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Waste Isolation Safety Assessment Program

Task 4
Third Contractor Information Meeting
Volume II

MASTER

J. F. Relyea, Chairman

Seattle, Washington
October 14-17, 1979

Prepared for the
Office of Nuclear Waste Isolation
under its Contract with the
U.S. Department of Energy

Pacific Northwest Laboratory
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Waste Isolation Safety Assessment Program

TASK 4
THIRD CONTRACTOR INFORMATION MEETING

VOLUME II

J. F. Relyea, Chairman

Held at
Battelle Memorial Institute,
Human Affairs Research Centers
Seattle, Washington 98105
October 14-17, 1979

June 1980

Prepared for
The Office of Nuclear Waste Isolation
under its contract with the
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Pacific Northwest Laboratory
Richland, Washington 99352

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PREFACE

The WISAP Task 4, Third Contractor Information Meeting was held in Seattle, Washington, October 14-17, 1979. The purpose of the meeting was to:

- present an overview of ONWI needs and schedules
- present an overview of WISAP goals and methodology
- reiterate Task 4 objectives
- present technical accomplishments of subcontractors during FY-1979.

We are grateful to Gary Brock of the Battelle Memorial Institute, Human Affairs Research Centers, and John Burlison of Pacific Northwest Laboratory, for careful recording of notes on the discussions, for preparing the transcripts, and for editorial assistance. Sue Gano of Pacific Northwest Laboratory provided additional assistance.

We also wish to thank Jody Marshall and Jolene Kitzerow of Battelle for their help in conference organization and logistical support. We are grateful to the rest of the Battelle-Seattle conference staff who were responsible for lodging, food, and audio-visual services.

Finally, the effort of guest speakers and attendees--whose participation led to lively discussions and program redirection and guidance--is much appreciated.

This research was supported by the Waste Isolation Safety Assessment Program (WISAP) conducted by Pacific Northwest Laboratory. This program was sponsored by the Office of Nuclear Waste Isolation, which is managed by Battelle Memorial Institute under contract DE-AC06-76RLO 1830 with the U.S. Department of Energy.

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INTRODUCTION

The Contractor Information Meeting (October 14-17, 1979) was part of the FY-1979 effort of Task 4 of the Waste Isolation Safety Assessment Program (WISAP): "Sorption/Desorption Analysis." The objectives of this task are to:

- evaluate sorption/desorption measurement methods and develop a standardized measurement procedure
- produce a generic data bank of nuclide-geologic interactions using a wide variety of geologic media and groundwaters
- perform statistical analysis and synthesis of these data
- perform validation studies to compare short-term laboratory studies to long-term in situ behavior
- develop a fundamental understanding of sorption/desorption processes
- produce X-ray and gamma-emitting isotopes suitable for the study of actinides at tracer concentrations
- disseminate resulting information to the international technical community
- provide input data support for repository safety assessment.

To accomplish these objectives, the experimental program initiated in FY-1977 is continuing with the assistance of ten scientific groups at national laboratories and private institutions.

The purpose of the Contractor Information Meeting was to:

- present an overview of ONWI needs and schedules
- present an overview of WISAP goals and methodology
- reiterate Task 4 objectives
- present technical accomplishments of subcontractors during FY-1979
- encourage information and idea exchange with other representatives of related programs
- solicit program critiques and peer review.

Conference participants included those subcontracted to WISAP Task 4, representatives and independent subcontractors to the Office of Nuclear Waste Isolation, representatives from other waste disposal programs, and experts in the area of waste/geologic media interaction.

Since the meeting, WISAP has been divided into two programs: Assessment of Effectiveness of Geologic Isolation Systems (AEGIS) (modeling efforts) and Waste/Rock Interactions Technology (WRIT) (experimental work). The WRIT program encompasses the work conducted under Task 4.

This report contains the information presented at the Task 4, Third Contractor Information Meeting. Technical Reports from the subcontractors, as well as Pacific Northwest Laboratory (PNL), are provided along with transcripts of the question-and-answer sessions. The agenda and abstracts of the presentations are also included. Appendix A is a list of the participants. Appendix B gives an overview of the WRIT program and details the WRIT work breakdown structure for 1980.

AGENDA

Sunday (October 14)

6:00-9:00 p.m.	Registration/Dinner

Monday (October 15)

8:00-9:00 a.m.	Overview of ONWI/WISAP/Task 4 R. J. Serne
	Session I: Experimental Methodology and Data Acquisition; Subtasks 4.1 and 4.2
9:00-9:45 a.m.	(1a) "Effects of Hydrogen Peroxide Pretreatment of Clay Minerals on the Adsorption of Sr-85 and Tc-95m Under Anoxic Conditions." J. F. Relyea and C. D. Washburne, PNL
	(1b) "Laboratory Studies of Pu-237 on Selected Minerals Under Anoxic Conditions." J. F. Relyea, R. J. Serne, R. W. Fulton, C. D. Washburne, and W. J. Martin, PNL
9:45-10:05 a.m.	(2) "Cesium Sorption on SiO_2 and Smectites." R. J. Silva, LBL
10:05-10:15 a.m.	Break
10:15-10:45 a.m.	(3) "Transport of Radionuclides in Geologic Media: Methods. P. Rickert, ANL
10:45-11:15 a.m.	(4) "Systematic Study of Nuclide Adsorption on Selected Geologic Media; Experimental Methodology and Data Acquisition." R. E. Meyer, ORNL
11:15-11:45 a.m.	(5a) "Strontium, Technetium, and Tritium Transport in Tuff and Sandstone Cores." H. C. Weed, LLL
	(5b) "Observations on a Batch Kd Technique Using Filtration at Various Stages." D. G. Coles, LLL
11:45-12:15 p.m.	Discussion
12:15-1:15 p.m.	Lunch
1:15-1:45 p.m.	(6) "Sorption of Technetium on Geologic Media Under Anoxic Conditions." C. W. Francis and E. A. Bondietti, ORNL

1:45-2:15 p.m.	(7) "The Kinetics and Reversibility of Radionuclide Reactions with Basalt, Granite, and Argillite." G. S. Barney, RHO
2:15-2:30 p.m.	Break
2:30-3:30 p.m.	(8a) "Sorption of Salt Dome Materials: Uranium (VI) and Technetium (VII)." B. R. Erdal, D. P. Bayhurst, S. J. DeVilliers, F. O. Lawrence, and E. N. Vine, LASL
	(8b) "Effects of Anoxic Conditions and Water Composition on Sorption-Desorption." S. J. DeVilliers, D. P. Bayhurst, W. R. Daniels, B. R. Erdal, F. O. Lawrence, and E. N. Vine, LASL
	(8c) "Behavior of Plutonium and Americium." W. R. Daniels and F. O. Lawrence, E. N. Vine, P. Q. Oliver, and S. Maestas, LASL
	(8d) "Dynamic (Column) Studies of Radionuclide Migration Rates." E. N. Vine, LASL
3:30-4:00 p.m.	Discussion
	Session II: Data Synthesis; Subtask 4.3
4:00-5:00 p.m.	(9) "Statistical Investigation of the Mechanics Controlling Radionuclide Sorption." T. C. Johnson and A. N. Mucciardi, Adaptronics
5:00-5:30 p.m.	Discussion

Tuesday, (October 16)

	Session III: Verification Studies; Subtask 4.4
8:00-8:40 a.m.	(10) "Testing a Site-Binding Electrical Double-Layer Model for Predicting Kd Values." L. W. Benson and R. J. Silva, LBL; G. A. Parks, Stanford University
8:40-8:55 a.m.	(11) "Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: The EQ3/6 Software Package." T. J. Wolery, LLL
8:55-9:15 a.m.	Discussion
	Session IV: Mechanism Studies; Subtask 4.5
9:15-9:55 a.m.	(12a) "Adsorption of Plutonyl by Aerated Soil Minerals." D. Rai, D. A. Moore, and R. J. Serne, PNL

	(12b) "Solubility of Plutonium Compounds and Their Behavior in Soils." D. Rai, R. J. Serne, and D. A. Moore, PNL
9:55-10:05 a.m.	Break
10:05-10:40 a.m.	(13) "Transport of Radionuclides in Geologic Media--Mechanisms." M. G. Seitz, ANL
10:40-11:10 a.m.	(14) "Systematic Study of Nuclide Adsorption on Selected Geologic Media-Mechanisms of Adsorption." R. E. Meyer, ORNL
11:10-11:40 a.m.	(15) "Sorption of Americium and Neptunium on Geologic Media." G. W. Beall and B. Allard, ORNL
11:40-12:00 noon	(16) "A Systematic Study of the Kd Values for 15 Sandstones Having a Wide Range of Mineralogical Composition." D. G. Coles, LLL
12:00-1:00 p.m.	Lunch
1:00-1:20 p.m.	(17) "Sorption of Radionuclides on Weathered Rocks." G. E. Brown, G. S. Barney, RHO
1:20-1:50 p.m.	(18) "Microautoradiographic Studies of Rock Thin-Sections and Cores." J. L. Thompson, W. R. Daniels, and S. Maestas, LASL
1:50-2:40 p.m.	(19) "Subsurface Migration of Radioactive Waste Materials by Particulate Transport." G. G. Eichholz, GIT
2:40-3:00 p.m.	(20) "The Valence States of the Actinides in Natural Waters and Sorption on Geologic Media Under Anoxic Conditions." B. Allard and G. W. Beall, ORNL
3:00-3:20 p.m.	Discussion
3:20-3:35 p.m.	Break
3:35-6:00 p.m.	Guest Speakers and Discussion (Sandia, USGS, Atomic Energy of Canada)
6:00 p.m.	Dinner

Wednesday (October 17)

8:00-12:00 noon	General Discussion of WISAP Task 4

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ABSTRACTS

(1a) Effects of Hydrogen Peroxide Pretreatment of Clay Minerals on the Adsorption of Sr-85 and Tc-95m Under Anoxic Conditions. J. G. Relyea*, and C. D. Washburne, Pacific Northwest Laboratory.

Treatment of three clay minerals with hydrogen peroxide affects the observed adsorption behavior of technetium relative to untreated clay under anoxic conditions. A possible adsorption mechanism of Tc is the reduction of TcO_4 to a more positively charged species. Oxidation of the clay by H_2O_2 would hinder the reduction of the TcO_4 by buffering the clay-water system at a higher Eh value.

(1b) Laboratory Studies of Pu-237 Sorption on Selected Minerals Under Anoxic Conditions. J. F. Relyea*, R. J. Serne, R. W. Fulton, C. D. Washburne, and W. J. Martin, Pacific Northwest Laboratory.

Plutonium Kd values were generally higher under anoxic conditions than ambient conditions in both 5.13N NaCl and 0.03N $CaCl_2$. Lower values for Kd(Pu) were observed in 0.03N $NaHCO_3$ under anoxic than in an ambient atmosphere and no significant differences were found in Kd(Pu) values in 0.03N NaCl for the two oxygen levels. Sorption of Pu was greatest on the phyllosilicates (illite, montmorillonite, vermiculite, and biotite).

The blank-corrected batch Kd method is not well suited for measuring low Kd values when the tracer nuclide is sorbed by the blank container. Measurement of the amount of nuclide sorbed by the blank container can be used to correct calculated Kd values; however, the process doubles the radioanalytical counting requirements over the normal blank-corrected batch method. Containers which do not adsorb tracer nuclides should be used, if possible.

(2) Cesium Sorption on SiO_2 and Smectites. R. J. Silva*, Lawrence Berkeley Laboratory.

No abstract available.

(3) Transport of Radionuclides in Geologic Media-Methods. Paul Rickert*, Argonne National Laboratory.

(1) Nuclide migration by infiltration versus that predicted by batch Kd, (2) batch experiments that reproduce column geometry, (3) analyses of radionuclides on particles by dialyses techniques, (4) leach-migration experiments, and (5) our new rock column holders with pressurized Teflon sleeves.

(4) Systematic Study of Nuclide Adsorption on Selected Geologic Media - Experimental Methodology and Data Acquisition. R. E. Meyer*, Oak Ridge National Laboratory.

Distribution coefficients have been determined as a function of solution variables for a variety of adsorption systems. Last year, we concentrated on studies of adsorption of a number of ions on clay minerals at low pH values where complications due to hydroloysis and precipitation are minimized. We also showed in the systems tested that essentially identical results were obtained using all three of our methods of measuring distribution coefficients, batch, column, and axial filtration. This year we have concentrated on extending adsorption studies to higher pH ranges more characteristic of natural systems, usually from about 4 to 10. The nuclides studies were Cs(I), Sr(II), Eu(III), I^-, Tc(VII), Am(III), Np(V), and U(VI) in various NaCl solutions and a simulated groundwater, all as a function of pH. Clay minerals included montmorillonite, kaolinite, illite, and attapulgite, and hydrous oxides included chromatographic alumina, Corundum, Gibbsite, and Hematite.

Iodide adsorption was studied in a variety of solutions for a number of minerals and rocks including most of the controlled sample rocks. The work on actinide adsorption (supported in part by the Division of Nuclear Sciences/BES) included studies of the adsorption of Am, Np(V), and U(VI) as a function of pH on a large number of rock-forming minerals. Strong increases with pH were observed for a number of systems including Sr(II) and Eu(III) on the hydrous oxides and Am(III) on many of the rock-forming minerals. For some cases, for example, Sr(II) on montmorillonite, little or no dependence on pH was found.

(5a) Strontium, Technetium, and Tritium Transport in Tuff and Sandstone Cores. H. C. Weed*, Lawrence Livermore Laboratory.

Radionuclide transport experiments have been conducted at room temperature and 10MPa confining pressure on cores of Thirsty Canyon tuff with tuff-equilibrated water and St. Peter sandstone with sandstone-equilibrated water. The radionuclides are Sr-85, Tc-95m, and T as HTO. Results will be presented in the form of concentration profiles for the cores, concentration vs. time curves for the effluent solutions, and sorption ratio values derived from these measurements.

(5b) Observations on a Batch Kd Technique Using Filtration at Various Stages in the Procedure. David G. Coles*, Lawrence Livermore Laboratory.

Simulated groundwater that has been equilibrated with various radiotracers is first filtered through an 0.4 μm pore size filter before contacting it with the geologic media being studied. Implications to the final Kd value derived using this technique are discussed. In particular, filtration is compared to simple centrifugation as a phase separation method.

(6) Sorption to Tc on Geologic Media Under Anoxic Conditions. C. W. Francis*, and E. A. Bondietti, Oak Ridge National Laboratory.

The influence of time, temperature, pH, Eh, Fe^{+2}, and Tc concentrations on the sorption-desorption of Tc on a basalt, granite, and shale was investigated. Loss of the TcO_4^- anion from the solution phase appears not to be due to sorption of the anion on the solid phase matrix, but rather due to the reduction to a lower oxidation state; probably TcO_2 which is highly water-insoluble. Loss of TcO_4^- increased with time. There appears to be an interaction between the reduction of TcO_4^- and temperature, viz, increasing temperature enhanced the initial reduction rate, but the rate exponentially decayed at high temperatures (72 vs. 22°C). Basalt significantly reduced TcO_4^- faster and in greater quantities than the granite or shale samples. On the order of 10^6 more Tc-99 was retained on anoxic basalt columns than Tc-95m; however, the apparent distribution coefficients (0.64 and 3.54 ml/g) were not appreciably different. The additions of Fe^{+2} prior to TcO_4^- additions did not affect TcO_4^- reduction; however, additions of Fe^{+2} to TcO_4^- suspensions readily reduced TcO_4^-. The reduced form of Tc is slowly oxidized to the TcO_4^- under oxic conditions. In Eh-pH monitored stirred suspensions, the most important variables influencing the loss of TcO_4^- are Eh and the solution to solid ratio of the suspension.

(7) The Kinetics and Reversibility of Radionuclide Reactions with Basalt, Granite, and Argillite. G. S. Barney*, Rockwell Hanford Operations.

Observations of sorption-desorption reactions of Cs, Sr, Np, Am, and Pu on basalt, granite, and argillite were extended to 218 days. Equilibrium concentrations of radionuclides in batch experiments were not reached for most radionuclides even after this lengthy equilibration time. In addition, reactions of the crushed rock with groundwaters (dissolution, hydrolysis, precipitation, etc.) did not reach equilibrium after 150 days. The dissolution of basalt is accompanied by the formation of colloidal particles which contain Si, Fe, Ca, and Al. These colloids sorb Cs, Sr, Am, and Pu during equilibration experiments. Some of the colloids pass through 0.3 μm filters (some are not retained even on 0.01 m filters) and therefore cause calculated Kd values to be too low.

Additional experiments were performed to determine the effects of radionuclide concentration on Kd values and to measure the reversibility of radionuclide sorption. Several improvements were incorporated into these experimental procedures. Spiked solutions were filtered to eliminate precipitation of tracers before equilibration and dried tracers were added to groundwater solutions to prevent alteration of solution composition by the tracer stock solution.

(8a) Sorption of Salt Dome Materials, Uranium(VI), and Technetium(VII).

B. R. Erdal*, B. P. Bayhurst, S. J. DeVilliers, F. O. Lawrence, and E. N. Vine.

Studies of the sorption of strontium, cesium, barium, cerium, europium, uranium, and americium on Hainesville salt dome materials were made under aerobic and anaerobic (less than 0.2 ppm oxygen) conditions. Results using a dilute brine and a bicarbonate water will be presented.

Results from investigations of the sorption-desorption of uranium (VI) and technetium(VII) on various Nevada Test Site (NTS) materials under aerobic and anerobic conditions, at ambient and elevated (70°C) temperature, will also be presented.

(8b) Effects of Anoxic Conditions and Water Composition on Sorption-Desorption. S. J. DeVilliers*, B. P. Bayhurst, W. R. Daniels, B. R. Erdal, F. O. Lawrence, and E. N. Vine.

The sorption-desorption behavior of several radionuclides under conditions of very low oxygen concentration (less than 0.2 ppm), as may be present in deep geologic formations, was studied using the batch technqiue. Samples of argillite, granite, and Yucca Mountain tuff from the NTS were used. Comparisons will be made between these measurements and those made earlier using the same materials.

The effect of groundwater composition on the measured sorption-desorption behavior for strontium, cesium, barium, cerium, and europium was studied using two groundwaters having rather different ionic strengths. The geologic materials used were argillite, granite, and tuff from the NTS, all ground to the same particle size. The dependence of the Rd values on the groundwater composition will be discussed.

(8c) Behavior of Plutonium and Americium. W. R. Daniels*, F. O. Lawrence, P. Q. Oliver, and S. Maestas.

The behavior of Pu and Am during batch sorption ratio measurements was studied. A multiple-centrifuging technique resulted in aqueous solutions of Pu which were not altered by subsequent filtration, even through membranes as small as 0.05 μm. This result implies that the particulates present in these solutions (pH = 8) were smaller than 0.05 μm and that the Pu species present did not sorb on the filter membranes, at least during the time required for filtration. Results for Am indicate that solutions prepared in the same way as the Pu still contain Am species which are removed by filtration.

The effects of passing various soloutions involved in the batch sorption ratio measurements through polycarbonate membranes were studied by a microautoradiographic technique.

The results from sorption-desorption studies on granite, argillite, and tuff will also be discussed.

(8d) Dynamic (Column) Studies on Radionuclide Migration Rates. E. N. Vine*.

The migration rates of radionuclides in columns of crushed material from three types of geologic media (argillite, granite, and tuff from the NTS), and some of the parameters affecting these rates, will be discussed and compared to data previously obtained by a static (batch) technique.

(9) Statistical Investigation of the Mechanics Controlling Radionuclide Sorption. A. N. Mucciardi*, Adaptronics, Inc.

Nonlinear, adaptive learning network (ALN) models were synthesized that predict Kd for seven radionuclides (Tc, Sr, Cs, Np, Am, I, Pu) as a function of solid adsorbent, contacting solution and nuclide properties. Factors that were considered in this year's work included: (1) analysis of reversibility (adsorption versus desorption Kd's), (2) comparison of the Kd predictor equation on dilute waters versus salt brine, (3) comparison of Kd predictor equations on individual adsorbents versus groups of adsorbents, (4) analysis of the ORNL Ion Exchange data base, and (5) identification of the key variables controlling Kd for each radionuclide. Results of the predictor equations on data not used for model synthesis will be presented.

(10) Testing a Site-Binding Electrical Double-Layer Model for Predicting Kd Values. L. V. Benson*, and R. J. Silva, Lawrence Berkeley Laboratory; and G. A. Parks, Stanford University.

No abstract available.

(11) Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: The EQ3/6 Software Package. Thomas J. Wolery*, Lawrence Livermore Laboratory.

The newly developed EQ3/6 software package computes equilibrium models of aqueous geochemical systems. The package contains two principal programs: EQ3 performs distribution-of-species calculations for natural water compositions; EQ6 uses the results of EQ3 to predict the consequence of heating and cooling aqueous solutions and of irreversible reaction in rock-water systems. The programs are valuable for studying such phenomena as the formation of ore bodies, scaling and plugging in geothermal development, and the long-term disposal of nuclear waste.

(12a) Adsorption of Plutonyl by Aerated Soil Minerals. Dhanpat Rai*, D. A. Moore, and R. J. Serne, Pacific Northwest Laboratory.

Plutonyl(VI) was added to aerated mineral suspensions (1 g mineral and 34 ml of 10 meq $CaCl_2$) maintained at pH 4. The concentration of Pu in 0.015 m filtered solutions was determined at different time intervals.

The maximum adsorption occurred within the first two hours. The minerals differed considerably in their adsorption capacities. The minerals in an increasing order of adsorption were: gibbsite $<$ kaolinite $<$ montmorillonite $\ll$ vermiculite $\leq$ biotite. In order to understand this difference in behavior of various minerals, cation exchange capacity, surface area, chemical nature of the surfaces, and the chemical makeup of the minerals were determined. The results showed that the very high adsorption of plutonyl by vermiculite and biotite was largely due to the presence of ferrous iron in their structure which reduced plutonyl to very highly adsorbable species Pu(III) and/or Pu(IV).

(12b) Solubility of Plutonium Compounds and Their Behavior in Soils. Dhanpat Rai*, R. J. Serne, and D. A. Moore, Pacific Northwest Laboratory.

The solubilities of $^{239}PuO_2(s)$ and $^{239}Pu(OH)_4(s)$ under natural environmental conditions were determined. These data were then used to predict the 1) nature of the solid phases present in contaminated soils, and 2) total concentration of Pu that can be expected in soil solutions when these Pu solids are present.

Based upon solubility measurements, an estimated value of the log K° (equilibrium constant) for the dissolution of $^{239}PuO_2(s)$ $[PuO_2(s) \leftrightharpoons PuO_2] + e^-$ was found to be -14.8. The estimated value of the log K° for the dissolution of $^{239}Pu(OH)_4(s)$ $[Pu(OH)_4(s) \leftrightharpoons PuO_2 + 2\ H_2O + e^-]$ was found to be -12.8.

Comparison of Pu concentration, in solutions in equilibrium with contaminated Hanford soils, with the $PuO_2(s)$ and $Pu(OH)_4(s)$ solubility lines indicated that $Pu(OH)_4(s)$ was absent from all the samples and that two of the samples contained $PuO_2(s)$. The presence of $PuO_2(s)$ was also confirmed by X-ray diffraction of Pu particles isolated from one of the samples.

(13) Transport of Radionuclides in Geologic Media - Mechanisms.
Martin G. Seitz*, Argonne National Laboratory.

(1) Non-linear adsorption isotherms related to concentration expected in groundwater after leaching solidified waste, (2) rock loadings and limits they place on nuclide immobilization, (3) competing cation effects, Rb-Cs as an example and (4) recommendations for more detailed groundwater analysis to serve the need of the repository designer.

(14) Systematic Study of Nuclide Adsorption on Selected Geologic Media: Mechanisms of Adsorption. R. E. Meyer*, Oak Ridge National Laboratory.

The adsorption experiments at low pH values (4 to 5) were designed to test the applicability of ideal ion exchange equations to the data. These equations predict that at loadings small compared to the capacity, slopes of plots of the logarithm of the distribution coefficient versus the logarithm of the sodium chloride concentration should be -2 for divalent ion adsorption, -3 for trivalent ion adsorption, etc. Such slopes were observed for a number of cases, especially at low pH, but, in general, slopes were somewhat less than the ideal values. For other adsorption systems, e.g. Eu(III) on montmorillonite at intermediate to high pH, little or no salt dependency was found. For some systems the logarithm of the distribution coefficient increased approximately linearly with pH. Loading studies show many cases where adsorption follows an essentially linear isotherm from trace to intermediate loadings and expected decreases in distribution coefficient as loading becomes significant with respect to the capacity. In other cases, more complicated dependencies of the distribution coefficient with loading was found. Various explanations for this loading behavior and the pH dependence of adsorption are considered with respect to our data.

(15) Sorption of Americium and Neptunium on Geologic Media. G. W. Beall* and B. Allard, Oak Ridge National Laboratory.

No abstract available.

(16) A Systematic Study of the Kd Values for 15 Sandstones Having a Wide Range of Mineralogical Composition. David G. Coles*.

Kd measurements have been made on 15 sandstones using a simulated brine as the aqueous phase. These sandstones were chosen for their wide range of mineralogical compositions and have been extensively characterized both physically and mineralogically. The effects of the Kd's for Se-75, Sr-85, Sb-125, Cs-137, Ce-144, and Pu-237 are discussed in terms of size fraction and mineralogical variation.

(17) Sorption of Radionuclides on Weathered Rocks. G. E. Brown*, Rockwell Hanford Operations.

Samples of crushed basalt, granite, and argillite were artificially "weathered" by continuous leaching with distilled water for six months. The leaching was performed both in air and in an oxygen-free stream of nitrogen gas. The "weathered" rock was then characterized to determine surface area, cation exchange capacity, and composition of the weathered surface of the rock. Comparisons were made of radionuclide sorption (after 14 days) on fresh rock, rock weathered in air, and rock weathered in N_2. Although there are some exceptions, sorption on rocks weathered in N_2 is less than rock weathered in air. This is possibly due to the lack of an $Fe(OH)_3$ coating on the rock weathered in N_2. The $Fe(OH)_3$ is known to scavenge cations and silica from solution. Sorption of Cs, Am, and Pu is strongly affected by weathering basalt and argillite.

However, the cation exchange capacity is changed very little. This suggests that ion exchange plays a minor role in sorption of these radionuclides.

(18) Microautoradiographic Studies of Rock Thin-Sections and Cores.

J. L. Thompson*, W. R. Daniels, and S. Maestas.

Characteristics of Pu-239 and Np-237 sorption on alluvium, tuff, granite, and argillite thin-sections as determined by microautoradiography will be discussed. Also several experiments will be described in which Sr-85 or U-238 was infused into solid rock cores, yielding sorption data which may be compared with that obtained by batch and column methods. Microautoradiographic examination of these rock cores will also be discussed.

