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**Laboratory Studies of Radionuclide Distributions
Between Selected Groundwaters and Geologic Media**

October 1—December 31, 1980

MASTER

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

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Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media

October 1—December 31, 1980

Compiled by

W. R. Daniels

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LABORATORY STUDIES OF RADIONUCLIDE DISTRIBUTIONS BETWEEN
SELECTED GROUNDWATERS AND GEOLOGIC MEDIA

Quarterly Technical Progress Report for
October 1 through December 31, 1980

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ABSTRACT

This quarterly report presents Los Alamos National Laboratory contributions to the Waste/Rock Interactions Technology program, Tasks 3 and 4, for the first quarter of FY-1981.

I. INTRODUCTION

This report covers the Waste/Rock Interactions Technology (WRIT) technical activities at the Los Alamos National Laboratory for the first quarter of FY-1981. Based on their applicability to the WRIT project, some results on tuff have been included from research supported by the Nevada Nuclear Waste Storage Investigations program and the Radionuclide Migration project, both managed by the Nevada Operations Office of the Department of Energy.

II. GEOLOGIC MEDIA - NUCLIDE INTERACTION STUDIES IN THE REPORTING PERIOD

Much of the activity during the first quarter of FY-1981 involved those sorption studies needed to continue studies of sorption isotherms and the effect of solution-to-solid ratios and to continue measurements of migration rates in crushed, fractured, and porous materials.

A. Dependence of Sorption on Element Concentration

Results from batch measurements of the element-concentration dependence of sorption ratios for cesium, strontium, barium, and europium on Climax Stock granite and Eleana argillite were reported earlier.¹ The studies have now been extended to cerium on argillite and granite and to plutonium on granite. The synthetic groundwaters and solid materials were described^{2,3} previously.

1. Isotherm Measurements with Cerium (S. J. DeVilliers and A. J. Mitchell). The <75- and 75-500- μm fractions of Climax Stock granite core CS-5 and the 250-355- μm fractions of Eleana argillite cores CN-1 and CN-2 were used. All contacts were for 3 weeks at ambient temperature under normal atmospheric conditions with the usual batch technique^{2,3,4} for cerium. Initial pH values were ~ 7.4 for the granite and ~ 8.2 for the argillite solutions. Only single measurements were made for each cerium concentration and particle size. A Ce(III) carrier solution was prepared by dissolving a weighed amount of the nitrate salt in deionized water. The ^{141}Ce stock solution was prepared by drying the tracer and then dissolving it in the appropriate rock-pretreated groundwater, as usual.¹ Five solutions of different concentrations were prepared for batch contacts by mixing appropriate volumes of carrier and tracer stock solutions and the appropriate rock-pretreated groundwaters. Concentration data for the solutions before contact with the rocks are given in Tables I and II. Five control samples without rock were carried along in the experiment.

Results for both granite and argillite samples and controls are given in Tables I and II; sample data are presented as sorption ratios while data for the controls are given as the percent of the input activity remaining in solution after contact and centrifuging. For the granite, a high R_d value was observed for the highest cerium concentration. The R_d values for the other four concentrations showed no particular trend although they did vary as much as a factor of four. Interpretation of these data is complicated by the observation that the data provided by the control solutions indicate that much of the cerium activity was lost by either precipitation or sorption on the containers. In

TABLE I
DATA FOR SORPTION OF Ce(III) ON GRANITE -
ISOTHERM MEASUREMENTS

Initial ^a Cerium Concentration (M)	R _d (ml/g)		¹⁴¹ Ce Left in Control Solution (%)
	<75 μm	75-500 μm	
4.94 x 10 ⁻⁹	125	72.4	44
4.43 x 10 ⁻⁸	139	71.2	84
8.85 x 10 ⁻⁷	91.3	32.4	30
1.01 x 10 ⁻⁵	215	133	11
6.82 x 10 ⁻⁵	11200	4300	6.2

^aBased on weighed amount of cerium added. Corrected for losses during preparation of feed solution.

