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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 August 1983 for B0290, "Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques and Procedures."

Sincerely,

Allen

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

AGC:il Enclosure

- cc: 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 P. S. Justus, Siting Section, HLW Technical Development Branch D. J. Brooks, HLW Technical Development Branch Branch Chief, Waste Management Branch, RES G. F. Birchard, Waste Management Branch, RES R. O. Chester N. H. Cutshall S. E. Herbes J. S. Johnson M. J. Kelly A. D. Kelmers J. H. Kessler S. Y. Lee A. P. Malinauskas R. E. Meyer S. K. Whatley R. G. Wymer AGC File

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MONTHLY PROGRESS REPORT FOR AUGUST 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 (FIN No. B0290) / NRC #50 19 03 1

TECHNICAL HIGHLIGHTS:

Technetium Studies:

A series of sorption/desorption experiments were carried out to confirm the reversibility of the sorption/solubility reaction(s) involving technetium (IV). As in the tests reported previously, hydrazine hydrate was used to establish reducing redox conditions, flint glass tubes were used, and the test temperature was 60°C. Synthetic groundwaters GR-1 and GR-2 were used and the solids were Sentinel Gap basalt, Buckhorn clinoptilolite, or blanks (controls without solids). The technetium concentration remaining in solution after sorption or desorption conditions was not sensitive to the presence or absence of added solids (basalt or clinoptilolite). Considerably more data scatter was encountered in these tests than in the previous tests; however, the average values for the final technetium concentration in solution (for experiments with an initial Tc concentration  $\geq 1E-6$  mol/L) were nearly identical for both sorption and desorption conditions and were close to the apparent solubility limit of about  $5E-7$  mol/L for Tc (IV) reported previously. The sorption tests gave an apparent technetium solubility limit of  $9.6E-7$  mol/L and the desorption tests an apparent limit of  $1.0 E-6$  mol/L.

The general conclusion is that an apparent solubility limit of about  $1E-6$  mol Tc(IV)/L is obtained in tests carried out in this manner, and the apparent solubility value is independent of the presence or absence of basalt or clinoptilolite. The apparent solubility limit is much higher than the saturated solution values of  $\geq 1E-14$  or  $1E-12$  calculated by BWIP. The sorption behavior of Tc(IV) in tests with  $< 1E-6$  mol/L technetium initially present remains unclear. Individual experimental results continue to be variable and not readily reproducible. In general, some Tc(IV) sorption seems to be occurring on the glass tube and the PVC cap liner, but little or no adsorption is occurring onto the basalt or clinoptilolite. The interpretation of the Tc(IV) sorption results is complicated by the precipitation of an unidentified component(s) of the synthetic groundwaters when they are heated to 60°C in the presence of hydrazine.

To explore the possible role of the flint glass tubes and precipitation in the synthetic groundwater on the sorption behavior of Tc(IV), a series of similar blank experiments were conducted in polypropylene plastic tubes. Both fresh and aged groundwaters were used, to see if slow changes in the silicate species could be responsible for the groundwater instability. These experiments were also prompted by some earlier scouting tests (not previously reported) in plastic tubes which had technetium solubility values higher than  $1\text{E}-6$  mol/L in the presence of hydrazine; these results were rationalized at the time as possibly being due to air diffusion through the plastic tubes. Thus, for these experiments, the plastic tubes were placed overnight in a vacuum and then exposed and filled in an argon atmosphere. Tests were run for 6 days at  $60^\circ\text{C}$  in an argon atmosphere with synthetic groundwater GR-2 containing  $0.04$  mol/L hydrazine hydrate and traced with  $1\text{E}-10$  to  $1\text{E}-4$  mol/L technetium.

Differences in technetium behavior were observed in the glass and plastic systems and possibly also between the fresh and aged groundwaters. An apparent solubility limit was not clearly established in either the glass or plastic tube test series, and technetium solution concentrations as high as  $1.6\text{E}-5$  mol/L were encountered in plastic tubes. In some cases, aged groundwater gave lower technetium solution values compared to fresh groundwater, while in other cases higher values were obtained. Clearly, the situation is not totally straightforward. Understanding the experimental results is hindered by the general lack of knowledge of the chemistry of Tc(IV). Little information has been published and the solution species which might exist in these systems are not well established. Technetium (IV) is known to form many organic complexes. Also, there are hints in the literature that Tc(IV) solutions may contain dimers and polymers. These could complicate understanding the system.

The experimental results continue to be of use to the NRC BWIP site analysis efforts in that they show much higher technetium solubilities than those calculated and employed by BWIP, i.e., the BWIP values are not necessarily conservative. Further, the results to date help reveal the potentially complex behavior which technetium may exhibit in geochemical environments and suggest caution in accepting simple predictions of technetium behavior in rock/groundwater systems. These results also suggest that technetium solubility and sorption results are sensitive to experimental details and that the experimental methods employed must be confirmed before the results are accepted.

