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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

WM-Record File  
Lum-PES  
B0290  
ORNL

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PDR ✓  
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Distribution:  
Bradbury ✓  
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Dear John:

Enclosed is the progress report for the month of June 1985 for B0290, "Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques and Procedures."

Sincerely,

Susan K. Whatley, Manager  
Repository Licensing Analysis  
and Support  
Chemical Technology Division

SKW:bek

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  
K. C. Jackson, Geotechnical Branch  
D. J. Brooks, Geotechnical Branch  
Branch Chief, Waste Management Branch, RES  
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SKW File (2)

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MONTHLY PROGRESS REPORT FOR JUNE 1985

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, J. G. Blencoe, G. K. Jacobs, and R. E. Meyer

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

PROGRESS HIGHLIGHTS:

Hanford Site Information Evaluation

Materials and Methods:

The materials and methods used in the evaluation of Hanford Site information have been previously described in annual and quarterly progress reports. No additional activity is planned under this subtask.

Radionuclide Sorption/Solubility Values:

We have started measurement of sorption isotherms for Np(V) with three basalt/groundwater systems (Cohasset basalt with synthetic groundwater GR-4, and Umtanum and McCoy Canyon basalts with synthetic groundwater GR-2) to compare the effectiveness of different basalt/groundwater combinations in retarding migration of neptunium in the site far field. Comparison of the three systems is of interest because the performance assessment modeling for the Hanford Site in the draft EIS (DOE/RL-0017) assumed that all basalts exhibit equivalent sorption properties for all radionuclides, and because neptunium may be one of the key radionuclides for the Hanford Site performance assessment. The batch contacts are under anoxic redox conditions at 60°C. These experiments were delayed because of apparent difficulties in preparing starting solutions containing neptunium present as essentially 100% Np(V). Valence state analyses of the starting solutions by solvent extraction techniques seemed to show that significant percentages of the neptunium were present as Np(IV) after chemical valence adjustment to form Np(V). As discussed in last month's report, it now appears that the solutions actually contained essentially all Np(VI) and that the indication of the presence of Np(IV) was caused by  $^{233}\text{Pa}$ , a decay product of  $^{237}\text{Np}$ , which was extracted from the solution by the solvent [thenoyltrifluoroacetone (TTA) in xylene] used in the analysis of Np(VI). Because  $^{233}\text{Pa}$  produces x-rays in the same energy range as the x-rays from the  $^{235}\text{Np}$  neptunium tracer, we obtained spurious Np(IV) concentration counts in the TTA extractant; we were counting  $^{233}\text{Pa}$  when we thought we were counting  $^{235}\text{Np(IV)}$ . This conclusion was reached from the results of experiments with a number of solutions which had different

ratios of  $^{237}\text{Np}$  to  $^{235}\text{Np}$ . Detectable amounts of  $^{233}\text{Pa}$  could be formed only in those solutions which contained the greatest amounts of  $^{237}\text{Np}$ , and in only those solutions were any significant counts detected in the TTA extractant. We have now prepared synthetic groundwater solutions containing Np(V), and we have begun the Np(V) sorption isotherms with McCoy Canyon and Umtanum basalts and synthetic groundwater GR-2. These isotherms will be completed in July, and the isotherm for Cohasset basalt and GR-4 will then be started.

All experiments currently planned to evaluate sorption of technetium onto basalts have been completed.

In the monthly report for April, we stated that we had begun an experiment to determine a 50-day sorption isotherm of uranium onto McCoy Canyon basalt from GR-2 under anoxic conditions at  $60^\circ\text{C}$ . Previous attempts to determine this isotherm had been aborted because most of the groundwater leaked out of the defective test tubes used in the experiment. Tubes from a new lot are being used in the current experiments. We had observed significant increases in  $R_s$  values between 14- and 50-day batch contacts under anoxic conditions at  $60^\circ\text{C}$  for Cohasset basalt and GR-4; sometimes by as much as a factor of ten. Values of  $R_s$  after 14 days ranged from 19.4 to 31.1 L/kg at the lower concentrations of uranium, and a  $R_s$  value of 335 L/kg was observed at the highest initial concentration of uranium,  $1.02 \times 10^{-4}$  mol/L (NUREG/CR-4236, Vol. 1). The largest value was caused mainly by precipitation of an insoluble compound of uranium, sodium boltwoodite (NUREG/CR-4236, Vol. 1). In the 50-day experiments reported previously, values of  $R_s$  ranged from 115 to 669 L/kg at the lower range of uranium concentrations, and a value of 1288 L/kg was observed for the highest concentration. The large increases in  $R_s$  values in the 50-day experiments, as compared to the 14-day experiments, were probably due to increased precipitation of sodium boltwoodite at all concentrations of uranium. This conclusion was reached since we observed large increases in uranium losses from all of the control samples (no basalt present) in the 50-day experiments. The values of  $R_s$  for McCoy Canyon basalt and GR-2 for all redox conditions (anoxic and oxic) were in the range of 2 to 5 L/kg, but a value at 50 days contact at  $60^\circ\text{C}$  had not been determined.

