PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS: ANNUAL REPORT FOR OCTOBER 1984 - SEPTEMBER 1985

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ABSTRACT

Information pertaining to the potential geochemical behavior of
radionuclides at candidate sites for a high-level radioactive waste
repository, which is being developed by projects within the Department
of Energy (DOE), is being evaluated by Oak Ridge National Laboratory for
the Nuclear Regulatory Commission. During this report period, emphasis
was placed on information concerning the Hanford Site in southeastern
Washington. Our evaluation of technetium sorption information for the
Hanford Site was completed. We conclude that the experimental
methodology and results reported to date by DOE for technetium sorption
do not unequivocally demonstrate that significant retention of
technetium will be provided by phases present in the basalts at the
Hanford Site. More detailed information from DOE on the geochemical
behavior of technetium (Tc) may be desirable if the performance
assessment strategy for the Hanford Site will require geochemical
retardation of Tc by the site geology. Preliminary data obtained under
a parallel NRC/RES project suggest that the solubility of Tc(IV) oxides
in sodium chloride and GR-4 solutions is in the range of 10^{-8} to 5 x
10^{-8}mol/L. This range is in good agreement with estimates for
"expected" values and lower by several orders of magnitude than
"conservative" values for the Hanford Site. The control of U(VI)
solutions at an initial concentration of ~10^{-4} mol/L is apparently a
result of the precipitation of sodium boltwoodite. In uranium sorption
isotherm determinations, lower apparent concentration limits were
obtained in the synthetic groundwater GR-4/Cohassett basalt system
(~10^{-6} mol/L) than in the synthetic groundwater GR-2/McCoy Canyon
basalt system (~10^{-4} mol/L). The removal of neptunium from solution
by basalt/groundwater systems is apparently a function of both contact
time and basalt particle size. However, subsequent to previous reports,
we identified a problem with our counting procedure that renders this
conclusion qualitative at best. An evaluation was made of the
information developed by DOE on the native copper (Cu) deposits of
Michigan as a natural analogue for the emplacement of Cu canisters in a
repository in basalt at the Hanford Site. Although Cu will probably be
stable and relatively corrosion resistant in the basalt/groundwater
system at the Hanford Site, the DOE analysis alone does not
unequivocally support this conclusion. Further information on the
geochemical systems at both the Michigan Cu deposits and the Hanford
Site is desirable. Radionuclide solubility and speciation calculations
for representative groundwaters from the Yucca Mountain Site were
evaluated during this year. Our calculations confirm, in general,
previous results reported by DOE. However, agreement between the two
sets of calculations does little more than verify that the two computer
codes used in the separate analyses solve thermodynamic relationships
correctly and that the thermodynamic data used are consistent.
Experimental validation of calculated solubility and speciation
estimates for radionuclides is highly desirable. Samples of groundwater
and rocks from the Yucca Mountain Site were obtained and
characterization of the samples was initiated.

PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION
DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS:
ANNUAL REPORT FOR OCTOBER 1984 – SEPTEMBER 1985

1. EXECUTIVE SUMMARY

The purpose of this project, supported by the Nuclear Regulatory
Commission (NRC), is to evaluate methodologies and information related
to the geochemical behavior of radionuclides that may be employed by
the Department of Energy (DOE) in performance assessments of candidate
sites for high-level radioactive waste repositories. This project is
focused primarily on parameters related to (1) the solubility and
sorption behavior of radionuclides, and (2) geochemical conditions as
they affect radionuclide migration and waste package performance.
Emphasis was placed on information from the Hanford Site in
southeastern Washington. Future work will address information relevant
to the Yucca Mountain Site in Nevada. Information evaluated during
this past year includes the sorption behavior of uranium, neptunium,
and technetium in basalt/synthetic groundwater systems; geochemical
modeling to evaluate radionuclide solubility and speciation
calculations for Yucca Mountain; and an evaluation of the DOE analysis
of native copper deposits in the basalts of Michigan as a natural
analogue for the emplacement of copper canisters in the basalts at the
Hanford Site.

1.1 SAMPLE CHARACTERIZATION

The preparation and characterization of the basalt samples and
synthetic groundwater have been described previously (KELMERS 1985a).

Samples of tuff and J-13 groundwater from Yucca Mountain were received
and are being characterized before use in laboratory tests. Core
samples of the Topopah Spring tuff (the candidate repository horizon in
the unsaturated zone), the Calico Hills tuff (unit in the unsaturated
zone underlying the Topopah Spring), the Bullfrog tuff (first major
unit in the saturated zone), and an outcrop sample of the Topopah
Spring from Busted Butte were received and will be characterized for
their chemistry and mineralogy. Samples of J-13 well water were
analyzed and found to compare favorably with published chemical
analyses of this well water. A method of preparing a synthetic J-13
water was also developed. The behavior of radionuclides in actual and
synthetic J-13 water will be investigated to determine if the synthetic
water is suitable for use in sorption tests. Use of this synthetic
water could help alleviate problems associated with microbiological
activity present in actual J-13 well water.

1.2 TECHNETIUM

All currently planned work to evaluate technetium sorption and
solubility behavior in basalt/synthetic groundwater systems has been
completed. The following major conclusions were reached as a result of
this work:

1. Significant sorption is not observed under oxic redox conditions.

2. Significant sorption under anoxic conditions is observed only if the basalt is crushed and stored under an inert atmosphere and if stringent precautions are taken to exclude traces of air from the experiments.

3. Sorption isotherms are linear at low technetium concentrations under anoxic redox conditions.

4. Technetium sorption ratios are higher for the Cohassett basalt/GR-4 synthetic groundwater system than for the McCoy Canyon/GR-2 synthetic groundwater system.

5. The sorption ratios measured are not highly sensitive to the particle size of the basalt used in the anoxic tests.

6. The solubility limit for reduced technetium may be lower than the values of 10^{-5} to 10^{-6} mol/L that we reported previously. Solubility determinations are being explored in more detail under a parallel NRC/RES project.

7. Sorption of pertechnetate clearly involves reduction to a lower valence state, but the reactions involved are complex and not clearly understood.

Our results suggest that the experimental methodology and results reported to date for the Hanford Site do not unequivocally demonstrate that significant retention of technetium will be provided by the phases present in the basalts at the Hanford Site. DOE may need to obtain additional information to establish a better understanding of technetium geochemistry if the performance assessment strategy for the Hanford Site will require significant retardation of technetium to meet regulatory criteria.

1.3 URANIUM

The control of uranium U(VI) in solutions starting at an initial concentration of ~10^{-4} mol/L is apparently a result of sodium boltwoodite precipitation. In uranium sorption isotherm determinations, lower apparent concentration limits were obtained in the Cohassett basalt system GR-4 synthetic groundwater (~10^{-6} mol/L) than in the McCoy Canyon basalt system GR-2 synthetic groundwater (~10^{-4} mol/L). The reason for the different behavior in the two rock/water systems is not known, but may be related to precipitation kinetics or groundwater compositional effects.

1.4 NEPTUNIUM

The removal of neptunium from solution by basalt/groundwater systems is apparently a function of both contact time and basalt particle size.

However, the subsequent identification of problems during the counting procedure renders this conclusion qualitative at best.

1.5 GEOCHEMICAL MODELING

An evaluation was made of the information developed by DOE on the native copper deposits of Michigan as a natural analogue for the emplacement of Cu canisters in a repository in basalt. Although Cu will probably be stable and relatively corrosion resistant in the basalt/groundwater system at Hanford, the natural analogue analysis of DOE alone does not unequivocally support this conclusion. Further information on the geochemical systems at both the Michigan Cu deposits and the Hanford Site is desirable.

Radionuclide solubility and speciation calculations for the Yucca Mountain Site were evaluated during this year. Our calculations confirm, in general, previous results reported by DOE. However, agreement between the two sets of calculations does little more than verify that the two computer codes used in the separate analyses solve thermodynamic relationships correctly and that the thermodynamic data used are consistent.

2. INTRODUCTION

The purpose of this project is to provide technical support to the
Nuclear Regulatory Commission (NRC) in their analysis of information
being developed by the Department of Energy (DOE) on the potential
geochemical behavior of radionuclides at candidate high-level
radioactive waste repository sites. The emphasis of the project is to
provide an evaluation of information related to radionuclide solubility
and sorption behavior. These parameters are anticipated to play a
significant role in the performance assessment strategy of DOE for each
candidate site.

Most DOE site projects have relied on experimental determinations of
radionuclide solubility and sorption information and, to a lesser
extent, on geochemical modeling. Therefore, this project is
predominantly a laboratory effort complemented by geochemical modeling
where appropriate. Our evaluations emphasize the experimental methods,
results, and assumptions used by DOE in their analysis of repository
performance. Through these laboratory and modeling activities, we
evaluate DOE information for its uncertainty, accuracy, or
conservatism. This information can then be used by the NRC in their
assessment of DOE information and can be provided to DOE for their
consideration in addressing important aspects of repository performance
related to geochemistry. In this manner, it may be possible to resolve
many important technical issues before the final licensing activities.

This report discusses work performed during the past year and contains
information presented in three previous quarterly progress reports (see
page i) as well as new information. This report marks the end of our
current emphasis on the evaluation of information for the Hanford Site.
The Hanford Site was first emphasized because of the significant
quantity of geochemical information available. We are now beginning to
focus on information relevant to the Yucca Mountain Site in Nevada.
Yucca Mountain is also one of the leading candidate sites and a
significant amount of geochemical information has become available
during the last few years. We will be evaluating information related to
sorption and solubility controls on radionuclide migration, as well as
geochemical conditions within the thermally disturbed zone and thermally
undisturbed zone as they affect waste package performance and
radionuclide migration, respectively.

3. MATERIALS AND METHODS

3.1 HANFORD SITE MATERIALS

The preparation and characterization of the basalt samples and synthetic groundwaters used in the sorption experiments were described previously (KELMERS 1985a).

3.2 YUCCA MOUNTAIN SITE MATERIALS

3.2.1 Tuff Samples

3.2.1.1 Sample Characterization

Three core samples from drill hole USW-G1 and a sample of Busted Butte outcrop were received from the U.S. Geological Survey, Mercury, Nevada. The sources and descriptions of these samples are given in Table 3.1.

The tuff samples are being characterized by petrographic and x-ray diffraction (XRD) techniques. The samples selected for examination are small chips of outcrop and core material that are superficially

Table 3.1 Sources and descriptions of Yucca Mountain tuff samples[a]

Sample	Weight (g)	Rock unit	Depth (ft)[b]	Well
Core	1,779	Topopah Spring: lithophysal	1189.7-1190.3	USW-G1
Core	927	Topopah Spring: nonlithophysal	1226.8-1226.9	USW-G1
Core	1,767	Calico Hills: lithics in matrix	1474.8-1476.0	USW-G1
Core	1,778	Bullfrog: saturated	2314.4-2315.7	USW-G1
Outcrop	14,500	Topopah Spring	Surface	Busted Butte outcrop

[a]Information supplied by the U.S. Geological Survey, Mercury, Nevada.
[b]1 ft = 0.3048 meter.

similar to one another. Each rock is mottled and buff/brown in color, whereas the outcrop is somewhat darker than the core material. Both chips contain lithic fragments that were exposed by sawing during the preparation of the thin sections. Mineralogical investigation of these lithic fragments is being emphasized because many of the fragments have altered rims which, based on previous investigations (BISH 1982, VANIMAN 1984), may consist of clay minerals and zeolites produced originally by deuteric alteration. We believe it is possible that the minerals in these alteration rims, as well as the minerals in the outcrop material, may have been affected by weathering and, thus, could have sorptive properties different from those in the core material.

Preliminary examinations performed so far indicate that the lithic fragments, reaction rims, and groundmass material in the outcrop and core material may be significantly different mineralogically. We will attempt to quantify these differences when the XRD analyses are completed. The use of outcrop material in tests to predict behavior at depth will also be investigated.

