphasis was given to quantifying mineralogical and chemical differences between the samples; this information is useful for aiding interpretation of differences observed in radionuclide sorption experimental results with the different samples. The three basalt samples were acquired through various sources (MEYER 1985b, KELMERS 1984b and 1985) and were received without accompanying lithologic descriptions. Information regarding the sample location and textural unit (colonnade vs entablature) within the respective flows was not available.

Microanalysis of the samples was conducted using an optical microscope with point counting attachment, an electron microprobe with both wavelength and energy dispersive x-ray spectrometers, and a scanning electron microscope. Samples were prepared as polished thin sections for optical microscopy. Small chips (2 x 2 x 2 cm) were cut, embedded in epoxy resin, and polished for electron microscopy and spectrometry analyses.

The basalt samples had an aphanitic (microcrystalline) texture with varying grain sizes of less than 0.5 mm (Fig. 1). Primary mineral phases such as lath-shaped plagioclase and subequant tabular pyroxene grains were interlocked together by interstitial glassy mesostasis. Subhedral or dendritic magnetite, hollow acicular apatite, and granular iron sulfide (pyrite?) grains were distributed throughout the rock but were more frequently associated with the glassy mesostasis. Varying sizes and shapes of vesicles and microscopic cooling fractures were common in these samples.

The grain sizes of plagioclase and pyroxene in the McCoy Canyon and Cohasset samples (Fig. 1A and C) were coarser than those of the Umtanum sample (Fig. 1E). The point count results indicate that plagioclase is the most abundant phase (46%) in the McCoy Canyon sample, while mesostasis is the most abundant phase (36 to 41%) in the Umtanum and Cohasset samples (Table 2). The amounts of pyroxene were similar among all samples (25 to 30%). The plagioclase grains within a given sample had slightly different chemical compositions, particularly with respect to the amounts of sodium relative to calcium in the aluminosilicate matrix, but were within the compositional range of sodic anorthites ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). Compositional difference of the plagioclases among the samples were within the variations typically expected among the individual grains within a given sample. The pyroxene phase had significant compositional variations among the grains. Augite appears to be the predominant clinopyroxene in the samples. The compositional variation (iron vs magnesium) indicated that the iron-rich pigeonite phase occurs as a rim of augite grains. The relative abundance of the two phases, however, was not determined in this investigation.

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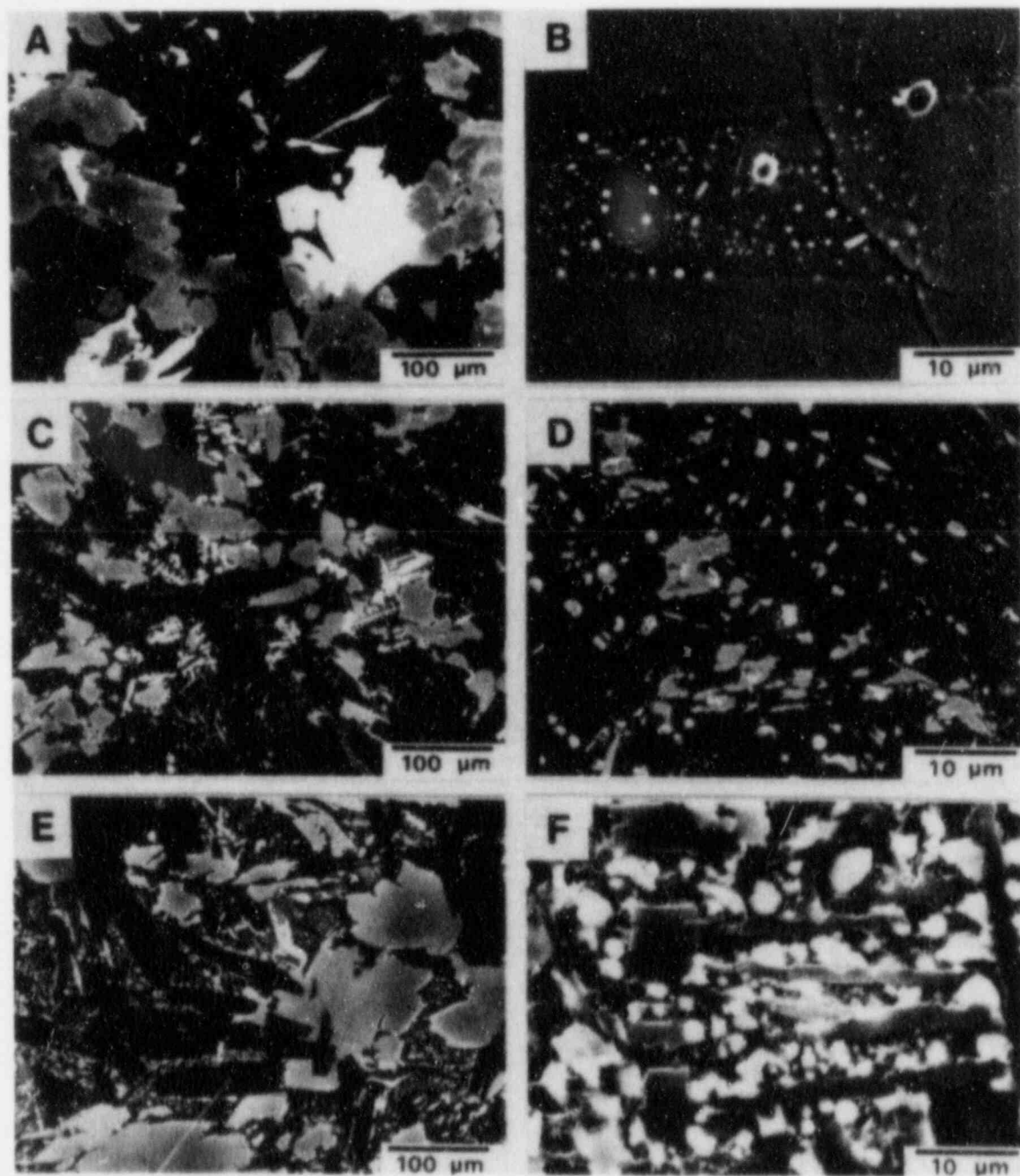


Fig. 1. Scanning electron micrographs showing different mineral phases in polished surface of McCoy Canyon (A and B), Umtanum (C and D), and Cohasset (E and F) basalt samples.

Table 2. Volumetric distribution of primary components of the McCoy Canyon, Umtanum and Cohasset basalt samples<sup>a</sup>

Component	Distribution (%)		
	McCoy Canyon	Umtanum	Cohasset
Plagioclase	46 ± 5 <sup>b</sup>	29 ± 4	27 ± 4
Pyroxene	30 ± 3	25 ± 4	25 ± 9
Mesostasis	20 ± 7	36 ± 6	41 ± 7
Magnetite	4 ± 1	10 ± 3	7 ± 2

<sup>a</sup>Total point counts = 927.

<sup>b</sup>Mean ± 1 standard deviation, with n = 3.

Interstitial glassy mesostasis was another major constituent of all the basalt samples. The mesostasis is formed from the residual liquid left over after crystallization of the plagioclase and pyroxene and is composed of glass and groundmass of amorphous and microcrystalline minerals (Fig. 1B, 1D, and 1F). In the McCoy Canyon sample, the mesostasis was dominated by glass with limited amounts of microcrystalline magnetite, apatite, and pyrite inclusions (Fig. 1B). The polished surface of the glass was smooth and solid. The microcrystalline granular magnetite was commonly associated with mesostasis, but relatively large subhedral to blade shape magnetite was associated with pyroxene phases. On the other hand, the mesostasis of the Umtanum sample had aphanitic texture with confused microcrystalline aggregates consisting of plagioclase, iron-rich grains and glass (Fig. 1D). The magnetite in the mesostasis had cruciate and dendritic patterns (Fig. 1C). The mesostasis of the Cohasset sample was dominated by numerous blebs (globules) loosely packed in open channels of the glass (Fig. 1F). The micron-to-submicron size globules (likely formed through exsolution of residual liquid) appear to be rich in iron but extremely heterogeneous in terms of chemical composition. Magnetite occurred as both small dendritic and subhedral forms in the mesostasis (Fig. 1E).

As suggested by the differences in the mineralogical composition, there were significant differences in the chemical composition of the mesostasis among the samples but only minor differences in chemical composition of whole (bulk) rock analyses (Table 3). The results of whole-rock analysis indicated that both the Umtanum and Cohasset samples had about 1% higher FeO content (all Fe present expressed as FeO) than the McCoy Canyon basalt sample. The Cohasset sample had ~1% higher CaO and MgO and ~3% lower SiO<sub>2</sub> than the others. However, the differences of SiO<sub>2</sub> and FeO among the mesostasis of the samples was as much as 11 and 12%, respectively. A high SiO<sub>2</sub> value indicates a high glass content, while a high FeO indicates high microcrystalline and/or glassy iron-rich minerals in the mesostasis. Some of the elements such as sodium and the trace elements were intentionally excluded in the calculation of the major oxide contents due to large uncertainties in the analyses.

in the mesostasis. Some of the elements such as sodium and the trace elements were intentionally excluded in the calculation of the major oxide contents due to large uncertainties in the analyses.

The mesostasis in the McCoy Canyon sample had the highest  $\text{SiO}_2$  and the lowest FeO contents, reflecting the high-glass and low-magnetite contents observed. In the mesostasis of the Umtanum sample, the amount of  $\text{SiO}_2$  was lower and FeO was higher than those in the McCoy Canyon mesostasis, although both mesostasis phases had higher  $\text{SiO}_2$  and lower FeO contents than those in the corresponding whole rock. The most significant aspect of the results was the chemical composition of mesostasis in the Cohasset sample. The FeO and  $\text{TiO}_2$  contents were not only the highest among the samples, but also were higher in the mesostasis than in the whole sample. The mesostasis composition of the Cohasset sample suggests that the globules which exsolved from the interstitial glass have a composition similar to the crystalline magnetite. A qualitative analysis (x-ray dot mapping) of phosphorous, fluorine, and sulfur distribution displayed a close association of these elements with the mesostasis of the samples (KELMERS 1984b).

Table 3. Chemical composition of bulk and selected mesostasis areas of the McCoy Canyon, Umtanum, and Cohasset basalt samples<sup>a</sup>

	Composition (%)					
	McCoy Canyon		Umtanum		Cohasset	
	Bulk <sup>b</sup>	Mesostasis <sup>c</sup>	Bulk <sup>b</sup>	Mesostasis <sup>c</sup>	Bulk <sup>b</sup>	Mesostasis <sup>c</sup>
$\text{SiO}_2$	56.1 ± 0.7	67.4 ± 3.3	56.6 ± 0.4	63.6 ± 2.1	53.6 ± 0.3	56.8 ± 2.6
$\text{Al}_2\text{O}_3$	18.0 ± 0.3	19.2 ± 3.3	17.3 ± 0.1	17.8 ± 3.3	17.6 ± 0.4	14.8 ± 2.3
CaO	7.7 ± 0.1	4.0 ± 1.9	6.8 ± 0.1	4.6 ± 1.3	8.6 ± 0.2	5.1 ± 1.1
MgO	3.6 ± 0.4	d	2.9 ± 0.3	d	4.4 ± 0.5	0.2 ± 0.3
FeO <sup>e</sup>	11.1 ± 0.3	3.7 ± 2.4	12.1 ± 0.2	8.9 ± 2.1	12.5 ± 0.4	15.9 ± 2.9
$\text{TiO}_2$	1.5 ± 0.1	0.8 ± 0.4	2.1 ± 0.1	1.4 ± 0.5	1.9 ± 0.1	3.6 ± 0.9
$\text{K}_2\text{O}$	1.7 ± 0.1	4.0 ± 1.4	1.8 ± 0.1	3.0 ± 0.7	1.2 ± 0.1	2.8 ± 0.4
$\text{PO}_4$	0.3 ± 0.1	0.9 ± 0.9	0.4 ± 0.1	0.7 ± 0.3	0.2 ± 0.1	0.8 ± 0.2

<sup>a</sup>Data should be used only for comparative purposes among the samples.

