

OAK RIDGE NATIONAL LABORATORY  
OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

WM DOCKET CONTROL  
CENTER

POST OFFICE BOX X  
OAK RIDGE, TENNESSEE 37831  
November 8, 1984

'84 11 13 PM 7

Dr. J. W. Bradbury  
Geotechnical Branch  
Office of Nuclear Material  
Safety and Safeguards  
U.S. Nuclear Regulatory Commission  
Room 623-SS  
Washington, D.C. 20555

Dear John:

Enclosed is the progress report for the month of October 1984 for B0290, "Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques and Procedures."

Also enclosed are some mailing address labels. When addressing mail, please use my entire address so as to reduce the possibility of loss and the receipt of information much faster.

Sincerely,

Susan K. Whatley, Manager  
Engineering Analysis And Planning  
Chemical Technology Division

SKW:kk  
Enclosure

cc: Office of the Director, NMSS (Attn: Program Support Branch)  
Division Director, NMSS Division of Waste Management (2)  
M. R. Knapp, Chief, Geotechnical Branch  
R. J. Starmer, Geotechnical Branch  
D. J. Brooks, Geotechnical Branch  
Branch Chief, Waste Management Branch, RES  
G. F. Birchard, Waste Management Branch, RES  
W. D. Arnold  
J. T. Bell  
J. G. Blencoe  
F. I. Case  
A. G. Croff  
N. H. Cutshall  
L. M. Ferris  
J. R. Hightower  
G. K. Jacobs  
A. D. Kelmers  
D. C. Kocher  
S. Y. Lee  
A. P. Malinauskas  
R. E. Meyer  
F. G. Seeley  
F. J. Smith  
R. G. Wymer  
G. C. Young  
SKW File

WM-RES  
WM Record File  
B0290  
ORNL

WM Project 10, 11, 16  
Docket No. \_\_\_\_\_  
PDR ✓  
LPDR ✓ (B, N, S)

Distribution:  
J. Bradbury | Joan-Ticket  
\*PHHe | \_\_\_\_\_  
(Return to WM, 623-SS) | C2

8412030646 841108  
PDR WMRES EXIORNL  
B-0290 PDR

1624



SKW  
11/07/84

## MONTHLY PROGRESS REPORT FOR OCTOBER 1984

PROJECT TITLE: Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques, and Procedures

PROJECT MANAGER: S. K. Whatley

TASK LEADER: A. D. Kelmers

SCIENTIFIC STAFF: W. D. Arnold, G. K. Jacobs, S. Y. Lee, R. E. Meyer, F. G. Seeley, and F. J. Smith

ACTIVITY NUMBER: ORNL #41 37 54 92 6 (FIN No. B0290)  
NRC #50 19 03 1

## HIGHLIGHTS:

Evaluative work with both neptunium and technetium is now being conducted under experimental parameters which closely simulate the in situ redox condition for the Hanford Site repository leading candidate horizon: anoxic redox conditions, Cohasset basalt, synthetic groundwater formulation GR-4, and elevated temperature. The sorption ratio and apparent concentration limit values being measured are compared with the "expected" and "conservative" distribution coefficient and solubility values recommended by the BWIP for site performance assessment modeling [SD-BWI-DP-001] and with "conservative best estimate" values summarized in the Site Characterization Plan [DOE/RL 82-3].

Technetium sorption onto Cohasset basalt under anoxic redox conditions was higher than that previously observed with McCoy Canyon basalt under similar test parameters ( $R_s$  of 10 to 12 L/kg vs 3 to 5 L/kg). The higher sorption with Cohasset basalt, as compared to McCoy Canyon basalt, may correlate with the larger amount of mesostasis and higher iron content of the mesostasis in the Cohasset basalt sample. Our  $R_s$  values are lower than the "expected"  $K_d$  value of 15 L/kg or the "conservative best estimate" value of 29 L/kg reported by the BWIP.