We are now using much more careful oxygen removal techniques in our anoxic experiments than we did in last year's determinations with McCoy Canyon basalt reported in NUREG/CR-4236, Vol. 1. Anoxic 50-day experiments with McCoy Canyon basalt in GR-2 were therefore begun to see whether these more stringent oxygen-removal techniques will cause the sorption ratios for uranium to exceed the 2 to 5 L/kg range which we had observed in all previous experiments with this system, and to see whether increasing the duration of the experiment from 14 to 50 days will cause the same large increase in sorption ratio as was observed with the Cohasset/GR-4 system. These experiments were completed this month, and the results are shown in Table 1.

Table 1. Sorption of uranium on McCoy Canyon basalt from GR-2  
Anoxic conditions, 60°C, 50 days

Initial concentration of uranium (mol/L)	Average Rs calculated from standards <sup>a</sup> (L/kg)	Average Rs calculated from controls <sup>a</sup> (L/kg)	Loss of uranium from control (%)	Rs values for 14-day tests <sup>b</sup> (L/kg)
$1.15 \times 10^{-7}$	$6.3 \pm 0.8$	$4.8 \pm 0.7$	9.0	$3.9 \pm 0.2$
$1.10 \times 10^{-6}$	$5.5 \pm 0.4$	$1.1 \pm 0.3$	29.5	$2.5 \pm 0.2$
$8.85 \times 10^{-5}$	$4.9 \pm 0.4$	$-3.9 \pm 0.5$	60.7	$2.0 \pm 0.4$
$1.00 \times 10^{-4}$	$48.0 \pm 1.7$	$-4.3 \pm 0.3$	90.9	$35 \pm 7$

<sup>a</sup>In column 2, values of Rs are 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 are 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 in the samples, and the resulting sorption ratios are negative. The results given are the average of three determinations.

<sup>b</sup>Reported in September, 1984, monthly. All test conditions were the same except for the 14-day duration of test. Initial concentrations of uranium were slightly different from those in the first column, but they were always within 15%.

For the three lowest concentrations, the values of Rs for the 50-day experiments are about twice as high as those for the 14-day experiments. At the higher concentrations of uranium, the value of Rs, 48 L/kg, is about 35% higher than the value from the 14-day test. The large losses from the control experiments suggest precipitation of uranium again, probably as sodium boltwoodite, as we have already observed with some systems. However, we did not directly observe the formation of a precipitate because so little could have been formed that it would be very difficult to see the precipitate in the translucent polypropylene test tubes. In other experiments previously reported (NUREG/CR-4236, Vol. 1), sodium boltwoodite formed from  $10^{-4}$  mol/L solutions of uranium in GR-2.

The relatively small increases in Rs at the two lower concentrations of uranium suggest that the more stringent oxygen removal techniques used in these experiments did not cause a large difference between the 14- and 50-day experiments.

#### Geochemical Modeling:

No activity.

Yucca Mountain Information EvaluationMaterials and Methods:

Work is progressing on adaption of one of the glove boxes to contain a CO<sub>2</sub> air mixture.

Radionuclide Sorption/Solubility Values:

No progress to report this month.

Geochemical Modeling:

No progress to report this month.

## GENERAL ASPECTS

None

## MEETINGS AND TRIPS

None

## REPORTS AND PUBLICATIONS

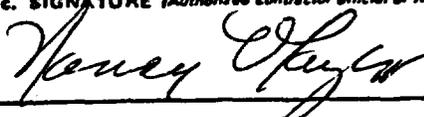
The draft quarterly progress report for January-March 1985 was sent to the NRC Project Manager for review and comment.

## PROBLEM AREAS

None

## COST/BUDGET REPORT

Expenditures were \$31.5K for the month of June and \$375.3K for the fiscal year to date. A detailed cost/budget report will be sent under separate cover.

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