<sup>b</sup>Mean ± 1 standard deviation, with n = 4.

<sup>c</sup>Mean ± 1 standard deviation, with n = 10.

<sup>d</sup>Not detectable (<0.1%).

<sup>e</sup>All Fe present is expressed as FeO.

Several samples having an edge which appeared to have been altered by contact with groundwater or exposure to ambient environmental conditions were selected in order to look for microfracture-filling secondary minerals. A fracture starting from the weathered surface and extending ~3 mm toward the interior was found in a piece of the Cohasset sample (Fig. 2A). The fracture was loosely packed with secondary minerals, small granular (zeolite?) and coated (smectite?) materials (Fig. 2B), and partially altered fragments of primary minerals (Fig. 2C). Unaltered fractures without filling materials were also observed in an interior part of the sample (Fig. 2D). For the sorption experiments, small pieces of basalts were selected to avoid pieces having a weathered surface before the final size reduction (as described in Sect. 3). Thus, the material used in the batch and column experiments should not have significant amounts of such alteration products.

#### 4.2 COMPARISON WITH PUBLISHED INFORMATION

The mineralogy and petrography of the candidate horizons have been studied in detail by the BWIP and the findings published in various reports (BENSON 1979, NOONAN 1980, TEAGUE 1980, LONG 1981, SCR 1982, BENSON 1982, LONG 1983, ALLEN 1983). The recently published report that identifies the candidate repository horizons (LONG 1983) concluded the following:

In spite of the general similarities among Grande Ronde Basalt flows, there are slight differences among the candidate horizons. The most significant differences are grain size, abundance of glass, mesostasis and interstitial alteration products, as well as relative abundance of secondary minerals in fracture fillings. It must be stressed, however, that all four flows (Rocky Coulee, Cohasset, McCoy Canyon, Umtanum) are more similar mineralogically than they are different, and any benefit to radionuclide isolation reflecting the differences in glass, mesostasis, and alteration product abundances is likely to be small.

In comparison with other factors such as geophysical and geohydrological parameters, the geochemical and mineralogical factors may play insignificant roles for selection among the flows for the repository horizon. However, the significance of mineralogical and geochemical differences between the flows should not be underestimated for understanding geochemical processes, including radionuclide retardation, mineral weathering, and autogenic in the repository near-field and far-field environments. While effects of the observed morphological, mineralogical, and compositional differences among the samples on the radionuclide sorption properties have not been directly determined experimentally, one might expect to have higher sorption values when the ferrous iron-rich mesostasis of the Cohasset and Umtanum samples is in contact with redox-sensitive radionuclides such as neptunium(V) or technetium(VII). Therefore, the mesostasis could be not only a predominant source of solubilized elements in the groundwater, but also a predominant sorption site for selected radionuclides which undergo reduction and chemisorption reactions.



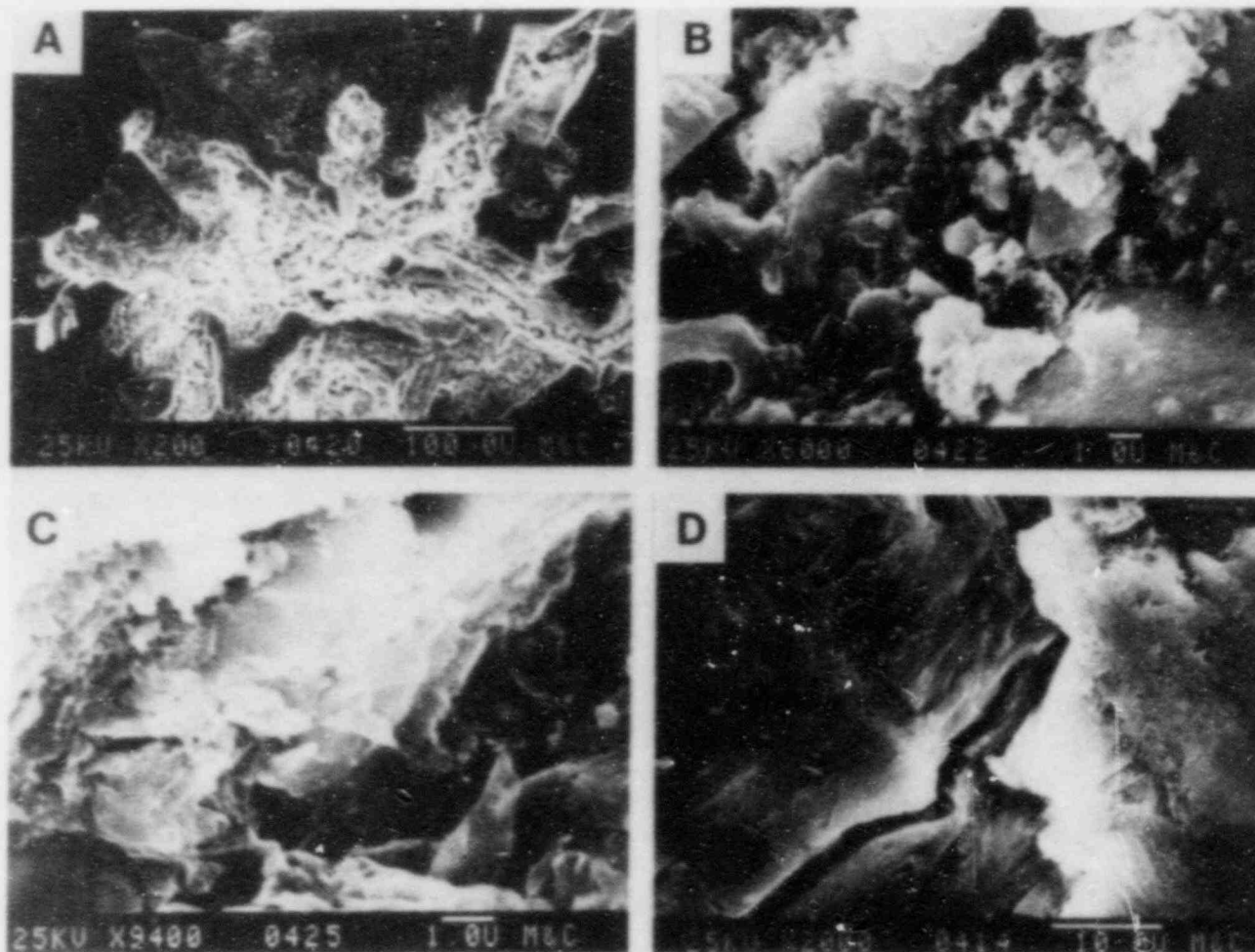


Fig. 2. Scanning electron micrographs of Cohasset basalt sample showing (Unit of bars =  $\mu\text{m}$ ); (A) microfracture with fracture filling secondary minerals, (B) higher magnification of secondary minerals, (C) partially weathered fracture surface, and (D) unaltered microfracture.



Direct comparison between our results and the published data is difficult because our results are based on a single sample from each flow. Furthermore, the origins of the samples, in terms of intraflow structures, were not known. The microscopic analyses indicated that our McCoy Canyon sample might have been obtained from a colonnade zone, and the Cohasset and Umtanum may have been obtained from entablature zones. The abundance of mesostasis and dendritic iron oxide grains observed in the Cohasset and Umtanum samples are characteristics of entablature material formed under a high cooling rate (LOFGREN 1980) and suggest that these samples may have been obtained from entablature zones. The presence of crystalline euhedral magnetite and acicular apatite with a lesser amount of mesostasis suggests that our McCoy Canyon sample may be colonnade material formed under a slower cooling rate. Similar morphological and mineralogical differences were observed from a colonnade and entablature sample with the Umtanum flow (ALLEN 1983).

Modal distributions of primary components in our McCoy Canyon and Cohasset samples were within the range of the published data for corresponding textural units in the individual flows; the Umtanum sample was closer to that of colonnade material rather than entablature material, although the morphological features suggested that our sample was a typical entablature (Table I-2 in LONG 1983). The grain sizes of the Cohasset and McCoy Canyon samples were coarser than the Umtanum flow sample, regardless of their interflow positions. The glass has been suggested as an inherently metastable basaltic phase and likely to be most chemically reactive with groundwater (APTED 1982). Furthermore, the crystalline and amorphous groundmass of the mesostasis can be expected to play an important role as a sorption medium for radionuclides. Therefore, it is important to consider the possible impact of differences in morphology, mineralogy, and chemical composition of the mesostasis among the basalts on radionuclide sorption or apparent concentration limit results.

The chemical composition of the bulk and glassy mesostasis of candidate repository horizons was reported by LONG (1983). The report concluded that compositional variations of bulk samples within individual and among the basalt flows was minor. Significant variations of major oxides in glass analyses among the flows were noted, but the variations within individual flows were as great as variations among the flows. Minor differences were also observed between the bulk chemical compositions of our samples and the published values. Our values were within the ranges of their maximum and minimum values despite the absence of  $\text{Na}_2\text{O}$  values for our data. Comparison of the chemical analysis results for glass is impossible because our results represent a composition of both microcrystalline and glass material in the glassy mesostasis while the published results represent only glass phase.

With respect to the comparison of sorption ratio values measured with the different basalt samples in our work (KELMERS 1984a, KELMERS 1984b, KELMERS 1985) as well as results previously published for basalt samples from different flows (SALTER 1981b), the results of this mineralogical characterization study suggests caution in ascribing differences observed in sorption ratios with samples from different flows as being characteristic of the flows.

Rather, it seems equally plausible, at least for radionuclides such as technetium and neptunium that undergo reduction and chemisorption reactions, that the observed difference in sorption ratios could result from intra-flow variation of colonnade vs entablature composition. In both our recent work and that previously published (SALTER 1981b), the textural unit from which the basalt samples were obtained was not identified. A significant shortcoming of the information for site performance assessment may be the lack of knowledge of intraflow vs interflow differences in sorption behavior.

## 5. TECHNETIUM

### 5.1 APPROACH TO HANFORD SITE INFORMATION EVALUATION

Technetium has been identified as one of the key radionuclides in a nuclear waste repository in basalt (BARNEY 1980). This conclusion was based on the quantity of technetium in the high-level waste, the potential release from waste and migration through the repository to the accessible environment, and the biological hazard of technetium. The published information relative to the Hanford Site on technetium solubility in synthetic groundwaters and sorption onto basalts, secondary minerals, and interbed materials is summarized in Table 4.

Table 4. Summary of technetium solubility and sorption values published for the Hanford Site

	Redox condition		Reference
	Oxidizing	Reducing	
Solubility, mol/L:			
	-----	$10^{-12}$	SALTER 1981a
	-----	$>10^{-14}$	EARLY 1982
	-----	$>10^{-14a}$	SALTER 1983
	-----	$10^{-9b}$	SALTER 1983
	-----	$10^{-5c}$	SALTER 1983
Sorption, L/kg:			
Basalt	0	29	SCR 1982
	0 to 7	29	SALTER 1981c
Secondary minerals	0	50	SCR 1982
	0	-----	SALTER 1981b
Interbed	0	70	SCR 1982
	2 to 3	46 to 104	BARNEY 1982

<sup>a</sup>Calculated solubility for Eh = -0.3 V.