(19) Subsurface Migration of Radioactive Waste Materials by Particulate Transport. G. G. Eichholz*, Georgia Institute of Technology.

The objective of this work is the study of the uptake of dissolved radionuclides leached from waste material by water onto suspended colloidal particulates and their subsequent transport through permeable media. Vertical column packed with basalt, limestone and other media have been set up to observe the migration of labeled particles. It has been shown that such particles do, in fact, migrate and are absorbed to a degree depending on the type of particle and bed medium rather than physical hindrance. The attachment on waste ions on such particles has been observed from distilled water, rock-equilibrated and saline waters and, as expected, depends on concentration, competition with other dissolved ions, pH and effective surface area. The latter does not necessarily stay constant since agglomeration of kaolin particles occurs in brines. The implication of this on migration in salt beds and in adjacent strata is also being studied.

(20) <u>The Valence States of the Actinides in Natural Waters and Sorption on Geologic Media Under Anoxic Conditions</u>. B. Allard* and G. W. Beall, Oak Ridge National Laboratory.

No abstract available.

TECHNICAL REPORTS

VOLUME II

ONWI REPORT NO.

SYSTEMATIC STUDY OF NUCLIDE ADSORPTION ON SELECTED GEOLOGIC MEDIA

ANNUAL PROGRESS REPORT

Covers period:
October 1, 1978 – September 17, 1979

COMPILED BY R. E. MEYER

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SYSTEMATIC STUDY OF NUCLIDE SORPTION ON SELECTED GEOLOGIC MEDIA

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ABSTRACT

This report summarizes the past year's work concerning the adsorption of nuclides of interest to nuclear waste on clays, hydrous oxides, and other geologic media as a function of the pertinent variables of salt concentration, pH, and loading. Most of the adsorbent-adsorbate systems were investigated in the pH range 5-10 and the salt concentration range of from about 0.01 M to 5 M NaCl in order to cover the most probable compositions of groundwaters in the region of waste repositories located in bedded salt formations or salt domes. A batch method was generally used to obtain the data, but for some special conditions, the axial filter was used. For adsorption on clay minerals at pH values of about 5 where hydrolysis reactions are not likely to occur, a strong salt dependence was observed, and the data could be fairly well described by ideal ion exchange equations. As the pH was increased, for some of the systems, e.g. for Eu(III) adsorption on montmorillonite, distribution coefficients increased significantly with pH and the salt dependence decreased or disappeared entirely. For adsorption of Sr(II) and Eu(III) on hydrous oxides, usually a form of Al_2O_3, significant increases in distribution coefficients with pH were observed and the salt dependence was very small, but often increasing somewhat as the pH was increased. Distribution coefficients for adsorption of I^- on a large variety of minerals and rocks were almost always very small, generally almost zero, and only for a few adsorbents under special conditions were distribution coefficients as high as 10 liters/kilogram observed. These results demonstrate that a large number of experiments are required for a complete and systematic investigation of a single nuclide-adsorbent system but also show that the dependence of the distribution coefficient on the variables show regularities which may be used to interpolate and extrapolate the data to non-tested conditions.

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INTRODUCTION

Estimation of the migration rates of nuclides in geologic formations requires reliable information concerning the adsorption behavior of the nuclides on the various minerals present in the formation. As is known from basic studies on the adsorption behavior of ions from aqueous solutions onto inorganic materials, adsorption behavior may be strongly dependent upon such variables as pH and salt concentration as well as on the properties of the adsorbent. Furthermore, the functional dependence may be very large; for example, a ten-fold increase in distribution coefficient is observed for some systems if the pH is varied a single unit. The adsorption behavior of a system is therefore best represented by a series of functions with respect to the pertinent variables.

It is clear that because of the many variables involved, investigation of a single adsorbate-adsorbent system requires a great deal of experimentation. It is probably therefore impossible to attempt a complete description of all possible nuclide-mineral systems pertinent to nuclear waste disposal because the variety of systems is truly enormous. In an attempt to reduce this problem to manageable levels, we have chosen to investigate systematically a few minerals, representative of classes, over a wide range of conditions with initial emphasis on the variables of pH, salt concentration, and loading.

We have chosen to concentrate our determinations in the salt concentration range of 0.01M to 5M (usually either $CaCl_2$ or NaCl). Current policy in the United States appears to be directed toward placing the first nuclear waste repositories in deeply bedded salt deposits or in salt domes. Any breach of such a repository will therefore probably result in groundwaters in this concentration range. It is quite important to determine the dependence of adsorption on salt concentration because it is impossible to predict the actual salt concentrations in the groundwaters, and for some adsorption systems, the dependence of distribution coefficient on salt concentration is significant. Investigation in this intermediate to high salt concentration range is important also because literature data in this range are sparse and somewhat fragmentary.

Much of our initial work was carried out with Cs(I), Sr(II), and Eu(III). The solutions were maintained at pH 5 in order to avoid possible problems with hydrolysis and precipitation. These measurements allowed us to determine the extent to which relatively simple ion exchange equations could be used to represent the data. During the past year, we have concentrated upon extending these results to higher pH values more representative of natural systems.

Most of the work reported here was taken with two mineral classes, the clays and the hydrous oxides. These two classes were chosen because they are ubiquitous in formations and because they tend to have high capacities and high selectivities for many of the nuclides. For some nuclides, e.g. I^-, we have also investigated adsorption behavior with a number of other rocks and minerals.

We have also supported work done by B. Allard (on leave from the Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg, Sweden) of the Transuranium Research Laboratory here at ORNL concerning actinide adsorption on rock-forming minerals. Here the approach was to investigate the adsorption of certain actinide species on selected rock-forming minerals over a wide range of pH in a simulated groundwater, in 4M NaCl, and for some systems other concentrations of NaCl. This work was done largely by Gary Beall and Bert Allard. As mentioned above this work was supported in part by our WISAP (ONWI) funding and also by Basic Energy Sciences/DOE, Division of Nuclear Sciences. We shall include only a brief summary of their work in this report because most of their work will be covered in separate reports.

Last year our report was in the form of a sesquiannual report (Meyer 1978) which covered the first 1-1/2 years work funded by the WISAP Program and also by our sponsors in Fossil Fuel Extraction, Department of Energy. This related work deals with two topics of interest to the field of enhanced oil recovery, (1) Ion Exchange Characteristics of Enhanced Oil Recovery Systems, which is in part concerned with alkaline earth/alkali metal ion equilibria in oil-bearing geologic formations, and (2) Selection of Multiple Tracers for Enhanced Oil Recovery Systems, which is a study of the conditions under which the adsorption of various inorganic ions might be low enough to be useful for tracer monitoring of the chemical floods used in certain methods of tertiary oil recovery.

Since much of our initial work dealt with material of interest to both of our sponsors, such as method development, we combined the results in a single report last year. This year, which involved mostly accumulation of results, we separate the reports even though there still are some areas of common interest.

METHODS AND MATERIALS

METHODS

In view of the wide variation in results from studies of adsorption on minerals in the literature from different laboratories, development of methods has been an essential component of our activities. The need for an enormous number of measurements in a systematic investigation dictates that these methods be rapid, as well as reproducible and accurate. We have used three methods so far to obtain adsorption information: batch equilibration experiments, column methods, and axial filtration. Each method has different advantages and disadvantages for the various experimental situations of interest to us.

In last year's sesquiannual report, we explained the operation of our axial filter and column methods of determining distribution coefficients, and we showed that these methods give results identical to the commonly used batch method. Because of the great number of measurements necessary and because of the necessity of fairly long-term equilibration times for some systems, we decided this year to concentrate on using a modified batch method for most of our results.

In our batch equilibrations, weighed amounts of purified and properly pretreated clay are shaken with known volumes of solution, and the reduction of concentration of the adsorbate in the solution is determined after separation of solid and solution by centrifugation or other means. Whenever possible, radiometric methods were used for analyses, otherwise atomic absorption analysis was used. Results are expressed as distribution coefficients, *D*, the amount adsorbed per unit weight of adsorbent divided by the amount per unit volume of solution at equilibrium.

In order to accomodate the great number of samples we use for a single adsorbent-adsorbate system, we reduced the size of the sample and centrifuge tube to as small as practical, usually 7-15 ml. The amount of sample used was determined by estimating (usually from preliminary experiments) the weight to volume ratio necessary to give a significant reduction of the adsorbate in the solution.

Distribution coefficients are calculated from the equation

$$D = \frac{c_i - c_f}{c_f} \frac{V}{w} \tag{1}$$

where D is the distribution coefficient in liters/kilogram,

c_i is the initial concentration of the nuclide in the solution in any convenient unit, usually counts $\cdot$ min^{-1} $\cdot$ ml^{-1},

c_f is the final concentration of the nuclide,

w is the weight of the sample in kilograms,

V is the volume of the solution in liters.

Distribution coefficients given in this report are related to dried material, in the case of clay usually freeze-dried. Usually the adsorbent was pre-equilibrated with the solution in order to stabilize the pH and establish equilibrium conditions. After equilibration and separation by centrifugation, a volume V_a of tracer solution was added. In this procedure, the volume was computed as follows

$$V = V_a + \frac{(w_t - w)}{\rho} \tag{2}$$

Here w_t is the weight of the sample plus the residual water left after centrifugation, and ρ is the density of the solution. Similarly, the concentration of the initial tracer solution was reduced by the factor $\frac{V_a}{V}$ in order to account for the dilution by the residual water. Adsorption on the tubes was also measured and generally found to be negligible.

We have also used the axial filter method to some extent this year to measure distribution coefficients. This system was described in last year's sesquiannual, and we therefore give only a brief description here. A cylindrical rotor, wrapped with a filter of pore size in the μm range is rotated at rotational velocities on the order of several thousand RPM within an outer chamber which contains a slurry of the adsorbent. After preequilibration with the medium of interest by pumping it through the chamber and through the filter into an exit in the axle, the medium with the adsorbate is introduced at a fixed rate and the adsorbate concentration in the effluent is followed with time (loading cycle). After the solid reaches equilibrium with the incoming medium, i.e. when the effluent concentration equals the influent, adsorbate-free solution is introduced and the concentration of the effluent is again followed with time (eluting cycle).

Equations have been derived for computation of distribution coefficients by comparison of effluent concentration curves with time between what is expected from dilution and what is observed when adsorbent is present. The determination is simplest when distribution coefficients are independent of loading of adsorbent by adsorbate and when half-times of the adsorption reactions are much less than the average residence time of the medium in the chamber. In such cases, a plot of the appropriate adsorption function vs throughput volume is linear, and the results for loading and elution coincide. In this mode, the axial filter is used essentially as a stirred-tank reactor, with a single theoretical plate (the effluent completely equilibrated with adsorbent in passage through the chamber).

This method has the advantage of being able to conveniently measure distribution coefficients for highly dispersible solids for which liquid-solid separation after batch equilibration is difficult. Use of the method also offers a quick method of checking the reversibility of adsorption. We have used this method a number of times this year to confirm our batch determinations and to check if the adsorption reactions are reversible. In all cases determinations done with both methods under identical conditions gave the same results.

We have made extensive improvements on the system this year and have investigated the effects of non-linear isotherms and the possibilities of investigating kinetics of adsorption reactions with the system. This work was largely sponsored by the Division of Chemical Sciences, Basic Energy Sciences/ Department of Energy, and these results have now been presented in two papers (Triolo, Harrison, and Kraus, 1979; and Egozy, 1979).

In connection with the use of the axial filter to measure low values of distribution coefficients, we have also considered the possible effects of ion exclusion or Donnan equilibrium on the measured value of the distribution coefficient by both the batch and axial filter methods. Errors in the distribution coefficient can be introduced by this effect if it is sufficient to exclude to a significant degree electrolyte from the water in the adsorbent. In calculating the distribution coefficient, we normally assume that the water associated with the clay after centrifugation has the same composition as that in the clear supernatant solution. If it is not, an error will be introduced in the calculation. We currently are considering ways to estimate the magnitude of this error by devising experimental methods to measure the extent of ion exclusion. This error normally should not be large but might be significant for systems with which low distribution coefficients are observed.

We have measured capacities of our adsorbents by a variety of techniques. Probably the best method is as follows: A chloride solution of an index cation, e.g. NaCl or $CaCl_2$, was equilibrated with the adsorbent several times until analysis of the solution resulted in essentially 100% index cation solution. After separation by centrifugation, the adsorbent along with the residual solution was washed several times with the nitrate salt of another cation, e.g. NH_4NO_3. The total index cation and chloride content of the wash solutions was then determined. Considerations of charge balance gives the following equation; assuming a monovalent chloride MCl:

$$M^+_{res} + M^+_{ads} + C_{anion} \cdot w = Cl^-_{res} + Cl^-_{ads} + C_{cat} \cdot w \qquad (3)$$

where M^+_{res} and Cl^-_{res} refers respectively to the number of equivalents of cations and chloride ions in the residual solution, M^+_{ads} and Cl^-_{ads} refer to the number of equivalents of adsorbed cation and chloride ions, C_{anion} and C_{cat} are the anion and cation exchange capacities of the adsorbents in equivalents/kg, and w is the weight of the sample in kg.

Therefore:

$$M_t^+ - Cl_t^- = (C_{cat} - C_{anion})w \tag{4}$$

where $$(M_t^+ = M_{res}^+ + M_{ads}^+,\ Cl_t^- = Cl_{res}^- + Cl_{ads}^-) \quad . \tag{5}$$

Thus, the difference in the amounts of index cation and chloride ion give the difference in cation and anion exchange capacities of the clay. If the cation capacity is much larger than the anion capacity, as is often the case, the method gives C_{cat}; otherwise C_{anion} will have to be determined independently. This method has the advantage of taking into account the possibility of ion invasion or exclusion in the interlayer or between clay particles residual water; the concentration of the electrolyte in the residual water may be less than that in the external solution. For materials like montmorillonite which are difficult to centrifuge, this difference in concentration and the amount of water involved can make this correction significant.

Using this technique, as reported in last year's sesquiannual, we obtained a value of about 0.95 equivalents/kg for the exchange capacity using 0.1 M NaCl, 0.1 M $CaCl_2$, and 0.01 M $CaCl_2$ as the index cation solutions. When we used 0.01 M NaCl, a lower value of the exchange capacity was found. We do not know the reason for this.

We have also used other methods to measure the capacity including a column method which we described in last year's sesquiannual.

MATERIALS

Our samples of clay minerals include the following:

A. Source clays, Department of Geology, University of Missouri.
    1. STx-1 Ca-Montmorillonite (White), Gonzales County, Texas.
    2. SWy-a Na-Montmorillonite, Crook County, Wyoming.
    3. CMS-P Fl-1 Attapulgite, Florida.
    4. CMS-K6a-1 Kaolin, well crystallized, Georgia.

B. Reference clay minerals from Ward's Natural Science Establishment.
    1. Montmorillonite #27, Belle Fourche, South Dakota.
    2. Montmorillonite #31, Cameron, Arizona.

C. Also a French Montmorillonite from Henry Thomas, University of North Carolina (Chapel Hill).

D. Oklahoma Illite, Beaversbend.

E. From Baroid Corporation, Houston, Texas.
   1. Synthetic Montmorillonite.
   2. Aquagel, a spray-dried purified Montmorillonite.

Our initial experiments have been performed with all of these clays, but more recently we have concentrated on those from the University of Missouri. We have purified some of these by the methods of Jackson (M. L. Jackson, "Soil Chemical Analysis - Advanced Course", 1956). After removing the sand fraction, the clay is treated with sodium acetate - acetic acid, pH 5, reagent to remove carbonates, then with 30% H_2O_2 to remove organic matter, and finally with sodium dithionite and citrate to remove hydrous iron oxides. Some of the clays were purified only to the point of removing carbonates.

Our samples of oxides include the following:

A. Fisher Chromatographic Alumina (γ AlOOH)

B. Natural Oxides - obtained from Ward's Natural Science Establishment.
   1. Corundum (Al_2O_3), 75% α and 25% β alumina (X-ray analyses).
   2. Gibbsite ($Al_2O_3 \cdot nH_2O$).
   3. Hematite (Fe_2O_3).

Other minerals include Serpentine ($3\ MgO \cdot 2\ SiO_2 \cdot 2\ H_2O$), Augite (Pyroxene), Hornblende, and Galena (PbS). These minerals and the natural oxides were ground with a mortar and pestle and sieved to a size fraction of about 0.04 to 0.06 mm.

The following rocks, obtained from Batelle Northwest, were also used for some of the nuclides. They were used as received: Anhydrite, Culebra, Dolomite, Magenta Dolomite, Conasauga Shale, Westerly Granite, Sentinel Gap Basalt, Oolitic Limestone, and Green Argillaceous Shale. Characterization of these rocks has been given by Ames (1978).

THEORY AND EQUATIONS

Many rocks and minerals, especially the clays, have ion exchange properties. It is desirable to determine the extent to which they behave as ideal ion-exchangers in order to know whether we can use ideal ion exchange equations for interpolation and extrapolation of adsorption data to unknown conditions.

Consider the ion-exchange equilibrium represented by the following equations:

$$pM_1^{n+} + n\bar{M}_2^{p+} \rightleftarrows p\bar{M}_1^{n+} + nM_2^{p+} \tag{6}$$

where the bars over the terms represent adsorbed species. We may write for the equilibrium expression

$$K = \frac{\bar{c}_{M_1}^{\,p} \cdot c_{M_2}^{\,n}}{c_{M_1}^{\,p} \cdot \bar{c}_{M_2}^{\,n}} \cdot \Gamma \tag{7}$$

Here c represents the concentrations of the components in the liquid and adsorber phases, K is the equilibrium constant, and Γ is the appropriate quotient of the activity coefficients. If the capacity of the adsorber is C, then assuming no invasion of co-ions,

$$p\bar{c}_{M_2} = C - n\bar{c}_{M_1} \quad . \tag{8}$$

Here C is expressed in equivalents per unit weight.

If M_1 is present in the adsorber at trace loading, i.e. at only a few percent of capacity, then

$$\bar{c}_{M_2} \approx C/p \tag{9}$$

$$\frac{K}{\Gamma} \approx D_{M_1}^{\,p} \cdot \frac{c_{M_2}^{\,n}}{(C/p)^n} \tag{10}$$

and

$$D_{M_1} \approx \left(\frac{C/p}{c_{M_2}}\right)^{n/p} \cdot (K/\Gamma)^{1/p} \tag{11}$$

where the distribution coefficient is given by

$$D_{M_1} = \frac{\bar{c}_{M_1}}{c_{M_1}} \quad . \tag{12}$$

Assuming K/Γ to be constant, rearrangement of Equation 11 and differentiation yields

$$\frac{d \log D_{M_1}}{d \log c_{M_2}} = -n/p \quad . \tag{13}$$

Thus for exchange of Sr(II) with Na(I) we would expect a slope of -2 at low loading when log D_{Sr} is plotted vs log c_{Na}. For exchange of Eu(III) with Ca(II) at low loading, a slope of -3/2 is expected.

If Equation 11 is not valid, i.e. if loading proceeds to the point where it is significant with respect to the capacity, then

$$D_M = \left(\frac{C - n\bar{c}_{M_1}}{p c_{M_2}}\right)^{n/p} \cdot (K/\Gamma)^{1/p} \quad . \tag{14}$$

As loading increases, the term, $n\bar{c}_{M_1}$, becomes significant with respect to C, and the distribution coefficient decreases relative to the value at trace loading.

For some systems, we find behavior fairly close to that predicted by these equations, e.g. for Sr(II) adsorption on the clay minerals, as we have shown in last year's sesquiannual report. The degree to which these equations are followed is shown in Table 1 which summarizes data on adsorption on four clay minerals at pH 5. For illite the equations are almost ideal for a slope of -2 is observed as predicted from Equation 13. For the other clays the relations hold only approximately, and the absolute values of the slopes are less than 2. There are probably many reasons for this. In deriving the equations, we have assumed that the activity coefficient product is constant.

This is most certainly not true; activity coefficient ratios in the aqueous phase can be estimated fairly well for these systems, and if these are taken into account the slopes of the plots of log D vs log c (Equation 13) are altered somewhat, but correcting for this ratio does not necessarily give slopes closer to ideal behavior. Further discussion of the data given in Table 1 is given below in the Results section.

We have also assumed that the total cation concentration in the adsorbent is equal to the capacity (Equation 8). If substantial coion invasion occurs, which is likely at high concentrations of external electrolyte, then this relation is no longer true for charge balance would then require an increase in the total number of cations in the adsorbent as the concentration of external electrolyte increases.

From a practical standpoint, another highly likely possibility is the presence of several types of adsorption in a mineral sample. This could most simply be due to the presence of an impurity at low concentrations but with a high selectivity for the adsorbate in question; there could also be more than one kind of adsorption 'site' on the same mineral.

The equations given above are derived on the assumption of a fixed capacity resulting from a fixed charge 'imbalance' in the adsorber lattice. However, many adsorbers have properties sensitive to pH, and the adsorption behavior in such cases becomes much more complicated for one must now consider the interaction of several cations with the pH-sensitive group. Although there are many theories in the literature concerning some aspects of the behavior of such adsorbers, there are no generally accepted quantitative and general theories which describe all aspects of behavior as a function of solution composition and pH. Certain general characteristics are known however from experiment, and it is probably worthwhile to repeat them here (cf. Helfferich, 1962). The charge on the exchanger lattice, which may be equated to the capacity, will depend upon the pH, since e.g. the removal of a hydrogen ion will reduce the positive or increase the negative charge. However, the charge will also depend on the concentration and nature of the competing cations so that it is not accurate to speak of a fixed capacity at a given pH. From the practical standpoint, this means that a complete description of such an adsorption system should include a study of the pH dependence of adsorption as well as the concentration dependence of all competing cations including the adsorbate in question. This does not mean that there will necessarily be a dependence on the concentrations of the cations, i.e. a salt dependence. In fact, unlike "ideal" ion exchange, there appear to be situations where there is no appreciable salt dependence. In this discussion, we are referring solely to the effect of pH on the solid adsorber and not on the solution species.

RESULTS

ADSORPTION OF Cs(I)

Last year we presented data concerning the adsorption of Cs(I) on the sodium form of various samples of montmorillonite at pH values of 5 and 8. There were some significant differences in the data among the various samples although there seemed to be no effect of pH. Also, the absolute values of the slopes of log D vs log $c_{\mathrm{Na(I)}}$ were significantly less than unity for some of the samples. We showed later that there was an effect of loading of Cs(I) on adsorption on both the sodium and calcium forms of montmorillonite, such that values of D at trace loading were somewhat greater than those at intermediate values. This loading effect could partially account for the difference among the clay samples since the experiments were not always done at the same loading. This effect may also account for some of the deviations from the ideal value of -1 for the slopes of plots of log D vs log $c_{\mathrm{Na(I)}}$ because at the more dilute concentrations of NaCl the distribution coefficients were much higher and consequently the loading greater.

In order to check the pH dependence of Cs(I) adsorption, a large number of experiments were done in the pH range of 5 to 10 for adsorption on the sodium form of Wyoming montmorillonite. For these experiments, a freeze-dried sample of completely purified montmorillonite (Jackson's procedure) was used, and the cesium concentration was trace, on the order of 10^{-10} moles/liter. The results shown in Figure 1 show that there is no significant effect of pH on this adsorption reaction, and also that the effect of NaCl concentration is significant. It is clear from Figure 1 that the slopes of plots of log D vs log $c_{\mathrm{Na(I)}}$ would be somewhat less than -1. This effect could also be partly due to the loading effect mentioned above although we have not yet completely investigated this effect at very low concentration levels.

We have also investigated the adsorption of Cs(I) from NaCl solutions on hydrous oxides. Our samples of adsorbent include Fisher chromatographic alumina, corundum (Al_2O_3), Gibbsite ($Al_2O_3 \cdot nH_2O$), and Hematite (Fe_2O_3). In Figure 2 results are shown for the adsorption on the Fisher Al_2O_3. Only a moderate effect of pH is observed and there is little effect of NaCl concentration below about pH 8; above pH 8, a small decrease in *D* is observed when the NaCl concentration is increased. For adsorption on corundum, shown in Figure 3 , there is even a smaller effect of pH; however, there is a fairly significant effect of salt concentration, with the distribution coefficients decreasing significantly when the salt concentration is increased. We do not know the reason for this difference. In another series of experiments (Figure 4), mostly preliminary, with all of the natural oxides somewhat varied results were obtained. In this series of experiments the values we obtained for Cs(I) adsorption on corundum do not seem to be consistent with those given in Figure 3. Values of *D* seem higher than they should be considering the salt dependence shown in Figure 3. This may be due to a loading effect and to check this possibility, we are planning loading experiments for Cs(I) on the natural oxides. In the case of hematite there appears to be an effect of pH but this experiment will be repeated; these results for the natural oxides should be considered as preliminary.

ADSORPTION OF Sr(II)

Last year we showed that the adsorption behavior of Sr(II) on montmorillonite, kaolinite, illite and attapulgite at pH 5 could be described fairly well by ideal ion exchange equations. Plots of log *D* vs log $c_{Na(I)}$ were linear with slopes between about -1.5 to -2.0, which approach the ideal value of -2. Loading curves, that is plots of log *D* vs moles Sr(II)/kilogram of clay were almost ideal in shape in that values of *D* at very low loadings were the same as those at larger loadings and the distribution coefficient did not substantially decrease until loadings approached the capacity, i.e., Equation 14 was a fair approximation to the data. These Sr(II) adsorption data are summarized in Table 1 where capacities, the equations for the plots of log *D* vs log $c_{Na(I)}$, and K/Γ (see Equation 7) are given.

The results given above were for clay-solution systems maintained at pH 5 by acetate buffers. In order to extend these results to higher pH values, sodium chloride solutions were adjusted with NaOH and HCl to other pH values without use of buffers. The clay was then added and allowed to equilibrate, usually with further additions of acid or base to give approximately the desired pH value. Tracer Sr(II) was then added to the solution and the systems were allowed to equilibrate for at least 48 hours. Strontium concentrations were maintained at approximately 10^{-7} moles/liter in order to preclude possible problems with precipitation. The results for Sr(II) adsorption on the sodium form of montmorillonite, shown in Figure 5 , show that there was no significant effect of pH in the region investigated.

For Sr(II) adsorption on illite and kaolinite, however, different results were obtained. In the case of illite, Figures 6 and 7 , a small increase of D with pH was observed. Plots of log D vs log $c_{\mathrm{Na(I)}}$ were obtained from the data of Figure 6 and are shown in Figure 7 . Slopes of the lines are in good to fair agreement with the theoretical slope of -2, and the comparison of the data from this experiment with last years experiments at pH 5 in acetate-buffered solutions shows reasonable agreement. One should keep in mind, however, that small amounts of montmorillonite are frequently found with illite and that it would be difficult to detect the montmorillonite in the illite. Our loading curves obtained for illite last year (Figure 30, Sesquiannual Report, Meyer, 1978) however do not give any indications of any other significant adsorbent in the mixture.