Neptunium sorption ratio values were highly dependent upon the particle size of the basalt used in the test;  $R_s$  values ranged from 4.7 to 275 L/kg for coarse to fine particles. The neptunium remaining in solution after contact was principally in the +4 valence state, but some +5 and +6 valence state neptunium was also present. Neptunium sorption ratio values were much higher for these anoxic condition tests than those previously measured under oxic redox conditions and are higher than those recommended by the BWIP.

The mineralogical characterization of the three basalt samples used in our work (from the Cohasset, Umtanum, and McCoy Canyon flows) was completed. There are significant differences in the morphology and composition of the

mesostasis phase of the three samples. The Cohasset and Umtanum samples have a larger mesostasis fraction than the McCoy Canyon and the mesostasis also has a higher iron content. The McCoy Canyon mesostasis is primarily glass with only limited microcrystalline inclusions while the Cohasset and Umtanum mesostasis has less glass and correspondingly more microcrystalline material.

#### TECHNICAL PROGRESS:

##### Technetium Studies:

The performance assessment for the Hanford Site may take credit for technetium retardation due to solubility limits in groundwater and/or sorption onto the host rocks. The BWIP data package of solubility and sorption Kd values recommended for use in modeling applications [SD-BWI-DP-001] lists an expected Kd of 15 L/kg for technetium and a conservative value of 0 L/kg. The expected value is apparently based on experimental results obtained in the presence of hydrazine. An expected solubility limit of  $10^{-9}$  mol/L and a conservative value of  $10^{-5}$  mol/L are given in the data package. The conservative value is based on experimental results obtained in the presence of hydrazine. We have previously strongly questioned the validity of the use of hydrazine in experiments to simulate the repository redox condition [NUREG/CR-3851, Vol. 1] and, therefore, the technetium geochemical values given in the data package may be considered of uncertain applicability for modeling purposes.

We have been investigating the sorption ratio and apparent concentration limit values for technetium in anoxic redox condition batch contact tests at 60°C. We feel that this test methodology best simulates the in situ redox condition. We are currently using Cohasset basalt (the leading candidate repository horizon) and synthetic groundwater GR-4 (the groundwater formulation which most closely simulates the Cohasset formation water composition). In previous work, we have shown that technetium sorption is observed only in the absence of oxidizing conditions and that the sorption ratio value measured is sensitive to contact time, temperature, groundwater composition, and the basalt sample used. We have suggested that sorption of technetium (initially present as the pertechnetate anion in solution) may result from reduction and chemisorption reactions involving the basalt surface.

During October, 14-d anoxic redox condition batch contact sorption tests were completed with Cohasset basalt and pertechnetate-spiked synthetic groundwater GR-4 at 60°C. As observed previously with McCoy Canyon basalt, moderate sorption was obtained from GR-4 with initial pertechnetate concentrations of  $10^{-12}$ ,  $10^{-8}$ , and  $10^{-6}$  mol/L, but essentially no sorption was observed from initial pertechnetate concentrations of  $10^{-4}$  and  $10^{-3}$  mol/L. The Rs values measured with Cohasset basalt were approximately three times those measured for McCoy Canyon basalt under the same experimental conditions. Values (mean  $\pm$  1 standard deviation) of the sorption ratio for the three initial pertechnetate concentrations for which sorption was observed are given in Table 1.

Table 1. Sorption ratios for technetium onto Cohasset basalt and McCoy Canyon basalt under anoxic redox conditions for 14 days at 60°C<sup>a</sup>

Initial Tc concentration (mol/L)	Rs (L/kg)	
	Cohasset	McCoy Canyon
10 <sup>-12</sup>	9.8 ± 0.7	3.5 ± 0.2
10 <sup>-8</sup>	16.2 ± 1.1	5.5 ± 0.7
10 <sup>-6</sup>	12.1 ± 2.7	4.0 ± 0.4

<sup>a</sup>Batch contact tests with synthetic groundwater formulation most representative of the specific flow; GR-4 for Cohasset, and GR-2 for McCoy Canyon. Groundwaters were spiked with <sup>99</sup>Tc and traced with <sup>95m</sup>Tc.