TABLE II
DATA FOR SORPTION OF Ce(III) ON ARGILLITE-
ISOTHERM MEASUREMENTS

Initial ^a Cerium Concentration (M)	R _d (ml/g)		¹⁴¹ Ce Left in Control Solution (%)
	Core CN-1	Core CN-2	
3.21 x 10 ⁻⁹	---	340	100
1.94 x 10 ⁻⁸	---	---	100
1.00 x 10 ⁻⁷	5900	---	2.5
8.64 x 10 ⁻⁷	140	5400	1.9
3.58 x 10 ⁻⁶	2600	2300	2.2

^aBased on weighed amount of cerium added. Corrected for losses during preparation of feed solution.

general, more activity was lost from the controls at the higher cerium concentrations. With the data for the most concentrated solution omitted, the average R_d value for the sorption of ¹⁴¹Ce on granite is 110 ml/g with a standard deviation of the mean of 20 ml/g, consistent with values reported³ earlier.

The sorption data for argillite are very erratic. Several of the liquid samples after contact did not show any ¹⁴¹Ce activity; therefore, R_d values

could not be calculated. The data obtained from the control solutions indicate that most of the activity was lost from the three most concentrated solutions.

In general, it can probably be stated that cerium solubility becomes a significant factor in removal of cerium from solution at concentrations greater than 10^{-7} to 10^{-6} molar.

2. Isotherm Measurements with Plutonium (W. R. Daniels, F. O. Lawrence, M. R. Cisneros, S. Maestas, and P. Q. Oliver). Plutonium isotherm studies for granite have been accomplished by using ^{237}Pu as tracer and adding ^{239}Pu to vary the concentration between 1.6×10^{-12} and 2.6×10^{-9} M. The procedures for batch measurements with plutonium were described in Refs. 1 and 4. The ^{237}Pu and total plutonium concentrations in the ^{237}Pu tracer solution, which was obtained from Argonne National Laboratory, were determined by mass spectrometry. The "Clinton" plutonium (>99.95 atom percent ^{239}Pu) was assayed by alpha counting. Initial traced, synthetic-groundwater ("feed") solutions were prepared by the usual technique, and actual plutonium concentrations at the start of contact with the crushed rock were calculated using the yields through the feed-preparation step as determined by ^{237}Pu gamma counting (Table III). Yields through the feed-preparation procedure were variable but showed some tendency to decrease with increasing plutonium added, perhaps due to precipitation.

Initial 3-week sorption experiments at five plutonium concentrations with two particle sizes of Climax Stock granite core CS-5, <75 μm and 75-500 μm , were followed by 3-week desorptions; both were in air at ambient temperature. Desorption results are not yet available; R_d values for the sorption experiments are given in Table III. Due to the small amount of ^{237}Pu available, only a single measurement was made for each combination of particle size and plutonium concentration. Additional measurements are planned. Within the accuracy of the limited data, a few general conclusions can be reached. There was no significant difference in sorption ratio for the different particle sizes. Although the lowest R_d value corresponds to the highest plutonium concentration, and the highest R_d value to the lowest plutonium concentration, there does not appear to be any real dependence of sorption ratio on element concentration. The pairs of measurements made with a given feed solution and two different particle sizes of granite tend to give similar R_d values, suggesting that the variation in feed solution, i.e., probably plutonium species, is more important than the variation in plutonium concentration. It should be noted that the average R_d value for all ten measurements of 290 ml/g with a standard deviation of the mean of 40 ml/g is

TABLE III
DEPENDENCE OF PLUTONIUM SORPTION RATIO
FOR GRANITE^a ON CONCENTRATION

Initial Pu Concentration ^b (M)		R _d (ml/g)	
Added	Actual	<75 μm	75-500 μm
3.6 x 10 ⁻¹²	1.6 x 10 ⁻¹²	460	530
4.7 x 10 ⁻¹¹	3.0 x 10 ⁻¹¹	170	170
4.4 x 10 ⁻¹⁰	1.9 x 10 ⁻¹⁰	300	350
3.9 x 10 ⁻⁹	1.3 x 10 ⁻⁹	280	300
3.9 x 10 ⁻⁸	2.6 x 10 ⁻⁹	140	160

^aClimax Stock granite core CS-5.