For kaolinite the data are somewhat more complicated for a strong pH dependence is observed as shown in Figure 8 . Except for the dilute solutions, a linear dependence of log D vs pH was found roughly to approximate the data. Comparison of these data with last year's data in buffered pH 5 solutions gives good agreement at concentrations of 0.2 M, 0.1 M, and 0.05 M but only fair agreement at 0.005 M NaCl. Also at the more dilute concentrations of NaCl shown in Figure 8 a very sharp dependence on pH was observed in the range 4-6. At the higher pH values, there is only about a factor of 10 difference between the values of D at the highest salt concentration, 0.5 M, and the lowest 0.005 M; Equation 13 predicts a factor of 10^4 difference. Since the initial concentration of Sr(II) was 10^{-7} M and the *D*'s are around 10^3 liters/kilogram, the loadings were less than 10^{-4} moles/kilogram, considerably below the capacity of kaolinite, ∿ 0.01 equivalents/kilogram. Thus none of the determinations of *D* shown in Figure 8 represent conditions near saturation of the capacity.

In summary, for all three clays, there is a strong salt dependence on adsorption, and ideal ion exchange equations represent the data fairly well except for Sr(II) adsorption on kaolinite at the higher pH values.

Shown in Figures 9 and 10are log *D* vs log $c_{Na(I)}$ plots for the adsorption of Sr(II) on montmorillonite at pH 5 for Wyoming montmorillonite which had been prepared and purified in different ways. For these conditions, we find no significant differences among the various samples of montmorillonite.

Figure 11shows the results of some preliminary experiments on the adsorption of Sr(II) on Fisher chromatographic alumina and the natural oxides at two concentrations of NaCl. In each case a fairly strong increase in distribution coefficient with pH was observed. Figures 12and 13show the results of experiments on chromatographic alumina at eight different concentrations of NaCl. Again there is a fairly strong dependence on pH with approximately a ten-fold increase of *D* for every unit increase in pH. Also at high pH values, the curves begin to show a salt dependence in agreement with the expected increase in cation exchange capacity as the pH is increased.

ADSORPTION OF Eu(III)

Last year we presented data at pH 5 for the adsorption of Eu(III) on the sodium form of montmorillonite. Below concentrations of about 1 M NaCl, plots of log *D* vs log $c_{Na(I)}$ were linear, and the slopes approach the theoretical value of -3, but above 1 M NaCl the distribution coefficients leveled off and tended to increase. We have now done the same experiment with Eu(III) adsorption on the calcium form of montmorillonite and found a similar effect as shown in Figure 14. Also in this figure, a decrease in *D* in solutions containing acetate is shown. Presumably the acetate complexes with Eu(III) and the complexed form is less adsorbed than the non-complexed form. We have also checked the loading behavior for this adsorption system,and the loading curve, Figure 15, at a $CaCl_2$ concentration of 0.05 M shows fairly normal behavior, i.e. the values of *D* at trace loading are the same as those at intermediate values and at the highest loadings decrease as the cation exchange capacity is approached.

The pH dependence of adsorption of Eu(III) on the sodium form of montmorillonite shows interesting behavior (Figures 16-19). There is a strong salt dependence on the adsorption reaction at pH values below about 5.5, but the distribution coefficients for all of the solutions increase sharply so that at higher pH values the plots almost coincide. There is also a suggestion that the values tend to level off at about 10^5 liters/kilogram.

A similar observation is noted for adsorption of Eu(III) on the sodium form of the Fisher alumina (Figure 20) except that the D's tend to level off at somewhat higher values of D, on the order of 10^6 liters/kilogram. Also for this case the distribution coefficients increase very sharply, almost five orders of magnitude when the pH is increased from about 3 to 7. Finally, for the natural oxides, shown in Figures 21 and 22, the distribution coefficients also increase very sharply in the pH range of 5 to 7 and tend to level off at values of D between 10^5 and 10^6 liters/kilogram.

In these experiments, ^{155}Eu(t 1/2 = 1.7 y) was used as a tracer. For the experiments with montmorillonite, the initial concentrations of Eu(III) were 10^{-6}M and for experiments with the oxides on the order of 10^{-9} to 10^{-10}M. Final concentrations for the montmorillonite experiments at the higher pH values were about 10^{-9}M and for the oxide experiments on the order of 10^{-11} to 10^{-12}M. Thus, if the estimated values of log $K_{sp} = -24.5$ and the first hydrolysis constant $[K_h = 10^{-7.8} = (EuOH^{++})(H^+)/(Eu^{+++})]$ given by Baes and Mesmer (1976) are only approximately correct, we calculated a solubility near pH 8 of about 10^{-6} to 10^{-7}M, well above the concentrations we observed. Of course there is always the possibility that these values of the constants may be incorrect.

CATION AND ANION EXCHANGE CAPACITY OF ALUMINA

In order to try to understand the behavior of these hydrous oxides we are measuring the uptake of Na(I) and Br^- on samples of the oxides. The procedure was to equilibrate samples of the adsorbent over several days and then measure the uptake by an isotope dilution method using ^{22}Na and ^{82}Br. The oxides were first preequilibrated with the appropriate solutions in order to insure complete uptake of the ions. The results of these experiments are shown in Figures 23-24 for Na(I) and Br^- uptake of Fisher alumina. As one would expect from a material with both weak acid and weak base properties, the cation exchange capacity increased with pH at higher pH values and the anion exchange capacity increased as the pH was lowered at lower values of the pH.

TEMPERATURE DEPENDENCE OF THE ADSORPTION OF SOME CATIONS ON ILLITE AND MONTMORILLONITE

Most measurements of distribution coefficients are determined at room temperature, usually 22-23°C. The temperatures of interest in the waste isolation program may vary from these temperatures depending on a number of conditions. It is therefore of some value to see if there may be a significant effect of temperature.

Determination of the temperature coefficient at elevated temperatures is complicated by the problem of separating the clay from the solution at the temperature of interest. This problem was solved in this work by removing a sample of the solution at temperature with a syringe attached to a small filter chamber fitted with a millipore filter. A small amount of solution was removed from the sample to determine the activity of the solution after adsorption. For the samples of montmorillonite, it was found that the sodium form would pass through the filter; however the calcium form which was less dispersible could be effectively separated by this device. We also used a sample of Oklahoma illite, a clay which we had used earlier for studies of Sr(II) adsorption and which we found relatively easy to separate.

The illite was prepared by removal of carbonates with pH 5 buffer, placed into the sodium form, and then separated into the 0.62 μm to 210 μm fraction by centrifugation. The clay was then washed several times with 1M NaCl and then three times with the solution prepared for equilibration. The clay was then added to a traced solution of the same composition. During the equilibration the suspension was rocked in a sealed test tube which was jacketed so that thermostated water could be circulated around it. A portion of the solution was removed for counting and then returned to the tube and the runs continued. In general, the suspensions were cycled from low to high and then to low temperature again in order to insure that the elevated temperatures did not affect the system. In general, equilibration times were several days at each temperature.

The montmorillonite samples were completely purified by the Jackson procedure and then freeze dried. They were treated the same way as the illite samples except that they were put into the calcium form by repeated contact with 1 M $CaCl_2$.

The results for these experiments are summarized in Table 2. The systems studied include adsorption of Sr(II) on the sodium form of illite and the calcium form of montmorillonite, and the adsorption of Cs(I) on the calcium form of montmorillonite. Temperatures investigated were room temperature and 80°C. In general, the effects of temperature were not large; the maximum change observed was about a factor of 3 (Cs(I)/Ca(II) system) decrease in D_{Cs} as the temperature was increased from room temperature to 80°C. The results of these initial experiments suggest that the divalent ions are preferred by the clay at the higher temperature.

ADSORPTION OF I^- ON MINERALS AND ROCKS

The adsorption of I^- on a large number of minerals and rocks was determined as a function of pH and salt concentration. The rocks that were used were those supplied by Battelle Northwest for the controlled sample program. For some of the samples the I^- concentration was determined at both 10^{-5}M and 10^{-8}M in order to see if there was an effect of loading. Analyses were carried out radiometrically using iodine-131.

The results are given in Table 3. In general distribution coefficients were very low, within experimental error essentially zero. There were some exceptions however. For kaolinite at 10^{-8}M I^-, there appeared to be a regular increase in D as the pH was lowered indicating possibly a very small anion exchange capacity at lower pH values. However even at pH 5.52 the distribution coefficient was only 1.14 liters/kilogram. For the Fisher alumina, the distribution coefficients increased as the pH decreased and at 0.01 M NaCl reached a value of 12.2 at pH 5.38. There was also a significant salt effect with the values of D decreasing as the salt concentration was increased. Such behavior is typical of weak base anion exchangers. The only other material to show any adsorption was Galena (PbS) which showed a regular increase in D as the pH decreased for both 10^{-5} and 10^{-8}M I^- and values of D of about 12-13 liters/kilogram at pH 5.6.

DISCUSSION

As we have shown in last year's annual report, adsorption behavior of alkali metal, alkaline earth, and rare earth ions on clay minerals can be fairly well described at pH 5 by "ideal ion exchange" equations. Significant exceptions were the adsorption of alkali metal ions at very low loading (10^{-5} to 10^{-4} moles/kilogram) on the calcium form of montmorillonite and the adsorption of Cs(I) on the sodium form of montmorillonite. In both of these cases, especially the former, distribution coefficients were higher at these low loadings than at intermediate loading levels, i.e. a linear isotherm was not followed in this loading region. Another variation noted last year was a leveling off of the distribution coefficient of Eu(III) adsorption on montmorillonite as the salt concentration was increased; at values above about 1M the expected linear decrease of the logarithm of *D* with respect to the logarithm of the salt concentration (cf. Equation 13) was not observed above 1 M salt concentration.

During the past year, one of our efforts was to extend these results on clay minerals to higher pH values more characteristic of natural systems, usually covering a range of from pH 5 to 10. At these higher pH values, some of the adsorption systems, such as Sr(II) adsorption on montmorillonite and illite, continued to follow ideal ion exchange equations but others did not. Thus, the adsorption of Sr(II) on kaolinite, which was highly pH dependent, did not follow ideal equations at the higher pH values. Also Eu(III) adsorption on the sodium form of montmorillonite at higher pH values no longer had a strong salt dependence and thus did not follow ideal ion exchange. Caution must therefore be used in the application of these equations to adsorption on clay minerals at higher pH values.

Another of our efforts this year was a study of adsorption on hydrous oxides, which are ubiquitous in formations and have been reported to have very great selectivity for multi-valent ions at higher pH values. The pattern of behavior of this class of minerals was somewhat different from that of the clay minerals. For Cs(I) adsorption, there was either no, or only a slight, pH dependence over the pH range in question, only a relatively small salt dependence, and the values of *D* were generally low, usually less than 10 liters/kg. For the multi-valent ions Sr(II) and Eu(III), a very large pH dependence on adsorption was observed, and only a very small or no salt dependence was found. Values of *D* were very high at higher pH values, reaching values of 10^4 to 10^6 liters/kg. The salt dependence that was found was generally observed only at the highest pH values investigated, presumably because of the increased cation exchange capacity of the hydrous oxides as the pH was increased. So far we have carried out these measurements with multi-valent ions primarily at trace loading because of the possibility of precipitation at higher concentrations of adsorbate. Thus 'ideal' ion exchange equations which are partially applicable to adsorption on clay minerals where cation exchange capacity is dominant were not at all applicable to hydrous oxides.

The data on adsorption on hydrous oxides however showed some consistent regularities which should simplify characterization of such adsorption systems. For example, it appears that distribution coefficients for multivalent-ion adsorption tend to follow a linear increase of log *D* with respect to the pH and in some cases, the slope of this line was near or close to unity.

It is perhaps not surprising that there is little or no salt dependence of adsorption on the hydrous oxides. These materials have properties similar to weak acid and weak base ion exchangers and therefore little cation exchange capacity would be expected at lower pH values, i.e. the weak acid groups are not significantly ionized until higher pH values are attained. Further it appears from the data that multivalent ions interact very strongly with the adsorbent, but Cs(I) does not. If Cs(I) is at least somewhat representative of the alkali metal ions then one would not expect Na(I) to interact strongly and to compete with multivalent ions. We have not yet however investigated salt dependence of these adsorbents for calcium salts as we have done for some of the clay minerals, since all of our experiments have been done so far in NaCl solutions. A salt dependence of Sr(II) adsorption on hydrous oxides might be expected if the salt is $CaCl_2$ or the salt of another multivalent ion.

In our studies of I^- adsorption, we found no significant adsorption on almost all of the materials investigated. Only for Al_2O_3 and for Galena (PbS) at low pH values were distribution coefficients as high as 12 liters/kilogram observed. Since these materials behave as weak base exchangers, some anion exchange capacity should be expected at lower pH values, as we observed. Galena (PbS) could act as a anion exchanger either if the sulfide group interacts with a proton to form an -SH group or if it is partially oxidized in the natural state to form an oxide or hydroxide.

This year we have extended our comparisons of adsorption on clays from various sources and purifications to a comparison of Sr(II) adsorption on montmorillonite on samples taken after each step of the Jackson purification procedure; no differences were found in distribution coefficients among the samples. However we have not yet tried this type of experiment with other adsorption systems, but it is of some interest to note that Eu(III) adsorption on Fisher chromatographic alumina gave about the same results as adsorption on corundum, the natural form of Al_2O_3.

Last year we presented in tabular form a comparison of our data with various values in the literature. Some of these comparisons we now know are strictly not valid because for some systems we have found strong pH dependencies and the pH was not always noted in the literature. The strong dependencies on the pH of adsorption of multivalent ions on hydrous oxides has been noted in the literature (Kraus, Phillips, Carlson, and Johnson, 1952). Tamura (1964) reported an increase of D with pH for Sr(II) adsorption on alumina. Kinniburgh, Syers, and Jackson (1975) have given data for adsorption of both Ca(II) and Sr(II) on precipitated and natural oxides of Fe(III) and Al(III) which show this strong pH dependence. Various theories have been advanced in the literature in an attempt to explain adsorption behavior of hydrous oxides (James and Healy, 1972a,b.c). However, to our knowledge there are not yet any generally accepted theories which satisfactorily explain the behavior of these minerals.

SUMMARY OF STUDIES ON ADSORPTION OF ^{241}Am and ^{235}Np ON ROCK-FORMING MINERALS

(This work was largely supported by the Basic Energy Sciences, DOE, Division of Nuclear Sciences.)

Distribution coefficients for ^{241}Am(III) and ^{235}Np(V) adsorption as a function of pH have been determined on a large number of rock-forming minerals from both a synthetic groundwater and 4 M NaCl. The determinations employed a batch technique using a solution to solid ratio of 20:0.5 (ml/gm). The groundwater composition was as follows (in ppm): Ca^{2+}, 14.8; Na^{+}, 56.2; K^{+}, 4.3; Mg^{2+}, 4.35; $CO_3{}^{2-}$, 100; SiO_2, 15.1; $SO_4{}^{2-}$, 11.2; and Al^{+3}, 0.0079. Analyses of the groundwater after exposure showed that, in most cases, the composition of the groundwater did not change significantly, and most of the changes were reasonable when the composition of the mineral is taken into account. The solids were prepared by grinding to a size fraction between 38 and 63 microns. The solids were preequilibrated three times with the groundwater, but not with the 4 M NaCl, before the tracers were added from a spiked tracer solution containing 0.1 N HCl. The initial concentrations of the sample solutions were $2x10^{-9}$M for Am and $2x10^{-11}$M for Np. pH values were adjusted by addition of HCl or NaOH. The distribution coefficients were measured after five days equilibration by removal of a solution aliquot and counting. The pH was then readjusted to a new value, and the solution was then allowed to equilibrate for another five days.

Figures 25-27 summarize the adsorption behavior of Am(III) as a function of pH on the major rock-forming minerals. Except for hornblende, apatite, marble, and dolomite, all the functions have approximately the same shape. With hornblende, a $CaCO_3$ impurity was found. These data show that distribution coefficients are quite low (note that the units are m^3/kg)* at low pH values but increase by several orders of magnitude to a maximum at about pH 7. The carbonate minerals dolomite and marble also exhibit high values of the distribution coefficient in the pH range shown, which was limited by the buffering capacity of the minerals. Figure 28 shows a comparison of the adsorption behavior of Am on quartz and montmorillonite as a function of pH in the dilute groundwater and in 4 M NaCl. Little difference is noted between quartz in the two solutions except at the lowest pH; for montmorillonite a strong salt dependence is noted at low pH values only. Thus ideal ion exchange equations can be used for the description of the salt dependence at low pH values but not

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*Values of D in m^3/kg are a factor of 10^3 lower than those expressed in ℓ/kg.

in neutral solutions. Also the values of *D* at low pH values for montmorillonite are much greater than those of quartz, and they are roughly proportional to their capacities (0.9 equiv/kg for montmorillonite and 0.002 equiv/kg for quartz).

For neptunium, similar adsorption behavior with pH was observed for the various minerals except that the sharp rise with pH did not occur until the pH was about 7-7.5 (Figure 30). Below this pH, distribution coefficients were fairly level. The order of increasing adsorption was about the same as for americium with the difference between distribution coefficients for quartz and biotite being about one order of magnitude. Studies in 4 M NaCl (not shown here) indicate a slight salt dependence which for most of the minerals is opposite to what would be expected from ideal ion exchange equations.

As part of an effort to study the sorption of actinide ions on whole rocks and to compare the results with predictions based on data obtained from pure minerals, we have carried out a series of actinide sorption experiments on the same well-characterized specimen of Climax Stock granite at varying conditions of Eh and pH. Qualitative trends in the sorption were evaluated through use of an autoradiographic technique.

All sorption experiments employed as the aqueous medium a synthetic groundwater with the same concentrations of principal constituents as that used in the studies on batch equilibration of minerals. In equilibrium with ambient air, the pH was ∿7.8 and was largely determined by the CO_2/HCO_3^- equilibrium. For experiments under anoxic conditions, N_2 gas was bubbled through the solution to remove O_2 and CO_2, which shifted the pH to ∿9.3. Radioactive concentrations, chosen to insure adequate deposition for an autoradiograph, were: ^{233}U, $6 \times 10^{-7}M$; ^{237}Np, $4 \times 10^{-5}M$; ^{238}Pu, $2 \times 10^{-9}M$; and ^{241}Am, $8 \times 10^{-10}M$. After each experiment of approximately 21 hours, the specimen was cleaned chemically, washed, then lightly ground with fine abrasive to expose a pristine surface.

The essential features of the autoradiograph "camera" are sketched in Figure 31. The Polaroid* type 57 sheet film (ASA 3000), a ZnS(Ag) scintillator film, and the radioactive surface of the granite were placed in firm contact by a pressure plate actuated by a mechanical system outside a light-tight box housing the components of Figure 31. This simple arrangement has proved to be very convenient and reproducible.

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*Polaroid Corporation, Cambridge, MA 02139.

Autoradiographs of the granite specimen after sorption from a solution of Am(III) under aerated and anoxic (N_2 purged) conditions suggested that a mildly reducing medium did not significantly alter the sorption. Moreover, the degree of sorption followed qualitatively the order observed in pure mineral experiments; namely, pyrite and biotite grains sorbed strongest, the feldspars less, and quartz least.

Some results with neptunium are illustrated in Figure 32. In these experiments, neptunium was expected to exist as the NpO_2^+ cation. Figure 2(a) shows an optical photograph of the Climax Stock granite specimen (2.7 x 3.1 cm) for comparison. Under aerated conditions, sorption of neptunium was observed to be strongest on the Fe(II)-containing minerals pyrite and biotite. Under nitrogen-purged conditions the specificity for these minerals appeared to be enhanced. Such results are consistent with a sorption mechanism involving the reduction of Np(V) to the much less soluble Np(IV) by Fe(II). As a test of this hypothesis, an experiment was made in which the surface of the granite was oxidized with concentrated H_2O_2 prior to exposure to the Np(V) solution. The autoradiograph of Figure 2(b) shows that general sorption was found across the whole surface, not specific for any mineral, as expected if all Fe(II) sites had been oxidized to Fe(III) prior to contact with Np(V).

Experiments with uranium showed low sorption on all minerals except biotite. The sorption of uranium, assumed to be present as UO_2^{2+}, appears to be related to the large cation-exchange capacity of biotite. Further, the sorbed uranium could be desorbed by re-immersing the specimen in 4 M NaCl, as expected if the sorption were due to simple, ion-exchange behavior.

Plutonium was expected to be present mostly as Pu(IV), and therefore, was also expected to be quite insoluble. Autoradiographs showed little effect of aerated or reducing conditions on the sorption; instead, the dominant pattern was one of general sorption across the surface, consistent with precipitation of PuO_2. A slight correlation with Fe(II) mineral sites implied that some PuO_2^{2+} was present. A solution treated with O_3, in which PuO_2^{2+} should have been the dominant species, exhibited a strong correlation with the Fe(II)-containing minerals, implying a reduction mechanism for deposition similar to that suggested for NpO_2^+.

The experimental details and a more complete discussion of the results of this work will be found in the following reports:

Publications About Adsorption Studies

1. G. W. Beall and B. Allard, "Chemical Factors Controlling Actinide Sorption in the Environment," Trans. Amer. Nucl. Soc. (TANSAO), 32, 164 (1979).
2. B. Allard, G. W. Beall, T. Krajewski and J. R. Peterson, "The Sorption of Americium on Major Rock-Forming Minerals, TANSAO, 32, 167 (1979).
3. T. Krajewski, G. W. Beall, B. Allard and J. R. Peterson, "Mineral-Contributed Anion Effects on the Retention of Trivalent Actinides in the Environment," TANSAO, 32, 168 (1979).
4. G. W. Beall, B. Allard, T. Krajewski and G. D. O'Kelley, "Chemical Reactions in the Bedrock-Groundwater System of Importance for the Sorption of Actinides," Symposium on Scientific Basis for Nuclear Waste Management, Boston, November, 1979; to be published in the Proceedings.
5. B. Allard and G. W. Beall, "Sorption of Americium on Geologic Media," J. Environ. Sci. Health, A14(6), 507 (1979).
6. T. Krajewski, "Anion Effects on the Retention of Selected Actinides on Geologic Media," Master's Thesis, University of Tennessee (January, 1980).
7. G. W. Beall, G. D. O'Kelley and B. Allard, "An Autoradiographic Study of Actinide Sorption on Climax Stock Granite," No. ORNL-5617 (December, 1979).
8. B. Allard, H. Kipatsi and J. O. Liljenzin, "Expected Species of Uranium, Neptunium and Plutonium in Neutral Aqueous Solutions," submitted to Radiochem. Radioanal. Lett.
9. B. Allard, G. W. Beall and T. Krajewski, "The Sorption of Actinides in Igneous Rocks," submitted to Nuclear Technology.

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Table 1

Distribution Coefficients and K/Γ Values for Sr(II) Adsorption on the Sodium Forms of Montmorillonite, Illite, Attapulgite, and Kaolinite Acetate Buffered, pH 5

Montmorillonite, Capacity 0.95 Equiv/kg

(Na^+)	D, l/kg	K/Γ
0.1	80	.89
0.2	23.3	1.03
0.6	4.65	1.85
1.1	1.75	2.34

$\text{Log}\ D_{\text{Sr(II)}} = -1.57\ \text{Log}\ c_{\text{Na}^+} + 0.31$

Illite, Capacity=0.101 Equiv/kg

(Na^+)	D, l/kg	K/Γ
0.005	13045	32.0
0.05	140.5	34.4
0.1	38.0	37.3
0.2	7.65	30.0

$\text{Log}\ D_{\text{Sr(II)}} = -1.64\ \text{Log}\ c_{\text{Na}^+} - 1.17$

Attapulgite, Capacity=0.138 Equiv/kg

0.005	1916	2.5
0.05	69.1	9.1
0.1	19.8	10.4
0.2	5.6	11.7

$\text{Log}\ D_{\text{Sr(II)}} = -1.81\ \text{Log}\ c_{\text{Na}^+} - 0.52$

Kaolinite, Capacity=0.0127 Equiv/kg

0.005	389	59.8
0.05	10.25	157.6
0.1	2.93	180.2
0.2	0.90	22.14

$\text{Log}\ D_{\text{Sr(II)}} = -1.64\ \text{Log}\ c_{\text{Na}^+} - 1.17$

Table 2

Temperature Dependence of the Adsorption of Sr(II) and Cs(I) on Illite and Montmorillonite

Conc. at Rm. Tmp. (M)	Rm. Tmp. (°C)	Rm. Tmp. D, ℓ/kg	80° D, ℓ/kg
Sr^{2+} from Na^+ Solutions onto Oklahoma Illite			
(Na^+)			
0.03	22	129	240
0.10	23.5	26.0	40
0.30	21.3	2.8	5.4
Sr^{2+} from Ca^{2+} Solutions onto Wyoming Montmorillonite			
(Ca^{2+})			
0.005	21	74	65
0.050	21	9.1	9.1
0.50	21	1.0	0.35
Cs^+ from Ca^{2+} Solutions onto Wyoming Montmorillonite			
(Ca^+)			
0.005	21	145	43
0.050	21	68	21.5
0.50	21	27.5	9.6

TABLE 3

Distribution Coefficients for Adsorption of I$^-$ on Kaolinite, Illite, and Alumina

Kaolinite (10^{-5} *M* I$^-$)

0.01 *M* NaCl		0.05 *M* NaCl		0.1 *M* NaCl		0.50 *M* NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)	pH	D(ℓ/kg)	pH	D(ℓ/kg)
5.11	0.17	5.01	0.48	4.94	0.74	5.05	0.51
5.51	0	7.06	0.63	6.97	0.61	6.42	0.25
6.91	.6						
7.24	-0.24						
7.64	-0.18						
9.71	0.15						

Kaolinite (10^{-8} *M* I$^-$)

0.01 *M* NaCl	
pH	D(ℓ/kg)
5.52	1.140
6.30	1.09
7.52	0.47
9.59	.020

Illite (10^{-5} *M* I$^-$)

0.01 *M* NaCl		0.05 *M* NaCl		0.1 *M* NaCl		0.50 *M* NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)	pH	D(ℓ/kg)	pH	D(ℓ/kg)
4.45	-0.13	5.20	+0.40	5.00	-0.70	4.75	0.67
5.18	-0.16	5.60	-0.40	6.22	-0.25	6.50	0.01
5.44	-0.34						
5.57	+0.28						
5.69	+0.31						
5.69	-0.55						
6.04	+0.17						
6.13	-0.09						
6.18	-0.04						
6.18	+0.36						
6.60	-0.40						
6.83	-0.10						

TABLE 3
(Continued)

Alumina (10^{-5} M I^-)

0.01 M NaCl		0.05 M NaCl		0.10 M NaCl		0.50 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)	pH	D(ℓ/kg	pH	D(ℓ/kg)
5.38	12.2	5.52	3.55	6.15	2.02	6.52	1.07
5.92	9.25	6.27	3.31	6.52	1.82	6.52	0.71
6.40	4.08					6.76	-0.90
6.70	4.57					7.13	2.15
6.88	3.12						
7.19	1.22						
7.55	2.63						
9.61	0.80						

TABLE 3 (continued)

Distribution Coefficients for Adsorption of I^- on Montmorillonite and 12 Minerals

(In this table, Granula refers to 20-50 mesh and powder to <50 mesh.)