The larger values of Rs observed with Cohasset basalt, as compared to McCoy Canyon basalt, could be due to the larger amount of mesostasis and higher iron content of the mesostasis for the Cohasset basalt relative to McCoy Canyon basalt (see section on sample characterization). It is plausible that the microcrystalline components of the mesostasis could be the most chemically reactive component of the basalt. The differences in technetium sorption ratio could also be due, at least in part, to differences in the synthetic groundwaters GR-2 and GR-4. We have previously shown that technetium sorption is sensitive to the groundwater composition. However, for both basalt samples there was essentially no measurable sorption when the initial concentration of TcO<sub>4</sub><sup>-</sup> in the solution was equal to or greater than 10<sup>-4</sup> mol/L. Possibly, the reducing capacity of the basalt sample may have been exceeded at these higher pertechnetate concentrations. The data do not suggest approach to an apparent concentration limit. In order to explore the sorption isotherm more completely in the intermediate concentration range, we have initiated sorption studies for both Cohasset and McCoy Canyon basalts at initial concentrations of 10<sup>-6</sup> to 10<sup>-4</sup> mol/L TcO<sub>4</sub><sup>-</sup>. Since the solubility limit of technetium given as "expected" by the BWIP is based on the calculated solubility of reduced technetium, it is important to attempt to understand the reactions occurring between TcO<sub>4</sub><sup>-</sup> in solution and the basalt surface which may result in the reduction of technetium.

#### Uranium Studies:

No progress to report this month.

### Neptunium Studies:

All laboratory work with neptunium is now being carried out under geochemical conditions representative of the Hanford Site far field environment. Cohasset basalt is being used since that flow now is the leading candidate repository horizon [RHO-BW-ST-28 P DRAFT]. Synthetic groundwater GR-4, the most recent groundwater formulation established by the BWIP, is being used since this formulation is reportedly more representative of Cohasset flow groundwater [P. F. Salter, BWIP, personal communication, 1984]. The tests are being conducted under anoxic redox conditions in an argon-filled controlled-atmosphere glove box to allow the basalt to establish the redox condition of the test; we believe that this test methodology best simulates the in situ far field redox condition in laboratory experiments. The tests are being conducted at 60°C in order to simulate the in situ far field temperature.

A potentially important licensing concern which we have previously raised [NUREG/CR-3851, Vol. 1] involves the sorption behavior of neptunium with basalt samples from different flows. Both our data [NUREG/CR-3851, Vol. 2] and results published by the BWIP [RHO-BWI-LD-48] suggest that sorption may be characteristically different with samples from different flows. Thus, the licensing concern is: Can neptunium sorption data measured in laboratory experiments with samples of a given basalt flow (Umtanum basalt in the case of much of the information published by the BWIP) be considered applicable for the description of neptunium sorption with other basalt flows? This concern is potentially significant to the NRC analysis effort since the BWIP reference Kd values recommended for use in site modeling calculations [SD-BWI-DP-001] were based on information collected in tests with Umtanum basalt, while the leading candidate horizon is now the Cohasset basalt. To explore this concern, we plan to construct sorption isotherms for neptunium with Cohasset, McCoy Canyon, and Umtanum basalts. First, however, a series of scouting tests with Cohasset basalt and synthetic groundwater GR-4 are being completed to help optimize the test parameters for the isotherm experiments. The effects of basalt particle size and of contact time on the sorption ratio are being explored.

Tests were completed this month to evaluate the effect of the particle size of the basalt sample used in the test on the neptunium sorption ratio value measured. Since we now believe that sorption of Np(V) includes a combination of reduction and chemisorption processes which involve the active surface of the basalt [R. E. Meyer, ORNL, manuscript in preparation], it seemed likely that the basalt-surface-area/groundwater-volume ratio of the batch contact tests could be an important experimental parameter. This parameter had not been previously explored in work related to the Hanford Site. All the results reported by the BWIP involved use of basalt particles in the 0.03-0.85 mm size range, while our previous work used particles of 0.044-0.210 mm size range.

