OAK RIDGE NATIONAL LABORATORY

OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

April 9, 1984

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

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Dear John:

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

Sincerely,

Susan K. Whatley, Manager
Engineering Analysis And Planning

SKW:kk
Enclosure
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MONTHLY PROGRESS REPORT FOR MARCH 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, N. H. Cutshall, G. K. Jacobs, J. H. Kessler, S. Y. Lee, and R. E. Meyer

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

HIGHLIGHTS:

Anoxic redox condition batch contact tests at 60°C showed no significant technetium sorption onto McCoy Canyon basalt from pertechnetate-traced synthetic groundwater GR-2. However, substantial technetium sorption was observed (Rs values of ~70 L/kg) at 27°C when a pertechnetate-traced 0.1 $\underline{M}$ NaCl solution was used in place of synthetic groundwater. These preliminary results suggest that the difference in technetium sorption behavior under anoxic redox conditions is not due to the contact methodology (batch $\underline{vs}$ column), but could be related to the solution composition (groundwater $\underline{vs}$ dilute sodium chloride). Additional batch contact experiments are underway to define procedures for anoxic condition experiments at 60°C.

Uranium sorption isotherms have been completed at 27°C for oxic, anoxic, and reducing (hydrazine added) redox conditions with McCoy Canyon basalt and synthetic groundwater GR-2. The sorption ratios obtained under oxic conditions showed little trend with uranium concentration and averaged ~1.6 L/kg. This is significantly lower than the "conservative best estimate" value of 6 L/kg for basalt under oxic conditions given in the BWIP Site Characterization Report, and higher than the value of 0.2±0.5 L/kg for Flow E basalt (the same as McCoy Canyon) under oxic conditions with synthetic groundwater GR-2 reported by BWIP [RHO-BWI-LD-48]. (Uranium sorption ratio values given in the BWIP report varied by two orders-of-magnitude for various basalt flows or groundwater formulations.) Uranium sorption values obtained under anoxic conditions were slightly higher (1.8 to 4.8 L/kg) and displayed an inverse relationship to uranium concentration, i.e., normal sorption behavior. Sorption ratios under reducing conditions bracketed (15 to 89 L/kg) the corresponding BWIP "best estimate value" of 40 L/kg. Under oxic conditions, the uranium(VI) species in synthetic groundwater GR-2 is calculated by MINTEQ to be the anion $UO_2(CO_3)_3^{4-}$ In general, anions exhibit poor sorption on geologic materials, thus our uranium sorption values may be in agreement with expected behavior. Additional uranium sorption work is underway at 60°C under anoxic conditions.

Column chromatographic tests with McCoy Canyon basalt and synthetic groundwater GR-4 at 25 and 70°C have confirmed the batch test technetium(VII) sorption ratio value of 0 L/kg. Technetium was not retarded and broke through the column in one void column. Tests with neptunium(V) have just been started, but preliminary observations suggest that Np(V) retardation may be sensitive to temperature, with greater Rf values obtained at higher temperatures. Additional neptunium results will be reported next month.

McCoy Canyon basalt was crushed and separated into a number of particle size fractions ranging down to <2 µm. X-ray diffraction and elemental analysis of the fractions did not indicate that any major differentiation of basalt minerals was occurring during crushing and size separation. The x-ray diffraction results suggest a slight enrichment of plagioclase in the +20 µm fractions and of x-ray-amorphous glass in the -20 µm fractions.

Under the geochemical modeling activity, the BWIP synthetic groundwater formulations GR-3 and GR-4 were modeled at 60°C to compare saturation indices and speciation results with previous calculations for 25°C. They were more oversaturated with respect to calcite, but less saturated with respect to fluorite and the silica phases.

The radionuclide solubility calculations published by BWIP [RHO-BWI-ST-39P] were checked using MINTEQ. Results generally were in excellent agreement. When the information in the data bases were consistent, similar to essentially identical solubilities were calculated. The few inconsistencies encountered were related to the data base information, not the calculational methodology. This emphasises the importance of having well-checked, internally consistent data bases for calculations related to repository licensing activities.

Modeling the actinide speciation reported by Cleveland et. al. from experiments with actual BWIP groundwater is proceeding slowly. MINTEQ does not converge well when modeling elements with multiple oxidation states. First indications are that Cleveland's results may not be confirmed by equilibrium arguments, and suggest that kinetic constraints may have played a large role in Cleveland's work. More careful modeling and sensitivity analyses are being carried out.

A statistical treatment of sorption data variance and standard deviation is underway. Improved, statistically valid methods of calculating variance and standard deviations for sorption ratio and desorption ratio values obtained from batch contact tests are being developed.