Montmorillonite (10^{-5} M I^-)

4.0 M NaCl

pH	D(ℓ/kg)
5.57	-0.097
6.18	0.181
6.74	-0.58
6.74	1.42
6.85	0.75
7.17	-0.10
7.84	0.40
8.58	0.24

Anhydrite (10^{-5} M I^-) (Granular)

0.01 M NaCl

pH	D(ℓ/kg)
8.49	0.074
8.58	-0.0076
8.75	-0.040
8.80	0.12
8.94	-0.031
9.28	0.017

0.20 M NaCl

pH	D(ℓ/kg)
8.36	-0.10
8.54	-0.13
8.95	-0.0077
8.97	-0.034
8.98	-0.020
9.54	0.099

Anhydrite (10^{-8}M I^-)(Granular)

0.01 M NaCl

pH	D(ℓ/kg)
8.29	0.027
8.49	0.0078
8.80	0.0017
8.80	0.048

Anhydrite (10^{-5} M I^-) (Powder)

0.01 M NaCl

pH	D(ℓ/kg)
7.89	0.16
7.95	0.0040
8.26	0.045
8.63	0.066
8.73	0.028
9.11	0.10

Anhydrite (10^{-8}M I^-)(Powder)

0.01 M NaCl

pH	D(ℓ/kg)
7.73	0.024
8.13	-0.055
8.65	0.063
9.08	0.027

TABLE 3 (continued)

Culebra Dolomite (10^{-5} M I^-) (Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
9.19	0.013	9.13	-0.0087
9.28	0.0062	9.20	-0.026
9.34	0.056	9.36	0.023
9.54	0.031	9.45	-0.011
9.56	-0.044	9.48	-0.046
9.68	0.13	9.61	0.098

Culebra Dolomite (10^{-8} M I^-) (Granular)

0.01 M NaCl

pH	D(ℓ/kg)
8.96	0.0027
9.17	-0.043
9.39	0.050
9.50	-0.053

Culebra Dolomite (10^{-5} M I^-) (Powder)

0.01 M NaCl

pH	D(ℓ/kg)
8.55	0.056
8.79	-0.023
9.21	-0.012
9.51	-0.11
9.52	-0.12
9.66	-0.015

Culebra Dolomite (10^{-8} M I^-) (Powder)

0.01 M NaCl

pH	D(ℓ/kg)
8.52	0.023
8.95	-0.059
9.52	-0.083
9.64	-0.070

Magenta Dolomite (10^{-5} M I^-) (Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
7.86	0.0042	7.82	0.012
7.91	0.047	7.89	0.032
7.93	-0.0068	7.93	-0.0069
8.20	0.11	8.27	0.019
8.21	-0.046	8.30	0.036
8.28	0.050	8.35	0

Magenta Dolomite (10^{-8} M I^-) (Granular)

0.01 M NaCl

pH	D(ℓ/kg)
7.98	0.022
7.98	0.027
8.14	0.0021
8.37	0.044

TABLE 3 (continued)

Magenta Dolomite (10^{-5} M I^-)(Powder)

0.01 M NaCl	
pH	D(ℓ/kg)
7.71	0.10
7.82	0.056
7.89	0.055
8.12	0.0048
8.22	0.019
8.53	0.12

Magenta Dolomite (10^{-8} M I^-)(Powder)

0.01 M NaCl	
pH	D(ℓ/kg)
7.69	-0.022
7.86	-0.023
8.14	0.010
8.71	0.060

Conasauga Shale (10^{-5} M I^-) (Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
7.94	0.0053	7.91	-0.057
8.04	-0.073	7.92	-0.059
8.04	-0.089	8.02	-0.075
8.06	-0.0065	8.09	-0.012
8.16	-0.0087	8.10	0.0083
8.19	-0.10	8.11	-0.040

Conasauga Shale (10^{-8} M I^-)(Granular)

0.01 M NaCl	
pH	D(ℓ/kg)
8.00	-0.022
8.07	-0.016
8.20	-0.015
8.21	0.0060

Conasauga Shale (10^{-5} M I^-) (Powder)

0.01 M NaCl	
pH	D(ℓ/kg)
8.06	0.36
8.25	0.048
8.40	0.074
8.54	0.27

Conasauga Shale (10^{-8} M I^-)(Powder)

0.01 M NaCl	
pH	D(ℓ/kg)
8.04	0.53
8.22	0.31
8.50	0.31
8.61	0.29

TABLE 3 (continued)

Westerly Granite (10^{-5} M I^-)(Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
8.26	-0.030	8.57	-0.048
8.34	-0.032	8.86	-0.040
8.50	-0.10	8.99	-0.061
9.02	-0.077	9.12	-0.022
9.03	-0.089	9.18	-0.067
9.35	0.0063	9.32	-0.0075

Westerly Granite (10^{-8} M I^-)(Granular)

0.01 M NaCl	
pH	D(ℓ/kg)
8.35	-0.074
8.69	0.031
9.00	-0.040
9.34	-0.058

Sentinel Gap Basalt (10^{-5} M I^-) (Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
7.35	-0.040	7.08	-0.013
7.37	-0.037	7.18	-0.034
7.47	-0.024	7.20	-0.013
7.49	-0.021	7.28	-0.033
7.70	-0.018	7.32	-0.011
8.54	-0.053	8.09	-0.010

Sentinel Gap Basalt (10^{-8} M I^-)(Granular)

0.01 M NaCl	
pH	D(ℓ/kg)
7.44	-0.051
7.50	-0.013
7.68	0.0050
8.41	0.0020

Oolitic Limestone (10^{-5} M I^-) (Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
7.88	0.010	8.06	-0.0064
7.94	0.012	8.20	0.036
8.11	-0.020	8.31	0
8.43	0	8.70	-0.017
8.48	-0.027	8.70	-0.025
8.54	0.0076	8.85	-0.036

Oolitic Limestone (10^{-8} M I^-)(Granular)

0.01 M NaCl	
pH	D(ℓ/kg)
8.02	-0.035
8.24	0.073
8.42	-0.039
8.55	0.010

TABLE 3 (continued)

Green Argillaceous Shale (10^{-5} M I^-) (Granular)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
8.31	-0.030	8.18	-0.075
8.38	-0.056	8.24	-0.020
8.45	-0.083	8.31	-0.039
8.60	-0.11	8.39	-0.047
8.60	-0.077	8.40	-0.014
8.66	-0.066	8.43	-0.0075

Green Argillaceous Shale (10^{-8} M I^-) (Granular)

0.01 M NaCl	
pH	D(ℓ/kg)
8.34	-0.072
8.45	-0.010
8.63	-0.059
8.64	-0.058

Serpentine (10^{-5} M I^-) (230-325 mesh)

0.01 M NaCl (Except as shown in parentheses)		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
7.49	1.32 (.019)	7.51	0.39
7.78	1.06 (.014)	7.82	0.26
8.04	1.07 (.012)	8.31	0.43
8.40	1.29	8.55	0.30
8.55	1.06	8.74	0.20
8.88	1.06	8.98	0.41
8.93	1.03	9.03	0.16
8.99	0.72	9.05	0.069
9.19	0.82	9.19	0.25

Serpentine (10^{-8} M I^-)(230-325 mesh)

0.01 M NaCl (Except as shown in parentheses)	
pH	D(ℓ/kg)
7.66	2.43 (.019)
8.12	2.19 (.013)
8.44	2.31
8.92	1.88
8.98	1.48
9.15	1.43

Augite (10^{-5} M I^-) (230-325 mesh)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
8.22	-0.14	8.39	-0.11
8.54	-0.042	8.67	-0.20
8.83	-0.25	9.03	-0.11
9.14	-0.055	9.30	-0.12
9.19	-0.12	9.32	-0.20
9.32	-0.082	9.42	-0.052

Augite (10^{-8} M I^-)(230-325 mesh)

0.01 M NaCl	
pH	D(ℓ/kg)
8.41	-0.079
8.88	0.0056
9.19	-0.18
9.33	-0.026

TABLE 3 (continued)

Hornblende (10^{-5} M I^-)(230-325 mesh)

0.01 M NaCl		0.20 M NaCl	
pH	D(ℓ/kg)	pH	D(ℓ/kg)
8.06	0.077	8.23	0.014
8.25	-0.13	8.52	-0.069
8.63	-0.19	9.05	0.047
9.22	0.027	9.36	-0.11
9.26	-0.12	9.38	-0.18
9.51	-0.15	9.61	-0.078

Hornblende (10^{-8} M I^-)(230-325 mesh)

0.01 M NaCl	
pH	D(ℓ/kg)
8.16	0.042
8.68	-0.10
9.21	-0.12
9.47	-0.052

Galena (10^{-5} M I^-) (230-325 mesh)

0.01 M NaCl	
pH	D(ℓ/kg)
5.56	11.97
6.30	6.72
6.30	5.40
6.49	7.04
6.58	6.22
7.60	1.35

Galena (10^{-8} M I^-)(230-325 mesh)

0.01 M NaCl	
pH	D(ℓ/kg)
5.59	12.97
6.54	7.28
6.61	6.11
7.80	1.36

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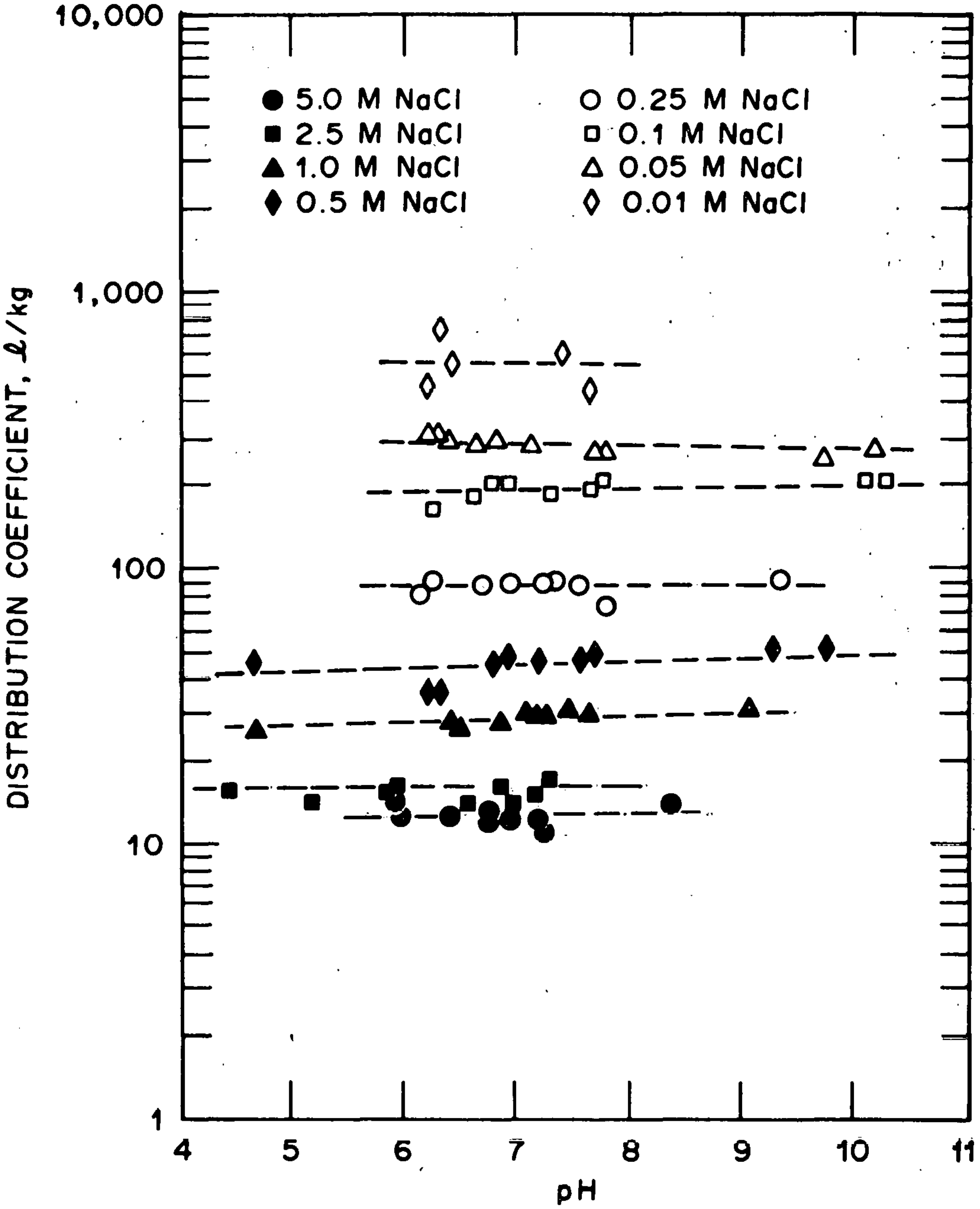
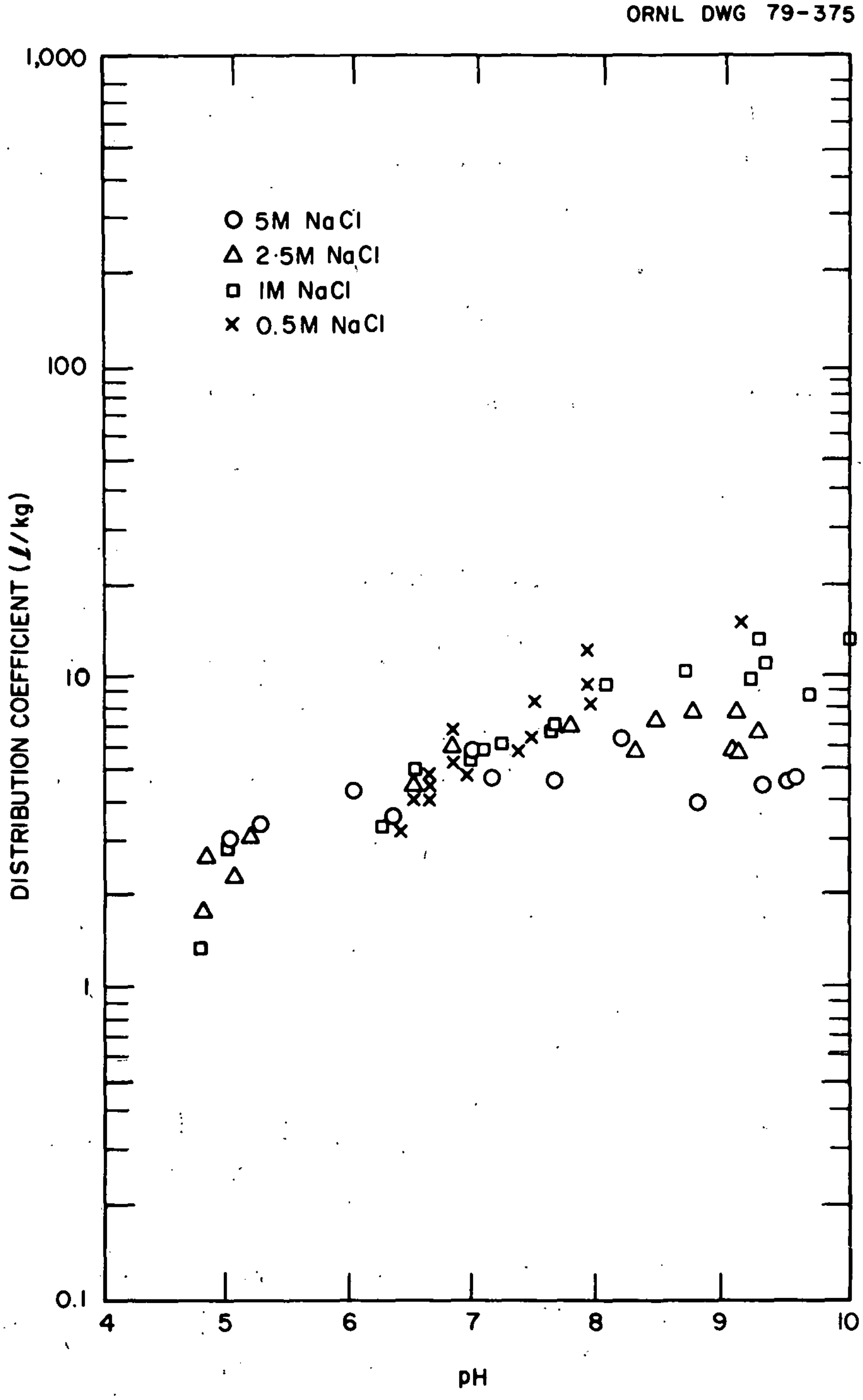


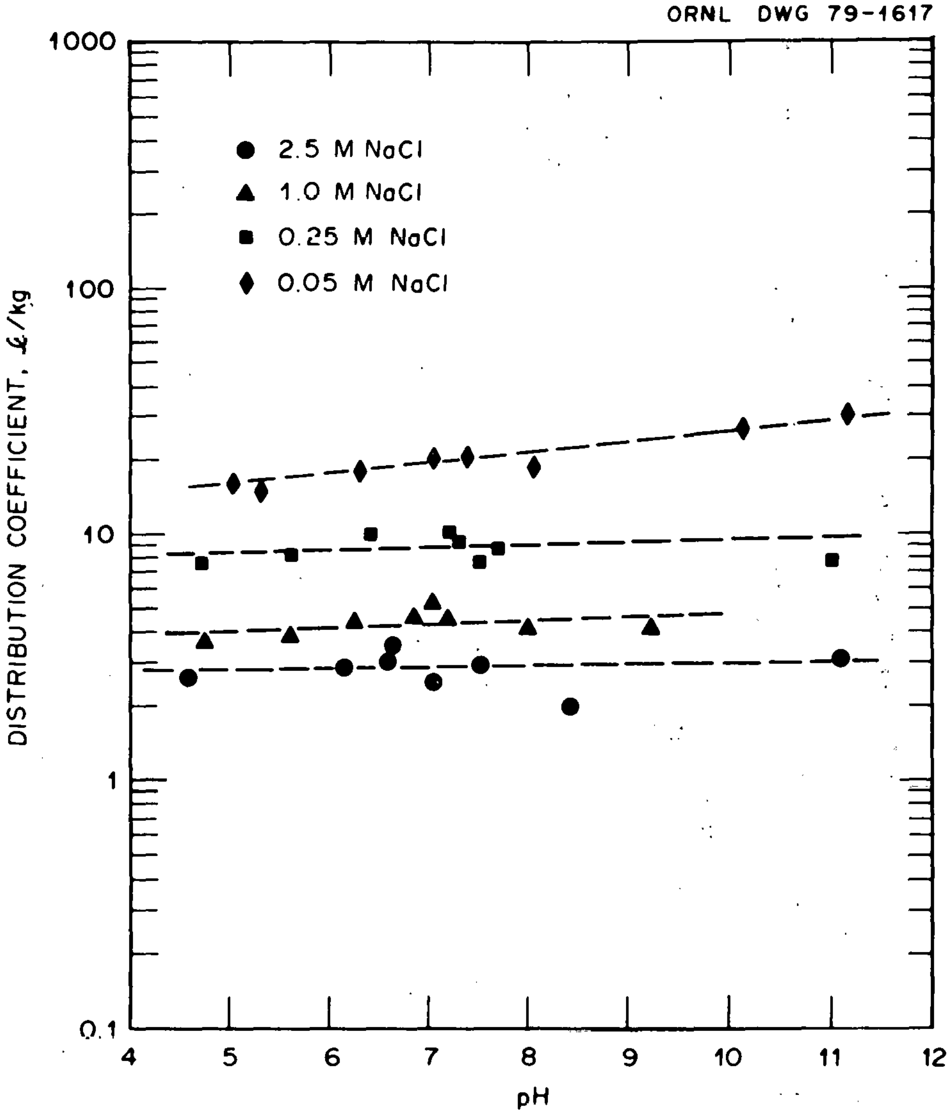
ADSORPTION OF Cs(I) ON THE SODIUM FORM OF PURIFIED WYOMING MONTMORILLONITE (trace loading, equilibration for 720 hrs)

Figure 1

Figure 2

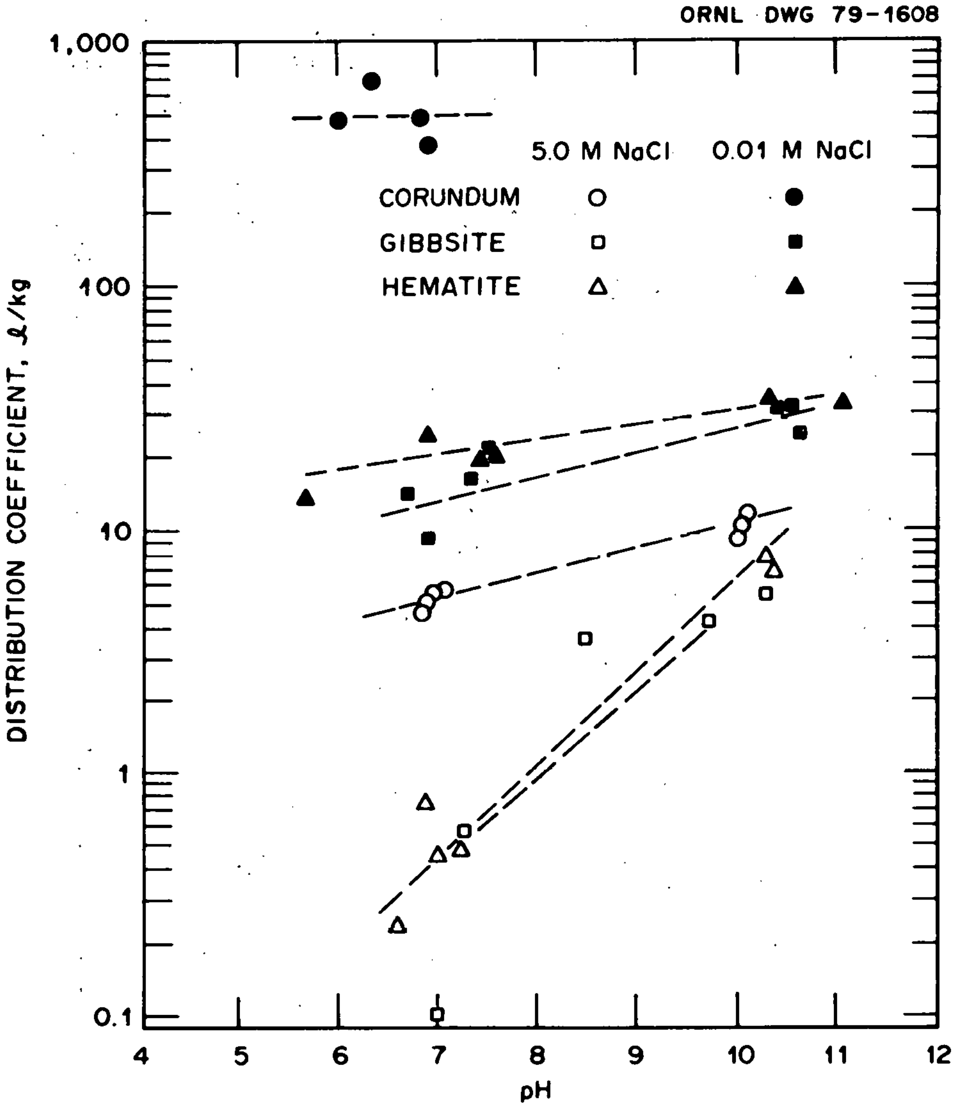


ADSORPTION OF Cs(I) ON THE Na FORM OF Al_2O_3 (TRACE Cs (I), EQUILIBRATION FOR 240 hrs.)