^bThe plutonium concentrations at 100% yield based on assay of the ²³⁷Pu and ²³⁹Pu solutions are shown as "added." The plutonium concentrations actually present at the start of the batch contacts, given as "actual," are lower because of losses during preparation of the feed solutions.

significantly lower than reported¹ previously. This difference may be due to the use of core CS-5 in the current studies and core CS-7 in the earlier ones; the cores are somewhat different in composition and are not perfectly homogeneous within a given core.

When the Freundlich equation $y = kc^n$, where y is the concentration on the solid in moles/g and c is the concentration in the aqueous phase in moles/l, is applied to the plutonium data, the parameters given in Table IV are obtained. The average value of 0.86 for n suggests non-ideal behavior and a tendency toward lower sorption at higher concentrations. This could arise as a result of saturation of available sorption sites, while a value of n greater than one

TABLE IV
FREUNDLICH ISOTHERM PARAMETERS
FOR SORPTION OF PLUTONIUM ON GRANITE

Fraction (μm)	n	k
<75	0.822	0.004
75-500	0.893	0.018

would suggest precipitation of the plutonium. As noted above, however, the limited number of data points and the apparent correlation between batch of feed solution and R_d value indicate a need for additional measurements before any definite conclusions can be reached.

B. Dependence of Sorption on the Solution-to-Solid Ratio (S. J. DeVilliers and A. J. Mitchell)

Batch sorption measurements were performed to determine the dependence of the sorption ratio on the solution-to-solid ratio. Procedures followed and data for 3-week contact times were reported^{1,3} earlier. Results for both 3- and 6-week contacts are given in Table V.

It can be observed that the sorption ratios of cesium and strontium on granite were more affected by the change in the solution-to-solid ratio than those of the other elements. The sorption ratios for cesium and strontium tend to increase with an increase in the solution-to-solid ratio. Sorption ratios for barium, cerium, and europium are essentially constant over the three solution-to-solid ratios for both contact times. In general, sorption ratios were larger for the smaller fraction size.

C. Radionuclide Sorption Experiments Using Solid Rock Cores (R. S. Rundberg, C. J. Duffy, S. Maestas, and N. A. Raybold)

Two cores of YM-49 tuff were cast in epoxy using the technique previously described.¹ One core, YM-49-b, was cast with stainless steel endcaps which had been sand-blasted to help the epoxy adhere to the steel. The other core, YM-49-c, was cast with stainless steel endcaps which have grooves cut on the perimeter for the same purpose. Water which had been pretreated with YM-49 tuff was passed through the columns for about 6 weeks at a pressure of 200 psi without confining pressure to pretreat the rock with the water. By the end of this period YM-49-b had developed a leak between the epoxy and the end cap. The remaining cores will be loaded with ^{237}Pu and ^{239}Pu to examine migration of plutonium through rock cores.

A new method of encasing permeable rock with epoxy for use in a low-pressure chromatography apparatus is being developed. The advantage of this technique is that the columns can be run on a laboratory bench top using a peristaltic pump, thus making it more convenient to run numerous solid-rock columns simultaneously. Two cores from the USW-G1 hole, G1-1982 and G1-2901, were encased in epoxy with a 1.5-cm-o.d. glass jacket. Water flow was achieved