TECHNICAL PROGRESS:

Technetium Studies:

We have observed different technetium sorption behavior in anoxic redox condition (air excluded) experiments conducted in different ways. Essentially no sorption of technetium onto McCoy Canyon basalt from pertechnetate-traced synthetic groundwater GR-2 was observed at 27°C in experiments conducted in a controlled-atmosphere glovebox with an argon atmosphere containing only 0.3 to 0.5 ppm oxygen. These results (described in the February Monthly Progress Report) were for experiments for both 14-day and 50-day contact periods with McCoy Canyon basalt crushed, sized, and stored in either air or argon. However, considerable sorption of technetium onto the same sample of McCoy Canyon basalt was earlier observed in a recirculating column experiment [NRC/RES FIN No. B0462] under similar anoxic conditions (controlled-atmosphere glovebox) when the pertechnetate-traced solution was 0.1 $\underline{M}$ NaCl adjusted to pH 9. In experiments done by Prof. R. L. Clark under our project last summer (see Letter Report L-290-2, "Studies of the Surface Character of Basalt and Its Ability to Adsorb Technetium"), some technetium sorption was observed on <325 mesh-size McCoy Canyon basalt from pertechnetate-traced synthetic groundwater GR-2 at 60°C in tests lasting for 99 days. (It should be noted that Clark's experiments were done in sealed glass containers with the fine fractions of basalt crushed in air, and a freeze-thaw technique was used to deaerate the GR-2 solution. The batch contact tests described last month were carried out in polypropylene test tubes and a larger-sized basalt fraction was used.) Prof. Clark's experiments suggest that some technetium sorption from synthetic groundwater GR-2 might be observed with -70/+325 mesh basalt if: the temperature was elevated to 60°C, the oxygen was more carefully excluded, and/or longer contact times were used.

Anoxic redox condition (air excluded) test methodology likely simulates or approximates actual BWIP repository conditions more realistically than the reducing redox condition experiments in an air environment with hydrazine added to the synthetic groundwater, as was done by BWIP. We are now attempting to resolve the differences in technetium behavior observed with the different anoxic condition experimental methodologies. It is important to at least qualitatively understand the sorption/precipitation reactions involved in the removal of technetium from solutions in contact with basalt in laboratory tests seems important in order to evaluate the BWIP data and BWIP description of expected technetium retardation in the engineered facility and/or the site or far field.

Procedure for Maintaining Anoxic Conditions at 60°C

At the present time, we do not have elevated temperature apparatus inside a controlled-atmosphere glove box to permit carrying out the batch contact tests within the glove box, as was done at 27°C. Therefore, some anoxic experiments at 60°C were carried out by adapting a procedure which is used to transfer materials from one controlled-atmosphere glove box to another. In this transfer procedure, Mason jars are filled inside a glove box with the materials and then sealed with the rubber-gasketed lids before transfer. For our sorption experiments, we prepared the samples inside a glove box. The test samples were placed into Mason jars along with several tubes which contained 5% Na_2SO_3 solution. The purpose of these tubes, which had caps with permeable membranes, was to attempt to chemically scavenge any oxygen that might enter the jars during the contact period outside the glove box. The jars were then taken outside the controlled-atmosphere glove box and the samples were contacted by shaking in an air thermostat at 60°C. After contacting, the jars were cooled in a vessel which was continuously flushed with argon. The jars were then taken back inside a glove box and opened for weighing, pH measurement, centrifugation to recover the solution, and sampling for ^{95m}Tc gamma counting.

Because the Mason jars were outside the glove box for long periods of time, there was some uncertainty that the rubber seal of the jar lid and the Na_2SO_3 scavenger adequately protected the basalt/groundwater samples from oxygen from air in leakage. We attempted to determine whether there was any significant amount of oxygen in the jars after the contact period by the following technique. A suction device was fitted to a Mason jar lid and connected directly to the glove box oxygen analyzer. Several Mason jars were prepared inside the glove box, brought outside for contacting, and then transferred back to the glove box to be opened. When the jars were opened, they were capped with the suction lid as quickly as possible and the   gen concentration was monitored. Two initial tests indicated that   oxygen was present in jars that had been outside the glove box for 14 ...rs. The first of these two jars was empty and the second contained   ur tubes filled with Na_2SO_3 oxygen scavenger solution. In both cases, the oxygen concentration indicated by the analyzer peaked in from one to one and a half minutes after the jars were opened. The peak concentrations were 17 ppm oxygen for the empty jar and 15 ppm for the jar with the oxygen scavenger tubes. The baseline oxygen concentration in the chamber at the time of these tests was 2.5 ppm oxygen. It appears that some air in leakage had occurred, but whether this was enough to affect the basalt/groundwater samples in the test tubes is not known.