<sup>b</sup>Highest value calculated from observed repository conditions multiplied by a factor of 10.

<sup>c</sup>Highest concentration value observed in sorption or solubility experiments in synthetic Grande Ronde groundwaters using 0.05 M hydrazine (published method of trying to simulate repository reducing conditions).

For oxidizing redox conditions, the various reports, including the Site Characterization Plan (SCR 1982), provide no estimate of the solubility limit of technetium, and recommend a sorption distribution coefficient of 0 L/kg (i.e., no sorption) for basalt, secondary minerals, and interbed materials. The pertechnetate anion,  $\text{TcO}_4^-$ , is the form of technetium in the +7 valence expected under oxidizing conditions in Grande Ronde groundwater. All pertechnetate salts are highly soluble in aqueous solutions, and pertechnetate anions are poorly sorbed onto geologic materials. One reference (PALMER 1981) has reported low sorption of pertechnetate under oxic conditions onto basalt. The reported mean distribution coefficient of  $4.7 \pm 8.9$  L/kg is a typographical error, and the correct value for that reference should be  $1.6 \pm 0.4$  L/kg (MEYER 1985a). Although not explicitly stated in the Site Characterization Report (SCR 1982), it would appear that no technetium retardation because of limiting solubility in groundwater or sorption onto repository host rocks is expected under oxic conditions at the Hanford Site.

According to the published information (SALTER 1981a, SALTER 1981b), pertechnetate dissolved in groundwater is expected to be reduced to technetium(IV), and the stable solid  $\text{TcO}_2$  is expected to precipitate under the reducing conditions predicted for groundwater under the repository environment. The available thermodynamic data for technetium(IV) are reported by Early (1982) to be limited and suitable only for estimating a limiting solubility of  $>10^{-14}$  mol/L, while Salter (1981a) reports a solubility of  $10^{-12}$  mol/L. These values of the solubility were apparently calculated from the equilibrium between  $\text{TcO}_2$  and  $\text{TcO}_4^-$  (CARTLEDGE 1955) for the Eh values expected under repository conditions from the expression

$$\text{Eh} = 0.738 + (\text{RT}/3\text{F}) \ln ([\text{TcO}_4^-] [\text{H}^+]^4),$$

where  $[\text{TcO}_4^-]$  is the activity of the pertechnetate ion and  $[\text{H}^+]$  is the activity of the hydrogen ion. Calculation of total solubility from this equation does not take into account the possibility of any significant solubility of technetium(IV) species. The pertinent data applicable to the hydrolysis and solubility of technetium(IV) have been reviewed recently by several authors (RARD 1983; PAQUETTE 1980; MEYER 1985b). When soluble technetium(IV) species are considered, one would expect that the total solubility would be greater than  $10^{-12}$  mol/L because it would include hydrolytic species of technetium(IV) in equilibrium with solid  $\text{TcO}_2$ . However, the existing data on hydrolysis of technetium(IV) species have not been adequately confirmed to allow prediction of total solubility with confidence. If the data in the literature are used (MEYER 1985b), then one can calculate an estimated solubility on the order of  $10^{-8}$  to  $10^{-6}$  mol/L of technetium(IV). The calculation is quite sensitive to the value selected for the solubility product of  $\text{TcO}(\text{OH})_2$  — the form of hydrated  $\text{TcO}_2$  selected for calculation of the solubility product (RARD 1983; MEYER 1985b).

From the published information, it appears that technetium retardation in the far field at the Hanford Site is expected to result from the low solubility of reduced technetium calculated under the anticipated site

redox potential (EARLY 1982). Additional retardation of reduced technetium due to moderate sorption onto basalt, secondary minerals, and interbed materials also is apparently expected under far-field conditions (SCR 1982).

## 5.2 EXPERIMENTAL RESULTS

### 5.2.1 Batch Results

The most significant set of results during the past year has been the measurement of technetium sorption onto McCoy Canyon basalt under highly anoxic redox conditions, and the demonstration that under these experimental conditions small but consistent values of  $R_s$  are obtained. We observed significant sorption only after we took the precaution of evacuating the plastic test tubes for three or more days as described above in the experimental section (Sect. 3.2.1.3). The results of these experiments are summarized in Table 5.

It appears from these results that the  $R_s$  values tend to increase by a factor of about 2 to 3 as the contact period is increased from 14 to 50 d; that is, steady state is not attained in 14 d. There appears to be no effect of increasing the contact temperature.

Table 5. Sorption ratios for technetium onto McCoy Canyon basalt under anoxic redox conditions<sup>a</sup>

Initial concentration Tc (mol/L)	Rs (L/kg)		
	14-d, 60°C	50-d, 27°C	50-d, 60°C
10 <sup>-12</sup>	3.5 ± 0.2	8.3 ± 0.1	11.1 ± 5.3
10 <sup>-8</sup>	5.5 ± 0.7	12.3 ± 1.0	9.9 ± 2.3
10 <sup>-6</sup>	4.0 ± 0.4	8.5 ± 0.2	3.6 ± 4.3
10 <sup>-4</sup>	~0	~0	~0
10 <sup>-3</sup>	~0	~0	~0

<sup>a</sup>Batch contact tests with synthetic groundwater GR-2 and basalt ground in argon. Values for  $R_s$  of ~0 in the table indicate that the precision of the <sup>95m</sup>Tc counting (difference between initial and final concentration) was insufficient to determine the extent of sorption. Some sorption of Tc probably occurred.

Sorption isotherms for these data are shown in Fig. 3. These isotherms do not indicate an apparent concentration limit. In order to attempt to determine the shape of the upper portion of the isotherm, we are conducting additional experiments in the range of initial concentrations 10<sup>-6</sup> to 10<sup>-4</sup> mol/L pertechnetate.

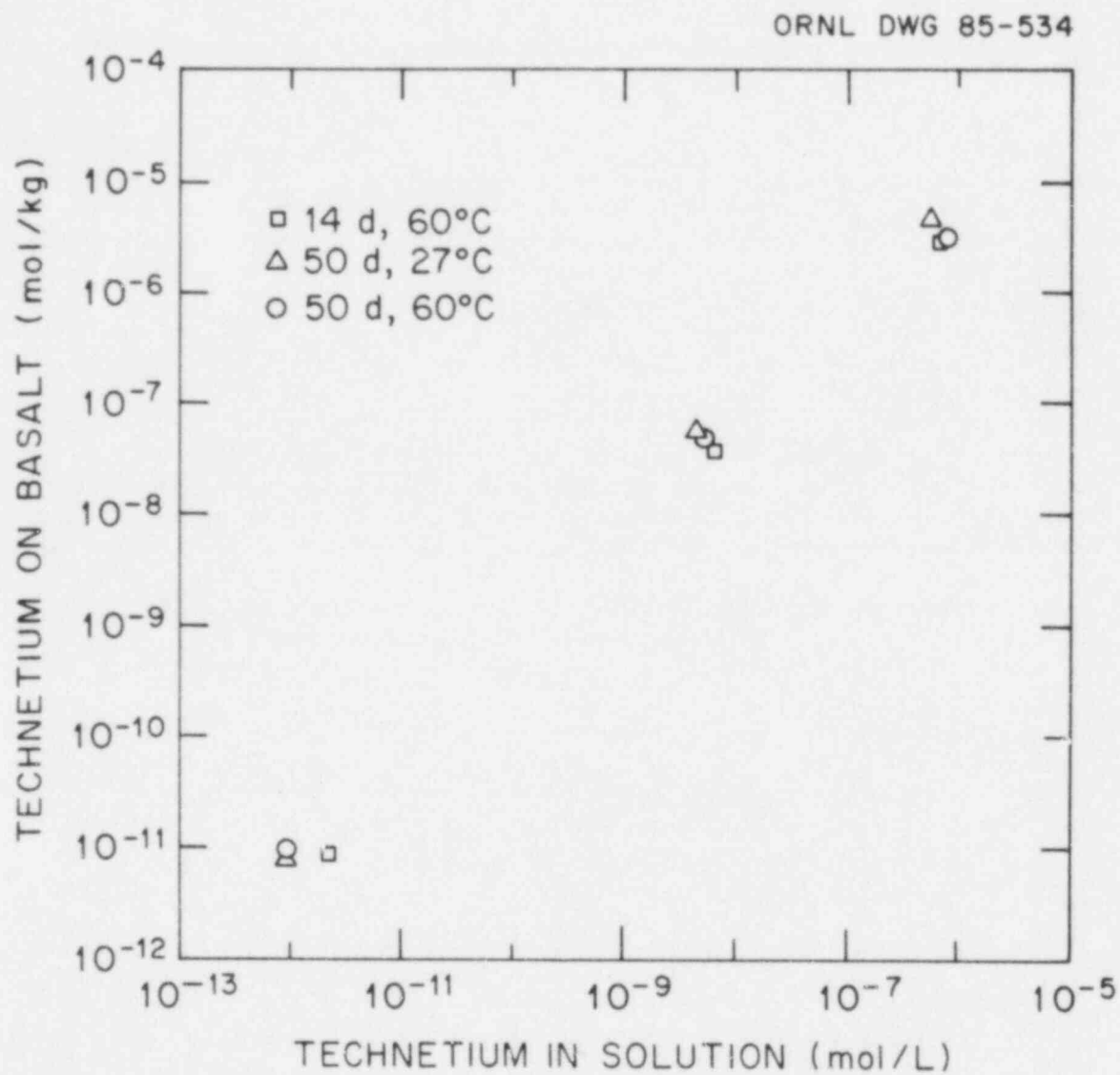


Fig. 3. Sorption of Tc on McCoy Canyon basalt; anoxic redox condition, GR-2.



After each experiment, a portion of the centrifuged solutions was analyzed for the valence distribution of the technetium. In general, for those cases where sorption of technetium was observed, we found reduced technetium in the final solution. For the runs that were initially  $10^{-6}$  mol/L in pertechnetate, we found concentrations of reduced technetium on the order of  $10^{-8}$  to  $10^{-7}$  mol/L after contact. It is difficult to say whether these concentrations are for true solution species of reduced technetium, but the data were obtained from centrifuged samples which should preclude the presence at least of larger colloidal material. It is interesting that these solution concentration values are in the range of the predicted solubilities of reduced technetium, as noted earlier.

In some earlier batch sorption tests with McCoy Canyon basalt, a greater sorption of technetium was observed when synthetic groundwater formulation GR-4 was used instead of GR-2. Results of these experiments are shown in Table 6 for technetium sorption onto basalt at 27°C using groundwater GR-4 instead of GR-2. A comparison of the various BWIP groundwater formulations has been reported previously [KELMERS (1985), Table 7]. Compared to GR-2, GR-4 has about 3 times the concentration of chloride ion and about 18 times less sulfate ion. Carbonate and silica compositions of the two are roughly the same. Groundwater GR-4 may be considered to be 0.01 M NaCl, containing silica, carbonate ions, and small amounts of  $K^+$ ,  $Ca^{2+}$ ,  $F^-$ , and  $SO_4^{2-}$ . In order to investigate the effects of groundwater components, a number of experiments were performed with solutions in which some of the components of GR-4 had been deleted (Table 6).