TABLE V
VARIATION OF SORPTION RATIOS FOR GRANITE WITH THE SOLUTION-TO-SOLID RATIO

Fraction (μm)	Solution:Solid Ratio	Contact Time (Weeks)	R_d (ml/g)				
			Cs	Sr	Ba	Ce	Eu
<75	5:1	3	795(6.5) ^a	61.0(2.5)	1450(2.5)	160(9.5)	513(9.6)
	10:1	3	1250(4.5)	44.8(2.3)	1170(1.5)	118(6.7)	403(6.6)
	30:1	3	2280(2.9)	122(2.2)	1190(1.2)	158(4.7)	585(4.3)
<75	5:1	6	946(6.9)	57.9(2.3)	1360(2.3)	287(11.0)	1070(11.4)
	10:1	6	1360(4.5)	52.3(1.9)	1400(1.5)	154(6.9)	544(6.7)
	30:1	6	2250(2.8)	68.7(1.8)	1220(1.1)	205(4.5)	816(4.1)
75-500	5:1	3	679(5.8)	34.5(2.6)	885(2.1)	105(8.6)	434(9.0)
	10:1	3	1010(4.1)	19.8(2.9)	839(1.5)	92.3(6.1)	320(5.9)
	30:1	3	2090(4.5)	160(2.1)	806(1.1)	158(4.7)	554(4.2)
75-500	5:1	6	790(6.0)	42.6(2.3)	983(2.1)	245(9.5)	988(10.3)
	10:1	6	1010(3.9)	36.8(1.9)	797(1.4)	103(6.2)	385(5.8)
	30:1	6	2190(2.8)	51.3(1.8)	884(1.1)	168(4.6)	627(4.1)

^aThe values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent and were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation. The estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

with a peristaltic pump. The G1-2901 core is highly fractured and thus requires very little pressure to attain sufficient flow. The G1-1982 core, however, contains no fractures and therefore requires a high pressure on the manifold tubing to achieve water flow through the core, which may reduce the lifetime of the tubing. A stable flow rate of about 1 ml/day through each core was achieved by adjusting the pump speed and individual manifold tubing pressures. The cores were equilibrated with pretreated groundwater; after about 4 weeks cracks were observed in the glass jackets of both cores. The occurrence of cracks in the glass jackets was surprising since x-ray diffraction results had not shown high concentrations of clays in these cores (J. R. Smyth, Los Alamos National Laboratory, personal communication, October 1980). It is not clear whether the cracking is due to swelling in the rock or the epoxy; however, rapid swelling was observed in some regions of G1-1982 tuff disks when they were treated with groundwater. This suggests the presence of clays like montmorillonite.

A core of G1-1982 was sealed into a plexiglass cylinder with the ends machined to 15 mm o.d. for use with the low-pressure column system. After being treated with groundwater for 2 weeks, the column was loaded with a tritium spike to measure the free column volume and the dispersion. After four weeks of water flow, the plexiglass shows no signs of damage.

The permeability of G1-1982 (partially welded Prow Pass Member) tuff was measured at 21.3°C over a range of effective confining pressures from 5 MPa to 29 MPa. A fit to the measurements was obtained using the following relationship:

$$k = 5.34 \times 10^{-18} / (1 + 12.55P)^{0.238},$$

where k is the permeability in m^2 and P is the pressure in MPa. This result is in good agreement with the flow rate of about 1.0 ml/day which was established in a G1-1982 core using a peristaltic pump. Based on the above permeability relationship a rate of 0.8 ml/day is predicted for a pressure of 50 psi.

Some preliminary experiments concerning fracture flow have been initiated using a small prototype of the proposed block experiments. An artificial fracture was formed by sealing together the edges of two machined surfaces of a tuff sample with a polyurethane sealant. The blocks had been predrilled to allow for groundwater and tracer injection into the fracture. This block will be used for mechanical tests and to aid in the development of suitable inlet

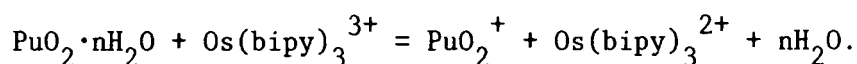
and outlet fixtures. In addition, a plexiglass model of a block experiment was constructed to aid in the design of a tracer injection systems. Dyes will be injected into the fracture to show visibly the shape of the tracer slug after injection. Systems such as this one, constructed from plexiglass, and tracer experiments using blocks with polished parallel faces should be informative.

A small hydraulic press and linear variable differential transformer (LVDT) displacement transducers were purchased for the block studies. The LVDT's will be used to precisely determine the aperture of the fracture in block studies.