Anoxic Condition Sorption Tests with Synthetic Groundwater GR-2 at 60°C

Using the Mason jar technique, we completed anoxic condition sorption tests at 60°C for technetium sorption onto -70/+325 mesh-size McCoy Canyon basalt. These were the first anoxic condition tests at 60°C, except for Clark's experiments in glass tubes with the fine-sized basalt. Synthetic groundwater GR-2 was used, and the basalt had been crushed, sized, and stored in an argon atmosphere. The groundwater contained 10^{-8} mol/L ^{99}Tc and tracer ^{95m}Tc. The contact time was 14 days in plastic (polypropylene) test tubes.

As in the anoxic condition tests at 27°C reported last month, essentially no sorption of technetium was observed. The sorption ratios for triplicate samples were 0±0.2 L/kg. The basalt used had been crushed, sized, and stored in an argon atmosphere. However, we are still not certain that the Mason jar technique maintained a sufficiently oxygen-free condition for us to conclude that these sorption ratios are representative of in situ far-field conditions.

Anoxic Condition Sorption Tests with 0.1 M NaCl Solution at 27°C

We also completed some anoxic condition batch tests this month at 27°C using 0.1 M NaCl as the solution instead of synthetic groundwater GR-2. The primary reason for these experiments was to test the Mason jar procedure described above by comparing the results of experiments done inside a controlled-atmosphere glove box and in the Mason jars outside the glove box. We selected 0.1 M NaCl as the solution because previous recirculating column experiments (NRC/RES FIN No. B0462) had shown that there should be substantial sorption of technetium onto basalt from the 0.1 M NaCl solution under anoxic conditions, but not under oxic conditions. In the batch contact tests this month, all of the pertechnetate-traced solutions and McCoy Canyon basalt samples were prepared inside the controlled-atmosphere glove box, and the Mason jar was loaded with three test samples, three control samples (no basalt), and four Na_2SO_3 scavenger tubes inside the glove box. The jar was taken outside the chamber for the contact period and then returned to the chamber for centrifugation, etc., as described above. The tests inside the glove box were conducted as previously described.

The results (Table 1) of a 14-day contact test at 27°C in Mason jars showed considerable technetium sorption. This indicated that not enough oxygen entered the Mason jars to affect the sorption of technetium for two of the three samples. (For one of the samples, the sorption was considerably lower.) The average of Rs the other two Mason jar test samples was 71.9 L/kg, nearly identical to the average of 69.2±3.9 L/kg for the triplicate samples contacted inside the glove box.

Table 1
Technetium Sorption Under Anoxic Conditions
onto McCoy Canyon Basalt from 0.1 $\underline{M}$ NaCl Solution at 27°C

Sample Tubes	pH	Mean count rate (counts/ks/mL)			Rs (L/kg)
		Standard	Controls	Sample	
Inside	8.9	67,432	57,168	7,272	69.6
glove box	8.9			7,117	72.9
	8.9			7,732	65.2
In Mason jars	9.0		64,052	17,176	28.7
outside	9.1			8,545	67.2
glove box	9.1			7,709	76.5

Conditions: 0.4 g McCoy Canyon basalt, -70/+325 mesh-size, ground,
sized, and stored in argon atmosphere; 4 mL 0.1 $\underline{M}$ NaCl
containing 10^{-8} $\underline{M}$ ^{99}Tc and tracer ^{95m}Tc; contacted
14 days at 27°C.

These moderately high Rs values indicate considerable sorption of
technetium by McCoy Canyon basalt from 0.1 $\underline{M}$ NaCl solution under anoxic
conditions. These tests, which were done by batch contact methodology,
tend to confirm the earlier recirculating column test results in 0.1 $\underline{M}$
NaCl (done under NRC/RES FIN #B0462) which showed substantial technetium
sorption. These preliminary scouting tests under anoxic conditions
suggest that the high Rs values observed with basalt and a sodium chloride
solution are not dependent on the contact method used. They do suggest
that differences in the solution compositions may be in some way respon-
sible for the differences observed in technetium sorption behavior; we
will be exploring this in more detail in the future. At the present time,
the cause of the apparent difference in technetium sorption behavior
observed between the sodium chloride solution and synthetic groundwater
must be considered unknown.

Some additional experiments are underway with the Mason jars left outside
the glove box for times longer than 14 days. However, this test procedure
involving the use of Mason jars outside the glove box has the disadvantage
that any intrusion of oxygen into the jars cannot be detected until the
end of the test. In addition, the transfer in and out of the glove box is
tedious and time consuming. A more useful approach to conducting anoxic
condition batch contact experiments at elevated temperatures may be to
heat and contact the samples inside the controlled-atmosphere glove box
where the oxygen concentration is continuously monitored. We are
exploring this procedure by constructing an air-bath thermostat inside one
of the glove boxes. This will be described in future progress reports.