The neptunium sorption ratio proved to be highly dependent upon the particle size of the Cohasset basalt used in the test (see Table 2). The Rs values ranged from 4.7 L/kg for the largest particles (-40/+70 mesh size) to 275 L/kg for the finest particles (-400 mesh size). Thus, the basalt

particle size range employed appears to play an important role in determining the sorption ratio value measured. In future tests, it probably will be desirable to give greater attention to the particle size range selected for the test. The results in Table 2 suggest that, under some conditions, the finer-sized particles in a given fraction could dominate the apparent test result.

These experiments under anoxic redox conditions with Cohasset basalt (Table 2) gave much higher neptunium sorption ratio values than the value of 1.7 L/kg established for the linear sorption isotherm in our tests under oxic redox conditions at 25°C with McCoy Canyon basalt [NUREG/CR-3851, Vol. 1]. The planned anoxic condition isotherm experiments will help establish if this greater sorption is due primarily to the change to anoxic instead of oxic redox conditions or to the use of Cohasset in place of McCoy Canyon basalt. Previously, increasing the temperature from 25 to 60°C under oxic conditions did not result in such a marked increase in sorption ratio values with McCoy Canyon basalt [NUREG/CR-3851, Vol. 2].

Table 2. Neptunium sorption as a function of Cohasset basalt particle size under anoxic redox conditions at 60°C<sup>a</sup>

Cohasset basalt fraction	Particle size ( $\mu\text{m}$ )	Mesh size	Surface area <sup>b</sup> ( $\text{m}^2/\text{g}$ )	$R_s^c$ (L/kg)
1	<420/>210	-40/+70	3.47	4.7 $\pm$ 1.2
2	<210/>105	-70/+140	4.60	14.5 $\pm$ 4.9
3	<105/>74	-140/+200	2.90	56.6 $\pm$ 8.8
4	<74/>44	-200/+325	2.70	202 $\pm$ 101
5	<44/>37	-325/+400	5.11	235 $\pm$ 9
6	<37	-400	1.94	275 $\pm$ 134

<sup>a</sup>Neptunium sorption tests involved contacting 0.4 g of the basalt fraction with 4.0 mL of synthetic groundwater GR-4 spiked with  $3 \times 10^{-7}$  mol/L  $^{237}\text{Np}$  (traced with  $^{235}\text{Np}$ ) under anoxic redox conditions for 14 d at 60°C.

<sup>b</sup>Surface area measured by BET nitrogen adsorption method.

<sup>c</sup> $R_s$  values are mean  $\pm$  1 standard deviation for three replicate samples.

As shown in Table 2, the surface area of the various fractions of Cohasset basalt (as determined by BET nitrogen adsorption) did not correlate well with the physical particle size range of the fractions. This was particularly puzzling since the neptunium sorption showed a strong positive correlation with decreasing particle size. We are further exploring the apparently anomalous relation of surface area to particle size.

The distribution of neptunium valence states was determined by solvent extraction techniques for the initial neptunium-spiked groundwater and for the solutions recovered after contact with the Cohasset basalt for 14 d. As shown in Table 3, most of the neptunium remaining in solution after the contact had been reduced from Np(V) to Np(IV). Some neptunium also remained in the +6 valence state after the contact. Additional information about the rate of change of the neptunium valence states will become available from the sorption rate tests underway.

Table 3. Neptunium valence state distribution after contact under anoxic redox conditions<sup>a</sup>

Cohasset basalt fraction (see Table 1)	Np concentration after contact (mol/L)	Np valence distribution (%)			
		(IV)	(V)	(VI)	Total
1	$1.2 \times 10^{-7}$	69.6	22.6	7.8	100.0
2	$8.6 \times 10^{-8}$	70.3	15.5	6.8	92.6
3	$3.9 \times 10^{-8}$	52.5	21.6	6.6	80.6
4	$1.7 \times 10^{-8}$	65.0	24.0	11.9	100.9
5	$1.2 \times 10^{-8}$	65.3	24.3	13.0	102.6
6	$7.9 \times 10^{-9}$	73.5	18.5	16.7	108.7

<sup>a</sup>The initial synthetic groundwater GR-4 was  $3.0 \times 10^{-7}$  mol/L in neptunium distributed as 19.3% Np(IV), 77.3% Np(V), and 4.6% Np(VI), for a total of 101.2%.