3.2.1.2 Crushed Sample for Sorption Experiments

A 2.4-kg sample of Topopah Spring tuff from the Busted Butte outcrop has been crushed for our initial sorption methodology tests. The procedure used in the preparation of this sample follows:

> The total weight of the two rocks of outcrop material received was ~14.5 kg. A portion (~4-kg) of the larger of the two rocks was crushed by wrapping the rock in heavy canvas and striking it with a 4.5 kg (10-lb) sledge hammer. The canvas was used to prevent possible contamination of the material with metal from the sledge hammer. The solids were inspected several times so that particles of canvas could be removed during the crushing procedure. The size was reduced further with a large porcelain mortar and pestle. When all particles passed through a 4-mesh screen, the crushed material was placed in an automatic Fritsch agate mortar and pestle and, using a relatively short intermittent grinding and screening technique, the particle size was reduced to less than 70 mesh (<210 μm) with a minimum amount of less than 325-mesh (<44-μm) particles. Approximately 2.4 kg of material was recovered in this manner. The sieve analysis is shown in Table 3.2.

3.2.2 Well Water Samples

Fifteen liters (4 gal) of J-13 well water were received from the U.S. Geological Survey, Mercury, Nevada. The water was shipped in plastic bottles painted to protect the water from light (i.e., to prevent biogrowth). The bottles were filled to the rim to eliminate any air space that could allow degassing of dissolved CO_2. The analyses for this well water (identified as J-13-2 in Table 3.3) have been completed. The composition compares favorably with reference J-13 well-water analyses (DANIELS 1982) except for a slightly higher concentration of

Table 3.2. Sieve analysis of crushed sample of
Busted Butte outcrop[a]

Sieve No. range	Weight (g)	Particle-size range (µm)	Percent of total
100-70	564.7	149-200	23.5
170-100	689.6	88-149	28.7
200-170	196.3	63-88	8.2
325-200	438.6	44-63	18.3
<325	512.7	<44	21.3
Total	2401.9		100.0

[a]Analytical samples (proportional to the above weight
fractions) were obtained from each of the particle-size fractions
by using a riffler (sample splitter). The remainder of the ground
fractions were combined, mixed for several hours in a V-blender,
and then riffled to appropriate size storage samples (50 and
100 g).

iron (0.21 vs 0.04 mg/L). The analyses for another sample of J-13 well
water received earlier (identified as J-13-1 in Table 3.3) are also
included. This earlier sample of well water was collected and shipped
in light-transmitting, commercial, distilled water jugs equipped with
snap caps. The jugs had leaked and there was a considerable amount of
air space above the water.

Although there was some concern about the condition of this sample as
received, the analyses also compared favorably with both the reference
J-13 and J-13-2 well-water analyses.

An interesting observation was made concerning the growth of algae in a
sample of J-13 well water removed from the stock jug and placed in a
window where it could receive sunlight for several weeks. This behavior
was explored because microbiological activity in J-13 well water had
been reported previously (BRYANT 1984; WOLFSBERG 1984). The algae first
appeared as tiny yellow/buff-colored dots that grew into colonies ~4
to 10 mm in diameter. After appearing to attain a maximum size in ~1
week, the colonies began to break up until the material was deposited as
a thin uniform layer on the bottom of the container. In ~2 weeks,
this layer of material had disappeared, and the solids appeared to have
gone back into solution. This whole process spanned a period of 1

Table 3.3 Analyses of J-13 well water

Constituent	Reference J-13[a] (mg/L)	J-13-1 (mg/L)	J-13-2 (mg/L)
Mg	2.1	2.0	1.9
Si	31.0	30.0	29.0
Fe	0.04	<0.03	0.21
Sr	0.05	0.034	0.03
Ba	0.003	<0.02	0.02
Ca	14.0	12.0	12.0
Li	0.05	b	<0.2
K	4.9	4.4	4.6
Al	0.03	<0.2	<0.2
Na	51.0	56.0	52.0
F^-	2.2	2.0	2.0
Cl^-	7.5	7.0	6.0
PO_4^{3-}	0.12	<5.0	<5.0
NO_3^-	5.6	11.0	9.0
SO_4^{2-}	22.0	18.0	16.0
CO_3^{2-}	0.0	0.0	0.0
HCO_3^-	120.0	102.0	104.0

Other analyses

pH	7.1	7.4	7.3
	b	6.8[c]	6.8[c]

[a]DANIELS 1982. W. R. Daniels et al., Summary Report on the Geochemistry of Yucca Mountain and Environs, LA-9328-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 1982.
[b]Not determined.
[c]These pH values were obtained immediately upon opening the jugs of well water; the higher pH values were taken after the samples had been removed and exposed to air for ~1 d.

month. This observation emphasizes the need to isolate samples of J-13 from light. The growth of microorganisms in the well water could affect experimental results (radionuclide sorption and/or solubility) as well as alter the well water composition.

3.2.3 Synthetic J-13 Well Water

To maintain a readily available source of water for use in our radionuclide sorption tests with a consistent composition similar to that of J-13 well water, we investigated the preparation of synthetic J-13 water. We were not able to prepare synthetic J-13 water by the procedure described by Soo (SOO 1984), because we could not dissolve silicic acid in hot $NaHCO_3$ solution as described in the published account. We therefore developed another method for preparing synthetic J-13 water by making up a series of concentrates and using a silica-containing solution that we had prepared previously for preparation of synthetic basalt groundwaters (KELMERS 1985a).

The synthetic J-13 well water was prepared by diluting the concentrates described in Table 3.4. The pH of the solution was adjusted from the initial value of 10.7 to 7.0 by bubbling CO_2 gas through the solution for a few minutes. Titration with 0.05 $\underline{M}$ HCl showed that the synthetic well water contained significant concentrations (Table 3.5) of carbonate and hydroxide ions before pH adjustment and essentially only bicarbonate ion after adjustment. (The solutions also contained dissolved CO_2 that was not detected by the titration procedure used.) After stirring in air overnight, the pH of the adjusted solution increased to 8.1. This increase in pH was presumably caused by loss of dissolved CO_2 from the solution. The adjusted solution pH decreased from 7.0 to 5.0 after overnight storage in a 100% CO_2 atmosphere, and it decreased from 7.0 to 6.4 after overnight storage in a 5% CO_2-95% air mixture. Neither solution was stirred during exposure to these two atmospheres. Similarly, a sample of actual J-13 well water that had been stored for ~2.5 months in a closed plastic bottle had a pH of 9.2, compared to the pH value of 6.8 when the sample was received and a pH of 7.3 after it had been exposed to air for 1 d. These results suggest that both actual and synthetic J-13 water readily lose dissolved CO_2 on exposure to air and that this CO_2 loss results in a significant increase in solution pH.

To avoid this increase in pH, a method of controlling the partial pressure of CO_2 (pCO_2) over the synthetic groundwater is necessary. A glove box was set up, and appropriate valves and flowmeters were installed so that various mixtures of air and CO_2 could be blended and put through the box in a once-through mode. A CO_2 monitor (PIR-200 Process Gas Analyzer from Horiba Instruments) was installed for measurement of the pCO_2. Mixtures of air and CO_2 were passed through the box, and the pH of synthetic J-13 groundwater was monitored as a function of the composition of the mixture. A mixture containing 1.5% CO_2 maintained the synthetic J-13 at a pH of approximately 7.

Table 3.4 Concentrates for preparation of synthetic J-13 well water

Concentrate No.	Volume for 1 L synthetic J-13 (mL)	Concentrates Constituents		Volume prepared (L)
1	100	0.04663 g	MgO	2.0
		81 µL	48% HF	
		0.02561 g	$Mg(NO_3)_2 \cdot 6H_2O$	
2	10	0.0100 g	$LiNO_3$	0.20
		0.00240 g	$Sr(NO_3)_2$	
		0.00183 g	$BaCl_2 \cdot 2H_2O$	
		0.00727 g	$Fe(NO_3)_3 \cdot 9H_2O$	
		0.01412 g	$Al(NO_3)_3 \cdot 9H_2O$	
		24 µL	$1 \underline{M} H_3PO_4$	
3	100	0.789 g	$CaSO_4 \cdot 2H_2O$	2.0
		0.06917 g	$Ca(NO_3)_2 \cdot 4H_2O$	
		0.2325 g	$CaCl_2$	
4	17.06	29.56 mg/mL	SiO_2	(Previously
		4.75 mg/mL	NaOH	prepared)
5	10	0.3195 g	$NaHCO_3$	0.20

Table 3.5. Carbonate, bicarbonate, and hydroxyl ion concentrations before and after pH adjustment of synthetic J-13

Sample	pH	CO_3^{2-}	OH^-	HCO_3^-	Total alkalinity
			Concentration (meq/mL)		
Unadjusted	10.7	0.00056	0.00158	a	0.00214
Adjusted	7.0	a	a	0.00210	0.00210

[a]None present.

At present, this flow-through system of passing air and CO_2 through the box is not used. Rather, pure CO_2 is added to the box until the pCO_2 is 1.5% as measured by the CO_2 monitor. The concentration of CO_2 in the box normally decreases only slowly with time, and a periodic manual introduction of CO_2 is adequate to maintain its partial pressure and, thus, the pH of synthetic groundwater at the appropriate level.

3.3 BATCH CONTACT METHODOLOGY

The complete test methodology for batch contact tests conducted under oxic, reducing, and anoxic redox conditions for the Hanford Site evaluation experiments was reported previously (KELMERS 1985a). These methods are being modified as appropriate to simulate the Yucca Mountain Site geochemical conditions.

4. TECHNETIUM

4.1 PUBLISHED SOLUBILITY AND SORPTION INFORMATION

The published information describing the sorption and solubility of technetium (Tc) in basalt/synthetic groundwater systems relevant to the Hanford Site candidate repository in the Columbia River Basalts has been reviewed and discussed (KELMERS 1984a, BLENCOE 1985). A review and discussion of the literature relevant to solubilities of Tc oxides was given in our annual report for the period October 1982 to September 1983 (KELMERS 1984b). Since these reviews were written we received a new report (BARNEY 1983) describing the kinetics of radionuclide sorption for basalt/groundwater systems. According to this reference, under oxidizing conditions, no sorption of Tc was observed on Cohassett basalt, but significant sorption was observed on Umtanum basalt. However, Barney (1983) attributes this sorption to contamination of the Umtanum basalt by particles of metallic iron introduced from the iron crushing apparatus during preparation of the basalt. Under reducing conditions maintained by added hydrazine, significant and fairly rapid sorption was observed for both Umtanum and Cohassett basalts (BARNEY 1983).

4.2 EXPERIMENTAL METHODS AND MATERIALS

The sorption ratios (Rs) given in this report were obtained by use of the batch contact method, in which samples of crushed and sized basalt were contacted with synthetic groundwater. The reduction in solution concentration of the Tc was measured after a prescribed period of time. The details of this method were described previously (KELMERS 1984b).