Table 6. Technetium sorption from simulated GR-4 groundwater and other solutions onto McCoy Canyon basalt<sup>a</sup>

GR-4 formulation	pH		Rs (L/kg)	Reduced Tc in contacted solution	
	Initial	Final		% of total	Total (mol/L)
Complete	9.7	9.3	$10.9 \pm 1.0$	7.8	$6.9 \times 10^{-14}$
No silica	10.2	9.3	$13.4 \pm 2.2$	9.6	$7.1 \times 10^{-14}$
	9.7	9.0	$27.5 \pm 3.5$	21.3	$9.6 \times 10^{-14}$
No carbonates	10.8	9.9	$9.9 \pm 1.5$	13.7	$12.2 \times 10^{-14}$
	9.7	9.1	$22.2 \pm 2.0$	11.4	$6.2 \times 10^{-14}$
No silica or carbonates	9.7	8.6	$53.1 \pm 8.9$	30.9	$6.8 \times 10^{-14}$

<sup>a</sup>Test conditions: anoxic atmosphere, 27°C, -70/+325 mesh McCoy Canyon basalt crushed and stored under argon, 14-d contact period, initial Tc  $10^{-8}$  M, centrifuged 30 min at 5000 rcf in argon. About 0.4 g of basalt was used with 4 mL of groundwater. The results were adjusted for a small loss (2-10%) of Tc onto the test tubes, as determined by control experiments.

For all of these groundwater compositions, we observed significant removal of technetium from solution by the basalt. However, for the solution that did not contain carbonate and silica, the sorption ratio was about five times that for GR-4. Smaller increases were noted when only either carbonate or silica were removed. There also appears to be a correlation between the final pH and the extent of sorption. Comparing the four samples (initially at pH 9.9), the value of  $R_s$  increased a factor of over 5 for a total pH change of 1.3 (pH 9.9 to 8.6). At this time, we do not know whether these groundwater composition effects were due to the final pH or to the absence of certain components of GR-4. Thus, the correlation with final pH could be the result of attack on the basalt (dissolution of the glass component?) which either released some species containing ferrous iron into the solution or made ferrous iron accessible at the surface of the basalt.

#### 5.2.2 Column Results

A series of column chromatographic experiments were carried out (KELMERS 1984b) to directly measure the technetium retardation factor under oxic redox conditions and to confirm the sorption ratio measured in our batch contact experiments. Tests at 25 and 70°C and flow rates of 0.48 and 0.96 mL/min yielded highly symmetric  $^{99}\text{Tc}$  elution peaks that coincided with the tritium peak from HTO; that is the retardation factor was 1, corresponding to a sorption ratio of 0 L/kg. No evidence for retardation of pertechnetate by McCoy Canyon basalt was observed in these oxic condition experiments. This result is in good agreement with our batch contact experimental results and with the general conclusion expressed by others that pertechnetate is not strongly sorbed by geologic materials.

### 5.3 DISCUSSION AND CONCLUSIONS

The sorption of technetium onto basalt is highly dependent upon a number of experimental parameters. For oxic redox conditions, there is general agreement among all investigators that little or no sorption of technetium is observed. Furthermore, the oxygen has to be removed with great care from the experimental apparatus in anoxic redox condition experiments with basalt for any sorption to be observed. (Sorption is referred to here in the general sense of technetium removal-from-solution by any process.) As we have shown in the experiments performed during the past year, when the oxygen was carefully removed to the low levels that our controlled-atmosphere boxes are capable of maintaining (see Sect. 3.2.1.3), moderate sorption on basalt was observed.

The link between these observations and the geochemical processes that produce these observations can best be elucidated by additional research regarding the mechanism of reduction and sorption of technetium onto basalt. In work being done under NRC FIN No. B0462, some of these mechanisms are being investigated. In that work (MEYER 1985b), it was concluded that the reduction of technetium probably is a heterogeneous reaction occurring at or on the surface of the basalt, rather than a homogeneous reaction occurring within the groundwater solution. Such a heterogeneous

reaction could first require a pertechnetate sorption step and then electron transfer (reduction) steps from the ferrous ions in the basalt to the sorbed technetium(VII) species. Because negative ions are not generally strongly sorbed by most minerals, the concentration of sorbed technetium(VII) on the surface is not likely to be high. For reduction to technetium(IV), a three-electron transfer would be required. If the basalt is covered by a thin passivating (nonconducting) layer due to oxidation or alteration, then the electron transfer could be hindered. The low concentration of  $\text{TcO}_4^-$  on the surface, the necessity for a three-electron reduction, and the presence of a passivating layer — all would tend to decrease the rate and/or extent of the technetium reduction reaction by basalt. The formation of this hypothetical passivating layer would likely be greatly influenced by small amounts of oxygen and subtle changes in groundwater composition. In the experiments with GR-4 (Table 6), we noted that GR-4 without silica or carbonates was essentially equivalent to a dilute NaCl solution containing small amounts of other ions. When this solution was used in the batch contact experiments, the sorption ratio was significantly greater than that for GR-4. In experiments done under NRC FIN No. B0462, NaCl solutions were often used in sorption experiments with both neptunium and technetium; the resulting sorption ratios were routinely much higher than those obtained in similar tests with synthetic groundwater formulations. Possibly, aggressive solution components like NaCl attack a passivating layer and expose ferrous ions; this behavior could explain the observation that sorption is much greater or faster from NaCl solutions.

The extent of sorption observed in a given experiment thus depends on a number of factors. We noted a slow but steady increase in  $R_s$  with time, and therefore the kinetics of the reaction likely is an important parameter. The kinetics might simply depend on the rate at which the passivating layers are attacked and the ferrous ions released or exposed. Experiments presented previously (KELMERS 1984c) showed that heat treatment of basalt in argon and high-temperature treatment with  $\text{H}_2$  will significantly increase the sorption rate. Such treatments could eliminate a passivating layer.

The identification of technetium as a key radionuclide, combined with the uncertainties expressed above in both the calculated solubility values and the measured sorption values, suggest that additional research may be needed to clarify those portions of the thermodynamic data and the general solution chemistry applicable to the proposed geochemical reactions. The complexity of the chemistry of reduced technetium, coupled with the very limited number of critical measurements available in the literature, necessitates that this research effort be experimental in nature and that apparent concentration limits and sorption values in addition to thermodynamic solubility products and stability constants are needed. The emphasis on technetium retardation by reduction at the Hanford Site to insoluble technetium(IV) species in the Site Characterization report (SCR 1982) indicates that the greatest concern by NRC should focus on solubility measurements. Significant concern should be directed toward confirmation of the postulated reduction reaction of technetium(VII) to technetium(IV) and to the evaluation of the solubilities of the reduced products.

#### 5.4 EVALUATION OF PUBLISHED TECHNETIUM INFORMATION FOR THE HANFORD SITE

The current conclusions from our experimental evaluation of the published information describing either the sorption behavior or apparent concentration limit for technetium relevant to the candidate repository site in the Columbia River basalt are summarized briefly in this section.

If an oxic redox condition is utilized in the site performance assessment analysis, then all investigators seem to be in agreement on the technetium sorption and solubility value to be employed in the analysis. No significant technetium(VII) sorption ( $R_s = 0$  L/kg) would be expected, and no solubility limit would be encountered. Thus, technetium released from the waste package into the groundwater would likely be modeled as migrating with the contaminated groundwater front, that is, the retardation factor would be one. Little additional laboratory work under an oxic redox condition seems warranted for basalt/groundwater systems.

If, on the other hand, the site performance assessment analysis elects to invoke a reducing redox condition, we feel that the available information on technetium is not sufficient at this time to make any defensible analysis of the technetium retardation to be expected. The published data for technetium under reducing conditions were obtained with the expectation that use of hydrazine adequately simulated the redox conditions in the repository. However, as we have described previously, there are many problems inherent in the use of hydrazine (KELMERS 1984a). Further, the use of any solution phase reducing agent in groundwater implies that technetium in the site will be reduced in solution. It is then apparently assumed that the reduced technetium will subsequently precipitate on the rock surfaces as the oxide or may simply sorb onto the host rock surface. However, our work to date indicates that the formation of reduced technetium is probably a heterogeneous reaction occurring on the surface of the basalt. Thus, the data published for the Hanford Site using hydrazine to simulate reducing conditions do not appear relevant to actual repository situations. For this reason, we have emphasized anoxic redox condition tests, and we feel that values of  $R_s$  obtained under these conditions will be more defensible for performance assessment modeling purposes.

## 6. NEPTUNIUM

### 6.1 APPROACH TO HANFORD SITE INFORMATION EVALUATION

Neptunium-237 has been identified as one of the key radionuclides, that is, those radionuclides likely to pose the greatest potential hazard during the storage of waste in a repository in basalt (BARNEY 1980). It was ranked as third most important in that study. Neptunium-237 is present in appreciable quantities in high-level waste, has a long half-life ( $2.2 \times 10^6$  y), and has a high biological hazard ranking.

Neptunium may be present in glass waste in the  $5^+$  valence state and could be leached into intruding groundwater as pentavalent species. In groundwaters typical of the Hanford Site, the neptunium(V) species present (in the absence of reducing reagents) may be  $\text{NpO}_2^+$  and one or more anionic carbonate complexes such as  $\text{NpO}_2\text{CO}_3^-$ ,  $\text{NpO}_2(\text{CO}_3)_2^{3-}$  or  $\text{NpO}_2(\text{CO}_3)_3^{5-}$  (MAYA 1983; LEMIRE 1984). The Np(V)-saturating solid phase may be  $\text{NpO}_2(\text{OH})$  (BAES 1976). In spent fuel, the neptunium probably exists as  $\text{NpO}_2$  in solid solution in the  $\text{UO}_2$  fuel matrix and could be released into intruding groundwater in the tetravalent state. The species  $\text{Np}(\text{OH})_5^-$  is calculated to be the dominant neptunium(IV) species in the Hanford Site groundwaters (EARLY 1982, EARLY 1983). However, the existence of  $\text{Np}(\text{OH})_5^-$  is questionable because there are no experimental data concerning its formation constant. If reducing conditions exist in the host rock/groundwater system as expected for the Hanford Site (SALTER 1981c; SCR 1982), then neptunium(V) released from glass waste also may be reduced to the tetravalent state and neptunium(IV) species in groundwater.

Neptunium is not expected to be strongly sorbed by host rocks at the Hanford Site. The Site Characterization Report (SCR 1982) and a more recent data package (SALTER 1983) contain "conservative best estimate" or recommended solubility and sorption ( $K_d$ ) values to be used in modeling calculations. The expected sorption ratio for neptunium was given as 10 L/kg, while a conservative value of 2 L/kg (expected value arbitrarily divided by 5) was given in Salter (1983). In the Site Characterization Report (SCR 1982), "conservative best estimate" values for the neptunium distribution coefficient were 10 L/kg under oxidizing conditions and 200 L/kg under reducing conditions. The reducing condition values were based on experiments in which hydrazine was added to try to simulate repository conditions. The Hanford Site sorption information has been separately reviewed and assessed (KELMERS 1984d).

The expected solubility for neptunium(IV) (calculated for  $\text{NpO}_2$  as the saturating solid phase) was reported (SALTER 1983) to be  $1 \times 10^{-10}$  mol/L; however, a conservative value of  $1 \times 10^{-5}$  mol/L was recommended since this concentration had been experimentally observed in reducing condition sorption tests which contained added hydrazine. Other neptunium solubility values have also been reported. Values for neptunium solubility of  $2 \times 10^{-7}$  mol/L under oxidizing redox conditions and  $1 \times 10^{-18}$  mol/L under reducing conditions were given in the Site Characterization Report (SCR 1982). Early (1982) and Early (1983) calculated a solubility of  $1 \times 10^{-10}$  mol/L in Grande Ronde reference groundwater. The Hanford Site solubility information has also been reviewed and assessed (BLENCOE 1985a).