ADSORPTION OF Cs(I) ON THE SODIUM FORM OF CORUNDUM (loading: 7 x 10^{-7} – 7.6 x 10^{-7} mole Cs(I)/kg, equilibration for 187 hrs)

Figure 3

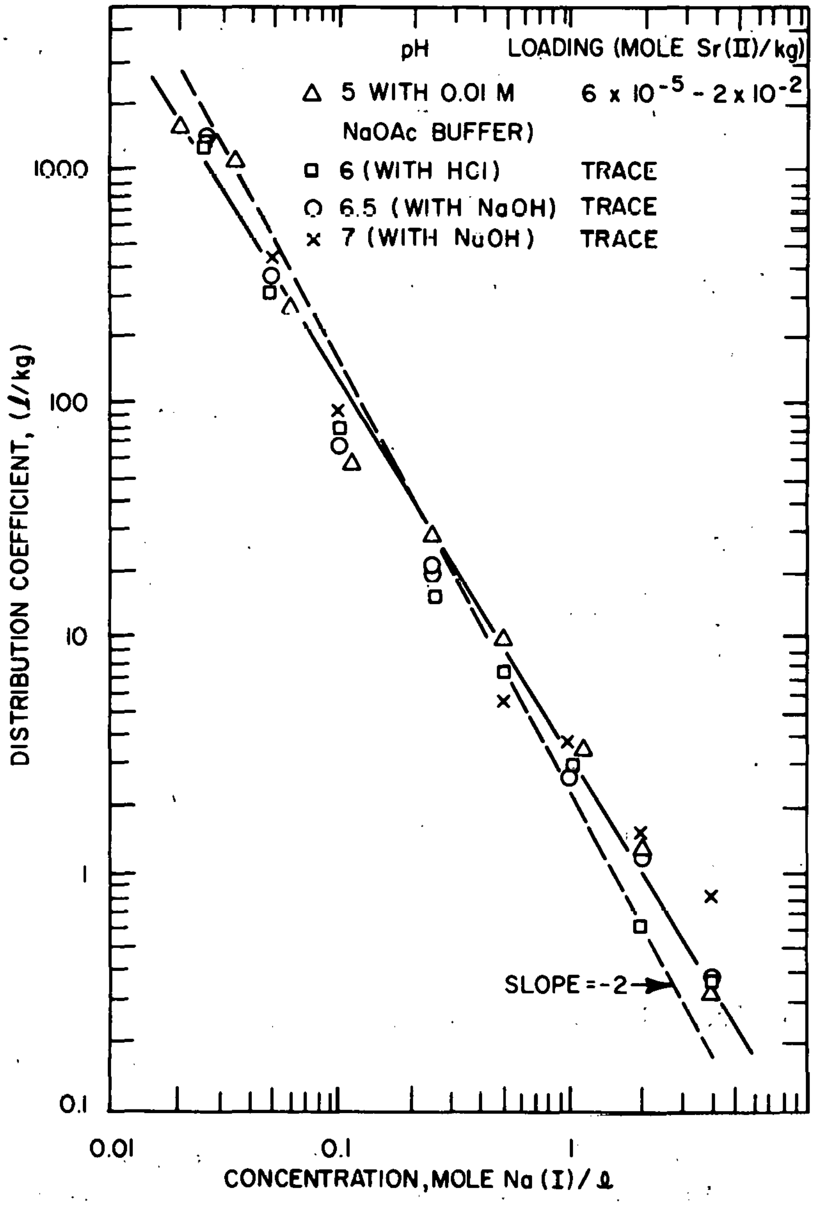


ADSORPTION OF Cs(I) ON THE SODIUM FORM OF NATURAL OXIDES (trace loading, equilibration for 348 hrs)

Figure 4

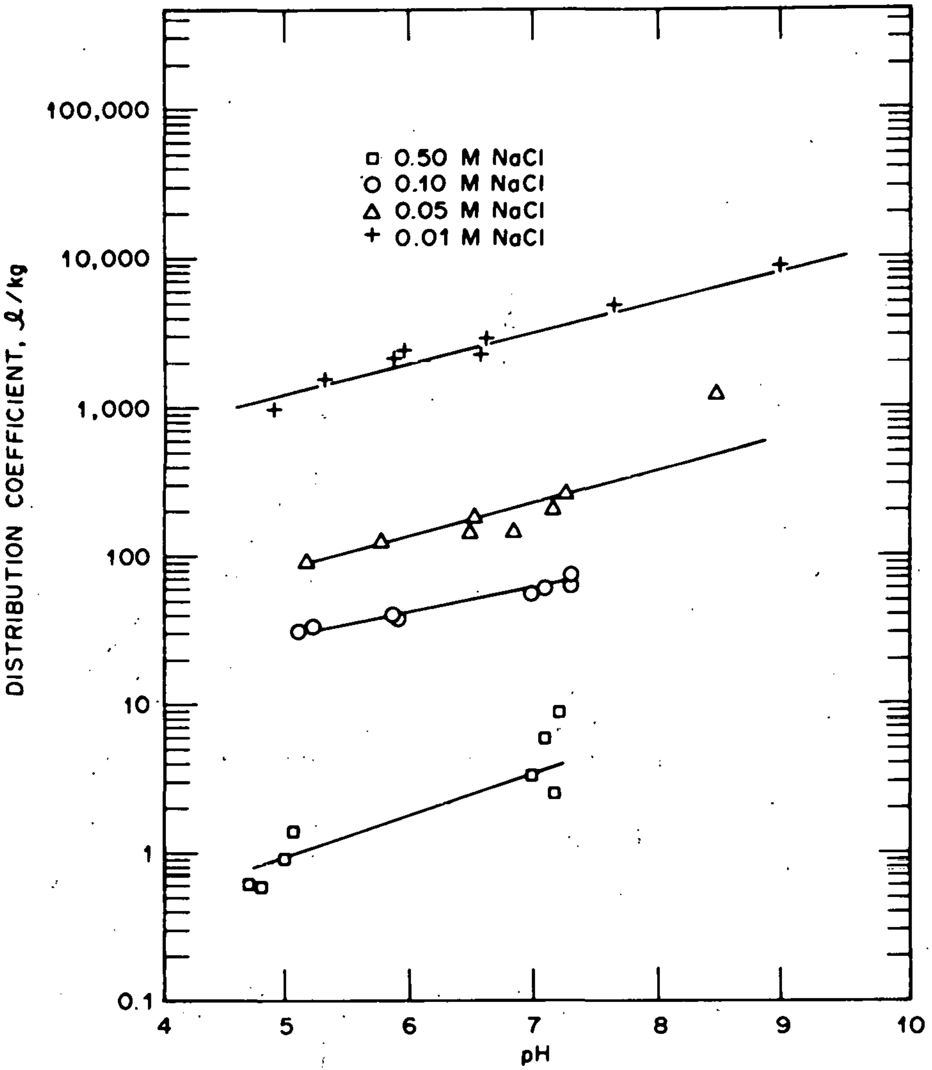
Figure 5

ORNL DWG 79-379



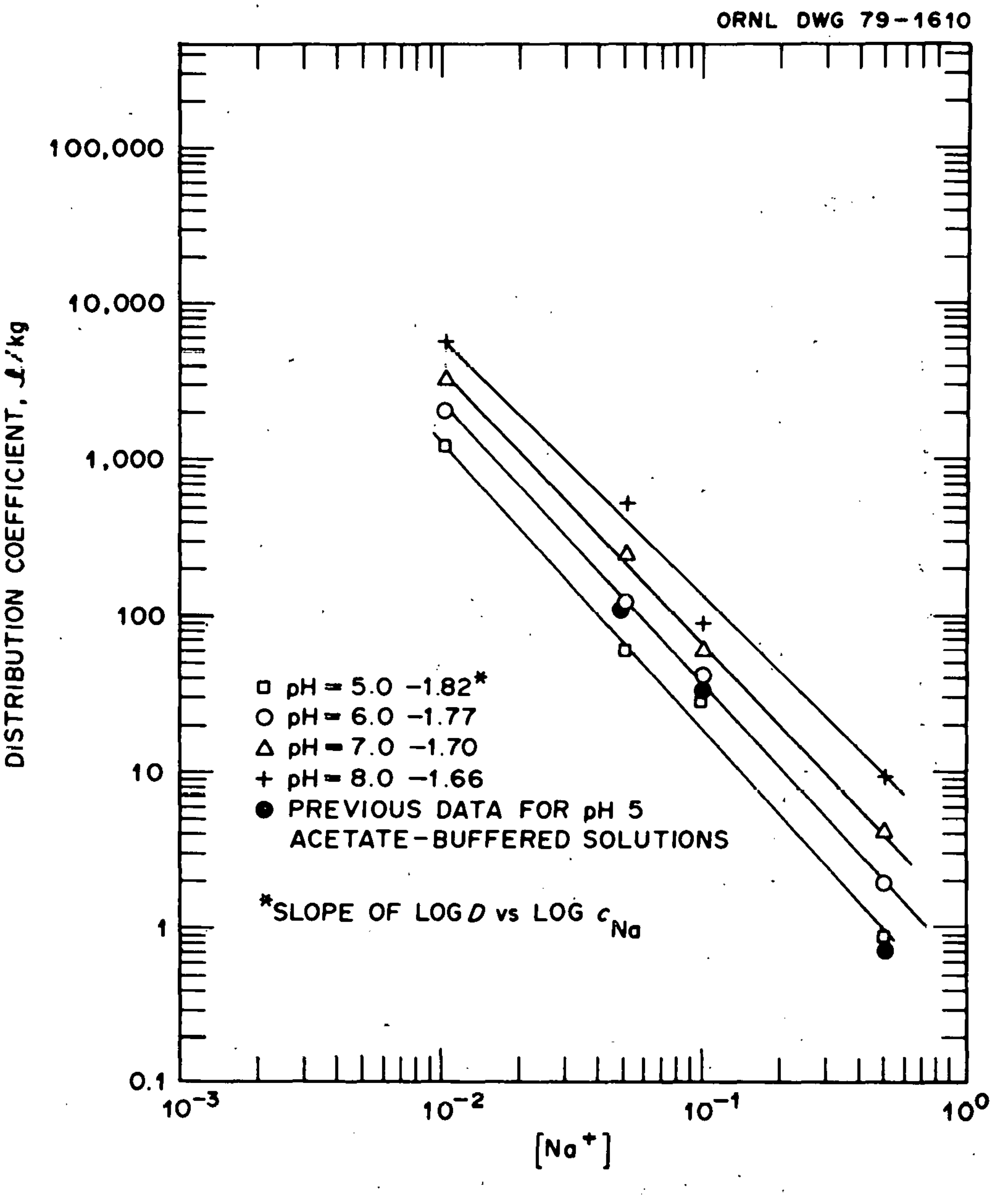
ADSORPTION OF Sr(II) ON THE SODIUM FORM OF PURIFIED WYOMING MONTMORILLONITE (NaCl + 0.01 M NaOAc OR NaCl + HCl OR NaCl + NaOH, SAMPLES WERE PREEQUILIBRATED, EQUILIBRATION FOR 48 hrs)

ORNL DWG 79-1609



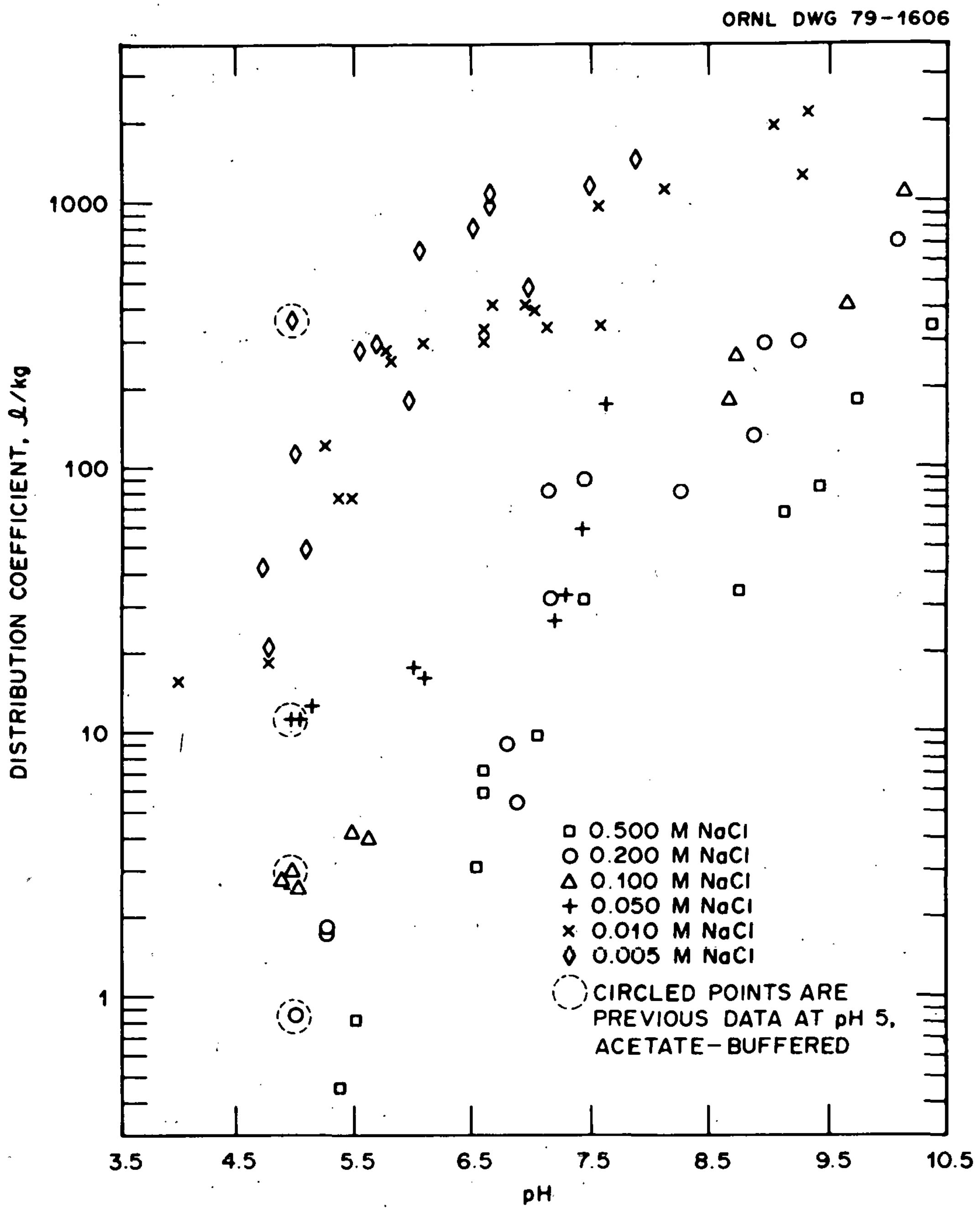
ADSORPTION OF Sr(II) ON THE SODIUM FORM OF ILLITE (trace loading, equilibration for 72 hrs)

Figure 6



ADSORPTION OF Sr(II) ON THE SODIUM FORM OF ILLITE (trace loading, equilibration for 72 hrs)

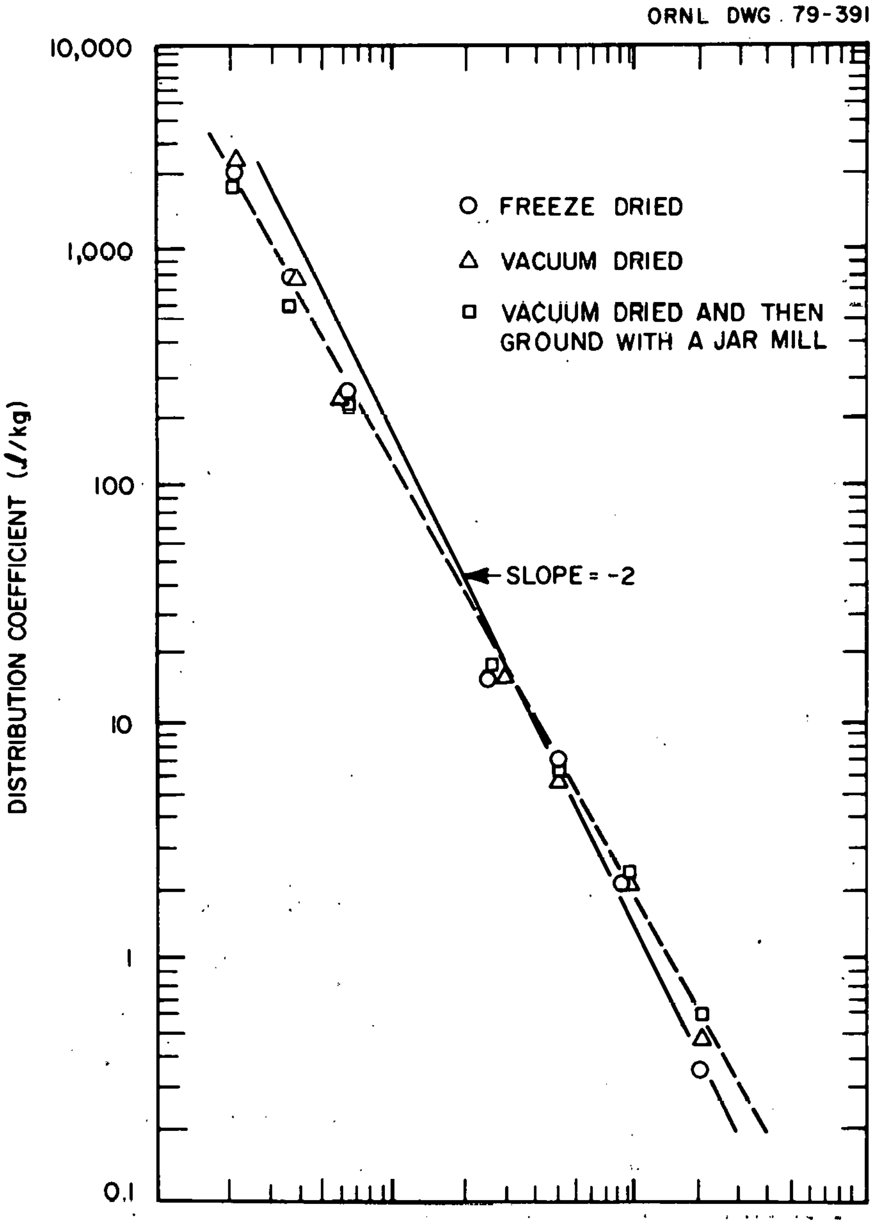
Figure 7



ADSORPTION OF Sr(II) ON THE SODIUM FORM OF KAOLINITE
(trace loading, equilibration for 72 hrs)

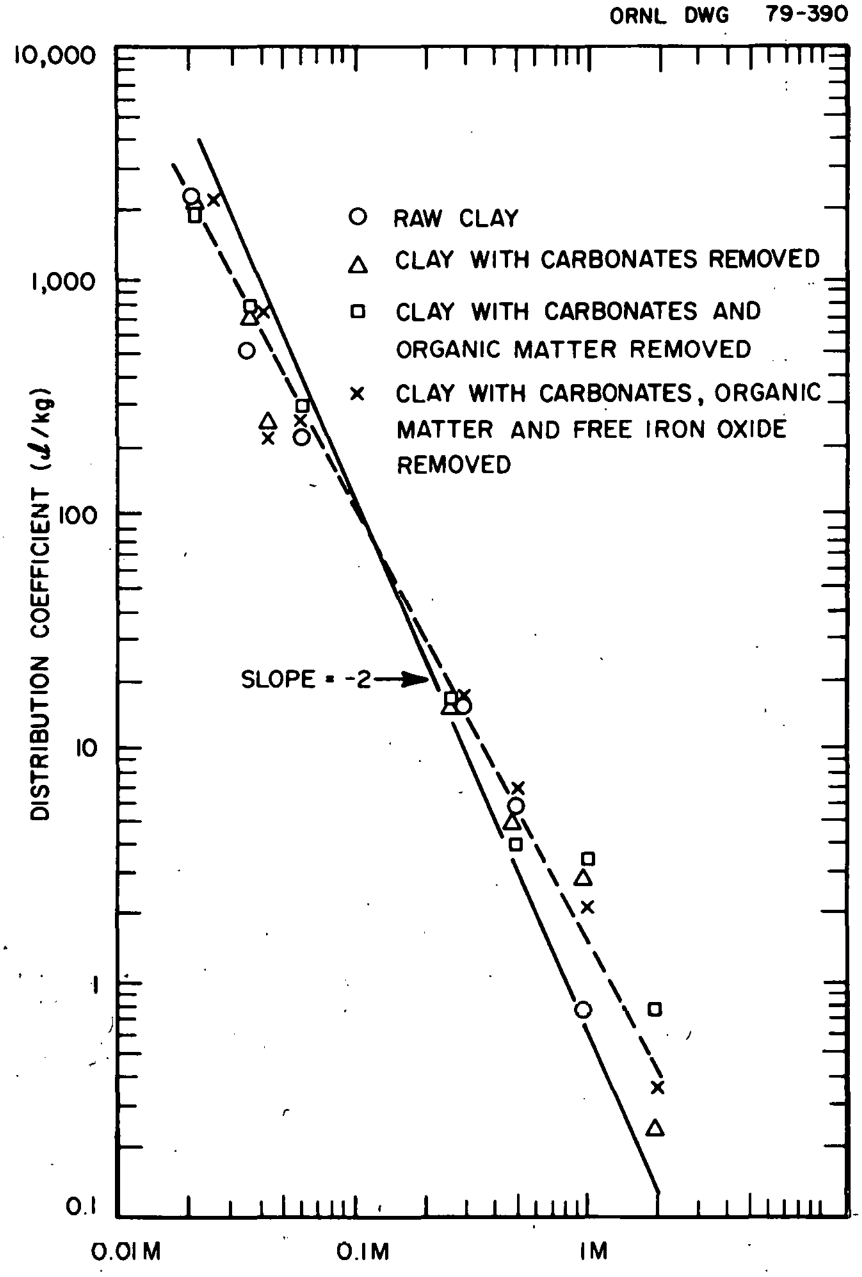
Figure 8

Figure 9

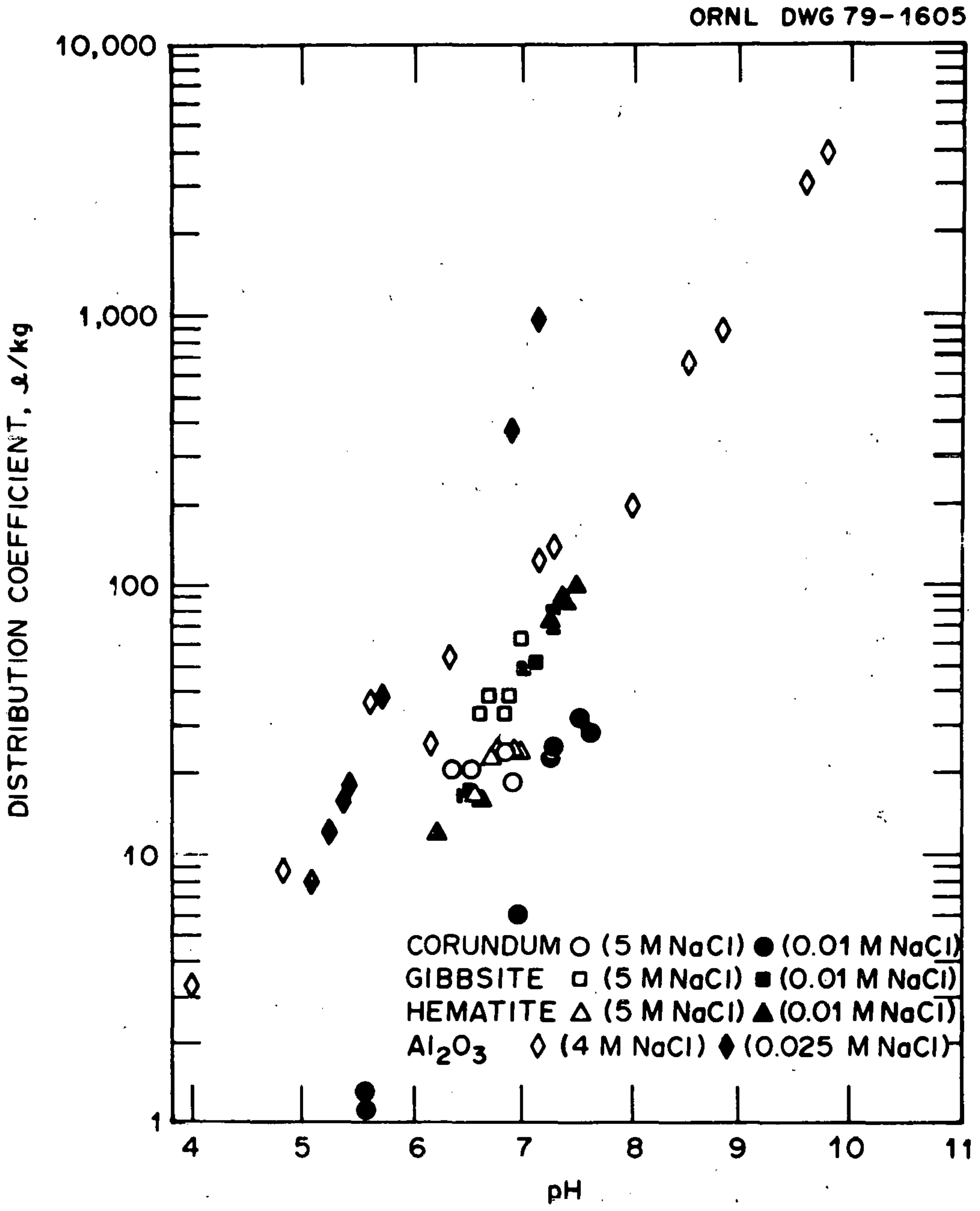


ADSORPTION OF Sr(II) ON Na FORM OF PURIFIED WYOMING MONTMORILLONITE FROM VARIOUS DRYING TECHNIQUES (TRACE Sr(II) LOADING, NaCl + 0.01 M NaOAc, pH 5, EQUILIBRATION FOR 117 hrs)

Figure 10



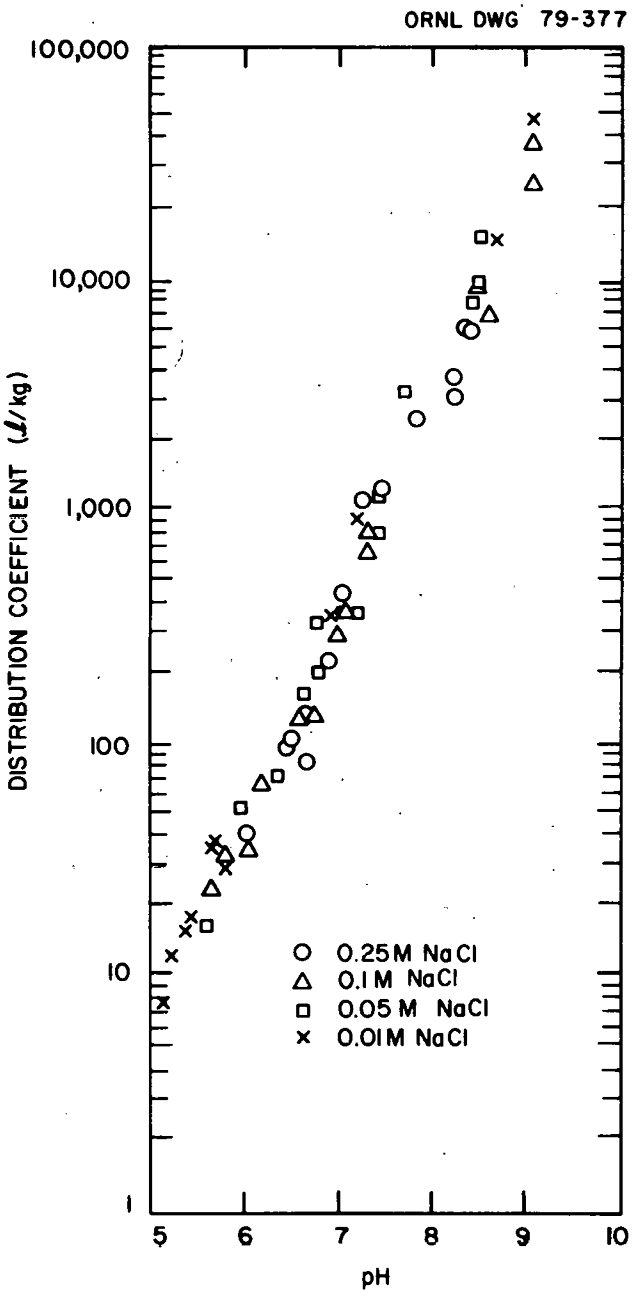
ADSORPTION OF Sr (II) ON Na FORM OF WYOMING MONTMONILLONITE OF DIFFERENT STAGES OF PURIFICATION (TRACE Sr (II) LOADING, NaCl + 0.01 M NaOAc, pH 5, EQUILIBRTION FOR 117 hrs)