4.3 RESULTS

4.3.1 <u>Sorption Isotherms</u>

Fifty-day isotherms were completed for the sorption of TcO_4^- onto Cohassett basalt from synthetic groundwater GR-4 under anoxic[1] conditions at two separate experiments conducted three months apart. In the earlier experiment, the pH values changed from initial values of 9.3 to approximately 7.5, and in the later experiment, the pH increased to approximately 8.8. Decreases in pH are always observed when GR-4 is contacted with basalt, probably due to reaction of the groundwater with the basalt. When plotted as a single sorption isotherm, the data from the two experiments are reasonably consistent with each other (Fig. 4.1). However, the values of Rs for the later experiment (lines

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[1]Anoxic has been defined as being air-absent conditions, whereas reducing was defined as having hydrazine or other reducing agents present (KELMERS 1985a).
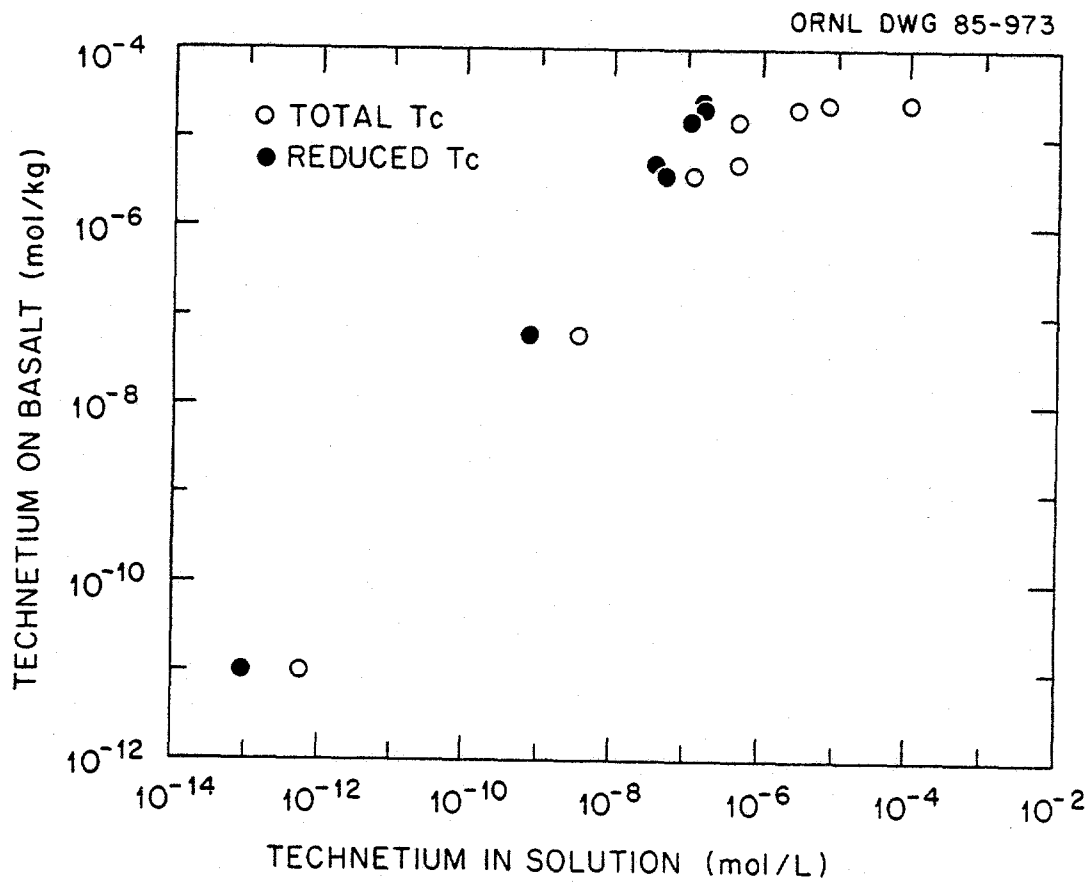
Fig. 4.1. Sorption isotherms for technetium on Cohassett basalt. Batch contact experiments were conducted under anoxic conditions with synthetic groundwater GR-4 at 60°C for 50 d.

Table 4.1. Technetium sorption by Cohassett Basalt from GR-4
at 60°C under anoxic conditions[a]

Initial TcO_4^- (mol/L)	Final pH	Rs (L/kg)	Final concentration of Tc (mol/L)	
			Total	Reduced
1.62×10^{-12}	7.5	17.7 ± 2.9	$5.7(\pm 0.5) \times 10^{-13}$	9.4×10^{-14}
1.00×10^{-8}	7.4	18.3 ± 5.6	$3.4(\pm 0.6) \times 10^{-9}$	7.5×10^{-10}
5.00×10^{-7}	8.8	32.8 ± 2.7	$1.2(\pm 0.1) \times 10^{-7}$	4.8×10^{-8}
1.00×10^{-6}	7.5	12.1 ± 7.3	$4.7(\pm 1.3) \times 10^{-7}$	3.4×10^{-8}
2.00×10^{-6}	8.8	23.6 ± 11.1	$4.7(\pm 1.1) \times 10^{-7}$	1.0×10^{-7}
5.00×10^{-6}	8.7	7.4 ± 1.4	$2.9(\pm 0.2) \times 10^{-6}$	1.5×10^{-7}
1.00×10^{-5}	8.7	3.2 ± 0.2	$7.5(\pm 0.2) \times 10^{-6}$	1.5×10^{-7}
1.00×10^{-4}	7.4	0.3 ± 0.3	$9.7(\pm 0.3) \times 10^{-5}$	-

[a]Test conditions: About 0.4 g Cohassett basalt was contacted for 50 d at 60°C with 4 mL of synthetic groundwater GR-4 containing $^{99}TcO_4^-$ traced with $^{95m}TcO_4^-$. The basalt was 70 to 325 mesh size, ground and stored in argon. Separation of solutions from the solids was carried out by 30-min centrifugation at 5000 rcf (relative centrifugal force). Results are averages (with standard deviations) of three determinations. Reduced technetium concentrations were determined by solvent extraction of Tc(VII); the remaining unextracted technetium was counted and reported as reduced technetium. Because a single determination of reduced technetium was made at each initial concentration, no standard deviations are given for reduced technetium.

3, 5, 6, and 7 in Table 4.1) are slightly high compared to those from the earlier experiment which had lower final pH values. This observation suggests that Rs values for sorption of Tc on basalt probably tend to increase somewhat with pH. The concentrations of reduced Tc as determined by solvent extraction techniques are also shown in Fig. 4.1. At the three highest concentrations of technetium, the values for the concentrations of reduced technetium may be in error and slightly too high because only a single solvent extraction could be used. There may have been incomplete extraction of TcO_4^- from the solution because of the relatively high concentration of TcO_4^- compared to the concentration of reduced technetium.

4.3.2 Effect of Basalt Particle Size

Experiments were conducted to measure the effect of particle size on the sorption of technetium on basalt. Two experiments were completed, the

first with the same samples of crushed and sized basalt used for similar experiments with neptunium described in Section 5. Because the results from this first experiment were unexpected in that there was little dependence of sorption on surface area, we repeated the experiment with basalt that had been freshly crushed and sized under anoxic conditions. The basalt that had been used in the previous experiment had been stored several months in an argon-filled controlled-atmosphere box. Although the oxygen level is kept to a low level in the boxes (<1 ppm oxygen), even this small amount of oxygen could react with the basalt and affect the sorption of Tc. It seemed advisable to prepare a new batch of crushed and sized basalt and use it as soon as possible after preparation (approximately one week).

The results of experiments concerning the effects of particle size on sorption of Tc are given in Table 4.2. In the table, comparison is made between experiments with the freshly ground and sized basalt and those with the sized basalt that had been stored for several months. With the stored basalt, there is essentially no correlation between particle size and sorption ratio. In fact, the sorption ratios are surprisingly uniform and range from 21.6 to 33.2 L/kg. For the experiments with the freshly crushed and sized basalt, the three largest size fractions have almost the same sorption ratio, averaging 15 to 22 L/kg. For the two finer fractions, the sorption ratios are about a factor of 4 to 5 larger, but the finest fraction does not have the larger sorption ratio. Thus, in this experiment, there is somewhat of a correlation between particle size and sorption ratio, but this correlation is not as strong as that obtained with neptunium in which the values range from 14.5±4.9 L/kg for 70 to 140 mesh size to 275±134 L/kg for <400 mesh size (See Section 5).

4.4 DISCUSSION

The 50-d data for Tc sorption on Cohassett basalt from synthetic groundwater GR-4 are compared to the 14-d data in Fig. 4.2 (KELMERS 1985a). There appears to be no significant difference between the 14- and 50-d data except perhaps in the 10^{-7} to 10^{-6} mol/L concentration range. Thus, the sorption reaction appears to reach a steady state within 14 d.

The isotherms shown in Fig 4.2 are linear with a slope of approximately one at the lower solution concentrations. At higher concentrations, the decrease of the slopes of the isotherms suggest a saturation sorption capacity of 2×10^{-5} to 3×10^{-5} mol/kg of basalt for the Cohassett/GR-4 system. For the sorption of Tc onto McCoy Canyon basalt from synthetic groundwater GR-2, the sorption capacity is about 5×10^{-6} mol/kg, 4 to 5 times smaller (KELMERS 1985c). The isotherm for reduced Tc is also linear and has a slope of approximately one (Fig. 4.1). The values of reduced Tc concentration at the upper portion of the isotherm may be high (See Section 4.1). The highest values of

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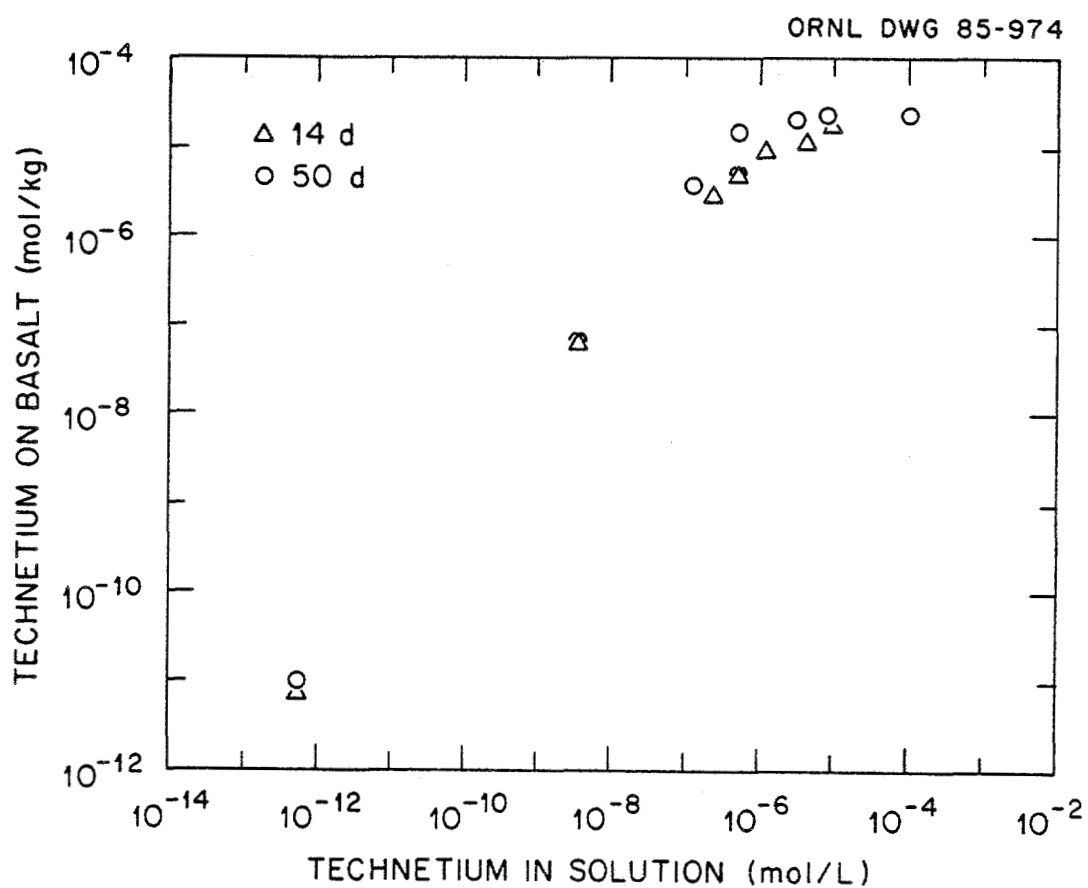
Fig. 4.2. Sorption isotherms for technetium on Cohassett basalt. Batch contact experiments were conducted under anoxic conditions with synthetic groundwater GR-4 at 60°C for 14 and 50 d.

Table 4.2. Effect of particle size on sorption of Tc(VII)[a]

Particle size range (microns)	Mesh size	Rs (L/kg) Stored basalt	Final pH	Rs (L/kg) Fresh basalt	Final pH
150-210	140-70	22.3±5.5	8.6	15.6±3.2	8.7
74-105	200-140	25.0±0.4	8.7	21.7±0.4	8.7
44-74	325-200	31.2±4.4	8.8	22.6±0.5	8.7
37-44	400-325	33.2±1.6	8.5	102.6±5.5	8.8
<37	<400	21.6±0.3	8.6	81.6±5.2	8.6

[a]Test conditions: About 0.4 g of Cohassett basalt was contacted with 4 mL of synthetic groundwater GR-4 containing $^{99}TcO_4^-$ traced with $^{95m}TcO_4^-$. Initial concentration of technetium was 10^{-8} mol/L. Contact time was 50 d for the stored basalt and 14 d for the fresh basalt. Conditions were anoxic at 60°C. Separation was carried out by 30 minutes centrifugation at 5000 rcf. The stored basalt had been stored in argon about three months before use; the fresh basalt was ground and sized about one week before use. Results are averages (with standard deviations) for three determinations.

the concentration of reduced Tc observed in solution are on the order of 10^{-7} mol/L. At these concentrations, only a small fraction of the total Tc is reduced. The shape of the isotherm for reduced technetium is not sufficiently well defined to say whether or not a solubility controlling phase is limiting the concentration. However, this concentration is not too far above the solubility limit of 10^{-8} to 5×10^{-8} mol/L currently being obtained for NaCl solutions and synthetic groundwater GR-2 (MEYER 1986).