We have been experimentally evaluating these neptunium sorption values under oxidizing redox conditions (air present) with McCoy Canyon basalt and representative synthetic groundwater. Recent work (MEYER 1984a) has shown that most of the neptunium sorbed onto basalt is reduced to the tetravalent state; thus, we have concerns relative to the reversibility of the sorption process(es) occurring in these oxic redox condition batch contact tests. Our oxic condition work was done in order to evaluate the published neptunium sorption information, most of which was obtained under oxic test conditions. While we now question the relevance of reducing redox conditions established in laboratory experiments by the addition of hydrazine (KELMERS 1984a), a few experiments were also carried out under such conditions to evaluate published information. Experimental work under anoxic redox conditions (careful exclusion of air from the basalt, groundwater, and test environment) is under way and will be described in future reports. These anoxic redox condition tests may best model the Hanford Site in situ redox condition in laboratory experiments.

## 6.2 EXPERIMENTAL RESULTS AND DISCUSSION

### 6.2.1 Oxic Redox Condition

Most of the experimental work with neptunium during this report period was directed toward evaluation of the sorption behavior of neptunium(V) under oxic redox conditions (air present). Emphasis was given to the geochemistry of neptunium(V) under oxic conditions since this may be the repository situation representing both the highest solubility of neptunium in groundwater and the lowest neptunium sorption onto host rocks, that is, it is the geochemical condition of greatest potential neptunium mobility at the Hanford Site. The experimental methodology and detailed results have been previously described (KELMERS 1984a; KELMERS 1984b; KELMERS 1985) and are not repeated here. In this report, we have attempted to put our results with neptunium(V) into perspective with our current understanding of neptunium sorption by basalt and with the reported Hanford Site neptunium sorption information.

#### 6.2.1.1 Sorption

A linear sorption isotherm was obtained with McCoy Canyon basalt for neptunium(V)-spiked synthetic groundwater GR-2 under oxic redox conditions at 24°C for batch contact tests at initial neptunium concentrations of  $10^{-7}$  to  $10^{-12}$  mol/L (KELMERS 1984a). The sorption ratio ( $R_s$ ) values (Table 7) were independent of contact time (1 or 4 weeks), use of crushed basalt with or without pretreatment with synthetic groundwater GR-2, and separation technique after contact (centrifugation or centrifugation followed by filtration). The average sorption ratio for the 48 data points that establish the linear portion of the sorption isotherm (Fig. 1 of KELMERS 1984a) was  $1.7 \pm 0.9$  L/kg (mean  $\pm$  1 standard deviation). (Each data point was the average of three replicate experiments.) Since neptunium(V) apparently undergoes reduction to neptunium(IV) and chemisorption in basalt/groundwater systems (MEYER 1984a), it seems unlikely that the average sorption ratio of 1.7 L/kg obtained in these



tests with McCoy Canyon basalt and Np(V)-spiked synthetic groundwater GR-2 solutions represents reversible sorption of one or more neptunium(V) species. Rather, the sorption ratio probably represents a steady-state condition of a complex oxidation/reduction system involving reduction of neptunium(V) to neptunium(IV) by some basalt component and reoxidation of neptunium(IV) by oxygen from air. This model of neptunium(V) sorption is based on results from other work which showed that the neptunium sorbed onto basalt was primarily in the tetravalent state (MEYER 1984b).

Table 7. Summary of neptunium(V) sorption ratio values under oxic redox conditions<sup>a</sup>

Basalt	Temperature (°C)	Initial Np (mol/L)	Sorption ratio (L/kg) <sup>b</sup>	Number of tests
McCoy Canyon	24	$10^{-7}$ to $10^{-12}$	$1.7 \pm 0.9$	48
McCoy Canyon	24	$10^{-12}$	$2.8 \pm 0.4$	12
Umtanum	24	$10^{-12}$	$6.8 \pm 0.2$	6
McCoy Canyon	60	$10^{-12}$	$5.8 \pm 1.6$	6

<sup>a</sup>Batch contact tests in air at  $24 \pm 2^\circ\text{C}$ . All tests were with synthetic groundwater GR-2 containing neptunyl chloride ( $^{235}\text{Np} + ^{237}\text{Np}$ ). No effect of contact time (1 or 4 weeks) or pretreatment of the McCoy Canyon basalt with groundwater was observed on the sorption ratio. Separation of solution for analysis after contact was by centrifugation at 4100 rcf; in some tests the solution was then filtered through 25,000 mol. wt cut-off Amicon filters.

<sup>b</sup>Sorption ratio values are the mean  $\pm$  1 standard deviation of the average values for the number of tests shown (each test was carried out in triplicate).

Umtanum basalt gave a higher sorption ratio than McCoy Canyon basalt in tests at a neptunium concentration of  $10^{-12}$  mol/L Np (Table 7). The mean  $R_s$  value for Umtanum basalt was  $6.8 \pm 0.2$  vs  $2.8 \pm 0.4$  L/kg for McCoy Canyon basalt. Umtanum basalt has been reported by others to give better neptunium sorption (SALTER 1981b).

In tests at  $60^\circ\text{C}$ , the neptunium sorption ratio with McCoy Canyon basalt increased to  $5.8 \pm 1.6$  L/kg, compared to  $2.8 \pm 0.4$  L/kg at  $24^\circ\text{C}$ , at an initial neptunium(V) concentration of  $10^{-12}$  mol/L. The tests were run only for one time period (1 week), and therefore it is possible only to say that sorption increased with temperature. Additional work would be required to establish if this  $60^\circ\text{C}$  value represents a steady-state result.

### 6.2.1.2 Desorption

Desorption of neptunium sorbed onto McCoy Canyon basalt under oxic conditions was studied by contacting the neptunium-loaded basalt with a fresh sample of synthetic groundwater GR-2. The results showed substantial scatter in the desorption ratio ( $R_d$ ) values, but the  $R_d$  values were generally significantly greater than the  $R_s$  values. The desorption data points in Fig. 1 of Kelmers (1984a) do not describe a desorption isotherm, but probably only confirm that sorption and desorption represent different processes. As discussed in Meyer (1984b), desorption in oxic redox condition experiments may result from slow reoxidation of sorbed neptunium(IV) species. The results do clearly establish that the experimental system is not at equilibrium, that is, substantial sorption/desorption disequilibrium exists. This aspect of the neptunium geochemistry is addressed further in the following section.

### 6.2.1.3 Chromatographic Experiments

Column chromatographic experiments are useful in evaluating the effect of multiple radionuclide species or forms and sorption/desorption disequilibrium on the retardation factor and migration profile since the retardation factor ( $R_f$ ) is directly measured, rather than being calculated from the sorption ratio ( $R_s$ ), as in batch tests. In addition, the column elution profile directly shows the effective radionuclide retardation as a function of time or groundwater volume throughput. The column tests with neptunium(V) under oxic redox conditions at temperatures of 25 to 80°C (KELMERS 1985) showed evidence of substantial sorption/desorption disequilibrium. A fraction of the neptunium (25 to 50%) eluted with  $R_f$  values which yielded calculated  $R_s$  values close to those measured in our batch contact tests (Table 8); 2.5 vs 1.7 L/kg at 25°C and 6.1 vs 5.8 L/kg at 60°C (column vs batch experiments). The remainder of the neptunium was retarded further and eluted as a continuous trailing band. In general, peak broadening and trailing increased with temperature. Since both reduction and chemisorption reactions may be involved in the sorption of Np(V) by basalt, it is difficult to ascribe specific reactions to various regions of the elution profile.

Table 8. Neptunium(V) retardation and sorption ratios for McCoy Canyon basalt measured in chromatographic experiments at 25 to 80°C

Temperature (°C)	Np fraction <sup>a</sup> (%)	$R_f$ (dimensionless)	$R_s$ (L/kg)
25	50	10.5	2.5
45	47	21.5	5.4
60	44	24.2	6.1
80	25	45.8	11.8

<sup>a</sup>Fraction of the neptunium activity eluted in volume  $V_2 - V_0$ .

#### 6.2.1.4 Apparent Concentration Limit

An apparent concentration limit can be determined from batch contact tests by experimentally extending the sorption isotherm until it becomes vertical at higher radionuclide concentrations. An apparent concentration limit determined in this manner is a sum of the solubilities of all the radionuclide species present plus any colloiddally dispersed material containing the radionuclide, and thus is different from the thermodynamic solubility of a defined radionuclide solid phase. Measurement of the apparent concentration limit may be especially useful in quantifying the limiting amount of a given radionuclide that can be mobile in groundwater for situations such as neptunium in basalt/groundwater systems where the valence and speciation of the soluble neptunium species, possible presence of colloidal forms, and identity of the saturating solid neptunium-containing phase(s) are all unknown in the experiments.

The sorption isotherms shown in Fig. 1 of Kelmers (1984a) are bending upward at the highest neptunium concentrations and may be approaching an apparent concentration limit value at a concentration of  $10^{-6}$  mol/L. At least, the apparent concentration limit probably is not lower than that value. Additional tests to define the apparent concentration limit are planned.

#### 6.2.1.5 Sorption by Amicon Filters

The sorption of a small but consistent fraction ( $5 \pm 2\%$ ) of the neptunium in synthetic groundwater GR-2 by Amicon filters was reported in Kelmers 1984b. While the experimental evidence pointing to the loss of neptunium from solution to the Amicon filters seems irrefutable, recent results (for example, data in Table 9) which indicate that these groundwater solutions of neptunium(V) contain significant amounts of neptunium(IV) and possibly traces of neptunium(VI) suggest caution in ascribing this loss of neptunium from solution to sorption of neptunium(V) by the Amicon filters. At the present time, we have discontinued the practice of testing for the presence of colloiddally dispersed neptunium after batch contact by filtration through 25,000 mol. wt cut-off Amicon filters since this step may be introducing a small but consistent bias in the sorption ratio values.

#### 6.2.2 Reducing Redox Condition

Strongly reducing redox conditions are expected to be established in the basalt/groundwater system (SALTER 1981c, SCR 1982). Hydrazine hydrate was added to the synthetic groundwater formulations in published experiments in order to simulate a low Eh (redox potential) in laboratory experiments which were exposed to air, following a method described by Barney (1981); these laboratory tests were identified as "reducing condition" experiments. We have previously expressed strong concerns as to the validity or applicability of this laboratory approach for simulating repository redox conditions (KELMERS 1984a). However, in order to help evaluate the published neptunium sorption information obtained in the presence of hydrazine, we conducted a number of batch contact tests in which 0.1 mol/L hydrazine hydrate was added to synthetic groundwater GR-2.

Table 9. Effect of hydrazine on neptunium valence<sup>a</sup>

Np valence <sup>b</sup>	Starting solution	Hydrazine hydrate added			
		Anoxic conditions		Oxic conditions	
		1 Day	1 Week	1 Day	1 Week
(IV)	6.2%	14.5%	18.4%	19.2%	12.9%
(V)	82.2%	82.1%	78.2%	81.9%	81.2%
(VI)	3.0%	2.3%	3.5%	2.5%	2.8%
Material balance	91.4%	98.8%	100.1%	103.6%	96.9%

<sup>a</sup>Tests were at 25 to 27°C; no basalt present. The solution was synthetic groundwater GR-2 containing 0.1 mol/L hydrazine hydrate. The neptunium was added as neptunyl chloride ( $^{235}\text{Np} + ^{237}\text{Np}$ ) to  $3 \times 10^{-7}$  mol/L.

<sup>b</sup>Valence measured by solvent extraction methods as described in Sect. 3.