ADSORPTION OF SR(II) ON THE SODIUM FORM OF NATURAL OXIDES AND Al_2O_3 (trace loading, equilibration for more than 7 days)

Figure 11

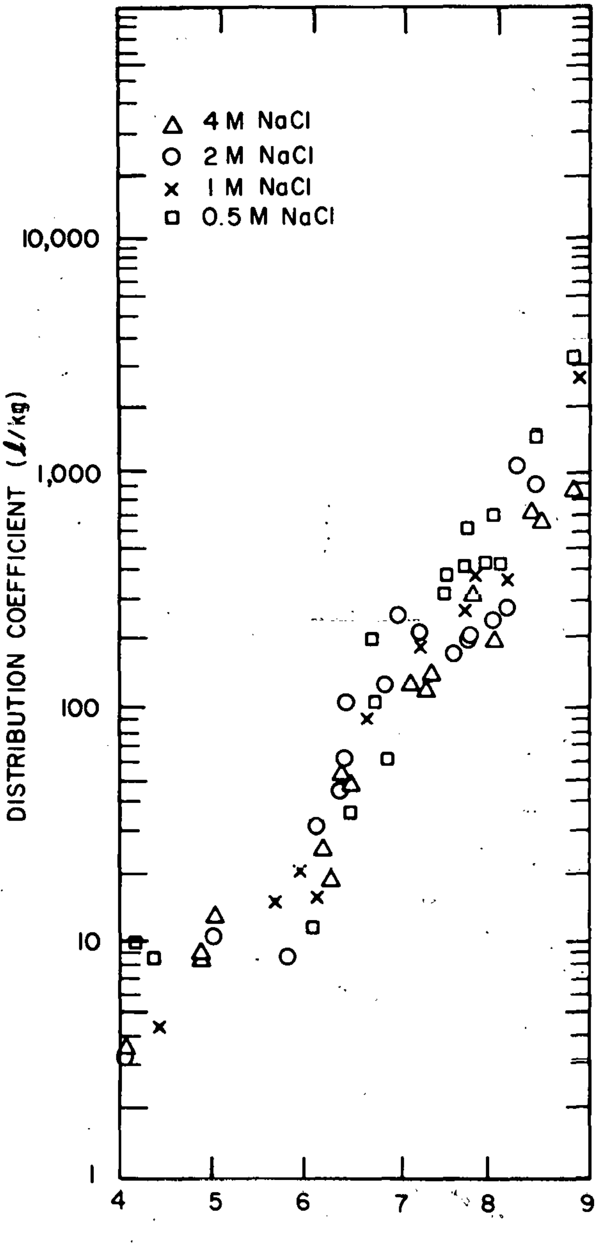
Figure 12



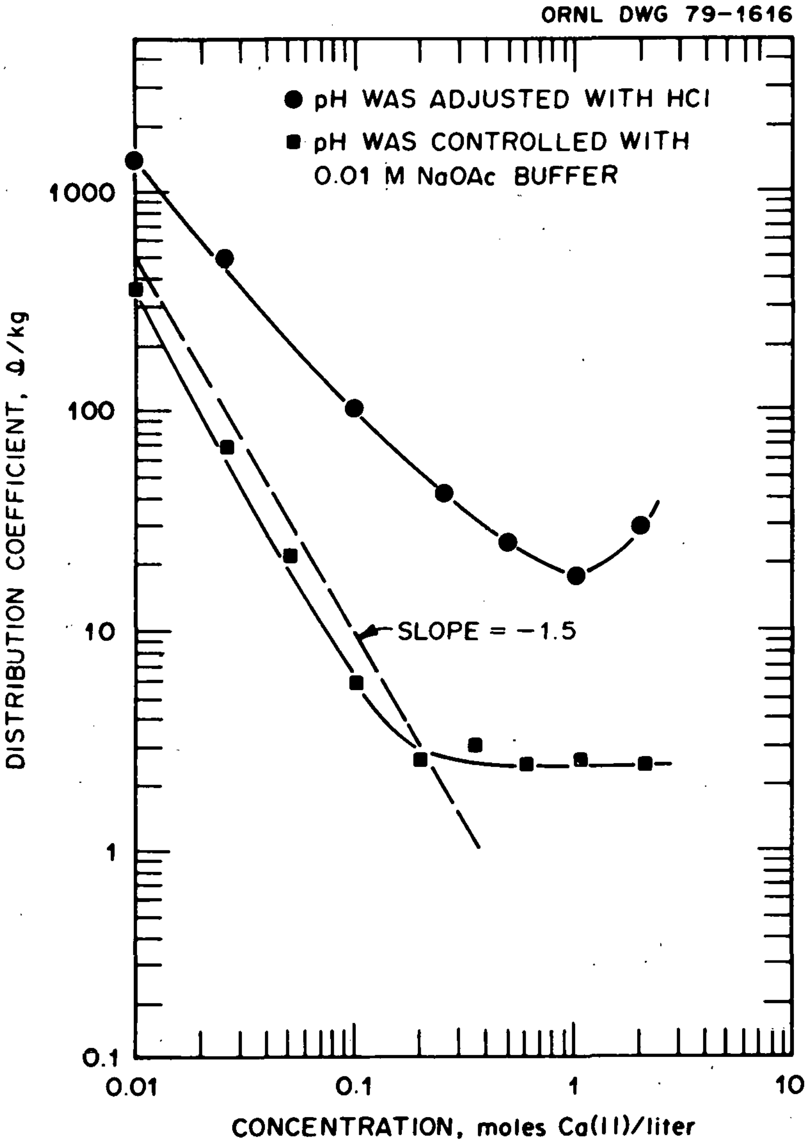
ADSORPTION OF Sr (II) ON THE Na FORM OF Al_2O_3
(TRACE Sr (II), EQUILIBRATION FOR 168 hrs)

Figure 13

ORNL DWG 79-378

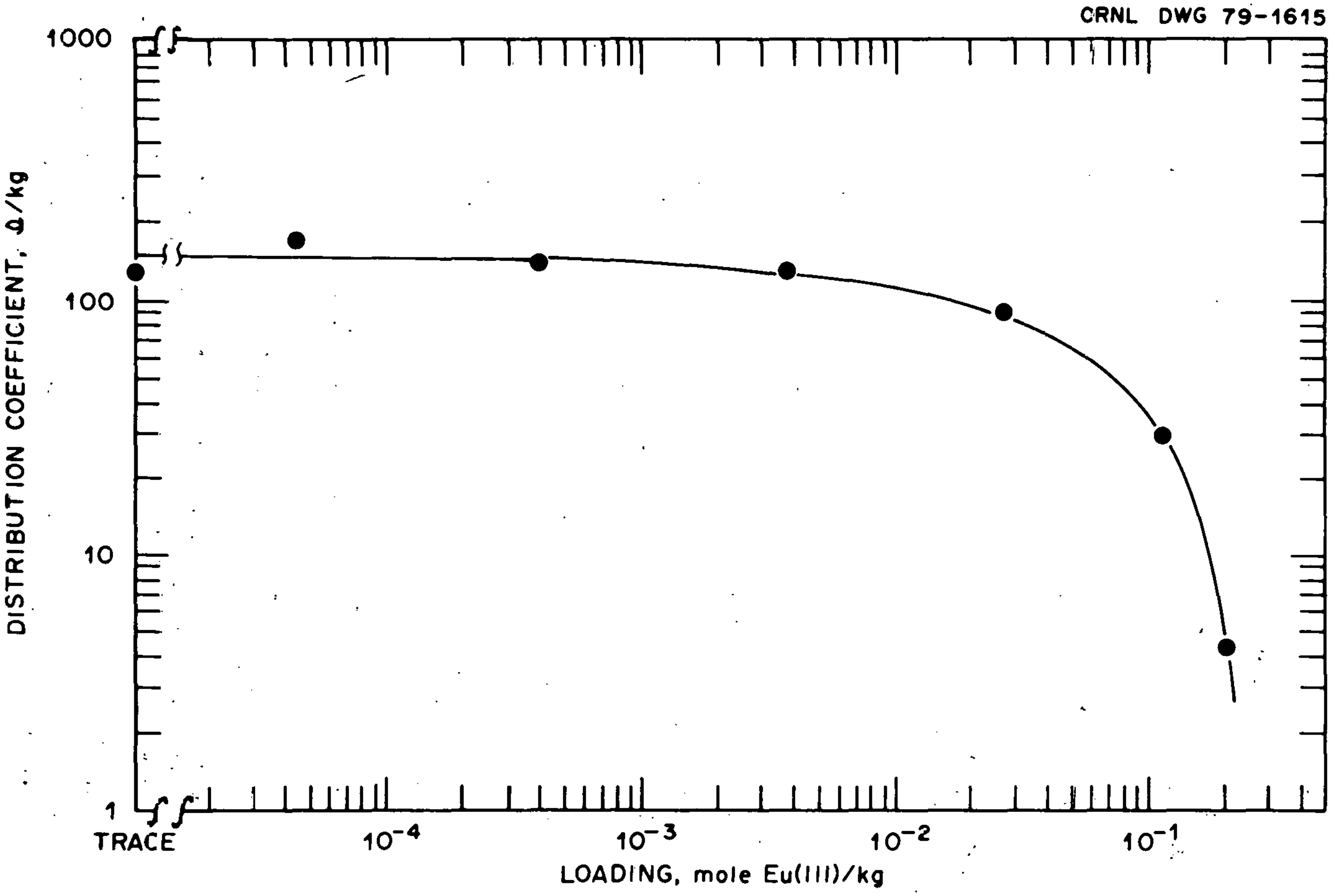


ADSORPTION OF Sr (II) ON THE Na FORM OF Al_2O_3 (TRACE Sr(II), EQUILIBRATION FOR OVER 62 hrs)



ADSORPTION OF Eu(III) ON THE CALCIUM FORM OF PURIFIED WYOMING MONTMORILLONITE ($CaCl_2$ + 0.01 M $Ca(OAC)_2$, loading 3×10^{-3} to 4×10^{-2} moles Eu(III)/kg, or $CaCl_2$ + HCl, pH 5, trace loading, samples were preequilibrated, equilibration for more than 76 hours)

Figure 14



EFFECT OF LOADING ON DISTRIBUTION COEFFICIENTS OF Eu(III) ON THE CALCIUM FORM OF PURIFIED MONTMORILLONITE (0.05 M $CaCl_2$ + HCl, pH 5, samples were preequilibrated, equilibration for 24 hrs)