The results from the particle size experiments suggest that there may be a different mechanism for technetium sorption on basalt than for the sorption of neptunium on basalt. If the sorption of technetium follows a simple first-order sorption mechanism, there would likely be a dependence on surface area or particle size as was found for neptunium (KELMERS 1985b). Because a strong particle-size dependency is not present, the mechanism of the sorption of Tc onto basalt might be quite complex. The difference in the results from the experiments with stored and freshly ground basalt suggests that even slight exposure to air greatly decreases the ability of basalt to sorb Tc.

4.5 CONCLUSIONS

We have now completed all of the experiments planned for the investigation of Tc sorption on basalt. The major results for this portion of our work may be summarized as follows:

1. Under oxic conditions, significant sorption of TcO_4^- is not observed with McCoy Canyon or Cohassett basalt/groundwater systems -- confirming the observations of Salter et al. (SALTER 1981a,b). This observation is attributed to the fact that anions are not generally adsorbed by minerals, especially in alkaline solutions, and that under oxidizing conditions, the basalt/groundwater system is not capable of reducing TcO_4^- to species of lower valence state which could be either sparingly soluble or easily adsorbed.

2. Significant sorption of Tc on basalt is observed only if extremely stringent precautions are taken to remove oxygen from the test system. These precautions include conducting all operations of the experiment in a controlled atmosphere box filled with argon containing <1 ppm oxygen and evacuating the plastic test tubes for several days before use to remove the last traces of oxygen that may be dissolved in the plastic.

3. Significant sorption of Tc on basalt is observed only if the basalt is ground and stored in an inert atmosphere. Exposure of basalt to an atmosphere containing even 1 ppm of oxygen was observed to gradually diminish the effectiveness of the basalt to remove Tc from the solution.

4. Sorption isotherms are linear and have a slope of one at concentrations of Tc from trace to about 10^{-7} mol/L. This result implies that the sorption ratio is constant at these concentrations of Tc. A constant value for the sorption ratio simplifies modeling the transport of Tc because it is difficult to incorporate varying values of Rs into transport models.

5. Technetium sorption ratios are somewhat higher on Cohassett basalt in synthetic groundwater GR-4 compared to McCoy Canyon basalt in synthetic groundwater GR-2. In addition, sorption isotherms indicate a saturation capacity of from 2×10^{-5} to 3×10^{-5} mol/kg for Tc sorption onto Cohassett basalt from GR-4 and a capacity of about 5×10^{-6} mol/kg for sorption onto McCoy Canyon basalt from GR-2. It is possible that the greater sorption observed with the Cohassett system resulted from characteristic differences in the quantity and Fe(II) content of the Cohassett basalt mesostasis (KELMERS 1985a). It is also possible that differences in the composition of the two different synthetic groundwaters could account, in part, for the greater sorption observed with the Cohassett system.

6. Unlike the sorption of neptunium on basalt, the sorption of Tc on basalt is not very sensitive to particle size. This sensitivity disappeared completely for basalt stored for several months in the controlled-atmosphere boxes containing argon with <1 ppm oxygen.

7. The use of hydrazine to simulate reducing conditions is a questionable procedure. The chemical path of the reduction of Tc with hydrazine is quite complex and does not correspond necessarily to that expected in repository environments. Also, a procedure using a reducing agent to produce lower valence states of elements implicitly assumes that the repository environment will cause reduction. In fact, one of the principal uncertainties is whether the repository environment will be capable of producing reducing conditions. The reasons for these conclusions pertaining to hydrazine have been discussed in considerable detail previously (KELMERS 1984c).

In our earlier work with technetium and neptunium in basalt systems (KELMERS 1984b), we obtained sorption isotherms on basalt in the presence of hydrazine. We reported apparent concentration limits for Tc that were approximately 10^{-6} mol/L when the experiments were conducted in glass test tubes and approximately 10^{-5} mol/L when the experiments were done in plastic test tubes. The plastic test tubes probably contained oxygen that reoxidized Tc(IV) to Tc(VII). In these earlier experiments, we did not distinguish between Tc(VII) and Tc(IV) (or other possible lower valence states). In addition, some of the reduced Tc may have been present as colloids. In some later experiments, considerable Tc was filtered out of the solution by ultrafiltration. The nature of the colloids is unknown, but there was some evidence that the colloids may be associated with the silica in the solutions. We now feel that our values for these apparent concentration limits are too high.

8. The sorption of Tc on basalt has been investigated in more detail in the NRC research program, Valence Effects on Solubility and Sorption (NRC FIN No. B0462), and some aspects of the mechanism have been clarified. Results to date (MEYER 1983, MEYER 1984, MEYER 1985) are briefly summarized below.

   a. Valence analysis shows that much of the Tc sorbed on the basalt is reduced to a lower valence state, probably Tc(IV). The Tc sorbed on basalt is difficult to remove from the surface of the basalt. Thus, substantial sorption/desorption disequilibrium exists with this system.

   b. Sorption of Tc onto basalt is quite sensitive to the composition of the solution; for example, sorption from pure NaCl solutions is significantly greater than that from synthetic basalt groundwaters.

c. The kinetics of Tc sorption appear to be quite slow. In column tests, Tc was only slowly removed from solution over periods of several months.

d. If basalt/groundwater systems are capable of reducing Tc, then solubilities of reduced oxides might control the maximum solution concentration of Tc. Therefore, the solubilities of Tc(IV) oxides are being determined over the pH region 1 to 10 in various solutions (MEYER 1986). The results obtained so far at 25°C in sodium chloride and in synthetic groundwater GR-4 solutions indicate that solubilities of Tc(IV) oxides are approximately 10^{-8} to 5×10^{-8} mol/L in the pH region 4 to 9. The species of Tc(IV) were determined by a solvent extraction procedure that distinguished between species of Tc(IV) and Tc(VII). Extrapolation of these results to the higher temperatures expected in basalt formations will require measurements at temperatures higher than 25°C.

4.6 EVALUATION OF PUBLISHED INFORMATION

A variety of Tc solubility values have been published for the Hanford Site (Table 4.3). Initially, calculated solubility values of $\geq 10^{-14}$ mol/L were reported for the reducing conditions expected to exist in the repository (EARLY 1982, 1984). The value 10^{-14} mol/L was calculated solely from the Tc(VII)/Tc(IV) redox equilibrium assuming that the only aqueous species of technetium is TcO_4^-. The solubility was reported as $>10^{-14}$ mol/L because it was recognized that species of Tc(IV) in equilibrium with the Tc(IV) oxides may also be present in solution. The more recent references have tended toward higher solubility values based, in part, on experimental observations. The work supported by NRC/Research (NRC FIN No. B0462) to obtain a more accurate measurement of the solubility of Tc(IV) oxides suggests that the solubility may be in the range of 10^{-8} to 5×10^{-8} mol/L. Thus, the conservative value given in Salter et al. (SALTER 1983) may be greater than the actual solubility for Tc(IV) solids in basalt groundwaters, and the expected value may be close to the actual solubility.

The Tc sorption ratio values reported for the Hanford Site are summarized in Table 4.4. With the exception of tests involving Umtanum basalt, essentially no sorption was observed under oxidizing conditions and Rs values of 0 L/kg were reported. Under reducing conditions (hydrazine added), or with Umtanum basalt even under oxidizing conditions, sorption ratios of 20 to 30 L/kg were reported. Contamination of the standard Umtanum basalt sample by iron particles from the grinding equipment used to pulverize the sample was suggested as the cause of this apparently anomalous sorptive capacity (BARNEY 1983, MEYER 1984). Although it may be coincidental, we also obtained Rs values in the range of 20 to 30 L/kg under anoxic conditions with a sample of Cohassett basalt that was not contacted by iron apparatus at any time during preparation.

Table 4.3 Technetium solubility values published for the Hanford Site

Reference	Technetium solubility (mol/L)	Comment
EARLY 1982, EARLY 1984	$\geq 10^{-14}$	Eh = -0.3 V
SALTER 1983	1×10^{-9} 1×10^{-5}	"Expected" "Conservative"
DOE 1984	5×10^{-4} to 2×10^{-8}	

Table 4.4 Technetium sorption values published for the Hanford Site

Reference	Rs (L/kg)	Comment
SALTER 1981	0	Flow E basalt, 23°C, oxidizing
	26.8 ± 21.9	Umtanum basalt, 23°C, oxidizing
	25 ± 5.2	Umtanum basalt, 60°C, oxidizing
	29 ± 2.5	Umtanum basalt, 23°C, reducing
SCR 1982	0	Oxidizing
	29	Reducing
SALTER 1983	15	"Expected"
	0	"Conservative"
DOE 1984	0 to 15	

If Tc is present in the solution in the oxidized (VII) state, then it will most likely be present as the anion TcO_4^-. As with other anions, TcO_4^- is not likely to be sorbed by the rocks and minerals present in basalt formations under the normal conditions of the groundwaters. Thus, if Tc(VII) is to be significantly sorbed, it must be reduced and either sorbed, precipitated, or otherwise incorporated into a solid. We have demonstrated that exceptional conditions must be met before basalt can be shown to sorb Tc(VII) in laboratory experiments. If even small amounts of oxygen are present in the groundwaters, there is not likely to be significant sorption. Thus, if DOE is to emphasize significant sorption of Tc(VII) by basalt in an actual repository situation, then they must demonstrate (1) that the oxygen level is at least as low as the level maintained in our anoxic boxes, and, perhaps most important, (2) that the surface of the basalt which contacts the groundwater has a potential for reducing Tc(VII) comparable to that of freshly ground basalt. Furthermore, even if these two conditions can be demonstrated, then the limited saturation capacity for technetium sorption onto basalt must be taken into account in calculations of retardation (see Section 4.4).

The geochemical conditions pertinent to the retardation of Tc migration at the Hanford Site will be different in the engineered facility and in the far-field site. Basalt used for backfill or overpack will probably have been mined and exposed to air during surface storage. Even if basalt is freshly crushed immediately before use, it will likely be exposed to air for significant lengths of time in the repository before anoxic conditions are established. Thus, it is possible that this basalt will have little, if any, effective capacity to reduce Tc. Temperatures used in the engineered facility may be considerably higher than the 60°C used in our experiments. The removal of dissolved oxygen by crushed Umtanum basalt has been investigated by Lane et al (LANE 1984). At 100°C, the lowest temperature investigated in these experiments, it was observed that the dissolved oxygen content of synthetic groundwater initially containing about 8.8 mg/L of dissolved oxygen (air-saturation) decreased to about 2 mg/L when the experiment was terminated after 3000 h. At 150°C, a decrease to 0.4 mg/L was observed after about 200 h. Thus, the removal process appears to be sensitive to temperature. Lane et al. (LANE 1984) suggests that the ferrous iron content of the basalt is involved in the removal process. However, these experiments did not distinguish between reduction of oxygen and diffusion of oxygen into microcracks of the basalt. Although we agree that the reduction of dissolved oxygen is a likely mechanism of removal, we also feel that sorption of dissolved oxygen is a possibility. The view that ferrous iron from basalt is involved in the removal of dissolved oxygen from the groundwater is supported by the work of White et al. (WHITE 1985). In White's work, it is suggested that removal of oxygen may also occur by diffusion into interior pore spaces. In our sorption experiments with Tc, the condition of <1-ppm oxygen in the argon atmosphere surrounding the apparatus corresponds to a dissolved oxygen content of $<4 \times 10^{-5}$ mg/L, assuming that the solution is at equilibrium with the <1 ppm oxygen content of the atmosphere in the

glove box. It is not known from the experiments of Lane et al. (LANE 1984) whether the basalt would ultimately reduce the dissolved oxygen content of the groundwater to levels comparable to 4×10^{-5} mg/L or less, and if it could, how long it would take. However, based on our experiments, we would not expect significant reduction of Tc until the oxygen content was reduced at least to these low levels. Further study of the kinetics of oxygen removal by basalt would, therefore, be desirable.