Uranium Studies:

The batch contact tests completed this month essentially finish the uranium sorption tests planned for 27°C. Tests have now been carried out with McCoy Canyon basalt both crushed, sized, and stored under argon in the controlled-atmosphere box and similarly prepared in air, and under oxic, anoxic, and reducing (hydrazine added) redox conditions. The uranium was added as U(VI) in synthetic groundwater GR-2. For the anoxic condition tests, the traced groundwater was sparged in the controlled-atmosphere box. The results are presented in Table 2.

Table 2
Uranium Sorption onto McCoy Canyon Basalt from Groundwater GR-2

Basalt Crushing Atmosphere	Initial Uranium (mol/L)	14-d Contact		50-d Contact	
		pH	Rs (L/kg)	pH	Rs (L/kg)
Oxic Conditions					
Argon	10^{-7}	9.0	1.6±0.2	8.9	1.7±0.3
	10^{-6}	9.0	2.0±0.3	8.9	1.7±0.2
	10^{-5}	9.0	1.3±0.1	8.9	1.2±0.1
	10^{-4}	9.0	1.8±0.1	8.9	1.4±0.1
Air	10^{-6}	9.1	2.0±0.2	9.1	1.8±0.1
	10^{-4}	9.0	1.6±0.2	9.0	1.4±0.1
Anoxic Conditions					
Argon	10^{-7}	9.7	4.0±0.1	9.5	4.8±0.8
	10^{-6}	9.6	3.8±0.1	9.6	3.4±0.1
	10^{-5}	9.6	2.3±0.3	9.5	2.5±0.3
	10^{-4}	9.6	2.0±0.2	9.5	2.4±0.2
Air	10^{-6}	9.6	2.0±0.2	9.5	2.4±0.2
	10^{-4}	9.6	1.8±0.1	9.4	1.9±0.6
Reducing (Hydrazine) Conditions					
Argon	10^{-6}	9.5	61.5±4.4	9.5	88.5±8.6
	10^{-4}	9.5	17.4±0.5	9.4	29.2±2.6
Air	10^{-6}	9.5	46.4±6.3	9.5	68.2±5.7
	10^{-4}	9.5	15.0±1.4	9.5	24.2±2.4

Contact Conditions: 27°C, 0.4 g -70/+325 mesh size McCoy Canyon basalt, 4 mL GR-2.
Solution Recovery: Centrifuged 30 min at 5000 rcf.
Rs Values: Mean ± one standard deviation for triplicate samples.

There seemed to be a small but consistent difference in the Rs values at a given uranium concentration and redox condition with air-crushed vs argon-crushed basalt. Significantly higher Rs values were obtained with the argon-crushed basalt under anoxic or reducing redox test conditions. The data for the anoxic condition tests suggests typical sorption isotherm behavior, with higher Rs values at lower uranium concentrations (Figure 1). The Rs values obtained when hydrazine was added to establish reducing conditions were much larger than those measured under oxic or anoxic conditions. It is possible that in the oxic and anoxic condition tests we are observing only sorption of uranium(VI), possibly the $UO_2(CO_3)_3^{4-}$ ion as calculated by MINTEQ for these conditions, onto the basalt. It is not clear if valence reduction is involved in the higher Rs values measured under anoxic conditions. The sorption reaction in the presence of hydrazine is unknown, but obviously is quite different and could involve chemical reduction of the uranium.

For the 50-day contacts, no significant change in the Rs values were observed compared to the 14-day values under oxic or anoxic conditions. Apparently these tests reached steady state in 14 days or less. In the presence of hydrazine, however, the sorption process seemed to be continuing since larger Rs values were obtained at 50 days. Again, the hydrazine-containing system seems to be behaving differently from the oxic or anoxic tests.

As we discussed last month, we are obtaining uranium(VI) sorption ratio values which are larger than those reported by BWIP for Flow E basalt (the same as McCoy Canyon) and we raised the question of flow specificity of uranium sorption behavior. This will be explored further when samples of additional basalt flows become available.

The uranium sorption tests will be extended to 60°C using test methodology established for technetium.

Neptunium Studies:

Neptunium experiments underway will be reported next month.