#### 6.2.2.1 Reduction of Neptunium by Hydrazine

A series of tests was conducted with synthetic groundwater GR-2 containing 0.1 mol/L hydrazine hydrate which had been spiked with our standard neptunyl chloride solutions to  $3 \times 10^{-7}$  mol/L neptunium. Solutions were held for 1 and 7 d under both oxic conditions (air present) and under anoxic conditions in the argon-filled glove box. The results (Table 9) show that the added hydrazine had no significant effect on the valence of the neptunium. Even in tests lasting for one week in the argon-filled glove box, the Np IV/V/VI ratio was not significantly changed. The simultaneous presence of three valence states of neptunium was surprising. We plan to explore this aspect further in future tests.

#### 6.2.2.2 Sorption and Desorption Ratios

Both sorption and desorption batch contact experiments were conducted under reducing redox conditions at 24 and 60°C (air present and hydrazine added to the synthetic groundwater) (KELMERS 1984b). The values measured for both sorption and desorption were much higher than those measured under oxic redox conditions.  $R_s$  values ranged from 250 to 18,100 L/kg, while  $R_d$  values were from 120 to 1,300 L/kg. Desorption ratio values at 60°C were lower than  $R_d$  values at 24°C or  $R_s$  values at 60°C. Since hydrazine did not reduce neptunium(V) to neptunium(IV) in solution, the increased sorption observed in these experiments does not necessarily represent the sorption behavior of a neptunium(IV) species such as  $\text{Np}(\text{OH})_4^-$ . Possibly the hydrazine reduces some basalt component [such as iron(III) to iron(II)] which in turn has favorable reduction reaction kinetics for neptunium(V). In any case, since experiments with added

hydrazine may not be applicable for repository assessment; this question may be moot, and we currently plan no further reducing redox condition tests.

### 6.3 CONCLUSIONS

1. In batch contact tests under oxic redox conditions at 24°C, a linear sorption isotherm was obtained with McCoy Canyon basalt and synthetic groundwater GR-2. The sorption ratio was  $1.7 \pm 0.9$  L/kg.
2. At 60°C (other experimental parameters the same), the sorption ratio for McCoy Canyon basalt increased about twofold.
3. Umtanum basalt gave about a twofold increase in the sorption ratio, as compared to McCoy Canyon basalt under the same experimental parameters (synthetic groundwater GR-2, 24°C, oxic redox conditions).
4. Desorption batch contact tests with McCoy Canyon basalt under oxic redox conditions at 24°C showed substantial sorption/desorption disequilibrium. The desorption ratios were considerably greater than the corresponding sorption ratios.
5. Column chromatographic experiments with McCoy Canyon basalt under oxic redox conditions confirmed the sorption ratio value measured at 24°C (2.5 L/kg vs  $1.7 \pm 0.9$  L/kg) and temperature effect trend observed in the batch contact tests (greater sorption at higher temperatures). The column test results also showed that a substantial fraction of the neptunium migrated much more slowly in the column and appeared to be only gradually released to the groundwater following sorption by the basalt. Such an elution profile is characteristic of sorption/desorption disequilibrium and is consistent with the higher desorption ratios measured.
6. Reducing redox condition tests (hydrazine hydrate added) gave much higher sorption ratio values than those measured under oxic redox conditions. This test methodology does not realistically simulate repository redox conditions, however, and these higher sorption ratios are not considered relevant for repository performance assessment calculations.

### 6.4 EVALUATION OF PUBLISHED NEPTUNIUM INFORMATION FOR THE HANFORD SITE

The most recently published compilation of radionuclide sorption and solubility values to be used in repository performance assessment modeling calculations (SALTER 1983) lists an expected distribution coefficient ( $K_d$ ) value of 10 L/kg and a conservative (expected arbitrarily divided by 5) value of 2 L/kg for neptunium. The expected value apparently is based on sorption batch contact test measurements under oxic redox conditions with Umtanum basalt. Oxic redox conditions gave the lowest (least favorable) value measured (Table 2 of SALTER 1983). In predicting the expected  $K_d$ , no credit was taken for the higher neptunium sorption recorded with secondary minerals or interbed material under oxic



conditions, or for all three materials (Umtanum basalt, secondary minerals, and interbed materials) under reducing redox conditions established by the addition of hydrazine.

The sorption ratio of  $1.7 \pm 0.9$  L/kg, which we obtained with McCoy Canyon basalt under oxic conditions at  $24^\circ\text{C}$ , is considerably lower than the expected value of 10 L/kg but is close to the conservative value of 2 L/kg (SALTER 1983). We observed increased sorption ratios with either increased temperature or use of Umtanum basalt instead of McCoy Canyon basalt.

Thus, our data suggest that the value of 2 L/kg in Salter (1983) may be representative of the actual, but not a conservative, sorption ratio value for neptunium with McCoy Canyon basalt at the repository temperature.

Several questions remain, however, which must be addressed in order to accept the expected or conservative neptunium distribution coefficient values given in Salter (1983) for performance assessment modeling calculations. These are:

1. Is sorption information obtained with one basalt flow (in the case of SALTER 1983, Umtanum basalt) valid for describing neptunium behavior in other basalt flows at the Hanford Site? This answer is particularly important since the leading candidate repository horizon now is the Cohasset flow rather than the Umtanum flow. Information in Salter (1981b) and the Site Characterization Report (SCR 1982), as well as the limited results reported here, show considerable difference in neptunium sorption values for different flows. For example, Table 8 of Salter (1981b) gives  $K_d$  values for neptunium in synthetic groundwater GR-2 under oxic conditions at  $23^\circ\text{C}$  (experimental parameters close to those for our oxic condition tests) of  $7 \pm 3$ ,  $0.5 \pm 0.1$ , and  $52 \pm 16$  L/kg, respectively for Umtanum, Flow E (the same as McCoy Canyon), and Pomona basalts. We similarly observed lower sorption with McCoy Canyon than with Umtanum basalt. The limited evidence available suggests that neptunium sorption behavior could be different for different basalt flows.
2. Is neptunium sorption information obtained at room temperature valid for modeling repository performance? Much of the published experimental work was at  $23^\circ\text{C}$ , and most of our work was at  $24^\circ\text{C}$ ; the repository far field will be at 52 to  $59^\circ\text{C}$ . Neptunium sorption onto Umtanum basalt was reported to be independent of temperature (Table 6-18 in SCR 1982); the  $K_d$  values given were  $30 \pm 13$  and  $31.2 \pm 4.7$  L/kg at 23 and  $60^\circ\text{C}$ , respectively. These  $K_d$  values are much larger and are not in agreement with the expected  $K_d$  value given in Salter (1983) or with our  $R_s$  value for McCoy Canyon basalt. We observed a substantial increase in the neptunium sorption ratio values with McCoy Canyon basalt as the temperature was increased in both batch contact and column chromatographic experiments. Additional work may be needed to resolve this question.
3. Are the neptunium sorption ratio values measured in batch contact tests valid for estimating accurate retardation factors for site performance assessment modeling? Only batch contact sorption test results have been published for basalt/groundwater systems, and the  $K_d$  values recommended for performance assessment analyses (SALTER 1983)



seem to be based solely upon these experiments. However, we have shown in both batch contact and column chromatographic tests that substantial sorption/desorption disequilibrium seems to exist. Under this disequilibrium condition, the values measured in batch contact sorption tests can be considered only as sorption ratios ( $R_s$ ) and not as equilibrium distribution coefficients ( $K_d$ ). Thus, the values in Salter (1983) or SCR (1982) may be useful in calculating bounding values of neptunium retardation, but they can not be utilized to calculate accurate retardation values. Our results, particularly the chromatographic column elution profiles, show that a substantial fraction of the neptunium would be retarded behind the elution position calculated from batch test  $R_s$  values, at least under oxic redox conditions. Thus, retardation factors calculated from the batch contact test sorption ratios may be considered conservative. Further exploration of this sorption aspect under more realistic repository geochemical conditions may be desirable.

4. Can neptunium sorption behavior be adequately modeled in site performance assessment calculations using only information for sorption onto basalt? The release pathway at the Hanford Site likely will include groundwater travel through the basalt flow tops (which may be lined with secondary minerals such as smectite clays, zeolites, and calcite), as well as through the interbed regions (BENSON 1979, 1982). Reported conservative best estimates of neptunium  $K_d$  values are higher for these other Hanford Site materials (SCR 1982). We have not measured sorption with these materials, in part because well-characterized samples of site material seem not to be available. Attention may need to be directed to this question in the future.

## 7. URANIUM

### 7.1 APPROACH TO HANFORD SITE INFORMATION EVALUATION

Uranium has been identified as one of the key radionuclides for a repository in basalt (BARNEY 1980). The information published on uranium solubility in synthetic groundwaters and sorption from these groundwaters onto basalt, secondary minerals, and interbed materials is summarized in Table 10. Generally, low solubilities and low-to-moderate sorption ratios are reported. Lower solubilities and higher sorption ratio values are reported for reducing redox conditions established by the addition of hydrazine to the test solutions than for oxic redox conditions. Information on both uranium solubility and uranium sorption is important for the NRC analysis activities since uranium will be the major component of the spent fuel waste form.

Table 10. Summary of published values for uranium sorption and solubility at the Hanford Site

	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
		$1.3 \times 10^{-11}$ to	
		$1.9 \times 10^{-9b}$	SALTER 1983
		$10^{-10c}$	SALTER 1983
		$10^{-6d}$	SALTER 1983
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	SCR 1982
Interbed materials	a	30 to 40	BARNEY 1982
		$20^e$	SALTER 1983
		$1^f$	SALTER 1983

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

<sup>b</sup>Computed for Eh = -0.3 V and a range of groundwater compositions.

<sup>c</sup>Highest calculated solubility multiplied by 10.

<sup>d</sup>Highest concentration value observed in sorption or solubility experiments in synthetic Grande Ronde groundwater containing 0.05 M hydrazine (published method of experimentally simulating the in situ repository redox conditions).

<sup>e</sup>Value expected under repository conditions.

<sup>f</sup>Conservative value to be used in geochemical modeling.

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 expected to be controlled by a combination of (1) low solubility under the reducing redox conditions anticipated for the basalt geochemical environment (EARLY 1982; EARLY 1983; SALTER 1981a; SCR 1982), and (2) moderate sorption onto basalt, secondary minerals, or interbed materials (AMES 1982; SALTER 1981c; SCR 1982; SALTER 1981b; BARNEY 1982). The Hanford Site sorption information has been reviewed separately (KELMERS 1984d).

## 7.2 EXPERIMENTAL RESULTS

The results of our preliminary sorption tests for uranium(VI) under oxic and anoxic conditions at 60°C are shown in Table 11. Included for comparison are the results previously reported for 25°C (KELMERS 1985). Low sorption ratio values of 1 to 4 L/kg were obtained. A precipitate was clearly observed in the blank test at an initial uranium(VI) concentration of  $10^{-4}$  mol/L. Because of the presence of basalt, we could not determine whether any precipitate was present in the parallel tests with basalt. The high  $R_s$  value at  $10^{-4}$  mol/L initial uranium concentrations suggests that some precipitation may have occurred.

## 7.3 DISCUSSION AND CONCLUSIONS

Uranium sorption isotherms obtained at 27 and 60°C under oxic and anoxic redox conditions were similar (Fig. 4). Little difference can be seen between the isotherms except for the higher apparent concentration limit for uranium at 60°C at the highest uranium concentration. This higher sorption ratio presumably is due to formation of a uranium-containing precipitate. The observed uranium sorption increased only slightly on going from 14- to 50-d contact times. Apparently, a steady-state condition was reached in these tests in 14 d or less. The presumed precipitation reaction observed in the  $10^{-4}$  mol/L solution is apparently somewhat slower, since the value of  $R_s$  doubled in going from 14 to 50 d.

Under reducing redox conditions, the  $R_s$  values were significantly higher than those under oxic redox conditions. These relatively high  $R_s$  values suggest that reduced uranium could have formed.