5. NEPTUNIUM

5.1 PUBLISHED SOLUBILITY AND SORPTION INFORMATION

A variety of neptunium (Np) solubility values have been published for the Hanford Site (Table 5.1). In general, experimentally observed or calculated solubility values for Np under oxidizing conditions have ranged from 10^{-5} to 10^{-7} mol/L. Much lower solubility values have been calculated for NpO_2 under the reducing conditions expected in the repository; these values have ranged from 10^{-10} to 10^{-20} mol/L. The most recent report, the Draft Environmental Assessment (DOE 1984), gives a range of solubility values from 10^{-7} to 10^{-9} mol/L for ^{237}Np (DOE 1984, Table 6-27). (It is not clear why only one specific isotope of neptunium was identified.) An earlier report (SALTER 1983) gave "expected" and "conservative" Np solubility values of 10^{-10} and 10^{-5} mol/L, respectively, for use in performance assessment calculations.

A variety of Np sorption or distribution coefficient values have been reported for the Hanford Site (Table 5.2). In general, values obtained under oxidizing conditions have been low to moderate, ~4 to 40 L/kg, but much higher values (200 to ~1000 L/kg) were reported under reducing conditions (hydrazine present).

5.2 SORPTION ISOTHERMS

Isotherms have been determined at 60°C under anoxic conditions for the sorption of Np onto basalt for the systems McCoy Canyon/GR-2 synthetic groundwater and Umtanum Basalt/GR-2 synthetic groundwater. The range of the initial concentrations of the neptunium was 4×10^{-11} to 10^{-6} mol/L. Solutions were traced with ^{235}Np and were made up to concentration with ^{237}Np. These isotherms are shown in Tables 5.3 and 5.4, and the isotherms are plotted in Fig. 5.1. The isotherms are linear in the concentration range shown, and there is little difference between the isotherms for the two basalts. Slightly higher sorption ratios were observed for McCoy Canyon basalt. Under these anoxic conditions, substantial sorption of Np was observed for both systems. Average values of Rs ranged from 79.5 to 143.2 L/kg for the Umtanum system and from 105 to 193.3 L/kg for the McCoy Canyon system. Valence analyses performed on the most dilute solutions showed that substantial amounts of Np(IV) were present in the final solution. In the case of the Umtanum system, almost all of the remaining Np in the solution at the end of the sorption run was Np(IV).

The isotherms were not extended to higher concentrations because the presence of ^{233}Pa, the decay product of ^{237}Np, interferes with the determination of Np in the counting technique that was used (counting tracer ^{235}Np with a NaI well counter). This problem did not exist at the lowest concentrations of Np, where ^{235}Np was used alone as the tracer. Neptunium-235, which has a half-life of 396 days, emits x-rays that can easily be detected by well-type NaI scintillation detectors. A multichannel analyzer with the region of interest set to exclude other

Table 5.1 Neptunium solubility values published for the Hanford Site

Reference	Neptunium (mol/L)	Comments
SALTER 1981b	$\sim 1 \times 10^{-5}$ $\sim 1 \times 10^{-18}$ to 1×10^{-20}	Oxidizing conditions Repository conditions
EARLY 1982, EARLY 1985	9×10^{-9}	Eh = −0.3 V
SCR 1982	2×10^{-7} 1×10^{-18}	Oxidizing Reducing
SALTER 1983	1×10^{-10} 1×10^{-5}	"Expected" "Conservative"
DOE 1984	1×10^{-7} to 3×10^{-9}	For [237]Np

Table 5.2 Neptunium sorption values published for the Hanford Site

Reference	Rs (L/kg)	Comment
SALTER 1981b	4.2 ± 0.9 30 ± 13 42 ± 11 1015 ± 164	Flow E basalt, 23°C, oxidizing Umtanum, 23°C, oxidizing Umtanum, 60°C, oxidizing Umtanum, 60°C, reducing (hydrazine)
SCR 1982	10 200	Basalt, oxidizing, "conservative best estimate" Basalt, reducing, "conservative best estimate"
SALTER 1983	10 20 10 2	Umtanum, oxidizing, measured Umtanum, reducing, measured "Expected" "Conservative"
DOE 1984	2 to 10	For [237]Np

Table 5.3 Isotherm for neptunium sorption onto Umtanum basalt
from synthetic groundwater GR-2[a]

Initial Concentration (mol/L)	Amount on solid (mol/kg)	Amount in solution (mol/L)	Rs (L/kg)
4.2×10^{-11}	3.94×10^{-10}	3.02×10^{-12}	130.5
	3.99×10^{-10}	2.70×10^{-12}	147.5
	4.03×10^{-10}	2.66×10^{-12}	151.8
Averages	$3.97(\pm0.05) \times 10^{-10}$	$2.79(\pm0.20) \times 10^{-12}$	$143.2(\pm11.2)$
1.0×10^{-9}	9.35×10^{-9}	6.85×10^{-11}	136.5
	9.44×10^{-9}	6.43×10^{-11}	146.9
	9.53×10^{-9}	6.56×10^{-11}	145.4
Averages	$9.44(\pm0.09) \times 10^{-9}$	$6.61(\pm0.22) \times 10^{-11}$	$142.8(\pm5.5)$
1.0×10^{-7}	9.25×10^{-7}	9.44×10^{-9}	98.1
	9.37×10^{-7}	8.46×10^{-9}	110.7
	9.28×10^{-7}	8.22×10^{-9}	112.9
Averages	$9.30(\pm0.06) \times 10^{-7}$	$8.71(\pm0.65) \times 10^{-9}$	$107.2(\pm8.0)$
1.0×10^{-6}	8.91×10^{-6}	1.19×10^{-7}	74.6
	8.97×10^{-6}	1.23×10^{-7}	73.1
	9.19×10^{-6}	1.01×10^{-7}	90.8
Averages[b]	$9.02(\pm0.15) \times 10^{-6}$	$1.14(\pm0.12) \times 10^{-7}$	$79.5(\pm9.8)$

Valence analysis:[c]

Initial conc. (mol/L)	Head count rate (counts$\cdot 10^{-3} \cdot 5^{-1} \cdot mL)^{-1}$	Valence distribution (%)		
		IV	V	VI
4.2×10^{-11}	9539(standard)	1.8	97.2	1.0
	6326(control)	21.5	77.8	0.62
	664(sample)	98.7	1.4	0

[a]Test conditions: 0.4 g of Umtanum basalt (-70/+325 mesh) contacted 14 d with 0.4 mL of synthetic groundwater GR-2 traced with [235]Np under anoxic conditions at 60°C; solution separated by centrifugation for 20 min at 5000 rcf. Concentrations $> 4.21 \times 10^{-11}$ mol/L were made up with [237]Np.

[b]Because considerable [233]Pa is present in the final solution, the data for this concentration are less accurate than those for the lower concentrations. The uncertainty is probably on the order of $\pm15\%$ and a few percent at lower concentrations.

[c]Valence analysis given only for the lowest initial concentration because of the presence of [233]Pa in the solutions of higher concentration.

Table 5.4 Isotherm for neptunium sorption on McCoy Canyon
basalt from synthetic groundwater GR-2[a]

Initial concentration (mol/L)	Amount on solid (mol/kg)	Amount in solution (mol/L)	Rs (L/kg)
4.2×10^{-11}	4.04×10^{-10}	1.97×10^{-12}	205
	4.00×10^{-10}	2.04×10^{-12}	196
	3.84×10^{-10}	1.95×10^{-12}	197
Averages	$3.96(\pm0.11) \times 10^{-10}$	$1.99(\pm0.05) \times 10^{-12}$	$193.3(\pm4.9)$
1.0×10^{-9}	9.35×10^{-9}	5.19×10^{-11}	180
	9.61×10^{-9}	5.00×10^{-11}	192
	9.81×10^{-9}	4.12×10^{-11}	238
Averages	$9.59(\pm0.23) \times 10^{-9}$	$4.77(\pm0.57) \times 10^{-11}$	$203(\pm30.6)$
1.0×10^{-7}	9.32×10^{-7}	9.32×10^{-9}	115
	9.21×10^{-7}	9.12×10^{-9}	101
	9.42×10^{-7}	6.41×10^{-9}	147
Averages	$9.32(\pm0.11) \times 10^{-7}$	$7.88(\pm1.37) \times 10^{-9}$	$121(\pm23.6)$
1.0×10^{-6}	9.20×10^{-6}	8.93×10^{-8}	103
	9.13×10^{-6}	8.38×10^{-8}	109
	9.17×10^{-6}	8.99×10^{-8}	102
Averages[b]	$9.17(\pm0.04) \times 10^{-6}$	$8.77(\pm0.34) \times 10^{-8}$	$105(\pm3.8)$

Valence analysis:[c]

Initial conc. (mol/L)	Head count rate (counts$\cdot10^{-3}\cdot5^{-1}\cdot$mL)$^{-1}$	Valence distribution (%)		
		IV	V	VI
4.2×10^{-11}	9583(standard)	4.0	93.4	2.6
	7600(control)	10.9	89.1	0
	432(sample)	28.7	57.5	13.8

[a]Test conditions: 0.4 g of McCoy Canyon basalt (-70/+325 mesh)
contacted 14 d with 0.4 mL of synthetic groundwater GR-2 traced with
^{235}Np under anoxic conditions at 60°C; solution separated by
centrifugation for 20 min at 5000 rcf. Concentrations >4.2 x
10^{-11} mol/L were made up with ^{237}Np.

[b]Because considerable ^{233}Pa is present in the final
solution, the data for this concentration are less accurate than
those for the lower concentrations. The uncertainty is probably on
the order of ±15% and a few percent at lower concentrations.

[c]Valence analysis given only for the lowest initial concentra-
tion because of the presence of ^{233}Pa in the solutions of higher
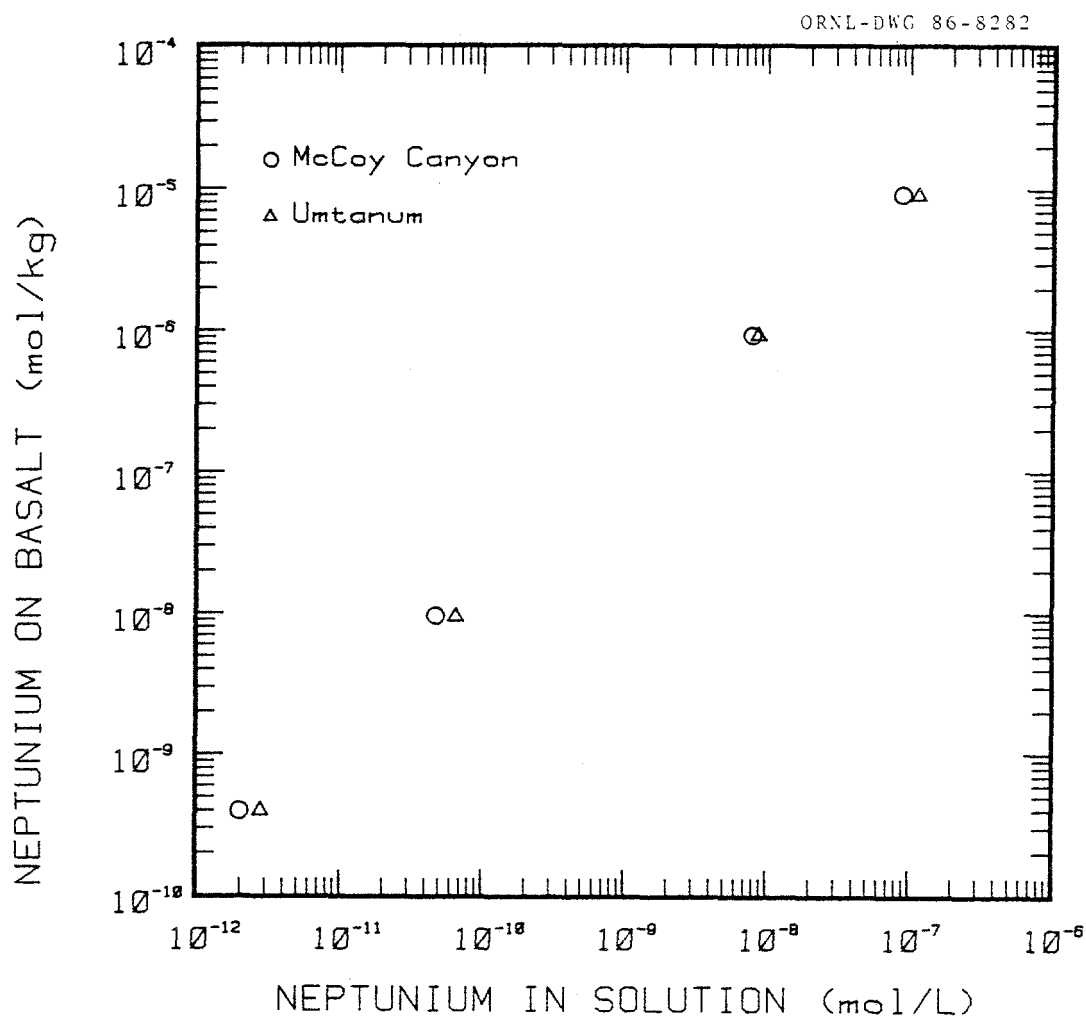concentration.

