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B0290

WM Project 10
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Dr. R. J. Starmer
Geotechnical Branch
Office of Nuclear Material Safety and Safeguards
U.S. Nuclear Regulatory Commission
427-SS
Washington, D.C. 20555

Distribution:
J. Justus Essen
H. H. C.
(AC... 10... 000-00)

Dear John:

Enclosed is the progress report for the month of September 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:arc
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
- P. S. Justus, Chief, Geotechnical Branch
- D. J. Brooks, Geotechnical Branch
- Branch Chief, Waste Management Branch, RES
- G. F. Birchard, Waste Management Branch, RES
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AGC
10/20/83

MONTHLY PROGRESS REPORT FOR SEPTEMBER 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:

Tentative conclusions reached previously concerning technetium sorption and concentration limits under reducing conditions (hydrazine) are as follows:

1. The sorption and concentration limit is not sensitive to the presence or absence of added solids (basalt or clinoptilolite).
2. The upper concentration limit of technetium in GR-2 groundwater is between 10^{-6} and 10^{-5} mol/L when measured in polypropylene plastic tubes, which is much higher than the 10^{-12} mol/L value employed by BWIP.
3. The upper concentration limit of technetium in GR-2 groundwater is between 10^{-7} and 10^{-6} mol/L when measured in flint glass tubes, which is markedly lower than the value measured in polypropylene plastic and indicates that experimental details are important in determining sorption values and concentration limits.

The activities during this report period concentrated on expanding on the above effects sufficiently to show that they are, in fact, real and to further indicate the limitations in experimental methodologies used to obtain geochemical values, and, thus, in the values themselves.

The apparent methodological problems engendered by the use of alternative materials of construction was investigated in two ways. The first was to conduct additional sorption/concentration limit measurements in different plastic materials. The measurements were made from tracer to 10^{-4} M technetium in GR-2 groundwater. The result was that insignificant differences were found between polypropylene, polyethylene, and polycarbonate plastic apparatus.

The second investigation of the effects of flint glass apparatus on technetium involved measuring concentration values in GR-2 groundwater less the constituents that had been previously determined to leach from glass (Al, B, Ba, Mg, Si) and then to add these constituents in separate experiments to determine their effects on the technetium remaining in solution. The results indicated that silicon and magnesium had a substantial effect on the technetium concentration values. The effect of the magnesium was to

decrease solution concentrations whereas the silicon had the opposite effect. Silica is known to have a complex solution chemistry in this pH range, involving the formation of large aggregates [see, e.g., J. Aveston, J. Chem. Soc. (1965), 4444]. If Tc species are complexed by these aggregates, they could be either kept in solution by them, or carried down if the silicate species precipitated. This area clearly has implications for the conduct of laboratory experiments and the values obtained therefrom; i.e., results obtained in glass apparatus are not appropriate because the apparatus is interacting with the experiment. Additionally, since there may be large amounts of HLW glass present in the repository, the effect of silicates on technetium may occur in the repository and, as noted above, it is not at all clear whether this will foster precipitation or mobilization of the technetium. At this point, we feel that detailed understanding of this area is required, but beyond the scope of the present project.

Another effect that was investigated concerned the extent to which hydrazine concentration affects the final concentration of technetium in GR-2 groundwater using plastic apparatus. Initial technetium concentrations ranged from tracer to 10^{-4} mol/L. Hydrazine concentrations of 0.07 and 0.1 mol/L were used. The results showed no significant effects of varying hydrazine concentration. However, the results obtained in this experiment as well as others has called into question whether experiments conducted in plastic tubes that have not been deaerated are valid. There are indications that this is the case, but a precise determination has thus far been obscured by the variation of other parameters. The degree to which this effect may be real, and, thus, affect the validity of results obtained in plastic apparatus (which is the case for BWIP) will be further investigated.

Finally, to ensure that the previously developed experimental results can be properly interpreted, it is necessary to know whether the technetium in the reducing experiments is, in fact, being reduced by the hydrazine introduced for this purpose. Such a determination is very difficult, but this was attempted on a number of solutions by extraction of Tc(VII) into chloroform containing tetraphenylarsonium chloride in a controlled-atmosphere box. Analysis of results is not complete, but preliminary indications are that larger-than-expected amounts of technetium are being found in the organic phase, and are, thus, presumably still in the +7 valence state. This experiment will be completed and reported during the next report period.