Chromatographic Studies:

Last month we determined the retardation factor (R_f) for technetium (TcO_4^-) under oxic redox conditions at 25°C with a flow rate of 0.96 ml/min. The results indicated that the R_f value was close to 1. There was no evidence for sorption, anion exclusion ($R_f < 1$), or precipitation of technetium on the McCoy Canyon basalt column. This month the flow rate was reduced to 0.48 ml/min and the column temperature was elevated to 70°C from room temperature (25°C). The results show again that there is no measurable retardation of technetium (Table 3), suggesting that changes of flow rate and temperature do not influence the sorption of TcO_4^- on the basalt column. These results confirm the sorption ratio of ~0 L/kg determined by batch contacts under oxic conditions.
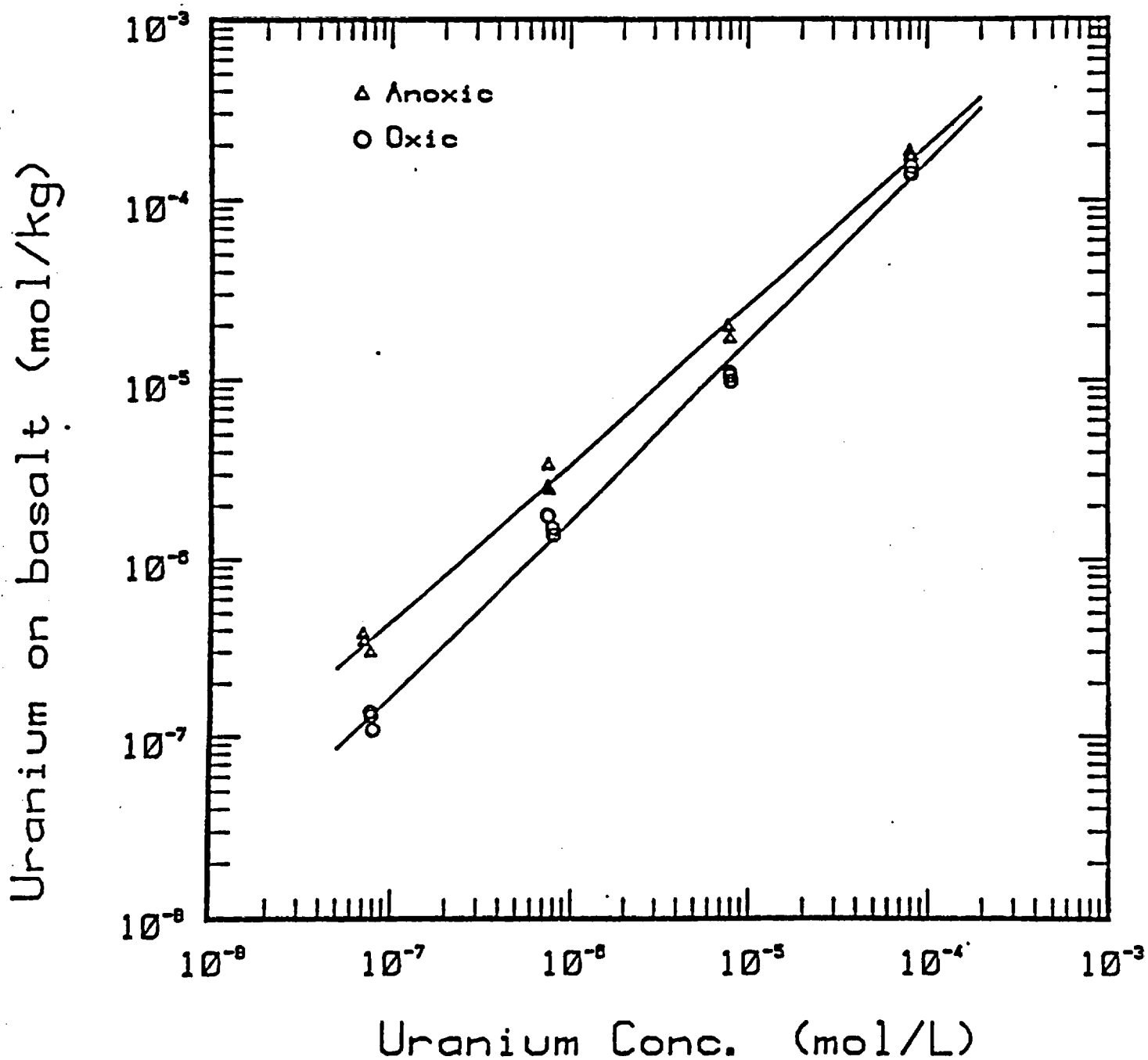
Sorption isotherms for U(VI) on McCoy
Canyon basalt from GR-2. Batch method.
27 C. 50 day equilibration. Basalt
ground in argon.