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Fig. 5.1. Sorption isotherms for neptunium onto McCoy Canyon and Umtanum basalts. Batch contact experiments were conducted under anoxic conditions with synthetic groundwater GR-2 at 60°C for 14 d.

radiation was used for determination of the count rate. The concentration of Np was determined by comparison of the count rate to the count rates of standards of known concentrations.

However, ^{235}Np, which is produced in small quantities by a charge-particle nuclear reaction in a cyclotron, is expensive, and therefore it was not used alone at concentrations greater than 4×10^{-11} mol/L. To study higher concentrations of neptunium, ^{237}Np was used in combination with ^{235}Np. Neptunium-237 is a long-lived nuclide (half-life = 2.14×10^6yr) which decays by alpha-particle emission to ^{233}Pa. Protactinium-233 is both a beta-particle and gamma-ray emitter (half-life = 27 d), and, unfortunately, its emission is in approximately the same energy region as ^{235}Np. The decay of ^{237}Np also produces a low energy gamma ray (86.5 keV) that is detected in the same energy window as the radiation from ^{235}Np and ^{233}Pa. Thus, when the NaI well detector was used, the relatively wide energy window detected radiation from ^{235}Np, ^{237}Np, and ^{233}Pa; consequently, ^{233}Pa complicated the determination of sorption ratios when it was present in significant quantities. The presence of ^{233}Pa also makes the valence analysis of Np unreliable, because protactinium is extracted by the same extractant (TTA in toluene) that also extracts Np(IV).

5.3 EFFECTS OF CONTACT TIME AND PARTICLE SIZE

In the report for the period October to December 1984 (KELMERS 1985a), experiments on the effects of contact time and basalt particle size on the sorption of Np onto basalt were reported. These tests were conducted under anoxic conditions using synthetic groundwater GR-4 and Cohassett basalt in batch contact experiments at 60°C. Contact periods of 1 to 60 d were employed for the experiments on the effects of time and a period of 14 d was used to study the effect of particle size. The initial concentration used for these experiments was 3×10^{-7} mol/L. At the time these experiments were done, the extent of the interference by ^{233}Pa in counting Np had not been determined. The initial concentration used in the experiments was high enough to cause considerable interference by ^{233}Pa. We estimate that about 20 to 30% of the counts from the 3×10^{-7} mol/L solution were not from ^{235}Np. The remainder of the counts were from ^{233}Pa and ^{237}Np, with the ratio dependent on the extent of achievement of secular equilibrium and on the sorption properties of protactinium. Thus, the data shown in Kelmers et al. (KELMERS 1985c) are inaccurate to the extent that ^{233}Pa is present.

The valence analyses shown are also inaccurate because the protactinium, if present, would indicate an apparent increased percentage of Np(IV), and the exact amount of protactinium present cannot be determined from the data. Therefore, the conclusions presented in Section 5 of Kelmers et al. (KELMERS 1985c) must be reconsidered. Specifically, it was stated in the report that the starting solutions contained a mixture of valence states. It is now known that the Np solutions used in these tests were essentially

completely Np(V). The presence of an unknown amount of ^{233}Pa also makes the valence state distributions given for these experiments incorrect; therefore, the conclusions given in Kelmers et al. (KELMERS 1985c) relative to valence state distributions during the test are not correct.

The general trends noted in the experiments are probably correct. Thus, the rapid decrease with time of Np in the solution was probably a correct observation, and it is likely that the solution concentrations are correct within a factor of roughly 50%. However, it is not possible to say whether the sorption ratios were still decreasing with time after 60 d, as was stated in Kelmers et al. (KELMERS 1985c). Similarly, the trends in the effects of particle size on sorption ratios reported in Kelmers (1985c) are probably correct only within a factor of roughly 50%. Unfortunately, there is no accurate way of knowing the errors precisely and whether they are consistently low or high from one sample to another.

5.4 EVALUATION OF PUBLISHED SORPTION AND SOLUBILITY INFORMATION

Our previous work under oxidizing conditions with McCoy Canyon basalt and synthetic groundwater GR-2 gave an average Np sorption ratio of 1.7 L/kg—close to the conservative value for the Hanford Site of 2 L/kg (SALTER 1983, DOE 1984). Our work under anoxic redox conditions with McCoy Canyon and Umtanum basalts and synthetic groundwater GR-2 described in this report has yielded much higher Np sorption ratios. As shown in Tables 5.2 and 5.3, sorption ratios of 79.5 to 203 L/kg were obtained. These values average somewhat lower than the reducing condition value of 200 L/kg given in the Site Characterization Report (SCR 1982), and are much lower than the value of 1015 L/kg initially reported in Salter et al. (SALTER 1981b) for reducing conditions (hydrazine present). Our anoxic condition values are much higher than the expected or conservative values for performance assessment calculations of 2 or 10 L/kg (SALTER 1983, DOE 1984).

6. URANIUM

6.1 PUBLISHED SOLUBILITY AND SORPTION INFORMATION

Uranium (U) has been identified as one of the key elements for a repository in basalt (BARNEY 1980). The information published on U solubility in synthetic groundwaters and sorption from these ground-waters onto basalt, secondary minerals, and interbed materials is summarized in Table 6.1. 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 U solubility and U sorption is important for the NRC analysis activities since U will be the major component of the spent fuel waste form.

Although not explicitly stated in the Site Characterization Report (SCR 1982), U 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, 1984; SALTER 1981a; SCR 1982), and (2) moderate sorption onto basalt, secondary minerals, or interbed materials (AMES 1982; SALTER 1981b,c; SCR 1982; BARNEY 1982). The Hanford Site sorption information has been reviewed separately (KELMERS 1984a).

6.2 SORPTION ISOTHERMS

Isotherms have been completed for the sorption of U onto Cohassett basalt from synthetic groundwater GR-4. Results for these determinations are given in Table 6.2, and the isotherms are plotted in Fig. 6.1. Significant increases in Rs values were observed when the duration of the test was increased from 14 to 50 d and, in some cases, the ratios increased by a factor of 10. Although we have no direct evidence, these large increases in Rs values in the 50-d experiments compared to the 14-d experiments could be, in part, a result of increased precipitation of sodium boltwoodite at all concentrations of U because we observed large increases in losses from all of the control samples in the 50-d experiments. The formation of sodium boltwoodite, $Na(UO_2)(SiO_3)(OH) \cdot 2.5H_2O$, was reported previously (KELMERS 1985a) to form in synthetic groundwater GR-2 at 60°C when the solution contains 10^{-4} mol/L U. The data in Table 6.2 also show large increases in Rs at the highest concentration of U for both the 14- and 50-d experiments. The sorption isotherms shown in Fig. 6.1 are typical of those found for sorption at low concentrations followed by precipitation at the higher concentrations.

We previously described sorption isotherms for U onto McCoy Canyon basalt from synthetic groundwater GR-2 (KELMERS 1985a). A 50-d

Table 6.1 Summary of published values for uranium sorption and solubility at the Hanford Site

	Redox Conditions		
	Oxidizing	Reducing	Reference
Solubility (mol/L)	10^{-4}	10^{-8}	SCR 1982
	a	2.1×10^{-10}	EARLY 1982
	a	2.0×10^{-10}	EARLY 1984
	a	10^{-8}	SALTER 1981a
		1.3×10^{-11} to	
		1.9×10^{-9b}	SALTER 1983
		10^{-10c}	SALTER 1983
		10^{-6d}	SALTER 1983
Sorption ratio (L/kg)			
Basalt (Flow E)	0.2 ± 0.5	17 ± 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

[a]No data given.

[b]Computed for Eh = -0.3 V and a range of groundwater compositions.

[c]Highest calculated solubility multiplied by 10.

[d]Highest concentration value observed in sorption or solubility experiments in synthetic Grande Ronde groundwater containing 0.5 $\underline{M}$ hydrazine (published method of experimentally simulating the in situ repository redox conditions).

[e]Value expected under repository conditions.

[f]Conservative value to be used in geochemical modeling.

Table 6.2 Uranium sorption onto Cohassett basalts[a]

Initial concentration (mol/L)	pH	Rs (L/kg)	
		14 d	50 d
9.8×10^{-8}	8.6 to 8.8	31.1 ± 4.5	313 ± 71
9.9×10^{-7}	8.5 to 8.8	30.7 ± 6.0	236 ± 48
1.05×10^{-5}	8.5 to 8.8	19.4 ± 1.8	115 ± 28
1.03×10^{-4}	8.5 to 8.7	355 ± 54	1288 ± 52

[a]Test conditions: About 0.4 g Cohassett basalt was contacted with 4 mL of synthetic groundwater GR-4 under anoxic conditions at 60°C. Basalt was -70/+325 mesh size, crushed and stored under argon. Separation was carried out by 30 min of centrifugation at 5000 rcf. Each Rs value is the average (with ± 1 S.D.) of three determinations and is calculated by comparison to the original standard solutions. Significant losses of uranium were observed from control samples (no basalt present) carried out in parallel with the basalt samples, especially for the two highest concentrations at 60°C.

isotherm was not shown in Kelmers et al. (KELMERS 1985a) for uranium(VI) sorption onto McCoy Canyon basalt from GR-2 under anoxic conditions at 60°C, because attempts to determine this isotherm had failed. We have now completed this isotherm, and the results are shown in Table 6.3, where they are compared with previously determined values for 14 d (KELMERS 1985a). These Rs values for McCoy Canyon basalt are much lower than those observed for the synthetic groundwater GR-4/Cohassett system. For the three lowest concentrations, the values of Rs for the 50-d experiments are about twice as high as those for the 14-d experiments. At the highest concentration of U, the value of Rs, 48 L/kg, is about 35% higher than the value from the 14-d test. The large losses from the control experiments suggest precipitation of U, probably forming sodium boltwoodite, as we have already observed with some systems previously. However, we did not directly observe the formation of a precipitate because so little could have been formed and it would be difficult to see it in the translucent polypropylene test tubes used. In other experiments previously reported (KELMERS 1985c), formation of sodium boltwoodite was observed from 10^{-4} mol/L solutions of uranium in synthetic groundwater GR-2 in the absence of basalt.