#### Chromatographic Studies:

No progress to report this month.

### Sample Acquisition:

There was no contact this month from NNWSI staff relative to the samples of Yucca Mountain materials which we requested [Letter Report L-290-6, May 22, 1984].

### Sample Characterization:

The mineralogical and chemical characterization of the three basalt samples (McCoy Canyon, Cohasset, and Umtanum) which have been used by our project was completed. Noticeable differences in terms of mineral distribution and chemical composition of the phases (particularly of the mesostasis) were observed among the samples. The results of point counts of mineral distribution indicated (Table 4) that the plagioclase phase is the major component of the McCoy Canyon sample while mesostasis is the major phase of the Cohasset and Umtanum samples. Pyroxene is the other primary mineral phase. The quantitative differences of the phases among the samples were small. There are some differences of grain size distribution, but the morphological features of plagioclase and pyroxene are very similar among the basalts. Magnetite, a minor phase in the basalts, has subhedral shapes with a large size variation in the McCoy Canyon sample, but has cruciate and dendritic forms of relatively uniform sizes in both the Cohasset and Umtanum samples. (Micrographs will be included in the Annual Report for FY 1984.)

The significant differences between the three basalt samples are the morphology and composition of the mesostasis phase. In the McCoy Canyon sample, the mesostasis is dominated by glass with limited amounts of microcrystalline magnetite, apatite, and pyrite inclusions. On the other hand, the mesostasis in the Cohasset and Umtanum samples has aphanitic texture with confused aggregates consisting of microcrystalline plagioclase and pyroxene and amorphous iron-rich globules exsolved from the interstitial glass. The chemical composition of the samples, analyzed by energy dispersive x-ray spectrometry, indicated (Table 5) only small differences in the bulk composition, but large differences in selected areas of the mesostasis. The bulk analyses showed that the Cohasset and Umtanum samples have higher iron content than the McCoy Canyon, the Umtanum sample has higher magnesium and calcium than the others, and the Cohasset sample has lower silicon than the others. However, the differences are only one to three percent, expressed as oxides. In the mesostasis, very large differences of  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$  and  $FeO$  were detected among the samples. The  $SiO_2$  and  $Al_2O_3$  concentrations, the dominant component of residual glass, are the highest in the McCoy Canyon. The  $FeO$  and  $TiO_2$  concentrations, the dominant components of the iron-rich globules and microcrystalline magnetite, are the highest in the Cohasset. The oxide values of the mesostasis of the Umtanum were in-between those of the mesostasis of the Cohasset and the McCoy Canyon samples.

Table 4. Volumetric distribution of primary components of the McCoy Canyon, Umtanum and Cohasset basalts<sup>a</sup>

Component	Composition (%)		
	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 (standard deviation) with n=3.

Table 5. Chemical composition of bulk and selected mesostasis area of the McCoy Canyon, Umtanum, and Cohasset basalts<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>
SiO <sub>2</sub>	56.1(0.7)	67.4(3.3)	56.6(0.4)	63.6(2.1)	53.6(0.3)	56.8(2.6)
Al <sub>2</sub> O <sub>3</sub>	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	11.1(0.3)	3.7(2.4)	12.1(0.2)	8.9(2.1)	12.5(0.4)	15.9(2.9)
TiO <sub>2</sub>	1.5(0.1)	0.8(0.4)	2.1(0.1)	1.4(0.5)	1.9(0.1)	3.6(0.9)
K <sub>2</sub> 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)
PO <sub>4</sub>	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. The FeO included ferric iron.