Experiments were started with neptunium using a [239]Np(V) tracer at column temperatures of 25 and 70°C with air-crushed McCoy Canyon basalt (2-45 μm fraction). Synthetic groundwater GR-4 was used as the eluant at a flow rate at 0.96 ml/min. The measured R_f value was 2.5 at 25°C and 22.6 at 70°C, and the corresponding sorption ratios (R_d) were 0.4 and 5.7 ml/g, respectively (Table 3). The elution curves had asymmetrical peaks with long skewed tailends. Small amounts (<1%) of [239]Np activity remained in the columns after the elution. These [239]Np(V) results are on the basis of only one experiment for each temperature. Further testing will be done to ensure that these preliminary results are confirmed. Oxidation states of [239]Np in the spike solutions and the eluted solutions will be determined for a better understanding of the retardation mechanism of Np(V) in the basalt column.

Table 3. Technetium(VII) and Neptunium(V) Retardation
in Column Experiments.

Radionuclide	Flow rate (mL/min)	Temp. (°C)	Volume[1] eluted (mL)	Peak[2] vol. (mL)	Retardation[3] factor, R_f	Sorption[4] ratio, R_d (mL/g)
Tc(VII)	0.96	25	0.73	2.16	1	0
	0.96	70	0.73	2.16	1	0
	0.48	25	0.73	2.16	1	0
	0.48	70	0.73	2.16	1	0
Np(V)	0.96	25	1.81	7.56	2.5	0.4
	0.96	70	16.39	21.6	22.6	5.7

[1]Total volume eluted before the elute activity reach 50% of the total spike activity, corrected for void volumes of the column fitting and tubing.

[2]Total volume where the activity of the eluate was between 0.01 and 0.99 of total activity eluted.

[3]The R_f was calculated from total volume eluted for radionuclides vs total volume eluted for HTO.

[4]The R_d was calculated from the equation $R_d = (R_f - 1)P/D_b$, where P = porosity (0.412) and D_b = bulk density (1.56 g/cm^3).

Sample Characterization:

An enrichment of minerals in a particular size fraction is frequently
observed after grinding and size separation of rock samples. Such
segregration results from the differences of hardness, shape, size, and
structure of the minerals in the rock. To test the possibility of preferential segregation during sample preparation of McCoy Canyon basalt,
the basalt sample was crushed in an agate mortar mounted on a vibrator.
The ground basalt was separated to 4 size fractions, -125/+45, -45/+20,
-20, and -2 μm by screening and gravitational sedimentation. The -125/+45
and -45/+20 μm size fractions were manually ground again with an agate
mortar and pestle to minimize the size effects on x-ray diffraction analysis (XRD). The results from wet chemical analysis of selected elements
and XRD peak intensity of plagioclase (0.321 nm) and titaniferous magnetite (0.252 nm) are given in Table 4.

Table 4. Elemental and X-ray Diffraction Analyses of Varying
Size Fractions of McCoy Canyon Basalt.

Size Fraction (μm)	Elemental Analysis (mg/g)					X-Ray Diffraction[1] (counts/sec)		
	Si	Al	Fe	Ti	Mn	I(P)	I(M)	I(P)/I(M)
-125/+45	194	122	6.5	5.0	0.06	68	24	2.83
-45/+20	201	109	8.5	6.9	0.08	72	21	3.43
-20	nd[2]	nd	nd	nd	nd	57	24	2.38
-2	205	106	10.4	7.9	0.73	47	19	2.47

[1] I(P) = intensity of a plagioclase peak (0.321 nm)
I(M) = intensity of a titaniferous magnetite peak (0.252 nm)

[2] nd = not determined

The elemental analysis shows a considerable increase of Fe, Ti, Mn concentrations in finer size fractions, suggesting an enrichment of Fe-Ti-Mn
rich components in the finer fractions. The XRD intensity of a magnetite
peak remained fairly constant among different fractions, but the intensity
of a plagioclase peak decreased noticeably in the -20 and -2 μm fractions,
resulting in lower intensity ratios of plagioclase to magnetite. The XRD
results suggest a slight enrichment of plagioclase in +20 μm size fractions
and x-ray amorphous glass in -20 μm size fractions. However, the effects of
such small compositional (elemental and mineralogical) differences on sorption behavior among varying size fractions of basalt samples may be hard to
determine. The findings do not suggest that major differentiation of basalt
components is occurring on crushing and size fractionation of material for
the sorption/solubility experiments.