III. CHEMISTRY STUDIES IN THE REPORTING PERIOD

A. Possible Inorganic Eh Moderators (T. W. Newton)

Work has begun on the development of Eh buffers or moderators for use in actinide solubility determinations. Couples consisting of certain complexes of Os(II) and Os(III) may have the required potentials, stabilities, and kinetic properties (Henry Taube, Stanford University, personal communication, April 1980). Current work involves the Os(II-III)(bipy)₃ couple, where bipy stands for 2,2'-dipyridyl. The potential is reported⁵ to be 0.878 V. This is such that the solubility equilibrium for plutonium is expected to be



Other couples with lower potentials will be required for other important solubility equilibria.

The compound $[\text{Os}(\text{bipy})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ was prepared from $(\text{NH}_4)_2\text{OsCl}_6$ by the method of Bailar.⁶ A spectrophotometric redox titration method was developed for assaying the compound. In this method aliquots containing 6 to 7 mg of the compound are diluted to about 140 ml and titrated in a special absorption cell with a 2 cm optical path. The titrant is a standardized Ce(IV) solution (about 0.05 N) delivered from a micrometer syringe; the wavelength used is 479 nm. The average precision of the method is $\pm 0.5\%$ based on five determinations.

Three determinations of the equivalent weight of two separate preparations gave widely varying results, ranging from 978 to 1210 g/equivalent. It was thus necessary to purify the compound by recrystallization from water. This was somewhat inconvenient due to the low solubility of the material (~ 1.55 g/l

based on our measurements). The equivalent weights found for two separate batches of recrystallized, air-dried material were both 889 ± 13 g/equivalent; the uncertainty is due primarily to the error associated with weighing 30 mg samples. The molecular weight of $[\text{Os}(\text{bipy})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ is 894, so the preparations are probably of satisfactory purity.

The absorption spectrum of the compound was determined using a Cary Model 14 spectrophotometer. The extinction coefficients of the principal features are listed in Table VI. The uncertainties are probably all about $0.03 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Solutions of $\text{Os}(\text{bipy})_3^{2+}$ are readily oxidized to the +3 state by chlorine gas. The spectrum of a neutral solution prepared in this way is summarized in Table VII. The spectra of solutions of $\text{Os}(\text{III})$ prepared by the titration of the $\text{Os}(\text{II})$ complex with $\text{Ce}(\text{IV})$ in 0.2-0.3 M H_2SO_4 were essentially the same as that indicated in Table VII.

Preliminary experiments to determine the stability of the $\text{Os}(\text{II})$ and $\text{Os}(\text{III})$ complexes were as follows. A sample of the $\text{Os}(\text{II})$ complex was refluxed with 6 M NaCl for 18 hours. After this rather drastic treatment the spectrum was found to be essentially unchanged. The $\text{Os}(\text{III})$ complex was refluxed for one hour with 6 M NaCl ; this gave a solution with a spectrum completely different from that of the starting material. However, when the solution was reduced with a small amount of $\text{Fe}(\text{II})$, the characteristic spectrum of $\text{Os}(\text{bipy})_3^{2+}$ was restored. In another experiment the $\text{Os}(\text{III})$ complex was allowed to stand in water for about 42 hours. This resulted in a 4.9% decrease in the absorbance at the 550-nm peak and small increases in the relative absorbances at the other peaks. Thus, the decomposition rate of $\text{Os}(\text{bipy})_3^{3+}$ is at least 2.8% per day at room temperature. When the same solution was heated to 90°C for 1.5 hours, evidence for significant further decomposition was observed. The absorbance at 550 nm decreased an additional 8%.

Further characterization of this tris bipyridyl system will involve studies of the electrochemical behavior when a potentiostat is used and of the kinetic behavior with trace concentrations of plutonium. Other future work will be the preparation of complexes with lower oxidation potentials.