Figure 15

Figure 16

Eu/Na exch.on montm.—0.1 M Na

Equilibration for 7 days

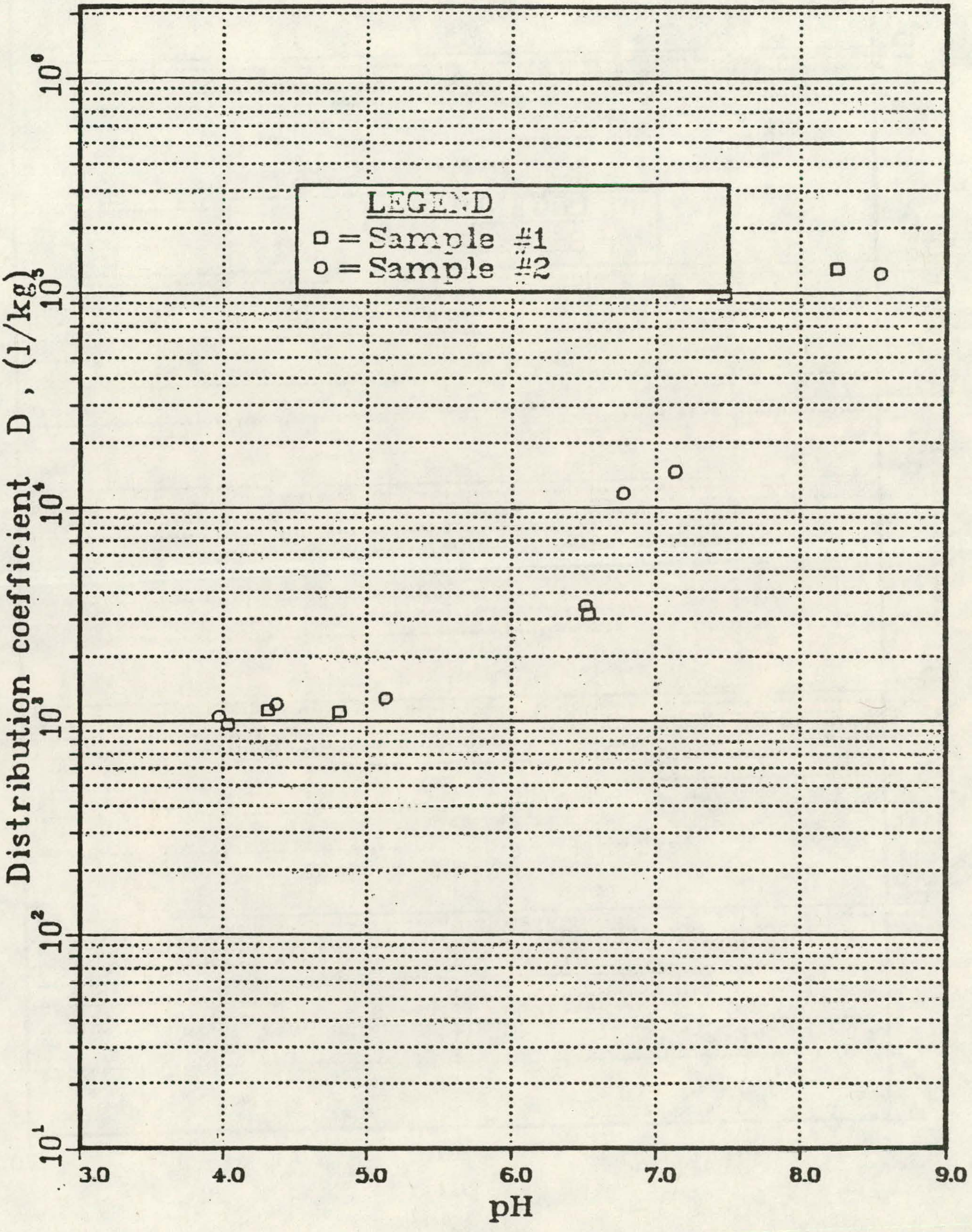


Figure 17

Eu/Na exch.on montm.–0.5 M Na

Equilibration for 7 days

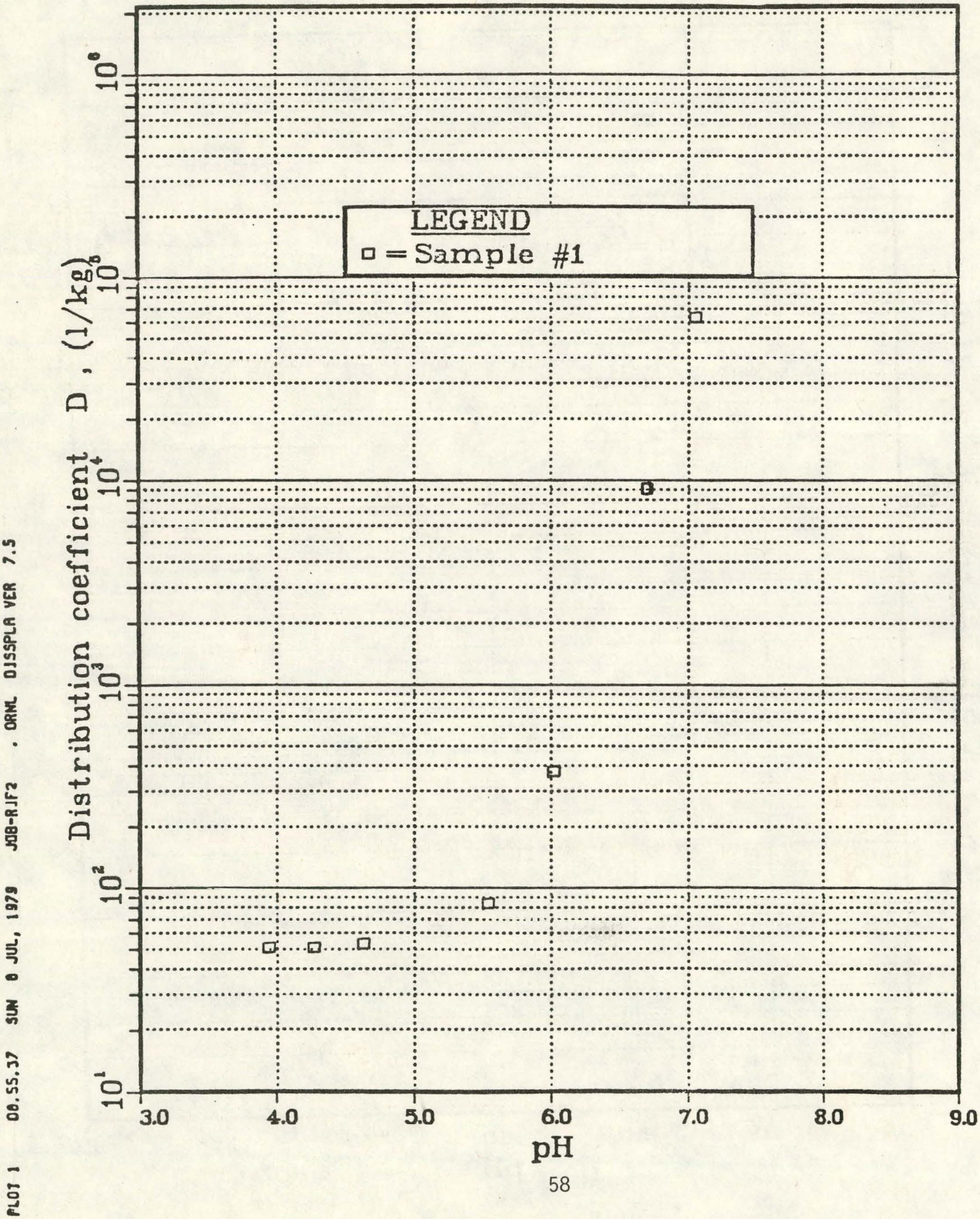


Figure 18

Eu/Na exch.on montm.–4.0 M Na

Equilibration for 7 days

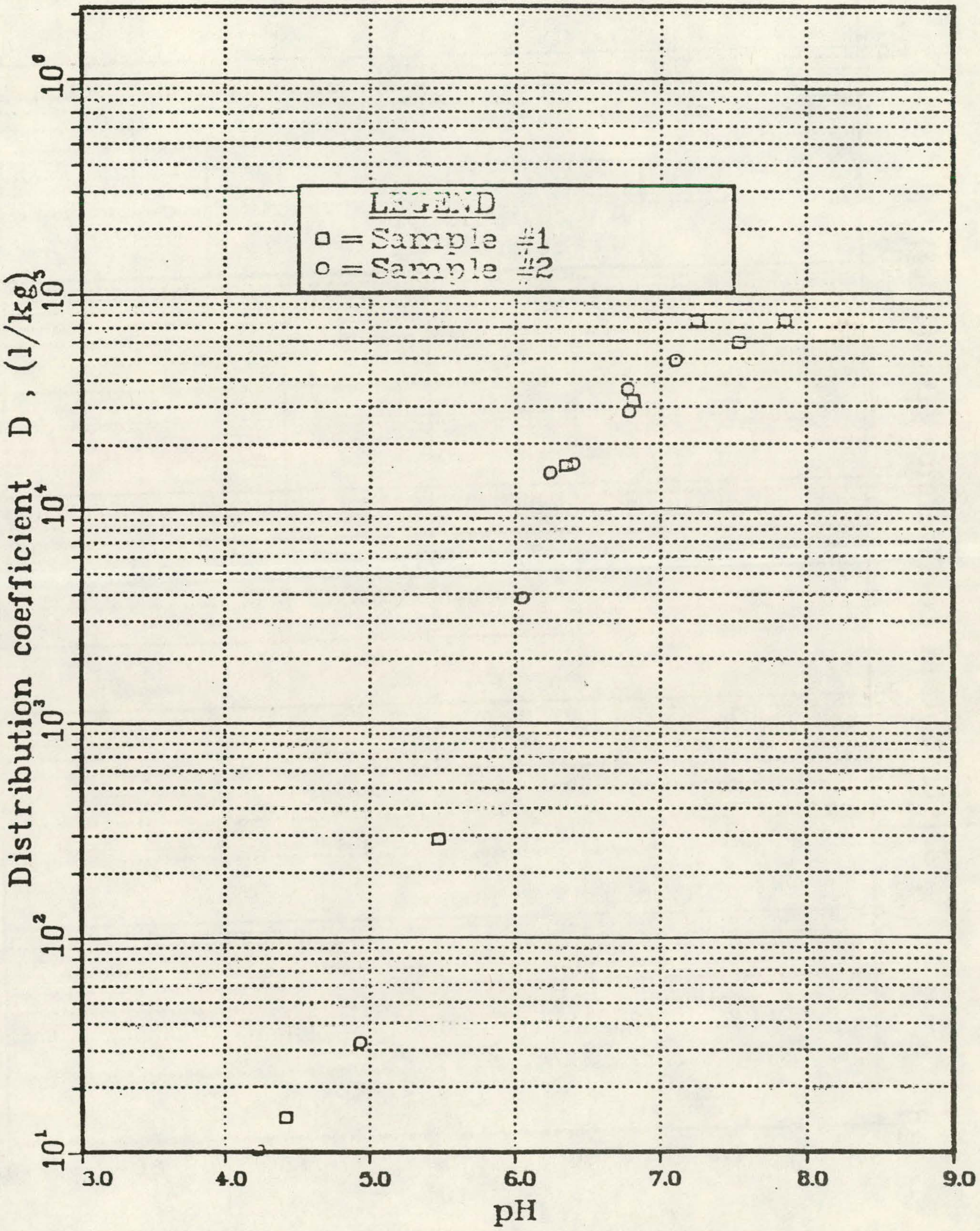


Figure 19

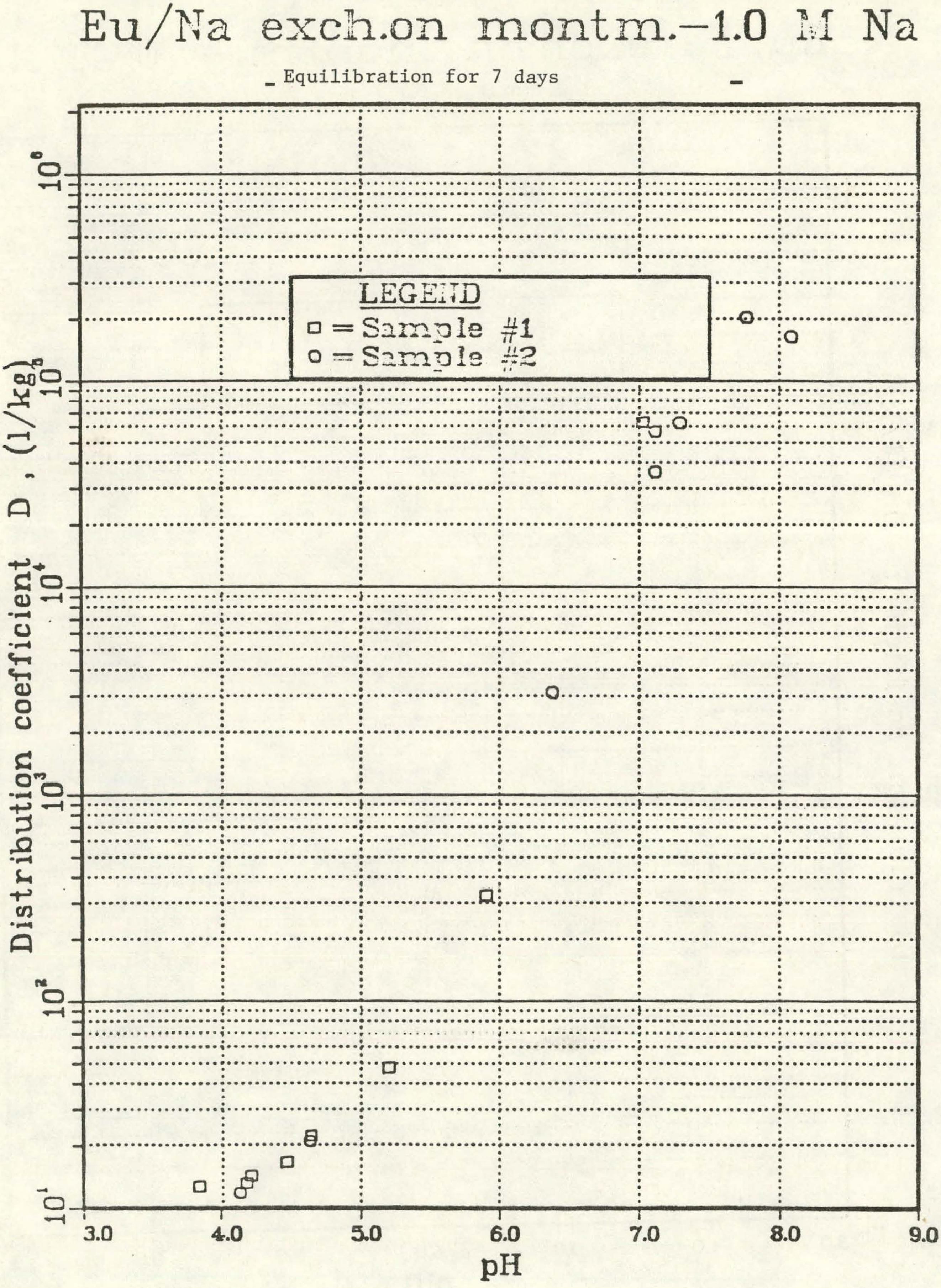
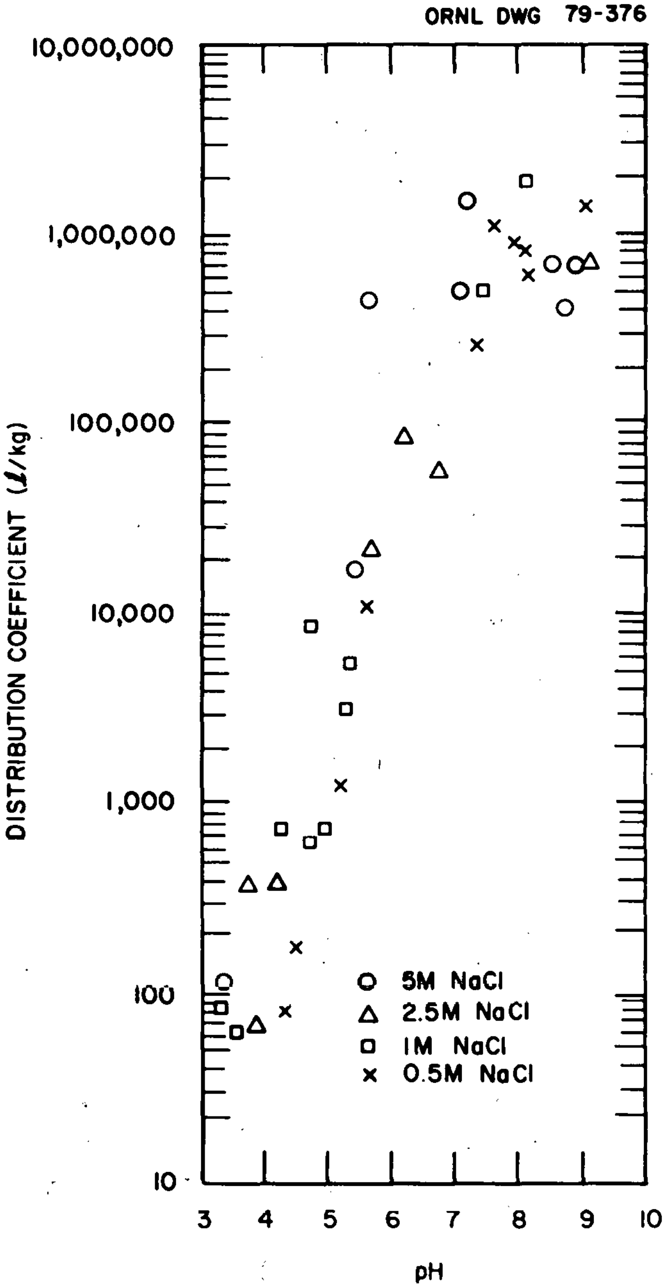
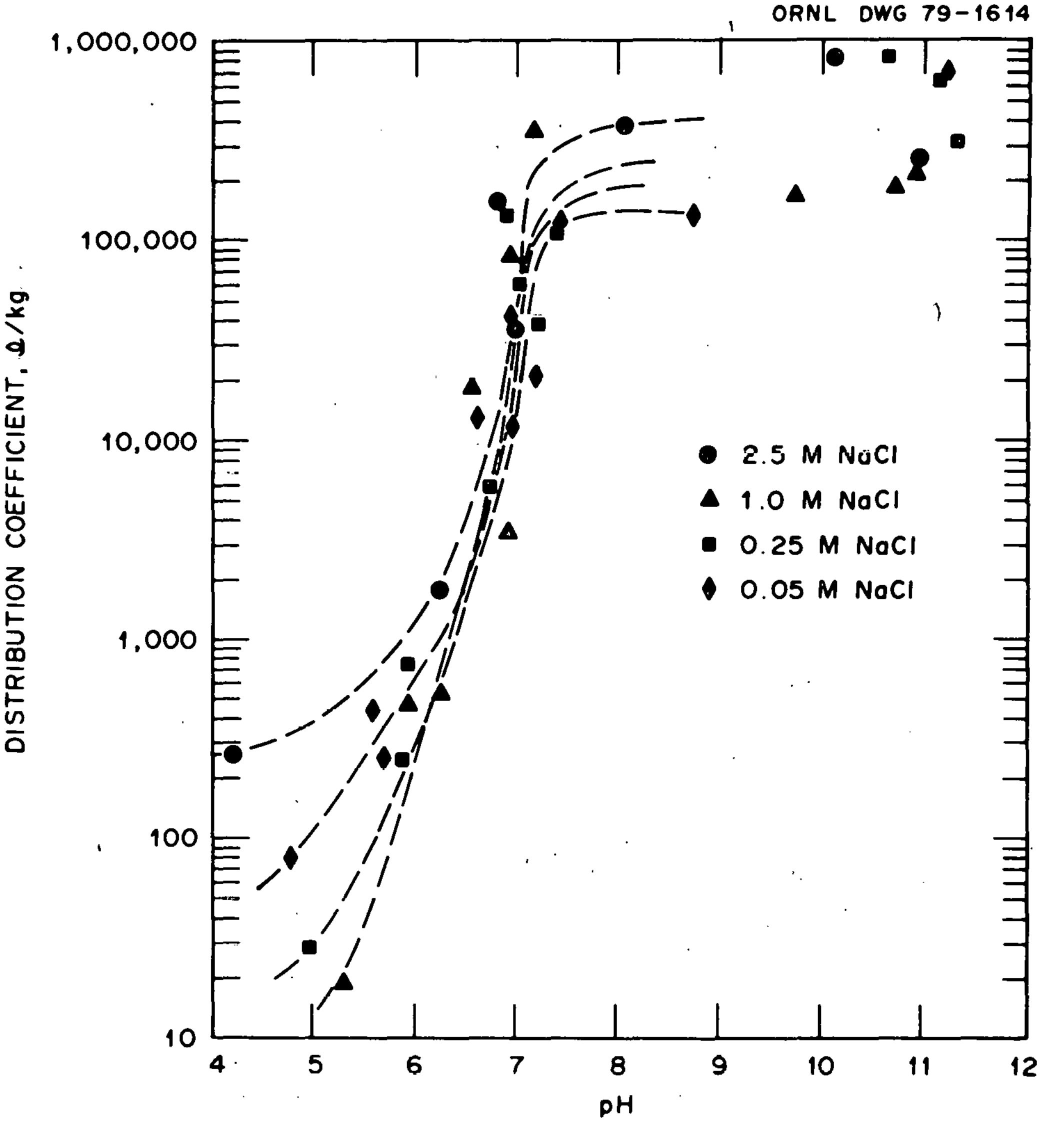

Eu/Na exch.on montm.–1.0 M Na
Equilibration for 7 days
LEGEND
□ = Sample #1
○ = Sample #2
Distribution coefficient D, (l/kg)
10^1
10^2
10^3
10^4
10^5
10^6
3.0
4.0
5.0
6.0
7.0
8.0
9.0
pH
LOT 1 08.56.50 3.JM 8 JUL, 1979 JOB-RIF3 . ORNL DISSPLA VER 7.5

Figure 20

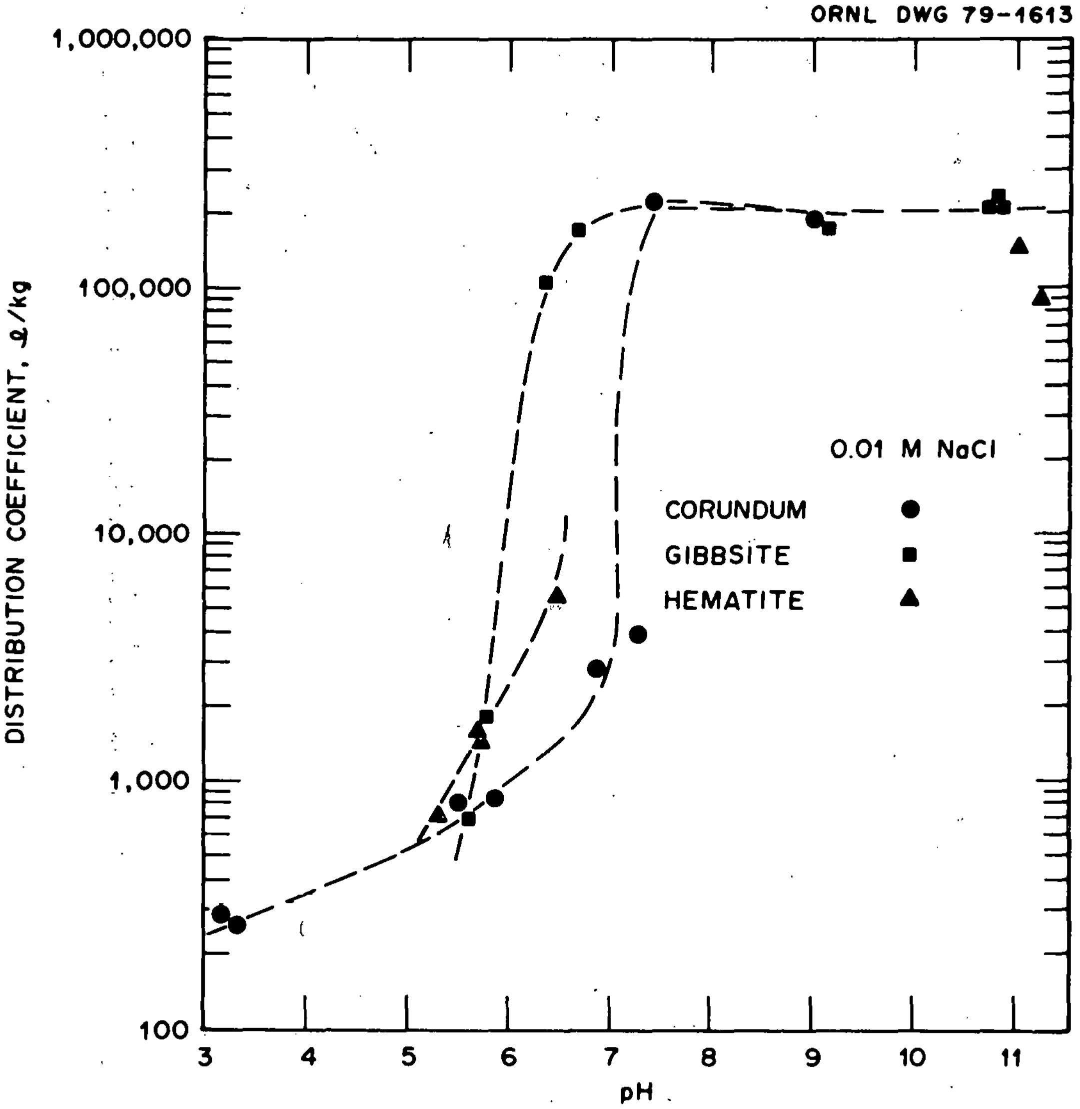


ADSORPTION OF Eu(III) ON THE Na FORM OF Al_2O_3 (TRACE Eu(III), EQUILIBRATION FOR 160 hrs.)



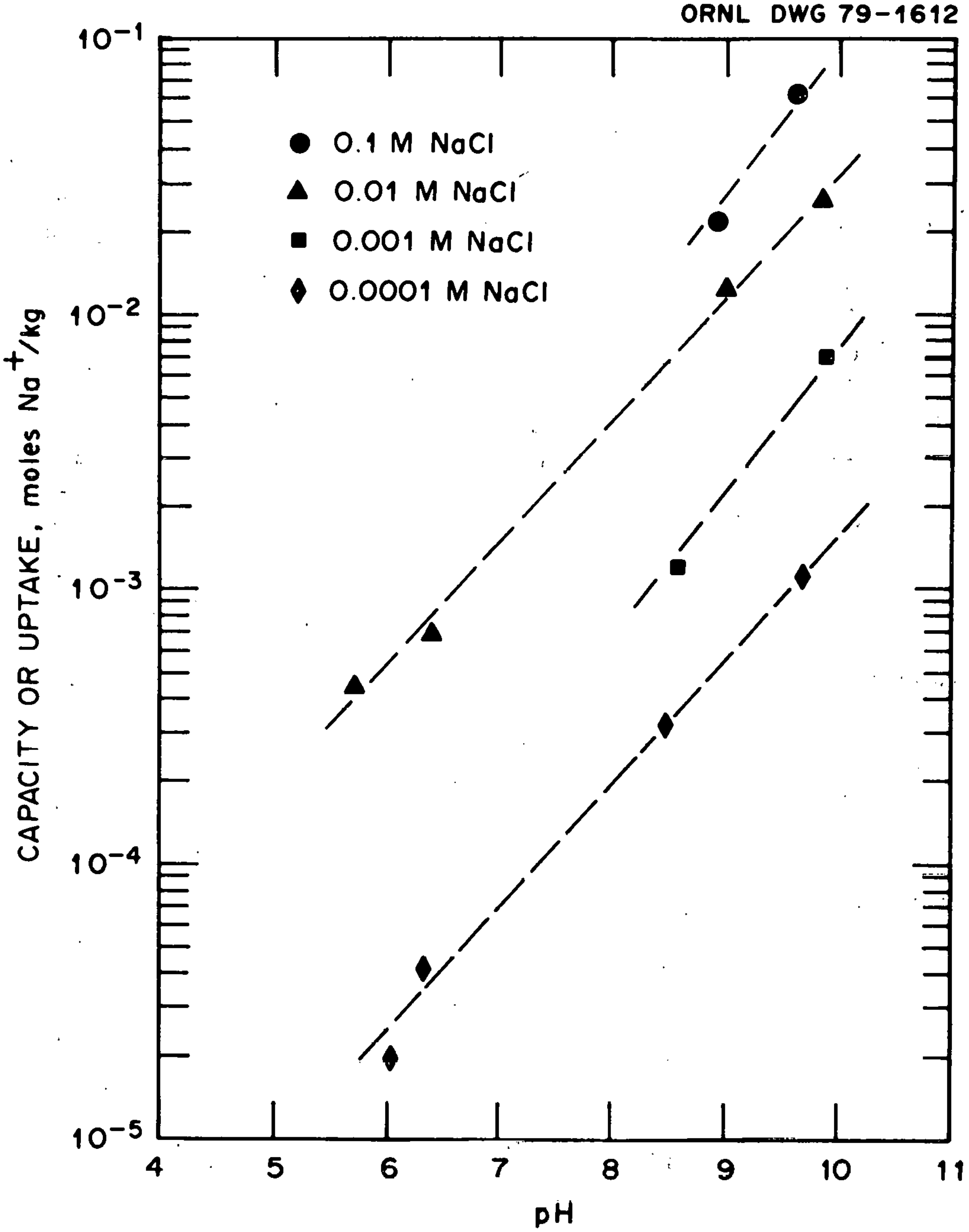
ADSORPTION OF Eu(III) ON THE SODIUM FORM OF CORUNDUM (loading: $1.9 \times 10^{-6} - 8.1 \times 10^{-5}$ mole Eu(III)/kg, equilibration for more than 192 hrs)

Figure 21



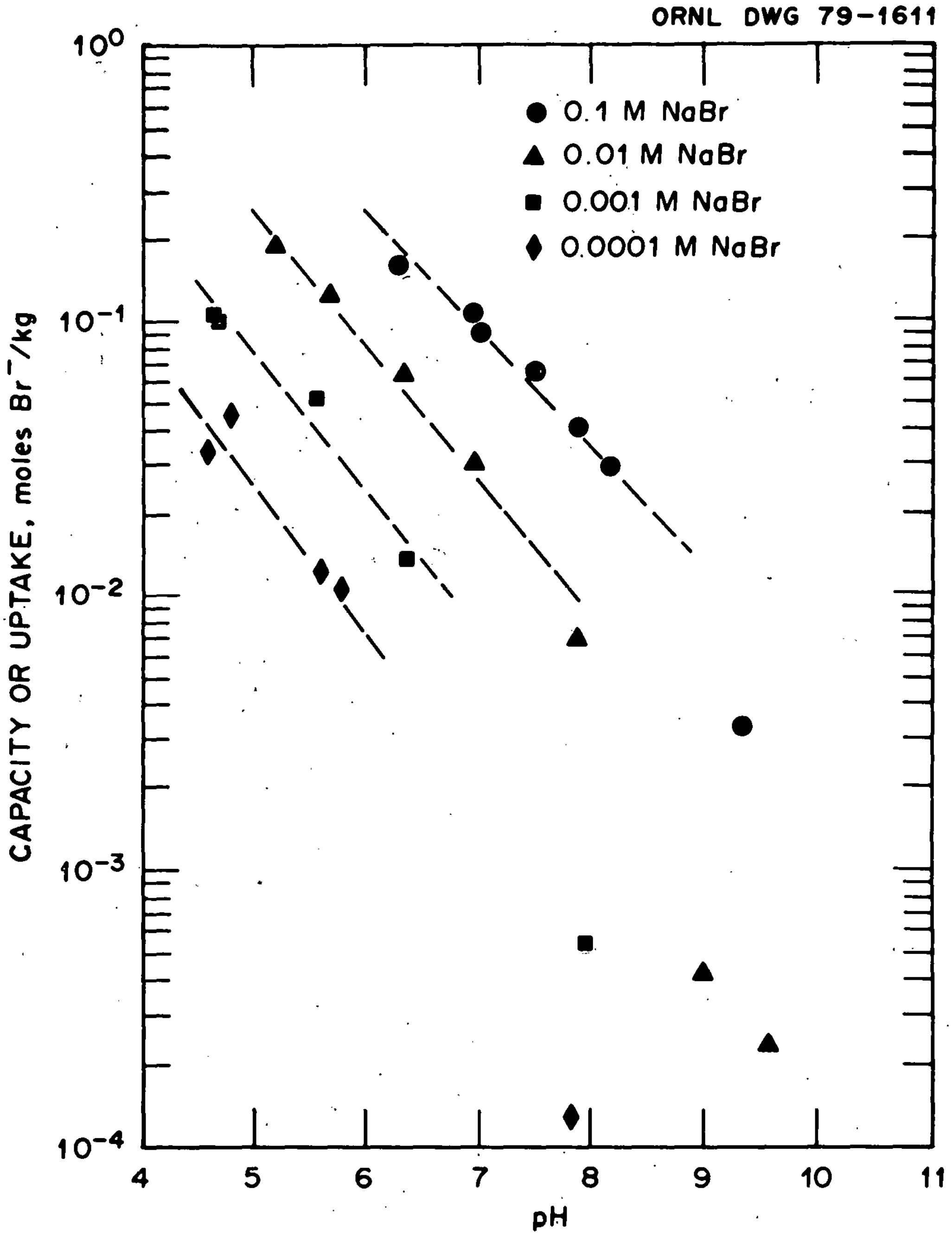
ADSORPTION OF Eu(III) ON THE SODIUM FORM OF NATURAL OXIDES (trace loading, equilibration for 300 hrs)

Figure 22



THE CATION EXCHANGE CAPACITY (OR UPTAKE) OF Al_2O_3 (equilibration for 480 hrs)

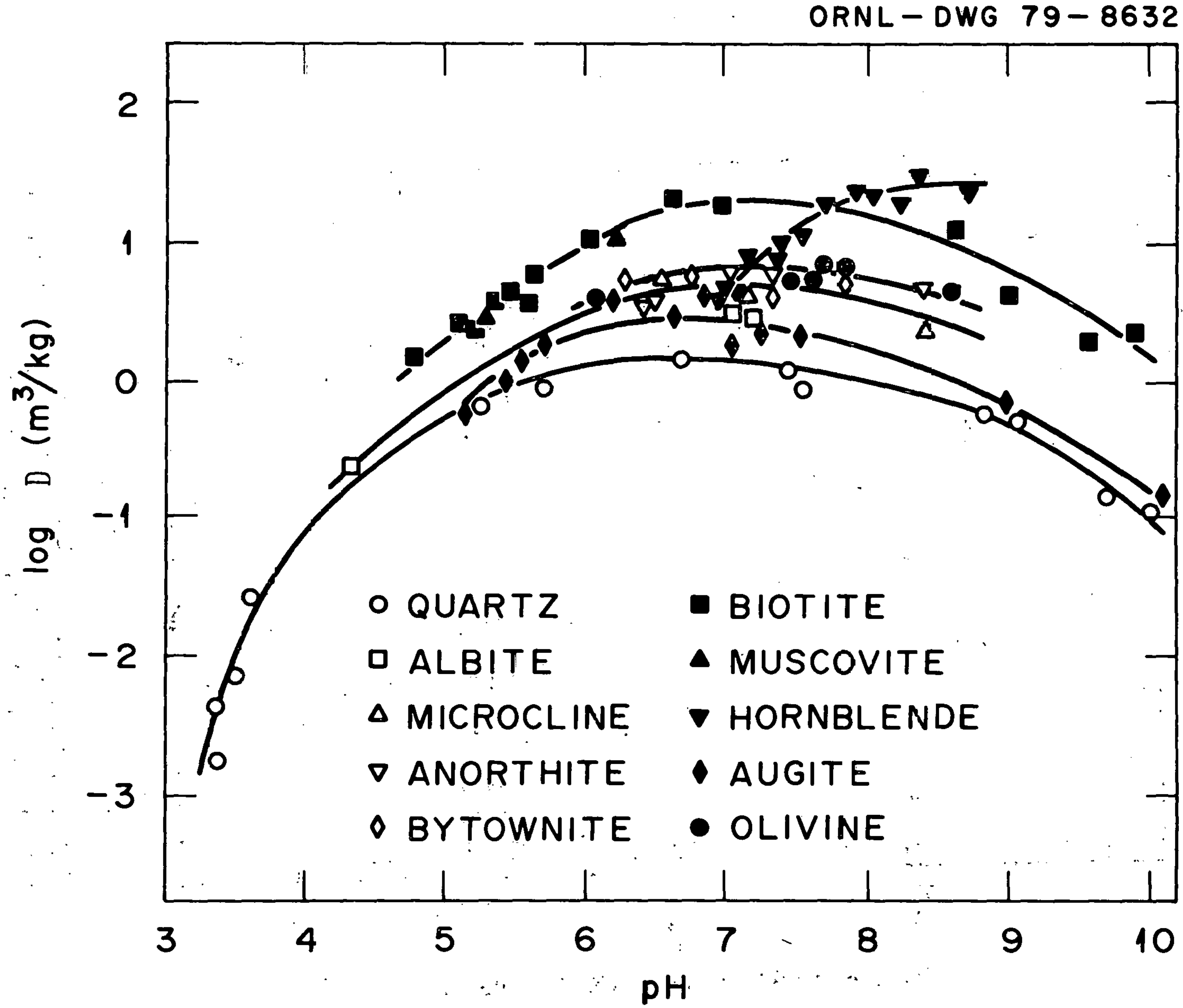
Figure 23



THE ANION EXCHANGE CAPACITY (OR UPTAKE) OF Al_2O_3 (equilibration for 72 hrs)

Figure 24

Figure 25



Adsorption of Am 241 on Various Rock Forming Minerals from a Synthetic Groundwater as a Function of pH.

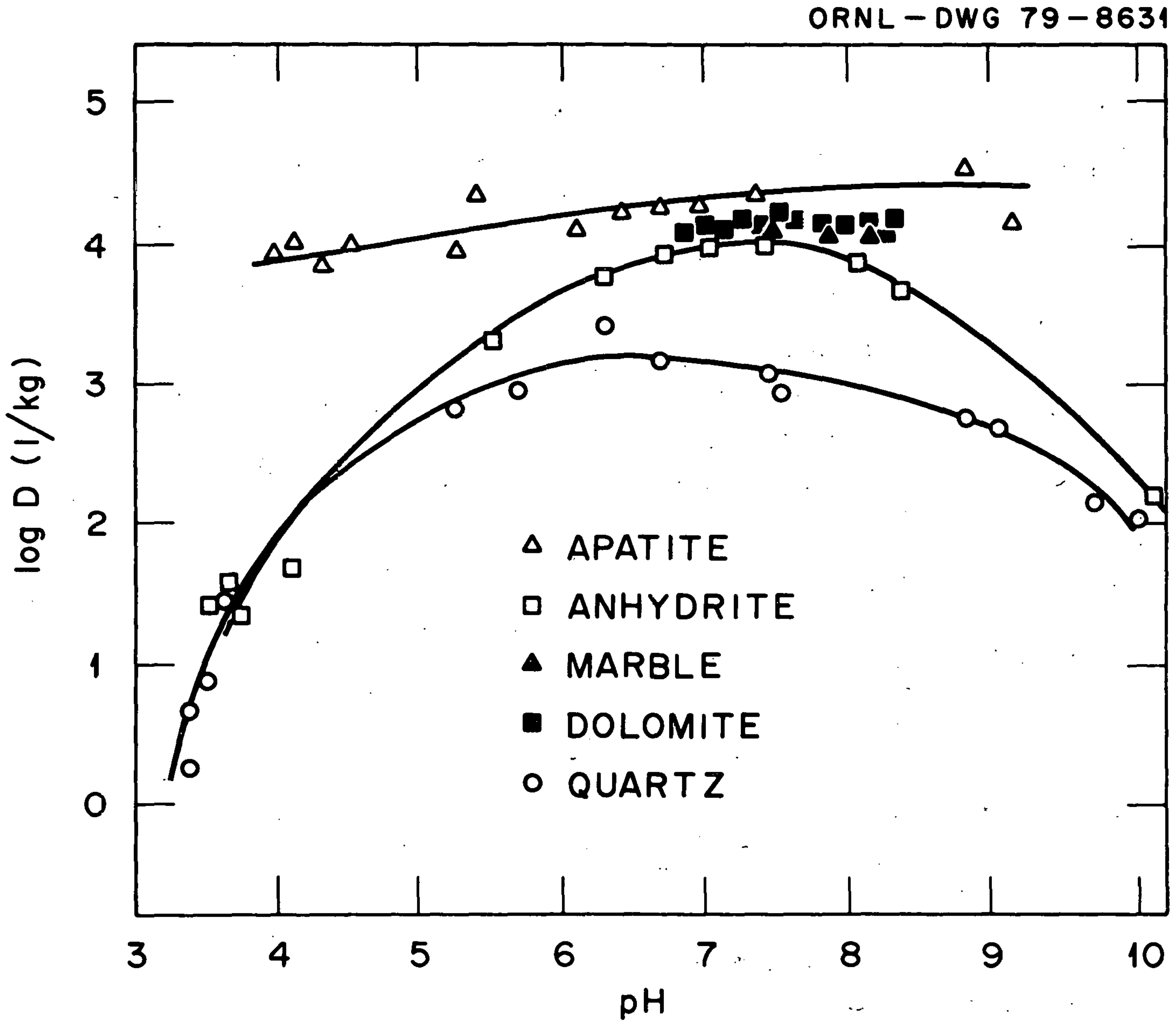


Figure 26

Adsorption of Am 241 on Various Rock Forming Minerals from a Synthetic Groundwater as a Function of pH.