<sup>b</sup>Mean (standard deviation) with n = 4.

<sup>c</sup>Mean (standard deviation) with n = 10.

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

### Geochemical Calculations:

No progress to report this month.

### General Aspects:

The following comments are in response to the NRC Project Manager's review of the September Monthly Progress Report.

#### Uncertainties in Sorption Ratio Values -

The technetium sorption ratio ( $R_s$ ) values are the mean  $\pm$  1 standard deviation for three replicate tests. One test constitutes a test tube containing a given weight of crushed basalt 0.4 g and a volume of technetium-containing groundwater 4 mL which are contacted by rocking for a fixed period of time. The  $R_s$  value for each test is the calculated concentration of technetium on the basalt divided by the measured concentration of technetium remaining in the groundwater after contact with the basalt. For technetium studies, we count the  $^{95m}\text{Tc}$  gamma peak in the initial groundwater solution (the groundwater is spiked with  $^{99}\text{Tc}$  and traced with  $^{95m}\text{Tc}$ ) and the  $^{95m}\text{Tc}$  remaining in solution after contact with the basalt and recovery of the solution by centrifugation. We assume isotopic equilibrium for technetium species, thus the ratio of  $^{95m}\text{Tc}$  activities represents the ratio of the  $^{99}\text{Tc}$  concentrations. This assumption probably is valid since both the  $^{95m}\text{Tc}$  and  $^{99}\text{Tc}$  stock solutions are pertechnetates; no other valences or species should exist in oxic technetium solutions. The concentration of  $^{95m}\text{Tc}$  sorbed onto the basalt is then calculated as the difference between the concentration of the contacted solution and the starting solution. It is not practical to attempt to count the  $^{95m}\text{Tc}$  on the basalt directly since included solution containing non-sorbed Tc can not be removed without disturbing the sorption steady state condition and, for less energetic isotopes, sample self-adsorption could quench the apparent count rate. No correction is made for sorption onto the test tube in the case of technetium. We routinely run control tests and have not measured significant loss from solution in blank or control tests (no basalt present) for technetium after we switched from glass to polypropylene test tubes about a year ago. Since the  $R_s$  value is a ratio of two numbers, one of which is obtained by difference, the precision is best for  $R_s$  values near 1 (50% sorption) and is considerably poorer for either high or low  $R_s$  values. Considering the extreme difficulty of having to do all this work inside a glove box in order to maintain anoxic redox conditions (work in a glove box goes about 5 to 10 times slower than on a bench top), we feel that the precision may be about as good as is practically achievable.

An additional experimental problem has surfaced in the most recent technetium work at 60°C under anoxic conditions. The capped polypropylene tubes occasionally allow some leakage or loss of solution during the contact period because the caps do not always fit perfectly or possibly by diffusion through the tube wall. In tests where there has been a measurable loss of solution, we assume that  $^{95m}\text{Tc}$  was lost from the test

tube in proportion to the volume loss and correct the calculated technetium concentration on the basalt for this loss. This correction represents another possible source of uncertainty in the final calculated  $R_s$  value. We are exploring the use of a different style polypropylene test tube from a different manufacturer to attempt to avoid this solution loss.

The experimental protocol for the neptunium samples is similar. We have regularly run blank or control tests in parallel and corrected the neptunium concentration measured in solution after contact for the loss from solution measured with the control samples. A small loss from solution for control samples is usually observed. As reported in this monthly progress report, we are finding Np(IV), Np(V), and Np(VI) in all our solutions. It was a little surprising to find three valence states present and this has led us to wonder if all three valence states of neptunium are present in the same species. If not, then the assumption that the  $^{235}\text{Np}$  tracer is in equilibrium with the  $^{237}\text{Np}$  spike could be open to question. The bulk of the neptunium in solution is  $^{237}\text{Np}$ , but since this is a low activity alpha-emitter, we have to trace it with  $^{235}\text{Np}$  which has a strong gamma peak and can be easily counted. If the two isotopes of neptunium are not in equilibrium, then the calculated  $R_s$  value which is based on  $^{235}\text{Np}$  might not be representative of the bulk  $^{237}\text{Np}$  sorption. We plan to address this aspect in future work. In particular, we are going to explore experimental methods of assuring isotopic equilibrium before the neptunium isotopes are added to the groundwater.