Hydrazine is not an expected repository constituent and may have complicated chemistry in these bicarbonate groundwaters (carbamate formation and/or metal complexation). Therefore, we plan to conduct most of the future technetium experiments under anoxic conditions (exclusion of air), rather than under reducing conditions established by the addition of powerful reducing agents such as hydrazine. The controlled-atmosphere glove box for this work has been received and is being made operational. Additional tests may further explore the effect of the test container on the results. Future work also will begin to explore other tuff mineral constituents in order to start confirming LANL sorption results reported for the Yucca Mountain candidate repository site.

### Neptunium Studies:

Sorption/solubility tests have been initiated to confirm the neptunium values reported by BWIP. This initial test series also is being utilized to establish a standardized experimental procedure. The first series of experiments are with basalt under oxic conditions; future tests will explore reducing conditions (with hydrazine hydrate, as reported by BWIP), anoxic conditions (argon atmosphere glove box), and secondary minerals and representative interbedded minerals as well as basalt. In these tests, Sentinel Gap basalt was crushed in air in an agate mortar and sieved to 70-235 mesh size. Groundwater GR-2 was used, traced with  $^{235}\text{Np}$  at  $3.8\text{E}-12$  mol/L. The tests were run for 7 or 28 days at  $24\pm 2^\circ\text{C}$ . Both centrifugation and filtration were used to separate the solids and solution after contact.

The resulting sorption ratio ( $R_s$ ) values ranged from 2.8 to 4.0 mL/g. The 7-day data indicated no differences in the  $R_s$  values for centrifuged or filtered samples, suggesting that there was no significant colloidal formation and/or sorption by the Amicon filters. The 28-day data appeared to suggest slightly higher  $R_s$  values than the 7-day data; however, there was a similar rise in the blanks (no basalt) and the filtered samples gave higher  $R_s$  values than the centrifuged samples. This could be consistent with an instability of the groundwater leading to the formation of a colloidal precipitate which has some neptunium sorption capability. After correction for the blanks, the 28-day  $R_s$  values were essentially the same as the 7-day values.

BWIP publications have given distribution coefficients for neptunium sorption on basalt under oxic conditions of 10 and 15 mL/g. Additional experimental work (underway) must be analyzed before we can say that the BWIP values can not be confirmed; however, the initial values obtained this month are significantly lower than the BWIP values.

A series of oxic condition sorption/desorption tests using both pre-equilibrated and fresh basalt and groundwater and a range of neptunium concentrations (to allow construction of sorption and desorption isotherms) are underway and will be reported next month. The two controlled-atmosphere glove boxes for the anoxic condition work have been installed and decontaminated. Preparations for connecting these through appropriate ports are essentially complete.

### Calculational Activities:

Computations of equilibrium speciation and saturation indices for BWIP groundwater data were continued using the standard PHREEQE data base. Data from four BWIP wells have been treated and the apparent saturation with respect to several minerals compared on both a vertical and north-south basis. Trends for carbonate minerals are toward increasing relative saturation with increased depth. These trends are apparent using in situ formation temperatures or using isothermal temperature calculations. The effect of pressure on apparent saturation trends

for carbonates still needs to be examined. Data for the northernmost well (DC-14) indicate a decreased oversaturation compared to quartz (all samples are out of equilibrium with quartz, probably because the reaction rate between quartz and these cool groundwaters is exceedingly slow) with increased depth. Data from the southernmost well (DC-15), on the other hand, show a uniform oversaturation with depth. Fluorite appears to be undersaturated in the groundwaters in the upper 300 m of the BWIP site, but is frequently oversaturated in the high fluoride groundwaters from the 1000-m depths.

The code for MINTEQ has been received from PNL and will be implemented on the ORNL computers.

#### MEETINGS AND TRIPS:

N. H. Cutshall, A. D. Kelmers, and J. G. Blencoe attended the annual NRC/RES program review at Reston, Virginia, on August 30-September 1.

#### REPORTS AND PUBLICATIONS:

The following paper was presented at the NRC/RES review meeting on August 30:

A. D. Kelmers, R. J. Clark, N. H. Cutshall, J. S. Johnson, and J. H. Kessler, "Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters: Description of Calculational and Confirmatory Experimental Activities."

#### PROBLEM AREAS:

None

#### COST/BUDGET REPORT:

Expenditures for the month of August were \$51K and FY 1983 expenditures to-date are \$363K. A detailed cost-budget report is given in the attached exhibit.