B. Behavior of Eh Moderator Systems (B. P. Bayhurst and A. E. Ogard)

A Vacuum/Atmospheres, controlled-inert-atmosphere glovebox and a Dri-Train purification system have been received from the vendors and are being installed.

TABLE VI
SPECTRUM OF $[\text{Os}(\text{bipy})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ IN WATER AT 23°C

Feature:	Valley	Peak	Shoulder	Valley	Peak	Valley	Peak	Valley	Peak
$\lambda(\text{nm})$:	347	366	385	409	435	459	479	543	589
$\epsilon \times 10^{-4} (\text{M}^{-1} \text{cm}^{-1})$:	0.84	1.06	0.99	0.87	1.26	1.18	1.34	0.31	0.37

TABLE VII
SPECTRUM OF $[\text{Os}(\text{bipy})_3]\text{Cl}(\text{ClO}_4)_2$ IN WATER AT 23°C

Feature:	Peak	Peak	Valley	Peak
$\lambda(\text{nm})$:	424	455	470	550
$\epsilon (\text{M}^{-1} \text{cm}^{-1})$:	820	420	260	650

This glovebox will be used for experiments pertaining to Eh buffer systems and other methods of producing and measuring low-oxygen-fugacity water systems. A two-month delay in the receipt of a Los Alamos-approved, hydrogen-gas manifold needed for the purification system will unfortunately delay use of the glovebox.

C. Characterization of Plutonium Oxidation States (F. O. Lawrence and M. R. Cisneros)

Work is continuing with equal emphasis on the preparation of trace amounts of plutonium in various oxidation states and the identification of different oxidation states by chemical separation. The identification procedures described by E. A. Bondietti of Oak Ridge National Laboratory are being used. Work has been started on the chemical separation of plutonium oxidation states from weakly acidic solutions.

IV. PROBLEM AREAS

The continued absence of the operating and capital equipment funds for FY-1981 has begun to impact on the probability of meeting the FY-1981 milestones and objectives. The two-month delay in receipt of a Los Alamos-approved, hydrogen-gas manifold needed for the purification system will delay use of the new controlled-inert-atmosphere glovebox.

V. ACTIVITIES PLANNED FOR NEXT QUARTER

The following is a brief outline of some of the activities planned for the period January 1 - March 31, 1981.

A. Migration Rate Studies - Fracture Flow

1. Continue or initiate nuclide migration studies using small (~1 inch diameter) whole-rock samples of granite or basalt.
 - a. Sr, Cs, Eu, U, Pu, or Am.
 - b. Low-pressure system: machined fracture, cleavage or tensile fracture, or open natural fracture.
 - c. High-pressure system: natural fracture.
2. Continue development of methods for performing nuclide migration studies on larger (i.e., perhaps more representative) samples of granite and/or basalt.

B. Migration Rate Studies - Crushed Material

Continue column studies using crushed granite or argillite for comparison with batch R_d results on the same crushed material.

1. Atmospheric conditions: Tc, Ce, Eu, U, Am.
2. Controlled-atmosphere conditions: Tc, U, or I.
3. Circulating system: Sr, Cs, Ba, Ce, Eu, Tc, Pu.

C. Sorption Measurements: Tc, Sr, Cs, Ba, Ce, Eu; Pu or Am.

Initiate measurements of sorption ratios (R_d) for tablets of granite and/or basalt as a function of element concentration, solution-to-solid ratio, oxygen and carbon dioxide concentrations, and concentrations of competing ions. Continue similar measurements using crushed material. Initiate studies of sorption kinetics on rock surfaces.

D. Materials Characterization

Continue materials characterization program. Initiate ion chromatograph measurements of anions.

E. Redox Moderator Studies

1. Continue preparation of possible inorganic redox moderator compounds. Examine various organic dyes for possible use as redox moderators.
2. Continue development of capability for distinguishing between (III+IV) and (V+VI) states of plutonium.
3. Continue assembly and testing of equipment for the study of the electrochemical behavior and stability of buffer systems.

