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

Dear John:

Enclosed is the progress report for the month of June 1983 for  
80290, "Laboratory Evaluation of DOE Radionuclide Solubility Data  
and Other Geochemical Parameters, Experimental Strategies,  
Laboratory Techniques and Procedures."

Sincerely,

*Allen*

Allen G. Croff, Manager  
Planning and Waste Management Analysis  
Chemical Technology Division

AGC:11

Enclosure

- cc: R. O. Chester
- N. H. Cutshall
- J. S. Johnson
- M. J. Kelly
- A. D. Kelmers
- J. H. Kessler
- S. Y. Lee
- A. L. Lotts
- R. E. Meyer
- S. K. Whatley

Office of the Director, NMSS (Attn: Program Support Branch)  
Division Director, NMSS Division of Waste Management (2)  
H. J. Miller, Chief, HLW Technical Development Branch  
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D. J. Brooks, HLW Technical Development Branch  
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MONTHLY PROGRESS REPORT FOR JUNE 1983

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

PROJECT MANAGER: A. G. Croff

ACTIVITY NUMBER: ORNL #41 37 54 92 6 (189 #B0290) / NRC #50 19 03 1

TECHNICAL HIGHLIGHTS:

Neptunium Studies:

Following transfer of the two controlled-atmosphere gloveboxes last month, cleanup and preparation of the boxes was begun for the anoxic condition sorption/solubility tests with basalt. Cleanup is proceeding more slowly than anticipated due to unexpectedly high levels of plutonium contamination in the boxes from previous use in a plutonium process line. Since it is important to reduce the contamination level as far as possible for our experiments, additional decontamination is being carried out.

Preparation of the  $^{235}\text{Np}$  and  $^{237}\text{Np}$  stock solutions has been completed and the oxic condition sorption/solubility experiments with basalt will be initiated next month.

Technetium Studies:

A distribution coefficient of essentially 0 mL/g for technetium with basalt and synthetic groundwater under oxic conditions was reported in our April monthly progress report and, similarly, a value of 0 mL/g was reported for clinoptilolite in May. (A  $K_d$  of 0 mL/g for technetium under oxic conditions is in agreement with values reported by BWIP in various publications and in the Site Characterization Report.) A zero distribution coefficient for technetium has been further confirmed this month in tests at 60°C with basalt samples out of contact with the atmosphere; no significant loss of technetium from solution occurred in experiments after up to 8 weeks of equilibration.

Work has now been started on technetium behavior at lower valence states at 60°C. Batch contacts with basalt are being carried out in the presence of hydrazine, a redox reagent used by BWIP to simulate the expected reducing conditions in the basalt beds at depth in the BWIP site. The technetium behavior was very different from that observed under oxidizing conditions. After about 3 days contact, about 70% of the technetium was removed from solution. If the removed technetium was assumed to be on the basalt, the tests would yield  $K_d$  values of 24 to 35 mL/g. These values are comparable to a  $K_d$  of 29 mL/g reported in the BWIP Site Characterization Report under reducing conditions.

However, it is not clear that the crushed basalt contributed significantly to the apparent technetium  $K_d$  values in the presence of hydrazine. The GR-1 and GR-2 synthetic groundwaters were not stable at 60°C and deposited a precipitate which adsorbed substantial quantities of technetium. In addition, there was substantial adsorption of technetium onto the glass tube and onto the PVC cap liner. Parallel blank samples (no basalt present) gave solution concentrations of technetium which were essentially equivalent to those in the presence of basalt. These observations raise concerns as to whether reported apparent technetium distribution coefficient for reducing conditions describe adsorption on basalt or on other solids precipitating from solution.

Above the linear isotherm region in the hydrazine-containing experiments, both in the presence and absence of basalt, there was a sharp rise in the apparent distribution coefficient values. These observations could be interpreted as indicating a solubility limit of about  $5E-7$  M Tc under these conditions. This number contrasts unfavorably, i.e., nonconservatively, with the calculated value of  $1E-12$  M technetium solubility under reducing conditions given in BWIP literature (RHO-BW-SA-192A). A recent report (RHO-BW-ST-39P) gave a calculated technetium solubility of  $>1E-14$  M. Additional tests are under way.

Reaction kinetics could be limiting the rate of the reaction of crushed basalt and oxidized technetium in the absence of air and/or surface oxidation of the basalt could be occurring during basalt sample crushing. Professor Ronald Clark of Florida State University is collaborating with us this summer and is exploring the effect of surface modifications of the basalt on apparent technetium adsorption behavior. Exposure of the crushed basalt to an inert gas or to hydrogen at elevated temperature prior to running batch sorption tests in the absence of air causes substantial removal of oxidized technetium from solution in comparison to experiments without this treatment. These preliminary results suggest that the basalt surface condition may be important, at least in the relatively short time scale of these tests compared to geologic storage times.

#### Calculational Activities:

Initial calculations of equilibrium speciation and solution saturation with respect to common minerals have been completed using PHREEQE for BWIP groundwater data provided by the NRC. The results indicate apparent supersaturation with respect to several minerals, particularly carbonates (calcite and rhodochrosite) and with respect to hematite and goethite. The apparent carbonate supersaturation may result from failure to account for pressure shifts in carbonate equilibria in these initial computations. The calculations will be repeated using pressure-adjusted equilibrium constants in order to test the pressure effects on the apparent supersaturation. If this does account for the apparent supersaturation, this would be consistent with the inference that the groundwater is at equilibrium with the designated carbonate minerals.

**Secondary Mineral Acquisition:**

Samples of clinoptilolite have been supplied for technetium and neptunium sorption measurements. Nontronite from Washington State has been ordered but not received. When the nontronite is in hand, we will proceed with a detailed characterization of these two secondary minerals.

**MEETINGS AND TRIPS:**

None.

**REPORTS AND PUBLICATIONS:**

None.

**PROBLEM AREAS:**

None.

**COST/BUDGET REPORT:**

Expenditures for the month of June were \$58.3K, reflecting the cost of installing and cleaning the two controlled-atmosphere glove boxes. Expenditures to-date are \$266K. A detailed cost-budget report is given in the attached exhibit.