Unfortunately, the chemistry of neptunium in alkaline solutions is poorly understood and we do not know what species may be present in the groundwaters. The Np(IV) species is usually assumed to be  $\text{Np}(\text{OH})_5^-$ ; however, there is no experimental evidence to support the presumed existence of this species. The Np(V) may be present as a mixture of  $\text{NpO}_2^+$  and several hydroxyl-carbonate complexes. Spectroscopic evidence of such complexes has been reported but the stability constants are unknown. The Np(VI) could be present as a number of species. In addition, stable fluoride complexes of all three neptunium valence states seem possible by analogy with uranium chemistry. These neptunium-containing groundwater solutions are likely quite complex chemically and sorption ratios measured represent the sum of the behavior of all the valence states and species present.

#### Solvent Extraction Methods of Determining Valence States -

The method for determining the neptunium valence is based on work done in the ORNL Analytical Chemistry Division in the late 1950's and at Hanford in the early 1960's. The following steps are involved:

1. A 1 mL sample of the neptunium-containing groundwater is taken and 8 M HCl is added to adjust the solution to 1 M HCl.
2. The Np(IV) is extracted with 0.5 mL of 1 M thenoyltrifluoroacetone in xylene and the organic extract is recovered by centrifugation and an aliquot is counted.

3. The aqueous phase from the preceding step is adjusted to 4 M HCl by the addition of 8 M HCl.
4. The Np(VI) is extracted with 0.5 mL of tri-n-octyl amine in xylene and the organic extract is recovered by centrifugation and an aliquot is counted.
5. The Np(V) in the aqueous phase from the preceding steps is determined by counting an aliquot.
6. The material balance is determined by summing the three counts from the solvent extraction procedure and comparing this value with the initial total count for neptunium. The percent valence distribution is calculated from the ratio of the individual measured values to the initial total count.

All these operations are conducted inside a glove box to eliminate valence changes which might occur due to oxygen in air. This analytical method involves a number of solution volume measurements and transfers, and three separate gamma counts; this leaves considerable margin for errors, either systematic or random, to creep into the result. Thus, we do not feel that great emphasis should be given to small differences in the valence percentages between various samples. This method is quite valuable, however, for identifying the major valence(s) present. It also is the only valence determination method which is applicable at the very low concentrations of neptunium involved in the sorption experiments.

The technetium valence state in technetium-containing groundwater samples is similarly determined by extracting the Tc(VII) with 0.05 M tetraphenylarsonium chloride in chloroform. The technetium activity remaining in the aqueous phase is reported as reduced technetium. We know of no analytical solvent extraction methods for Tc(IV) or other reduced technetium valence states. As with neptunium, the chemistry of lower valence states in alkaline solution is very poorly understood and we can only report the technetium as either Tc(VII) or reduced technetium.

#### MEETINGS AND TRIPS:

None

#### REPORTS AND PUBLICATIONS:

The progress report for the period January-March 1984 was typed on mats in final form and sent to the NRC Project Manager for issuance as NUREG/CR-3851, Vol. 2.

The progress report for the period April-June 1984 was revised after receipt of the NRC Project Manager's review. The report is undergoing the final editing and release process. After it is typed on mats in final form, it will be forwarded to the NRC Project Manager for issuance as NUREG/CR-3851, Vol. 3.

Preparation of the annual report for October 1983-September 1984 has been initiated. No quarterly progress report will be prepared for the period July-September 1984.

**PROBLEM AREAS:**

None

**COST/BUDGET REPORT:**

Expenditures were \$50.0K for the month of October. A detailed cost/budget report will be sent under separate cover.