VI. RECENT PUBLICATIONS AND ABSTRACTS

1. B. R. Erdal, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, D. C. Hoffman, F. O. Lawrence, J. R. Smyth, J. L. Thompson, and K. Wolfsberg, "Laboratory Studies of Radionuclide Transport in Geologic Media," in Underground Disposal of Radioactive Wastes, Vol. II, IAEA-SM-243/37 (International Atomic Energy Agency, Vienna, 1980), p. 367.
2. T. W. Newton, B. P. Bayhurst, W. R. Daniels, B. R. Erdal, and A. E. Ogard, "Preliminary Considerations Concerning Actinide Solubilities," in Waste-Rock Interactions Technology annual report for FY-1980.
3. E. N. Vine, W. R. Daniels, R. S. Rundberg, and J. L. Thompson, "Current Status of Crushed Rock and Whole Rock Column Studies," in Waste-Rock Interactions Technology annual report for FY-1980.
4. E. N. Vine, K. Wolfsberg, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, and F. O. Lawrence, "Current Status of Laboratory Sorption Studies," in Waste-Rock Interactions Technology annual report for FY-1980.

5. E. N. Vine, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, and K. Wolfsberg, "Radionuclide Transport and Retardation in Tuff," in Scientific Basis for Nuclear Waste Management, Vol. 3 (to be published).
6. W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver, "Sorption of Am and Pu on Various Geologic Media under Reduced-Oxygen Conditions," American Chemical Society regional meeting, New Orleans, Louisiana, December 10-13, 1980.

VII. ORAL PRESENTATIONS

1. T. W. Newton, B. P. Bayhurst, W. R. Daniels, B. R. Erdal, and A. E. Ogard, "Preliminary Considerations Concerning Actinide Solubilities," Waste-Rock Interactions Technology Annual Information Meeting, Seattle, Washington, October 13-15, 1980.
2. E. N. Vine, W. R. Daniels, R. S. Rundberg, and J. L. Thompson, "Current Status of Crushed Rock and Whole Rock Columns Studies," Waste-Rock Interactions Technology Annual Information Meeting, Seattle, Washington, October 13-15, 1980.
3. E. N. Vine, K. Wolfsberg, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, and F. O. Lawrence, "Current Status of Laboratory Sorption Studies," Waste-Rock Interactions Technology Annual Information Meeting, Seattle, Washington, October 13-15, 1980.
4. E. N. Vine, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, and K. Wolfsberg, "Radionuclide Transport and Retardation in Tuff," International Symposium on the Scientific Basis for Nuclear Waste Management, Materials Research Society, Boston, Massachusetts, November 17-20, 1980.
5. W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver, "Sorption of Am and Pu on Various Geologic Media under Reduced-Oxygen Conditions," American Chemical Society Regional Meeting, New Orleans, Louisiana, December 10-13, 1980.

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REFERENCES

1. W. R. Daniels, Ed., "Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media, Annual Report, October 1, 1979 - September 30, 1980," Los Alamos National Laboratory progress report LA-8586-PR (1981).

2. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Argillite," Los Alamos National Laboratory report LA-7455-MS (1979).
3. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, C. J. Duffy, F. O. Lawrence, S. Maestas, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Granite," Los Alamos National Laboratory report LA-7456-MS (1979).
4. B. R. Erdal, Ed., "Laboratory Studies of Radionuclide Distribution Between Selected Groundwaters and Geologic Media, Annual Report, October 1, 1978 - September 30, 1979," Los Alamos National Laboratory progress report LA-8088-PR (1979).
5. F. P. Dwyer, N. A. Gibson, and E. C. Gyarmas, "The Redox Potentials of the tris 2,2'-Dipyridyl Osmium II/III and the Tris o-Phenanthroline Osmium II/III Couples," J. Proc. R. Soc., N. S. W. 84, 80 (1950).
6. C. F. Liu, N. C. Liu, and J. C. Bailar, Jr., "Asymmetric Synthesis of Tris-(bipyridine) Complexes of Ruthenium(II) and Osmium(II)," Inorg. Chem. 3, 1085 (1964).

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