Geochemical Modeling:

Calculation of Synthetic Groundwater Saturation Indices and Speciation

The BWIP synthetic groundwater formulas GR-3 and GR-4 were modeled at 60°C using MINTEQ for comparison with the saturation and speciation results at 25°C reported in the February Monthly Progress Report. The results are shown in Table 5. As expected, the solutions are calculated to be more oversaturated with respect to calcite (since calcite solubility is inversely proportional to temperature) and less saturated with respect to flourite and the silica phases at the higher temperature. The formation of amorphous silica phases should be depressed by higher temperatures, as evidenced by the undersaturated state of the solutions at 60°C. It is possible that some of the instability problems with the synthetic groundwater solutions encountered in some of our experiments may have resulted from the fact that the tests were performed at 25°C rather than at 60°C. These BWIP synthetic groundwater formulations were designed to duplicate the major element analysis of groundwaters from various Grande Ronde basalt flows, where the ambient temperature is 55 to 59°C. Thus, the synthetic groundwaters should not necessarily be expected to be stable at lower temperatures.

Table 5. Saturation Indices for Synthetic Groundwater
GR-3 and GR-4 at 25 and 60°C

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

The calculated speciation of calcium and carbon in GR-3 and GR-4 at 25 and 60°C is given in Table 6. The most significant difference is in the increased amount of complexed carbonate. This difference may affect results for sorption tests at 60°C, relative to 25°C, for elements where carbonate complexation could be important. The speciation of other components was not significantly affected by the change in temperature.

Table 6. Distribution of Species in Synthetic Groundwater
GR-3 and GR-4 at 25 and 60°C

Component	Species	GR-3		GR-4	
		25°C	60°C	25°C	60°C
Calcium	Ca^{+2}	80	64	82	58
	$CaCO_3$ (aq)	9	24	16	39
	$CaSO_4$ (aq)	10	9	—	—
Carbon	CO_3^{-2}	26	28	24	27
	$NaCO_3^-$	4	22	4	20
	$CaCO_3$ (aq)	—	2	—	1
	HCO_3^-	69	47	71	50

Evaluation of BWIP Calculated Solubility Values

Solubility calculations for U, Pu, Am, Np, Pb, and Ni in synthetic
groundwater GR-3 at Eh = -0.3 V were performed using MINTEQ as a
comparative check of the calculational methodology and data base for
MINTEQ with those used by Early et al. [RHO-BW-ST-39P]. The
thermodynamic data for Pu, Np, and Am used in the MINTEQ calculations were
the same as those used by Early et al. As expected, the results were in
excellent agreement. Results for the most stable solids and dominant
aqueous species were identical to those calculated by Early et al., and
the solubility values were always within ± 20 % of the Early et al.
values.

The U, Pb, and Ni solubilities were modeled using the existing data base of
MINTEQ. Results for uranium were not in close agreement to those of Early
et. al. With the MINTEQ data base, UO_2 is calculated to be the most
stable phase with a solubility of 10^{-8} mol/L. Early et al. states that
$USiO_4$ is stable and has a solubility of $10^{-9.96}$ mol/L. The dominant
aqueous complex is calculated to be $U(OH)_5^-$ in both cases for GR-3 at this
low Eh value. This inconsistency has been confirmed to be the result of
different log(K) values for the formation of $USiO_4$. Early et al. used a
value of 9.07, whereas the MINTEQ data base contains a value of 7.62.
When the log(K) for $USiO_4$ was adjusted to be the same as that used by
Early et al., the calculated results were in close agreement. The value
in MINTEQ is probably more reliable, based on the validation study per-
formed on the MINTEQ uranium data base by Krupka et al. [PNL-4333].

Results for Pb using MINTEQ were in close agreement to those of Early et al. The stable solid, $Pb(OH)_2$, and dominant complexes, $PbCO_3$ (aq) and $Pb(CO_3)_2^{-2}$ were identical and the calculated solubilities were 1.8 x 10^{-8} mol/L (MINTEQ) and 2.4 x 10^{-8} mol/L (Early et al.). The small difference in calculated solubilities can probably be attributed to small differences in log(K) values contained in the two data bases.

Results for Ni were not in close agreement to those of Early et al. Again, the reason can be traced back to differences in the thermodynamic data bases. For the case of no sulfur speciation, $Ni(OH)_2$ was calculated to be the stable solid using MINTEQ, whereas Early et al. stated that NiO would be most stable. The nickel hydroxide was included in the data base used by Early et al., but the log(K) value for the formation reaction was two orders-of-magnitude smaller [ie., $Ni(OH)_2$ less stable]. The solubilities of the two phases $Ni(OH)_2$ and NiO were calculated to be 2.8 x 10^{-v} mol/L (MINTEQ) and 1.8 x 10^{-4} mol/L (Early et al.). For the case where sulfur was allowed to speciate into sulfate and sulfide species, $Ni(OH)_2$ was again calculated to be most stable using MINTEQ. Early et al. calculated NiS to be the stable solid. The formation constant for NiS in MINTEQ is approximately six orders-of-magnitude smaller (ie., NiS less stable) than that used by Early et al.; thus, NiS would not be expected to be stable using the MINTEQ data base. The solubilities calculated for the sulfur speciation case are the same as those stated above. The dominant aqueous complexes of $NiCO_3$ (aq) and $Ni(CO_3)_2^{-2}$ calculated by Early et al. were also calculated to be dominant in the MINTEQ runs.