The next report period will also involve initiation of anoxic experiments (no hydrazine) to determine the extent to which the technetium solubilities used by BWIP are appropriate to the actual situation at BWIP and to confirm the use of results obtained using hydrazine as a reductant.

Neptunium Studies:

The preliminary oxidic sorption tests have been completed. The results for freshly crushed basalt (in air) using neptunium at a tracer level ($\sim 3E-12M$) were reported last month. Neptunium concentrations up to $1.0E-6M$ were investigated for crushed basalt that had been equilibrated in GR-2 groundwater for a total of four weeks prior to the start of sorption. The test conditions were the same as reported for last month's results. Triplicate samples and duplicate blanks were run for all of the conditions reported. Sorption times were one and four weeks.

Table 1 gives the average R_s values for blank-corrected centrifuged and filtered samples. Centrifuging was at 4,100 rcf for 10 minutes; filtering was performed using a 25,000 MW cutoff Amicon filter. R_s values for the $1.0E-12M$ to $1.0E-6M$ neptunium concentration range were between approximately one and three ml/g. R_s values for the four-week equilibrations are only slightly higher (by about 0.5 - 1 ml/g) than for the one-week equilibrations.

There is a slight difference in the R_s values at one week between the basalt samples that had no pre-equilibration with GR-2 groundwater and those that did. The non-pre-equilibrated samples yielded slightly higher R_s values (by about 1 ml/g). However, this R_s difference disappears after four weeks. This result supports work at ANL (Vandegrift et al., 1983), which indicated that neptunium sorption was lowered for basalt fractures that had been exposed to flowing groundwater over fresh basalt fractures.

Although the R_s values are slightly higher at the highest concentration, there is no evidence that a solubility limit is being approached (maximum Np concentration to date: $\sim 1.0E-6M$). The maximum amount of activity removed from solution under any condition was always less than 30%.

These preliminary oxidic tests have consistently yielded R_s values lower than the conservative best estimate ($K_d = 10$ ml/g) for neptunium under oxidic conditions given in the BWIP SCR. However, further testing will be done to ensure that these results are real and comparable to the BWIP situation.

Reference: Vandegrift, G. F. et al., "The Interaction of Groundwater and Fresh Basalt Fissure Surfaces and its Effect on the Migration of Actinides and Fission Products," presented at the 185th National Meeting of the American Chemical Society, Seattle, Washington, March 20-25, 1983.

Table 1. R_s Values for Blank Corrected Neptunium Sorption Experiments in Basalt Under Oxidic Conditions

Starting Concentration	Equil. Time	R_s Centrifuged ^a	R_s Filtered
Pre-Equilibrated Values:			
1.E-6	1	2.1+/-0.2	2.6+/-0.2
1.E-8	1	1.1+/-0.4	1.0+/-0.5
1.E-10	1	1.6+/-0.6	1.4+/-0.6
3.E-12	1	1.0+/-0.5	1.4+/-0.4
1.E-6	4	2.9+/-0.3	3.3+/-0.3
1.E-8	4	1.4+/-0.5	1.5+/-0.5
1.E-10	4	2.4+/-0.6	2.5+/-0.8
3.E-12	4	2.3+/-0.9	3.0+/-0.9
Non-Pre-Equilibrated Values:			
3.E-12	1	2.8+/-0.3	2.6+/-0.3
3.E-12	4	2.8+/-0.3	3.0+/-0.5

^aRange is one standard deviation.

CALCULATIONAL METHODS: Debugging and adaptation of MINTEQ to the ORNL computer system is proceeding.

Contact with Lawrence Livermore Laboratory has been made to investigate best means for using the current version of EQ3/EQ6. A new version of the code has just recently been implemented at LLL and documentation is not yet available to indicate the changes that have been made. Since the code and the most recent alterations are designed for a CDC machine, adaptation to the IBM system at ORNL is a significant undertaking. Therefore, efforts are being made to use a direct computer link to apply the code at Livermore without moving it to ORNL.

MEETINGS AND TRIPS: None

REPORTS AND PUBLICATIONS: None

PROBLEM AREAS: None

COST/BUDGET REPORT:

Expenditures for the month of September were \$101.5K and expenditures for FY 1983 were \$464.4K. A detailed cost/budget report will be forwarded under separate cover.