6.3 DISCUSSION

Results from our experiments suggest that the behavior of 10^{-4} mol/L U solutions at 60°C in synthetic groundwaters GR-2 and GR-4 is largely controlled by a precipitation process. As reported previously (KELMERS 1985c), x-ray diffraction analysis of the light-yellow precipitate
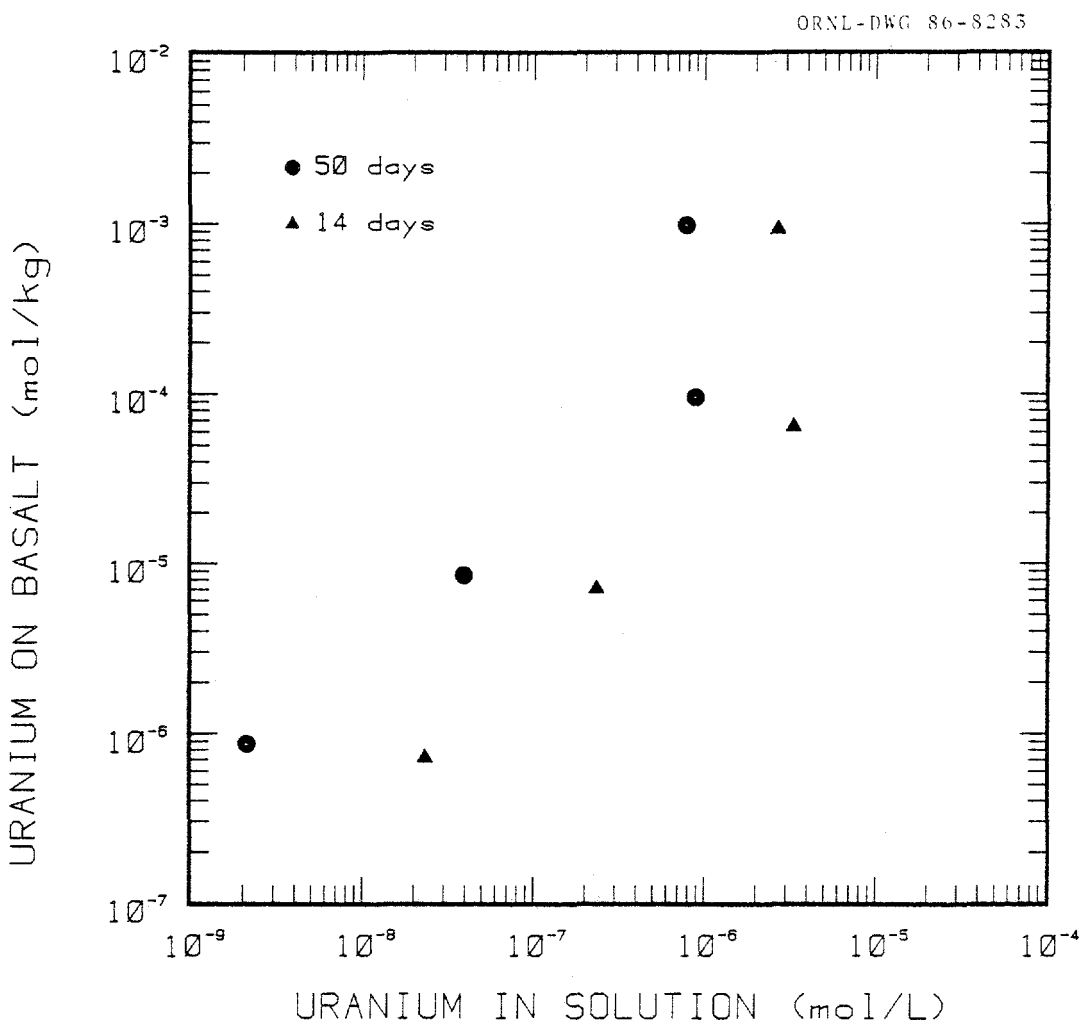
ORNL-DWG 86-8283

Fig. 6.1. Sorption isotherms for uranium on Cohassett basalt. Batch
contact tests under anoxic conditions with synthetic
groundwater GR-4 at 60°C.

formed from GR-2 and from GR-4, both initially 10^{-4} mol/L in U, indicated that the solid formed was sodium boltwoodite, $Na(UO_2)(SiO_3)(OH) \cdot 2.5H_2O$.

Plots of sorption isotherms of U on basalt for the two systems, synthetic groundwater GR-2/McCoy Canyon basalt and synthetic groundwater GR-4/Cohassett basalt, indicate apparent concentration limits of U at the upper solution concentrations. For the GR-2/McCoy Canyon system under anoxic conditions, a limit of over 2×10^{-5} mol/L is indicated by the 14-d isotherm and slightly under 2×10^{-5} mol/L after 50 d (Fig. 6.2). The 14-d isotherm was reported previously (KELMERS 1985a) and is given on Fig. 6.2 for purposes of comparison. In the absence of basalt, the control experiments with GR-2 (no basalt present) indicate lower concentration limits as indicated by the solution concentration of U at the highest initial concentration of U in Fig. 6.3. In this figure, a comparison is given between final solution concentrations for the control experiments and for the sorption tests with basalt. For the two higher U concentrations, the final control solutions contained less U than solutions with basalt. This behavior is unusual and at present we have no explanation.

For the synthetic groundwater GR-4/Cohassett basalt system under anoxic conditions at 60°C, considerably lower concentration limits were observed. As shown in Fig. 6.1, after 14 d the limit is about 3×10^{-6} mol/L, and 50 d after the limit is about 8×10^{-7} mol/L. The limits for the two systems vary by about a factor of 30. At this time, it is not possible to give the reasons for this variation. Extensive studies of the equilibrium solubility of sodium boltwoodite and of the kinetics of the precipitation reaction would be necessary for a complete understanding of this reaction. It is possible, for example, that the equilibrium solubilities of sodium boltwoodite in synthetic groundwater GR-2 and GR-4 might be similar, but that the kinetics of precipitation from solutions of GR-2 are much slower than those from GR-4. The lower concentration limits in the GR-2 control solutions shown in Fig. 6.3 compared to the limits in the solutions with basalt could also be a kinetic effect in that the presence of basalt might slow the precipitation reaction. Therefore, it would appear from our data that the equilibrium and kinetic properties of sodium boltwoodite formation should be investigated in more detail.

6.4 EVALUATION OF PUBLISHED SORPTION AND SOLUBILITY INFORMATION

The formation of sodium boltwoodite rather than schoepite as the stable solid phase shows the importance of identifying the solid phase present in experimental measurements and highlights the limitations of the existing thermodynamic data bases for compounds and conditions of interest to repositories. The formation of the U(VI) silicates has also been observed in experiments with simulated spent fuel (UO_2) plus synthetic groundwater GR-3 at elevated temperatures (APTED 1982). In our experiments with Cohassett basalt at 60°C, we have observed a concentration limit of approximately 8×10^{-7} mol/L, but we have no evidence that this is an equilibrium value. Thus, in a longer

Table 6.3. Sorption of uranium on McCoy Canyon basalt from synthetic groundwater GR-2 under anoxic conditions, 60°C, 50 d

Initial conc. uranium (mol/L)	Av Rs calc.[a] from standards (L/kg)	Av Rs calc.[a] from controls (L/kg)	% loss of uranium from control	Rs values[b] for 14 d (L/kg)
1.15×10^{-7}	6.3 ± 0.8	4.8 ± 0.7	9.0	3.9 ± 0.2
1.10×10^{-6}	5.5 ± 0.4	1.1 ± 0.3	29.5	2.5 ± 0.2
8.85×10^{-5}	4.9 ± 0.4	-3.9 ± 0.5	60.7	2.0 ± 0.4
1.00×10^{-4}	48.0 ± 1.7	-4.3 ± 0.3	90.9	35 ± 7

[a]In column two, values of Rs were determined by comparison of the final concentration of the uranium with the concentration of the standard solutions used initially. In column three, values of Rs were calculated by comparison with the control samples (no basalt present). These controls were equilibrated under the same conditions for the same length of time as the samples with basalt. For the two higher concentrations of uranium, the loss of uranium was greater in the controls than that in the samples, and the resulting sorption ratios are therefore negative.

[b]Reported in Kelmers et al. (KELMERS 1985a). All test conditions were the same except for the 14 d duration of the test. Initial concentrations of uranium in the 14 d test were slightly different from those in the first column, but they were always within 15%.

experiment, lower concentration limits might be observed. This value is comparable to the value of 10^{-6} mol/L given by Salter and Jacobs (SALTER 1983) for the highest concentration value observed in sorption or solubility experiments in synthetic Grande Ronde groundwaters containing 0.05 $\underline{M}$ hydrazine (published method of experimentally simulating in situ repository redox conditions). Other values given in Table 6.1 are somewhat lower than 10^{-6} mol/L. The value of 17 ± 2 L/kg given in Table 6.1 for the sorption ratio under reducing conditions is much lower than our values of from 313 to 1288 L/kg reported in Table 6.2. The values in Tables 6.2 and 6.3 probably include the effect of formation of sodium boltwoodite. Without further information on the equilibrium and kinetic properties of boltwoodite formation, it would be difficult to extrapolate these values of Rs to other conditions or to repository environments.
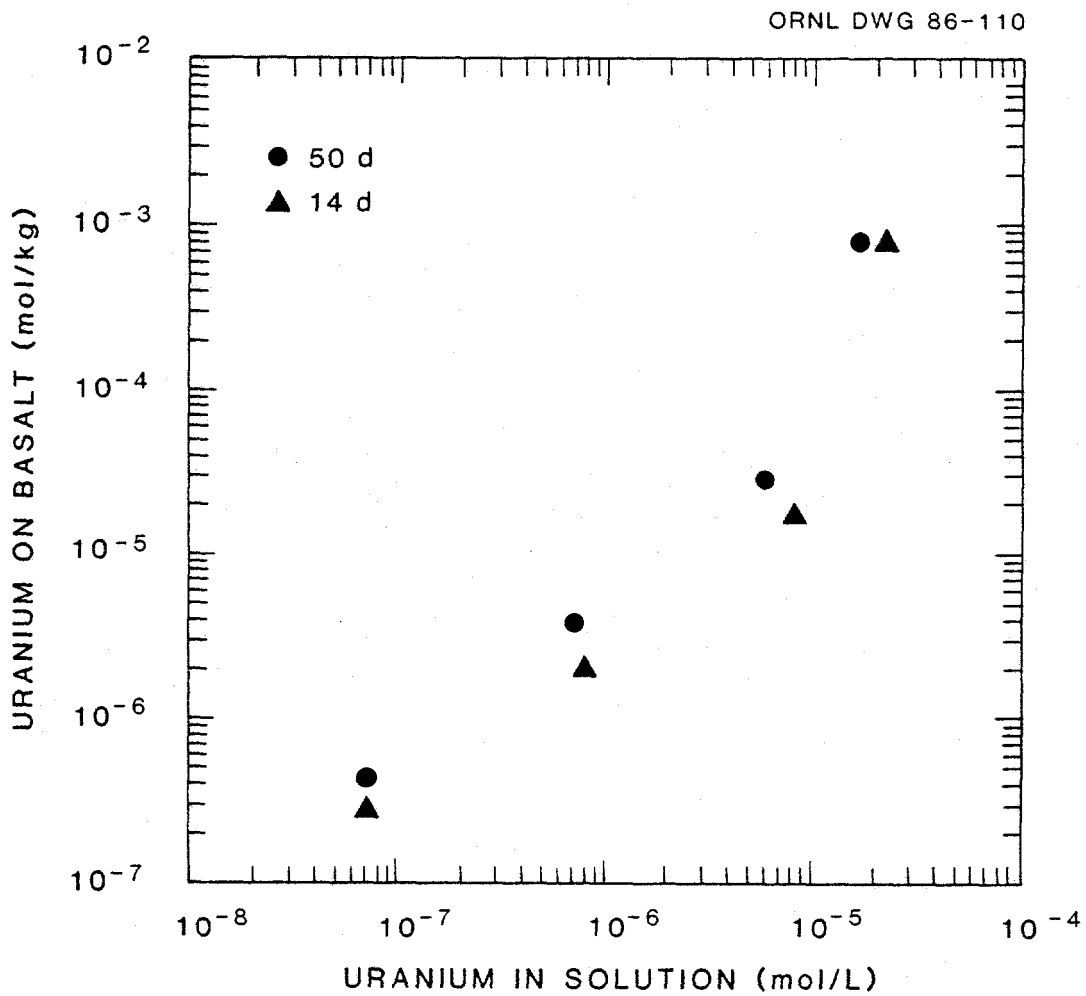
Fig. 6.2. Sorption isotherms for uranium on McCoy Canyon basalt. Batch contact tests under anoxic conditions with synthetic groundwater GR-2 at 60°C.
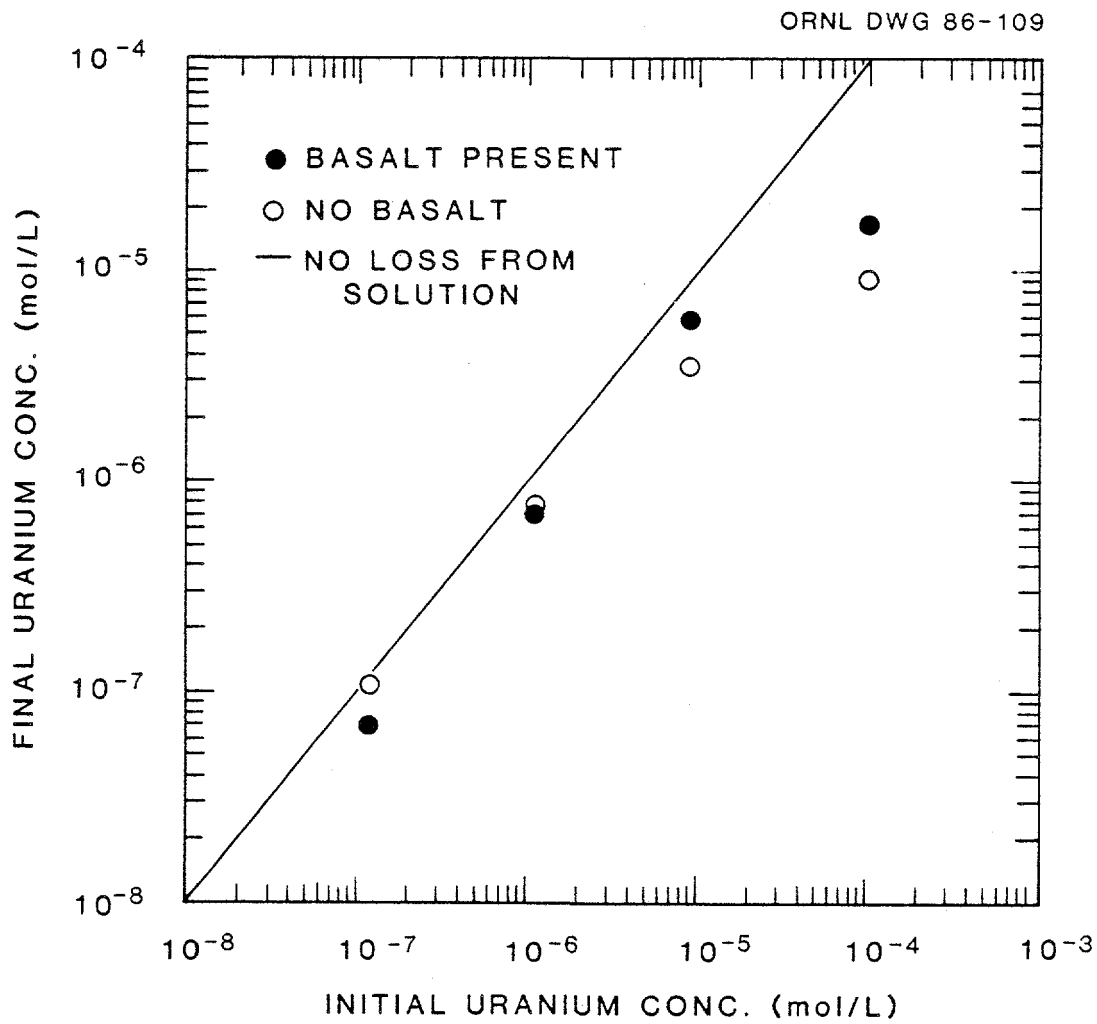
Fig. 6.3. Initial and final uranium concentrations for sorption isotherm experiments with McCoy Canyon basalt in synthetic groundwater GR-2 under anoxic conditions at 60°C for 50 d.