## 7.4 EVALUATION OF PUBLISHED INFORMATION FOR THE HANFORD SITE

Our preliminary  $R_s$  value of ~2.1 L/kg at 60°C under oxic redox conditions for the lowest initial uranium concentration is essentially the same as the value of  $1.6 \pm 0.3$  L/kg reported (SALTER 1981b) for the same experimental conditions with Flow E Basalt (the same as McCoy Canyon). No published data were reported at concentrations equivalent to our highest uranium concentration ( $10^{-4}$  mol/L), but for an initial concentration of  $10^{-5}$  mol/L, a value of  $7.75 \times 10^{-6}$  mol/L was given for the equilibrium concentration of uranium in the solution after the sorption experiment. This amount compares favorably with the value of  $8.0 \times 10^{-6}$  mol/L

obtained in our experiment. However, we observed a somewhat lower concentration ( $5.5 \times 10^{-6}$  mol/L) in a parallel blank experiment without basalt; perhaps the presence of basalt increased the amount of uranium in the solution; this will be explored further.

Table 11. Uranium sorption onto McCoy Canyon basalt from groundwater GR-2 under various conditions<sup>a</sup>

		Rs (L/kg)			
Contact temperature	Initial uranium (mol/L)	14-d contact		50-d contact	
		Oxic	Anoxic	Oxic	Anoxic
27°C					
Basalt crushed in argon:					
	10 <sup>-7</sup>	2.8 ± 0.2	4.8 ± 0.1	2.8 ± 0.3	3.7 ± 0.8
	10 <sup>-6</sup>	2.9 ± 0.3	4.0 ± 0.1	2.2 ± 0.2	3.4 ± 0.3
	10 <sup>-5</sup>	2.6 ± 0.1	2.9 ± 0.3	1.9 ± 0.1	2.6 ± 0.2
	10 <sup>-4</sup>	2.3 ± 0.1	2.1 ± 0.2	1.6 ± 0.1	2.2 ± 0.1
27°C					
Basalt crushed in air:					
	10 <sup>-6</sup>	1.7 ± 0.1	2.4 ± 0.2	2.1 ± 0.1	2.5 ± 0.2
	10 <sup>-4</sup>	1.6 ± 0.1	1.9 ± 0.2	1.7 ± 0.1	1.9 ± 0.6
60°C					
Basalt crushed in argon:					
	10 <sup>-7</sup>	1.8 ± 0.2	3.9 ± 0.2	2.2 ± 0.8	b
	10 <sup>-6</sup>	2.3 ± 0.4	2.5 ± 0.2	2.6 ± 0.4	b
	10 <sup>-5</sup>	2.4 ± 0.2	2.0 ± 0.2	2.6 ± 0.4	b
	10 <sup>-4</sup>	17 ± 1	35 ± 7	35 ± 2	b
Reducing conditions (hydrazine added to groundwater)					
		Rs (L/kg)			
		14-d contact		50-d contact	
27°C					
Basalt crushed in argon:					
	10 <sup>-6</sup>	64.3 ± 4.1		89.8 ± 8.7	
	10 <sup>-4</sup>	39.4 ± 1.3		50.8 ± 4.1	
27°C					
Basalt crushed in air:					
	10 <sup>-6</sup>	48.2 ± 6.5		69.3 ± 5.8	
	10 <sup>-4</sup>	34.8 ± 2.7		43.1 ± 3.5	

<sup>a</sup>Contact conditions: 0.4 g -70/+325 mesh-size McCoy Canyon basalt, 4 ml GR-2 at pH 8.9-9.7, solution recovery: centrifuged 30 min at 5000 rcf, Rs values: mean = one standard deviation for triplicate samples.

<sup>b</sup>Tubes leaked; repeat experiments in progress.

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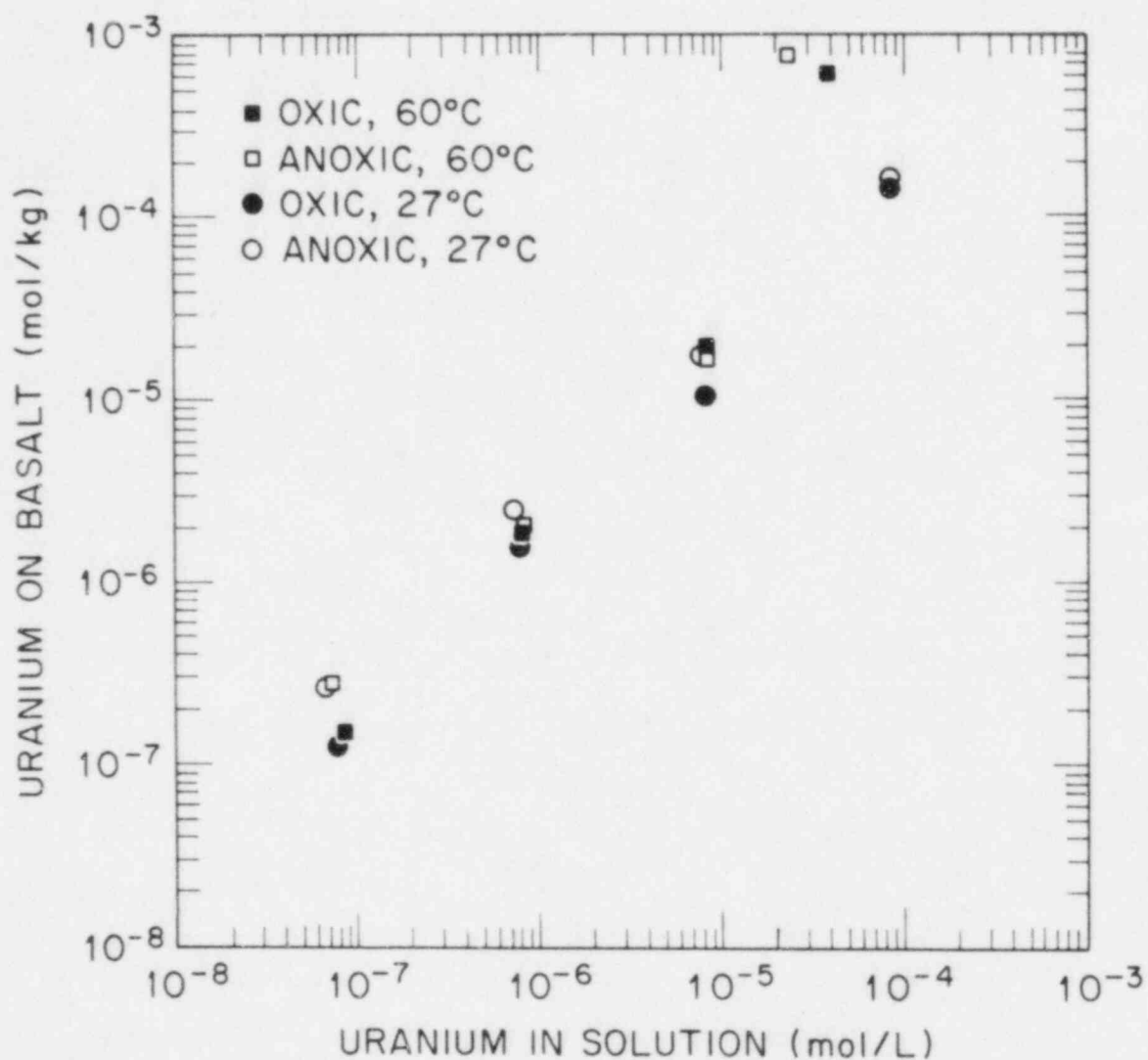


Fig. 4. Sorption isotherms for uranium(VI) onto McCoy Canyon basalt from GR-2. Conditions: 14-d contact; basalt crushed under argon.

At the present time, we believe that our results are in agreement with the published information for uranium sorption with Flow E basalt for oxic redox conditions. Additional experiments under oxic and anoxic conditions are being conducted to identify the uranium-containing precipitate and obtain a more accurate measurement of the apparent concentration limit for uranium(IV) in these basalt/groundwater systems under oxic and anoxic redox conditions. No additional work is under way for reducing redox conditions since we feel that these test conditions are not relevant to repository analysis.



## 8. STRONTIUM

### 8.1 APPROACH TO HANFORD SITE INFORMATION EVALUATION

Release of strontium from emplaced waste to the accessible environment is not considered to be solubility controlled at the Hanford Site (SALTER 1981a). Although strontium was not identified as a key radionuclide for a repository in basalt (BARNEY 1980), the sorption behavior has been extensively investigated (SALTER 1981a; SALTER 1981b; BARNEY 1981; SCR 1982). Salter (1981a) gives a distribution coefficient ( $K_d$ ) of 170 L/kg for sorption onto Umtanum basalt and 400 L/kg for Mabton interbed material as "current conservative estimates". Expected and conservative solubility values of  $10^{-4}$  mol/L and  $10^{-2}$  mol/L, respectively, are given in Salter (1983). In the same reference, the value for  $K_d$  expected under repository conditions is reported to be 90 L/kg and a conservative value for performance assessment modeling purposes of 30 L/kg is given.

Because of the relatively low hazard ranking, we have not given strontium a high priority in our work. As time has permitted, we have been determining sorption ratios for strontium onto basalt (KELMERS 1985). These experiments were generally done during the 14- and 50-d contact periods for the higher priority nuclides such as uranium and technetium.

### 8.2. EXPERIMENTAL RESULTS

In Table 12, data are given for sorption onto McCoy Canyon basalt (-70/+325 mesh size) from synthetic groundwater GR-2 at 27°C under oxic redox conditions. The contact periods were 14 and 50 d, and separation after contact was carried out by centrifugation at 5000 rcf for 30 min. These sorption ratio values are compared to data from Salter (1981b) obtained under essentially the same experimental conditions for the same basalt. Our data show slightly higher values of  $R_s$ , but the agreement is still good.

Table 12. Sorption of strontium onto basalt from GR-2

Initial concentration of strontium (mol/L)	$R_s$ (L/kg)		
	Our results		Published <sup>a</sup>
	14-d	50-d	
$10^{-12}$	$231 \pm 22.5$	$185 \pm 16$	178
$10^{-10}$	$224 \pm 11.7$	$182 \pm 11$	186
$10^{-8}$	$221 \pm 12.5$	$195 \pm 5$	182
$10^{-6}$	$217 \pm 3.5$	$207 \pm 6$	186

<sup>a</sup>Calculated from Table A-7, in 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, Wash., 1981.

### 8.3 DISCUSSION AND CONCLUSIONS

It is interesting that the sorption data that we have obtained are so close to that reported by Salter (1981b). Basalt is not a uniform material; yet our basalt samples exhibited almost the same values for  $R_s$  as that reported previously for the Hanford Site. This result is in contrast to our findings with technetium or neptunium, where our results were not in good agreement with the published data. If the sorption of strontium was due primarily to a minor basalt component whose percentage in the basalt was highly variable, then we might expect considerable difference in sorption for different samples. The similarity between our results and the published data suggest that sorption onto one of the major basalt phases may be an important process.

## 9. GEOCHEMICAL MODELING

### 9.1 INTRODUCTION

Geochemical models are anticipated to be an important tool in estimating the performance of high-level waste repositories. Although a comprehensive geochemical model is not available for performance assessment calculations, some of the site projects are using geochemical codes for calculating specific aspects of repository performance as well as to help interpret data from site characterization activities. Topics currently being addressed include interpretation of groundwater chemistry and estimating solubility-controlled concentrations of radionuclides in groundwater. Activities this year concentrated on evaluating calculated values and methodologies related to the candidate repository at the Hanford Site.