The results have shown that when information in the data bases are consistent, similar to essentially identical solubilities are calculated by MINTEQ or by Early et al. The solubility value inconsistencies described above are related to the data bases, and this emphasizes the importance of having well-checked, internally consistent data bases for geochemical modeling. During repository licensing, the codes may not be called into question, but the data bases may have to be verified and validated.

Actinide Speciation Calculations

Modeling the Pu, Np, and Am speciation reported by Cleveland from experiments with actual BWIP groundwater [Science 221, 271-273 (1983); Nucl. Technol. 62, 298-310 (1983)] was initiated. This work is proceeding slowly because MINTEQ does not converge well when modeling elements with multiple oxidation states. Careful initial guesses of the activities are required or MINTEQ will encounter fatal computational errors. First indications are that the results obtained by Cleveland will not be easily confirmed through equilibrium arguments. Rather, it appears that kinetic constraints may have played a large role in Cleveland's experimental work. However, more careful modeling and sensitivity analyses will be required to confirm this hypothesis.

General Aspects:

Statistical Treatment of Sorption Data Variance and Standard Deviation

There are several different methods of reporting sorption data developed
by batch contact tests. Frequently, only one number is given for a
sorption or desorption ratio value without any error bars. Researchers
that do report error bars for their data do not always indicate whether
these represent the range or extremes of values obtained, or are a
statistically calculated standard deviation. Further, some data may be
incorrectly expressed due to neglecting important terms that have some
distribution about a mean value. The underlying point is that the actual
standard deviation of a mean sorption or desorption ratio value for
several replicate samples is not the same as that calculated by assuming
that the values of the individual replicate samples have no variance. We
are developing a statistically valid method of calculating variances and
standard deviations for sorption and desorption data obtained by use of
radioactive tracers and standard counting techniques. This will be
described in detail in a subsequent Letter Report.

The method of calculating sorption or desorption ratios and their
variances will be evaluated in future data reporting. Although this
method has been developed specifically for the laboratory procedure used
in the actinide work, it is general enough to be employed by other
researchers. Variables or values that have been treated as "constant" in
this analysis can be included as variables if it becomes necessary in the
future.

Responce to NRC Project Manager's Comments

In the NRC review of the January Monthly Progress Report, comments were
included concerning the valence of technetium and neptunium in solution
after contact with basalt. Such questions go to the core of the problem
of understanding the reactions invo_ved in the sorption and/or
precipitation processes that resu!t in the removal of a radionuclide from
solution. We are actively involve! in exploring these questions and would
like to defer our responce to a future report. At the present time, we
can only describe some general observations. After a Np(V) or Tc(VII)
solution is contacted with basalt, essentially only the oxidized valence
of either radionuclide is detected in solution, regardless of the quantity
of radionuclide removed from solution during the contact. Conversely, if
the basalt is washed with HCl after contact, primarily only the reduced
valence [Np(IV) or Tc(?)] is detected in the HCl wash. Thus, we believe
that, in general, removal from solution of these two radionuclides must
involve a reduction reaction (not necessarily the same reaction for Np and
Tc) with some component on the basalt surface. The reduced radionuclide
could be bound through ion exchange or surface sorption, could be
precipitated as an insoluble oxide or other compound, or could be held on

the solid through interstitial substitution into an existing or newly derived basalt component. This is a complex system and understanding of the reactions involved for a given radionuclide may not always be quickly achieved. At least qualitative understanding may be necessary in order to know if experimentally measured values are conservative or nonconservative when extrapolated to repository containment times. We are continuing to develop an understanding of the geochemistry of technetium and neptunium in the basalt/groundwater systems (progress is reported under the respective headings this month), and in the future we can more fully respond to the questions raised.

MEETINGS AND TRIPS:

None

REPORTS AND PUBLICATIONS:

The Annual Report for FY 1983 has been completed and forwarded to the NRC Project Manager. It will be printed and issued by NRC as NUREG/CR 3730.

A draft copy of the Quarterly Progress Report for October-December 1983 has been prepared and forwarded to the NRC Project Manager for technical review. Following receipt of that review, a revised manuscript will be prepared. After editorial review, and patent and security release, it will be typed on mats and returned to the NRC Project Manager for issuance as an NUREG/CR report.

PROBLEM AREAS:

None

COST/BUDGET REPORT:

Expenditures were $53.2K for the month of March and $327.9 for the fiscal year to date. A detailed cost/budget report will be sent under separate cover.