7. SORPTION EXPERIMENTS WITH YUCCA MOUNTAIN SITE MATERIALS

During the latter part of this report period, experiments were initiated for the sorption of cesium and strontium onto tuff. These two elements were chosen because their behavior in aqueous solution is relatively simple. They each have a single valence state, and they do not hydrolyze or readily form complexes in the expected groundwater. Also cesium and strontium have been studied extensively by investigators in the Nevada Nuclear Waste Storage Investigations (NNWSI) project. Study of these two elements should provide a basis for evaluation of the techniques used by NNWSI. The first experiments were designed to explore effects of particle size, contact time, atmosphere control, nuclide concentration, and pretreatment of the tuff. A few preliminary results have been obtained in this report period concerning sorption of cesium and strontium. Further discussion of sorption on tuff will be given in future reports when more data have been collected and analyzed.

Work with europium was also initiated. Because americium is an important element, but is somewhat difficult to work with, europium was selected as a stand-in for initial experiments. The experience gained from the study of europium will be helpful in the study of americium.

8. NATURAL ANALOGUE FOR COPPER STABILITY

8.1 DOE METHODOLOGY AND INFORMATION

Crisman and Jacobs (CRISMAN 1982) studied the native copper deposits (~500 million years old) in the Portage Lake Volcanics near Hancock, Michigan, as a natural analogue for the emplacement of copper canisters in the proposed high-level nuclear waste repository in the basalts at the Hanford Site, Washington. Although copper is not currently a leading candidate material for the containment canister of high-level radioactive waste (HLW) or spent fuel, its inherent stability under some natural conditions (BIRD 1982) makes it desirable to maintain as an option, especially if it can be shown that the geochemical conditions in a repository may encompass the thermodynamic stability field of native copper.

Crisman and Jacobs (CRISMAN 1982) argued for significant similarity between the geochemical conditions, and the processes controlling them, in the basalt/groundwater system in Michigan and those in the deep basalts at the Hanford Site, Washington. We have evaluated this information (CRISMAN 1982) to determine whether there is a valid analogy between the basalt/water systems of Michigan and Washington, and if the data and interpretations of Crisman and Jacobs provide an adequate basis for reasoning by analogy that copper will have favorable corrosion characteristics in the deep basalts at the Hanford Site. Our evaluation assessed the quality of the data and considered alternative conceptual models for the interpretation of the data. This analysis was done to determine the validity of the analogy and the conclusions drawn from it pertaining to the potential performance of copper as a canister material.

8.2 EVALUATION OF DOE INFORMATION

Details of our evaluation have been reported previously (KELMERS 1985c); only a summary of the conclusions are presented here.

1. Although similar in bulk composition, the significant differences in mineralogy between the basalts at Michigan and those at the Hanford Site probably result in quite different mechanisms controlling the groundwater chemistry in the two systems. In addition, alternative controls on the groundwater chemistry were identified that were not considered by the DOE study. Therefore, any similarity in groundwater chemistry may be fortuitous, and additional information is required before firm conclusions can be made pertaining to analogous geochemical behavior between the two systems.

2. Although the basalt/water system in Michigan is probably "reducing," at least two redox indicators (native copper and iron-bearing phases) are not in equilibrium with the groundwater. The system may be in redox disequilibrium and, therefore, a single value of redox conditions as estimated in the DOE study may not be appropriate.

3. Based on the general similarities of the basalt/water system in Michigan to that at the Hanford Site, we agree with the conclusions of the DOE study to the extent that copper would probably be stable (or at least alter slowly) in the basalts at the Hanford Site. However, the DOE analysis alone is insufficient to unequivocally reach this conclusion, because of additional uncertainties (e.g., temperature and radiation effects).

9. SOLUBILITY AND SPECIATION CALCULATIONS FOR YUCCA MOUNTAIN

Solubility and speciation calculations using geochemical models (e.g., EQ3/6) are being used by NNWSI to estimate radionuclide source terms and to evaluate the nature of various geochemical characteristics of the Yucca Mountain Site (KERRISK 1983; KERRISK 1984; OGARD 1984). Calculations such as these are sensitive to the assumptions, boundary conditions, and thermodynamic data on which they are based. Therefore, we attempted to verify the solubility and speciation calculations performed to date that are relevant to the Yucca Mountain Site.

9.1 DOE METHODOLOGY AND INFORMATION

Ogard and Kerrisk (OGARD 1984) discussed aspects of the groundwater chemistry along various potential flow paths from the Yucca Mountain Site to the accessible environment. They presented results of solubility and speciation calculations for U, Pu, Am, Sr, Tc, and Ra in three different groundwater formulations representative of the subsurface hydrologic system at Yucca Mountain. They also presented results of calculations quantifying the pH and Eh buffering capacity of the groundwaters. For the solubility and speciation calculations, Ogard and Kerrisk used EQ3/6 to simulate the equilibration of each water with a specific solid phase to control the solubility of a given radionuclide. In this manner, they obtained an estimate of the total concentration and aqueous speciation for the radionuclide in the groundwater of interest.   The solubility and speciation calculations were performed for three representative groundwaters. The temperature assumed for the calculations is not given, but it is likely that 25°C was used, as data for elevated temperature are generally not available for the elements addressed.

9.2 EVALUATION OF DOE INFORMATION

To verify the DOE results, we repeated the solubility and speciation calculations of Ogard and Kerrisk (OGARD 1984) using MINTEQ (FELMY 1984). Only the calculations for U, Pu, Am, and Sr were evaluated because thermodynamic data for technetium and radium were not available in a compatible format for MINTEQ at the time our calculations were completed. This approach of independently calculating the solubility and speciation behavior of several radionuclides can yield useful insights into potential inconsistencies and problems associated with assumptions and thermodynamic data used. It must be emphasized, however, that laboratory validation of calculated values should be accomplished to ensure that any such calculations can be considered to be reliable within limits of reasonable assurance (NRC 1984). Details of our evaluation may be found elsewhere (KELMERS 1985c); a summary of the conclusions follows.

- Our calculated solubility and speciation for uranium and strontium was in excellent agreement with DOE results (OGARD 1984).

- We obtained good agreement with the calculated solubility for americium by DOE. However, we obtained a significantly different speciation scheme. Thus, agreement with the calculated solubility may be fortuitous.

- Results of the plutonium comparisons calculations were extremely sensitive to the thermodynamic data and assumptions. Significant effort will have to be made to evaluate, validate, and perhaps improve the thermodynamic data for plutonium before geochemical calculations will be reliable for this element.

Significant uncertainty remains in using calculated solubility and speciation results as a source term in performance assessment calculations. It would be desirable to perform uncertainty calculations to determine what effect, if any, uncertainties in analytical concentrations of elements and related parameters such as pH and Eh would have on the calculated solubility and speciation of radionuclides. Calculated solubilities must be confirmed experimentally to provide reasonable assurance that nonconservative assumptions are avoided. Some of the limitations associated with such calculations include (1) the assumption of equilibrium, (2) missing or invalid thermodynamic data, (3) incomplete accounting for all relevant and important geochemical processes, and (4) lack of experimental validation of calculated results. These limitations are discussed in more detail in NRC (1984).

10. IMPLEMENTATION OF EQ3/6

Information from the three candidate repository site projects (e.g., KERRISK 1985; EARLY 1985; and ONWI 1984) suggests that DOE will utilize the geochemical computer code EQ3/6 alone or in conjunction with other available geochemical models to help evaluate (1) geochemical conditions within the geologic setting, disturbed zone, and waste package, (2) sorption and solubility and speciation processes; and (3) the alteration of host rock, packing/backfill materials, and waste package components. Therefore, to improve the capability of our projects to provide the NRC with independent evaluations of geochemical information obtained by the DOE, we brought the EQ3/6 software package (WOLERY 1979) on-line at ORNL to supplement our existing available codes (e.g., WATEQ, MINTEQ, PHREEQE, GEOCHEM, MINEQL).

Version 3230B of the EQ3/6 software package (with instructions for upgrading EQ6U21 to EQ6U23) was implemented and tested on the ORNL computer system. In addition to the EQ3/6 code and its required supplementary code EQLIB, the codes MCRT and EQTL were also brought up on the ORNL computer system. MCRT and EQTL provide for the compilation, documentation, and management of thermodynamic data files required to run EQ3/6. The successful conversion of the codes was confirmed by running the test cases for each code which were included as part of the software package tape. However, a detailed evaluation of the codes will require that several test cases be made up to test the range of input options for each code.

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13. ABSTRACT (200 words or less)

Information pertaining to the potential geochemical behavior of radionuclides at candidate sites for a high-level radioactive waste repository, which is being developed by projects within the Department of Energy (DOE), is being evaluated by Oak Ridge National Laboratory for the Nuclear Regulatory Commission (NRC). During this report period, emphasis was placed on the evaluation of information pertinent to the Hanford site in southeastern Washington. Results on the sorption/solubility behavior of technetium, neptunium, and uranium in the basalt/water geochemical system are summarized and compared to the results of DOE. Also, summaries of results are reported from two geochemical modeling studies: (1) an evaluation of the information developed by DOE on the native copper deposits of Michigan as a natural analog for the emplacement of copper canisters in a repository in basalt, and (2) calculation of the solubility and speciation of radionuclides for representative groundwaters from the Yucca Mountain site in Nevada.

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