### 9.2 GROUNDWATER CHEMISTRY MODELING

A new synthetic groundwater formulation for the Hanford Site was released this year (SALTER 1984). The solution is apparently intended to simulate groundwater within the Cohasset candidate horizon for the testing of engineered components and radionuclide solubility and sorption controls. This new formulation (GR-4) and previous formulations (GR-1, GR-2, and GR-3) were modeled to evaluate the state of saturation of the solutions at 25°C. Solutions GR-3 and GR-4, representative of the Umtanum and Cohasset candidate horizons, respectively, were also modeled for 60°C in order to investigate possible effects of temperature on the state of saturation of the synthetic groundwaters because of the elevated temperatures encountered at the depths of these horizons at the Hanford Site (55 to 60°C).

Previously (KELMERS 1984b), GR-1, GR-2, and GR-3 have been modeled with the computer code PHREEQE (PARKHURST 1980). These solutions, in addition to GR-4, were modeled again with MINTEQ (FELMY 1984) in order to perform a check on the calculational approaches and thermodynamic data bases of the two computer codes. For calculations at 60°C, only MINTEQ was utilized. The compositions of the four groundwater formulations are listed in Table 13.

Table 14 contains calculated saturation indices ( $\log AP/K$ ;  $AP$  = ion activity product,  $K$  = equilibrium solubility product) for the groundwater formulations at 25°C. Saturation indices of zero indicate saturated conditions, while values less than zero indicate undersaturation and values greater than zero oversaturation. As seen in Table 14, the agreement between PHREEQE and MINTEQ is excellent. Both codes calculate the solutions to be oversaturated with respect to silica phases, fluorite, and calcite (except GR-1).

Results from calculations for GR-3 and GR-4 at 60°C are compared to results of calculations for 25°C in Table 15. The solutions are calculated to be oversaturated with respect to silica phases and fluorite at 25°C. At 60°C the solutions are calculated to be somewhat less

oversaturated, or even undersaturated, for these phases. Solutions supersaturated with respect to silica commonly precipitate amorphous suspensions. Formation of such a suspension during a solubility or sorption test at 25°C might render the results meaningless to the performance expected in an actual repository site where temperatures are commonly 50 to 60°C. Therefore, tests with GR-3 and GR-4 should closely approximate the temperatures representative of the candidate horizons.

Table 13. BWIP synthetic groundwater formulations

Species	Composition (mg/L)			
	GR-1 <sup>a</sup>	GR-2 <sup>a</sup>	GR-3 <sup>b</sup>	GR-4 <sup>c</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	---	---
HCO <sub>3</sub> <sup>-</sup>	81.5	75	[54.7] <sup>d</sup>	[92.0] <sup>d</sup>
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>Data taken from 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, Wash., 1981.

<sup>b</sup>Data taken from T. E. Jones, Reference Material Chemistry - Synthetic Groundwater Formulation, RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Wash., 1982.

<sup>c</sup>Data obtained from P. F. Salter, Rockwell Hanford Operations, Richland, Wash., personal communication, 1984.

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

Table 14. 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 15. 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

### 9.3 RADIONUCLIDE SOLUBILITY CALCULATIONS

The solubilities of selected radionuclides in the synthetic groundwater formulation GR-3 (see Table 13), have been calculated by Early (1982) and Early (1983). Calculations using PHREEQE (PARKHURST 1980) and MINTEQ (FELMY 1984) for the same elements as in the Early (1982, 1983) studies were performed to attempt to verify the calculations of Early.

Because of the importance of redox potential to the solubility of some radionuclides, Early (1982, 1983) calculated solubilities for a range of Eh values. This sensitivity analysis was not repeated in this study. Rather, the reference Eh value (-0.3 V) specified by Early was used in all calculations.

No attempt was made to evaluate the validity or correctness of the thermodynamic data used by Early. Rather, all calculations with PHREEQE used the same data as that in Early, with the following corrections for typographical errors: (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). Selected calculations were made with MINTEQ to allow some further comparisons: (1) the thermodynamic data of Early for Pu, Am, and Np were used in MINTEQ to compare the calculational methodologies of Early, PHREEQE, and MINTEQ, and (2) the data originally contained in MINTEQ for U, Ni, and Pb were used to evaluate possible effects of differing thermodynamic values on the results.

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 16. Agreement is generally excellent, although some numerical differences are present. These differences could be attributable to: (1) rounding errors, (2) activity coefficient corrections were not included in the calculations of Early (1982), or (3) differences in the thermodynamic data for the reference groundwater components (e.g., Ca, Na,  $\text{CO}_3^{2-}$ , etc.) in PHREEQE vs Early.



Table 16. Comparison of our calculated solubility relationships using PHREEQE with BWIP calculations

Element	Early (1982, 1984)			PHREEQE		
	$-\log M$	Dominant aqueous complex	Limiting solid	$-\log M$	Dominant aqueous complex	Limiting solid
Ni	3.74	$\text{NiCO}_3^0$	NiO	4.01	$\text{NiCO}_3^0$	NiO
Se	7.29	$\text{HSe}^-$	Se	7.25	$\text{HSe}^-$	Se
Zr	8.70	$\text{Zr(OH)}_5^-$	$\text{ZrSiO}_4$	8.56	$\text{Zr(OH)}_5^-$	$\text{ZrSiO}_4$
Tc	$\geq 14$	$\text{TcO}_4^-$	$\text{TcO}_2$	13.65	$\text{TcO}_4^-$	$\text{TcO}_2^b$
Pd	9.80	$\text{Pd(OH)}_2^0$	Pd	9.79	$\text{Pd(OH)}_2^0$	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	$\sim 8$	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.

<sup>b</sup>Rard (J. A. Rard, Critical Review of the Chemistry and Thermodynamics of Technetium, UCRL-53440, Lawrence Livermore National Laboratory, Livermore, Calif., 1983) and Isherwood (D. Isherwood, Lawrence Livermore National Laboratory, Livermore, Calif., personal communication, 1984) suggest that the thermodynamic properties are actually representative of  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ , not  $\text{TcO}_2$ . However, the compilation of Early lists the solid as  $\text{TcO}_2$ . (T.O. Early, D. R. Drews, G. K. Jacobs, and R. C. Rouston, 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, Wash., 1982).

Results of calculations using MINTEQ for Pu, Am, and Np 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 of calculations using MINTEQ and its accompanying data base for uranium were not in good agreement with the calculations of Early. For the MINTEQ calculations,  $\text{UO}_2$  is calculated to be the limiting solid phase with a solubility of  $1 \times 10^{-8}$  mol/L. Early calculates  $\text{USiO}_4$  to be the most stable solid with a solubility of  $2.1 \times 10^{-10}$  mol/L. This inconsistency results from the difference in the  $\log K$  for  $\text{USiO}_4$  in the two data bases. Early used a value of 9.07, whereas MINTEQ contains a value of 7.62. For both cases the dominant aqueous species is calculated to be  $\text{U}(\text{OH})_5^-$ .

Solubility calculations for lead using MINTEQ and its accompanying data base were in close agreement to those of Early. The limiting solid phases and dominant aqueous species were identical. The calculated solubilities were  $1.8 \times 10^{-10}$  mol/L and  $2.4 \times 10^{-10}$  mol/L for MINTEQ and Early, respectively. Possible reasons for the slight difference have been identified above. Additionally, small discrepancies between MINTEQ and Early in the thermodynamic data for lead may contribute to the small difference in calculated solubilities.

Solubility calculations for nickel using MINTEQ were not in good agreement with those of Early. As with uranium, the discrepancies can be attributed to differences in the thermodynamic data bases. For the case of Early where sulfur was not allowed to speciate into sulfate and sulfide,  $\text{Ni}(\text{OH})_2$  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 in MINTEQ. This difference results in the two different limiting solid phases and the difference in calculated solubilities;  $2.8 \times 10^{-6}$  mol/L - MINTEQ; and  $1.8 \times 10^{-4}$  mol/L - Early. For the case where sulfur is allowed to speciate into sulfate and sulfide species at  $E_h = -0.3$  V,  $\text{Ni}(\text{OH})_2$  was again calculated to be the limiting solid using MINTEQ. Results from Early conclude that  $\text{NiS}$  is the most stable solid. This discrepancy can be traced back to the fact that the  $\log K$  for  $\text{NiS}$  in MINTEQ is approximately  $1 \times 10^6$  times lower (i.e.,  $\text{NiS}$  less stable) than the value used by Early. For the  $E_h$  - pH conditions selected, nickel solubilities calculated assuming sulfur speciation and no sulfur speciation were identical (see also EARLY 1982, Fig.1). For all cases discussed above, the species  $\text{NiCO}_3^\circ$  and  $\text{Ni}(\text{CO}_3)_2^{2-}$  were calculated to be codominant by Early and using MINTEQ.

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. Calculations for U, Ni, and Pb utilizing the data base of MINTEQ emphasize the importance of having a well-documented

verified, and internally consistent data base. Differences in the thermodynamic values for only one reaction can significantly affect the results as was discovered for uranium and nickel.

#### 9.4 PLUTONIUM SPECIATION

An attempt was made to model the results of plutonium speciation experiments in selected basalt, granite, shale, and tuff groundwaters (CLEVELAND 1983). The geochemical model MINTEQ was used to simulate the distribution of soluble and insoluble plutonium, as well as the distribution of oxidation states, in the experiments of Cleveland (1983). This study was not completed for two reasons. First, the thermodynamic data base for plutonium is not complete and what is available is generally not well documented, verified, or validated. Therefore, results from any calculations would be highly uncertain. Second, notwithstanding the uncertainty, calculations with the data base of Early (1982) suggest that equilibrium controls are not important to the results of Cleveland. Rather, it appears that kinetic constraints among the redox couples of plutonium and precipitation reactions may be the dominant mechanism involved in controlling the distribution of soluble vs insoluble plutonium and its redox state found by Cleveland.

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13. ABSTRACT (200 words or less)

Geochemical information relevant to the retention of radionuclides by candidate high-level nuclear waste geologic repositories being characterized by Department of Energy (DOE) projects is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). Emphasis has been given to the experimental evaluation of key radionuclides relevant to the Hanford Site being characterized by the Basalt Waste Isolation Project (BWIP). In work by the BWIP, hydrazine was added to groundwater to simulate the reducing redox condition expected in the repository. Such laboratory methodology may not adequately model in situ repository geochemical conditions. We have been employing anoxic redox conditions to allow the basalt to establish the effective redox condition in batch contact sorption experiments. Sorption of Np(V) or Tc(VII) by basalt from synthetic groundwaters under anoxic redox conditions may involve chemisorption reduction reactions on the basalt surface. Our sorption ratio for neptunium under oxic redox conditions does not compare favorably with the value published by the BWIP. The published solubility of technetium under the reducing redox conditions expected by BWIP at the repository probably is based on calculations involving inadequate thermodynamic data. Under oxic redox conditions, our uranium sorption ratio was much lower than values reported by the BWIP. A mineralogical and chemical characterization was completed for the three basalt samples used in our work. Significant differences were seen in both the quantity and composition of the mesostasis. A potential deficiency in the information published by the BWIP is the absence of lithological information as well as mineralogical and chemical characterization for the basalt samples. Our geochemical modeling work suggested that code-to-code evaluation for geochemical calculations may be less important than a detailed evaluation of the data bases.

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Radionuclide sorption, radionuclide solubility, geochemical conditions, high-level waste repositories, basalt, neptunium, technetium, Basalt Waste Isolation Project (BWIP), uranium, hydrazine, mineralogical characterization, PHREEQE, MINTEQ, geochemical modeling, groundwater saturation, radionuclide speciation.

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