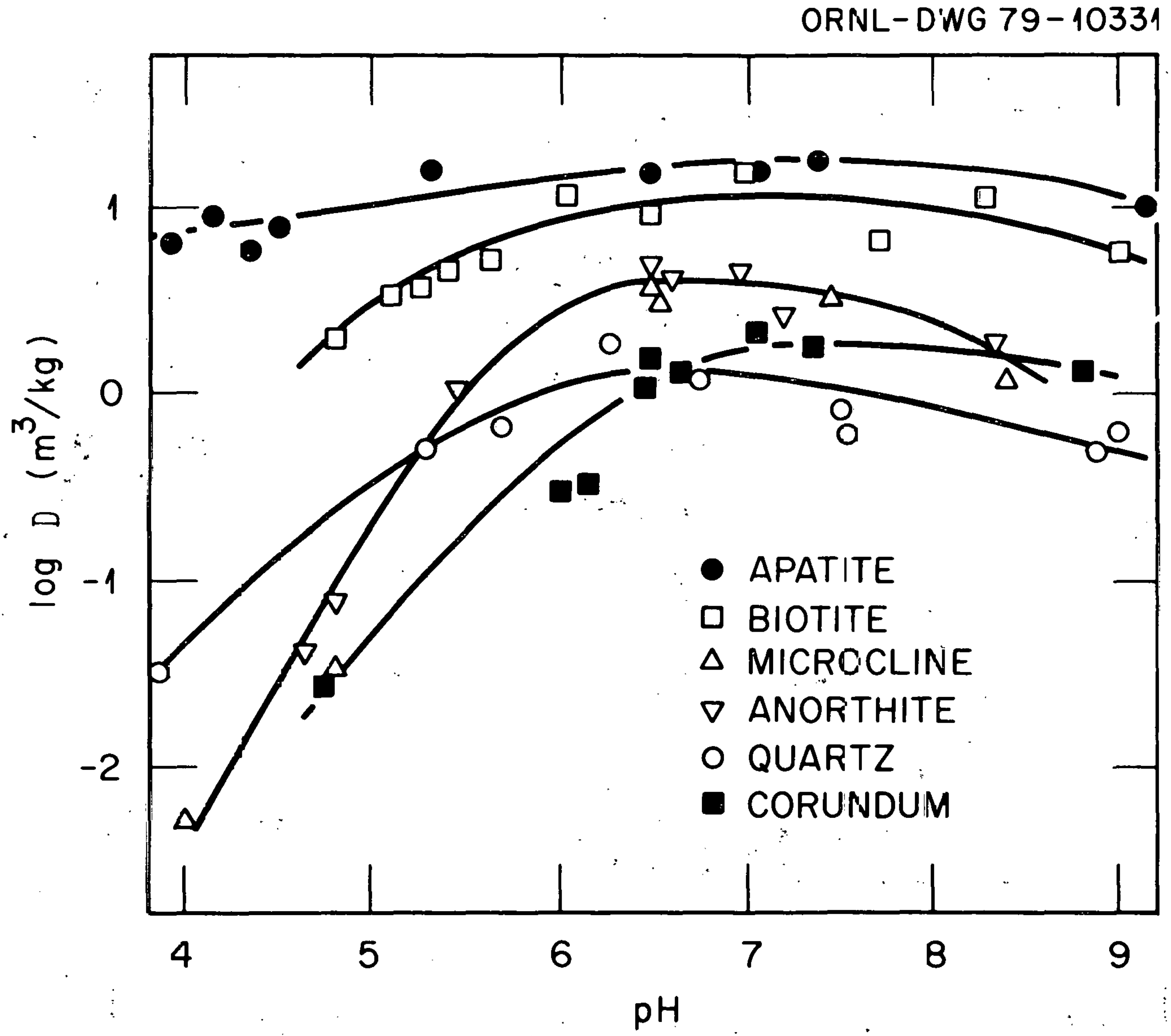
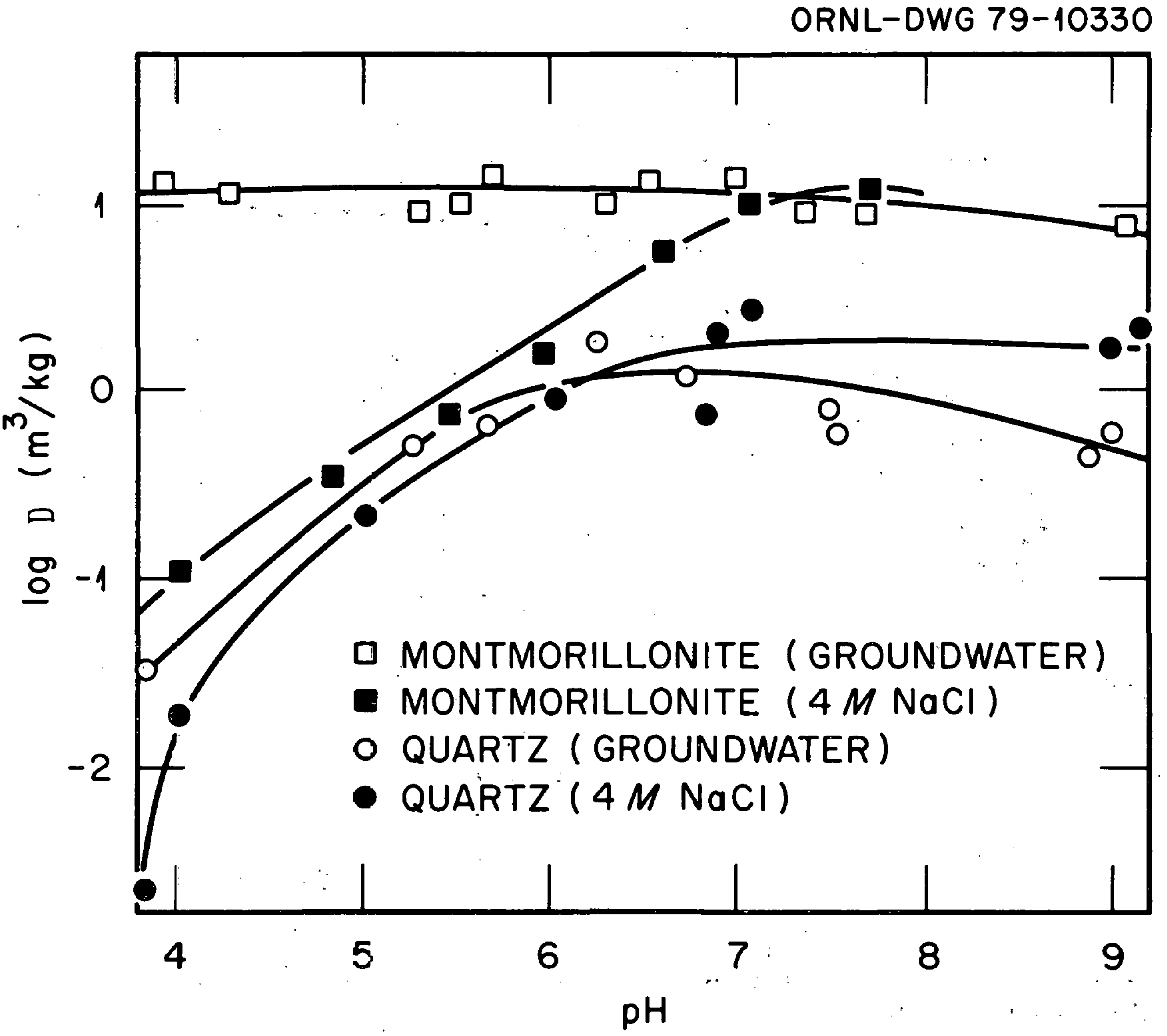


Figure 27

Adsorption of Am 241 on Various Rock Forming Minerals from a Synthetic Groundwater as a Function of pH

Figure 28



Comparison of the pH Dependence of the Adsorption of Am 241 from Synthetic Groundwater and from 4M NaCl

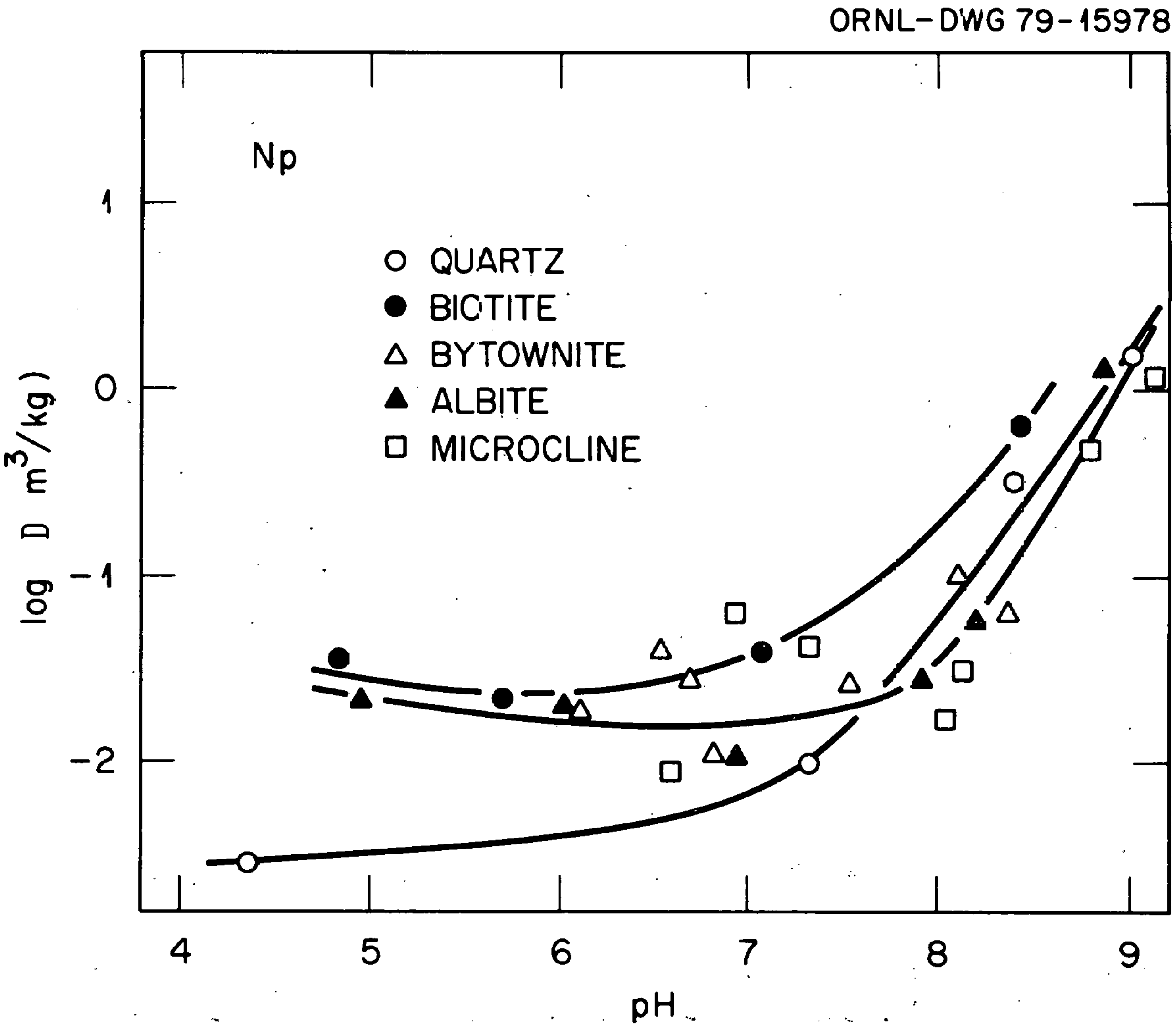


Figure 29

Adsorption of Np235 on Rock-Forming Minerals as a Function of pH from a Simulated Groundwater.

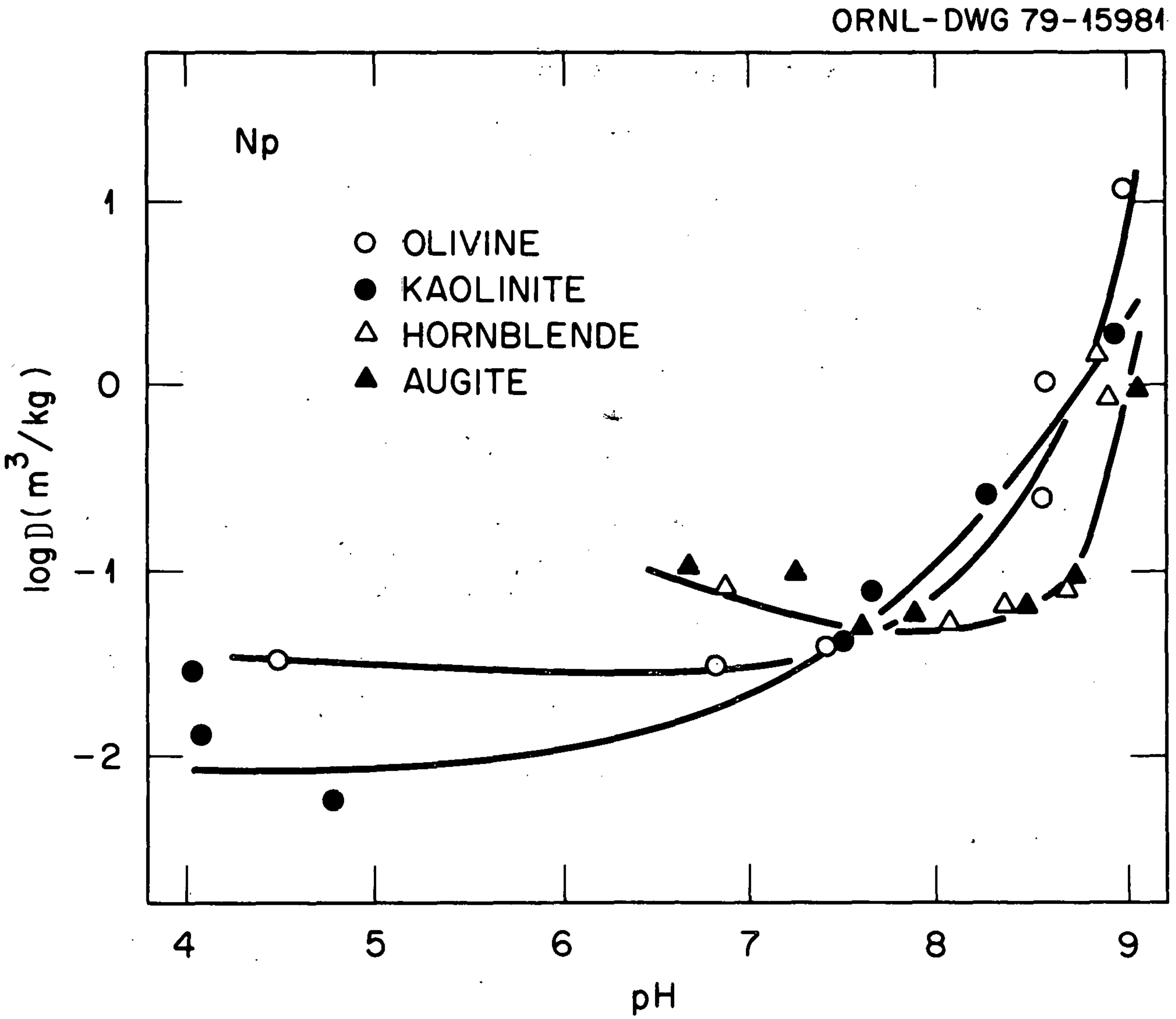
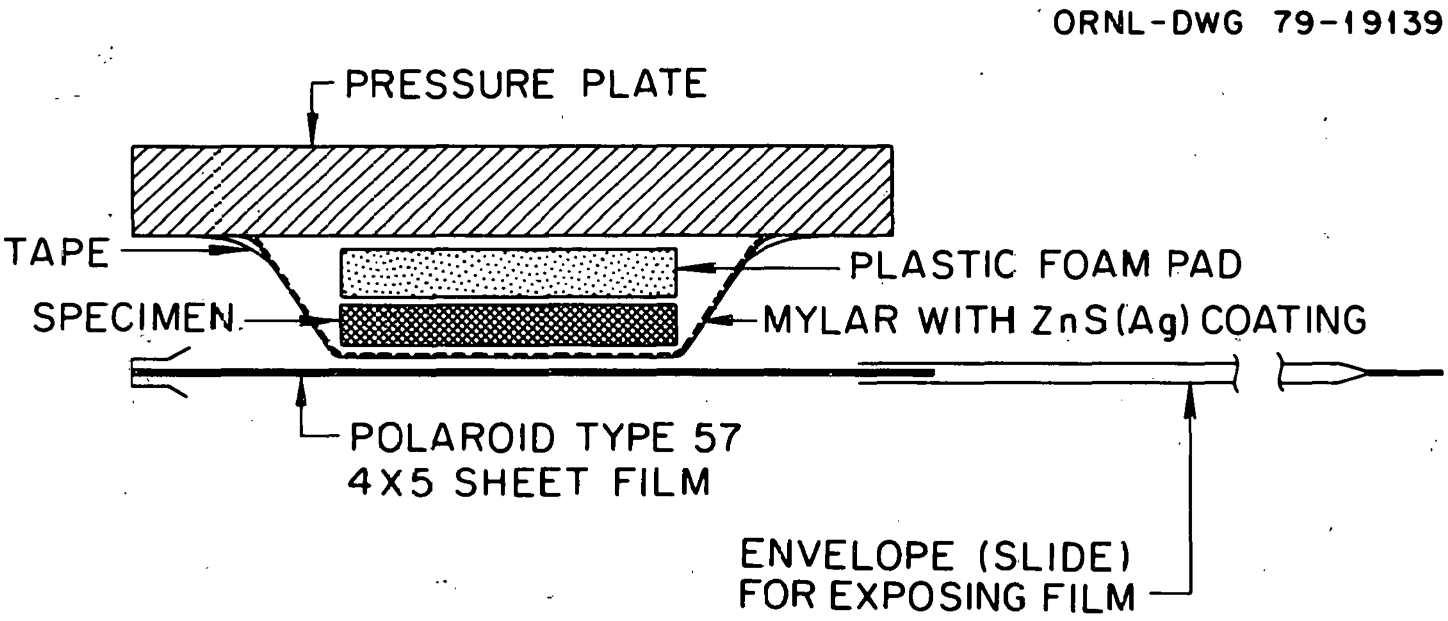


Figure 30

Adsorption of Np235 on Rock-Forming Minerals as a Function of pH from a Simulated Groundwater.



Simplified Diagram of autoradiograph camera, showing essential parts.

Figure 31

Sorption of neptunium from synthetic groundwater.
(a) optical photograph of specimen for comparison; (b), (c), (d) autoradiographs after sorption under conditions indicated.

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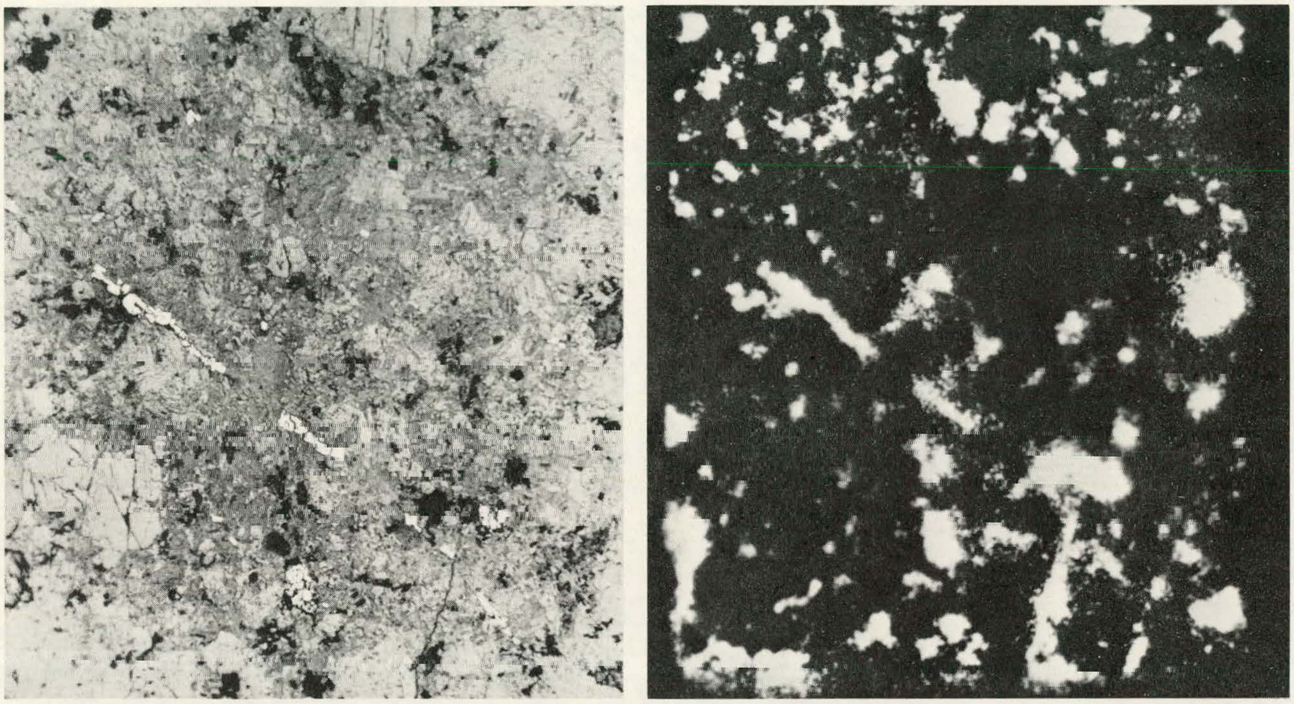
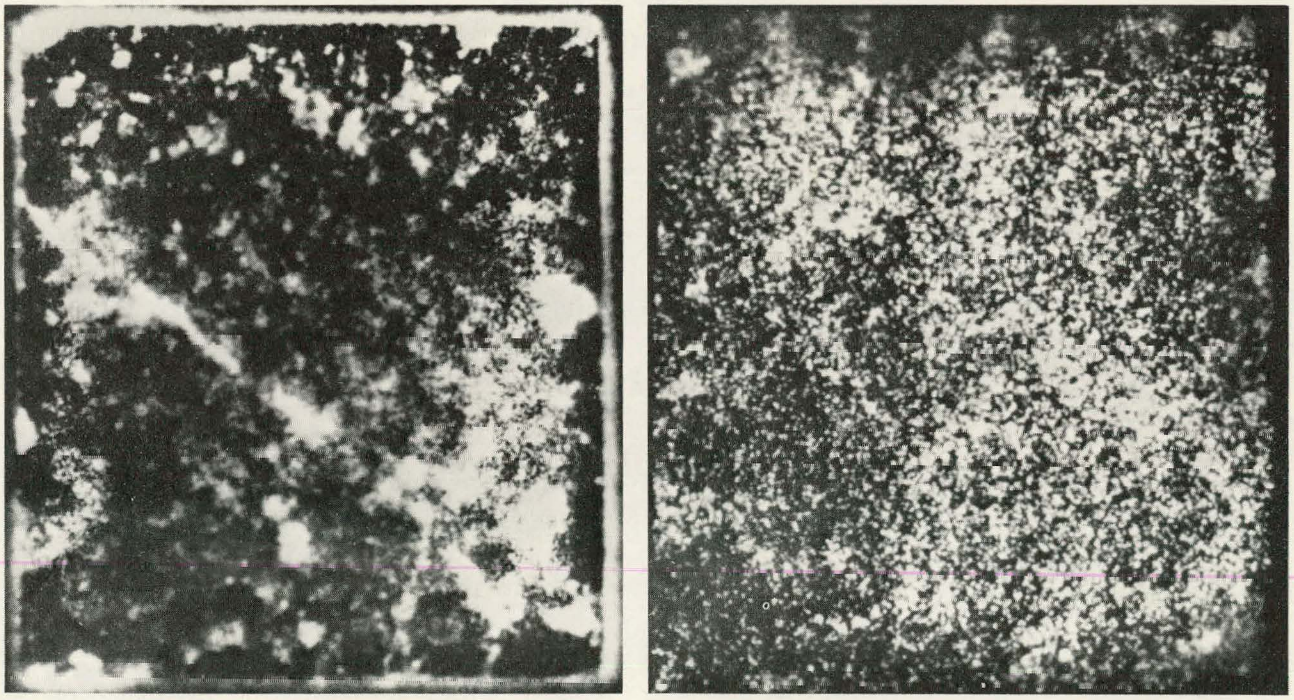


(*a*) CLIMAX STOCK GRANITE

(*b*) Np IN NITROGEN PURGED SOLUTION



(*c*) Np IN AERATED SOLUTION

(*d*) Np ON OXIDIZED SURFACE

Figure 32

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QUESTIONS AND ANSWERS

ORNL-I

Mineral Characterization

Q: What is the sodium form of alumina? Is that some surface saturation of alumina?

A: That's what you get; that just our terminology for taking the alumina and pre-equilibrating it to the sodium chloride a number of times at the pH in question before we do the experiment and add the tracers. What the actual form is, what the actual state of the surface is, is a good question. But at least all of the exchange capacity that is present at that pH, we saturated with sodium and chloride.

Clays Versus Oxides

Q: Is is correct to conclude from what you said that if you look at the repository control in the near-field you have essentially no sorption because you have brine?

A: Well, I wouldn't say so. It depends on the pH. If the pH is fairly low and the materials behave as ideal ion-exchangers, then there is little adsorption, but the oxides, in particular, hydrous oxides, do not behave in the same way that the clays do. If the pH is basic, even in fairly concentrated brine, the distribution coefficients are going to be enormous.

Pretreatment of Samples

Q: Do you really think that the Jackson treatment which strips the clay bare is going to provide the same materials that Mother Nature does?

A: We get that question almost every year, and I don't remember who it was; somebody said "You're taking all the charm out of science." I think it's useful in this kind of investigation to compare the steps in purification.

We've used the raw clay and we've used the pure clay and I would hope that we could use a--let's call it a synthetic approach that we could find out what's in the material whether we could identify how much of the clay materials are present, how much of the hydrous oxide material the low-capacity adsorbents and be able to get some kind of estimate, maybe not within the precision of 1%, but some kind of estimate of what the adsorption behavior is going to be.

Oxidation State

Q: Did you comment on how you maintained the oxidation states of the iodide? I guess I should really make the statement that we've had considerable difficulty in maintaining the iodine-131 as iodide.

A: But we're just doing experiments where we put some reducing agents in the presence of iodine to see if there's any difference between those and those just normally air-saturated and we didn't find any difference but we went ahead and did the experiments and they were fairly quick experiments; normally, it is a two-day shaking on those. We didn't find any great difference between those in which we put the various re-agents in and those that we didn't. We also, as you notice, added sodium iodide. It wasn't carrier free.

Ion Exchange and Competition

Q: Since you made your measurements at pH 5, could you confirm that in effect there was adsorption of cesium and sodium in accordance with what you would expect for a given exchange capacity, and if so, if you raised the pH to 7, which presumably is of greater interest in waste studies, could you just extrapolate those results in reference to solubility product?

A: The experiments that I showed range from pH 5 to pH 10. The second slide of the data showed no change in the distribution coefficient when the pH is changed from 5 to 10. That was only.....I believe I showed it only for sodium montmorillonite that had been purified and in alumina.

Q: I was thinking of those cesium and strontium tests in the presence of varying concentrations of sodium where it seemed to me that the adsorption was exactly what you would expect from the different concentrations.

A: Yes, it was certainly true for strontium. For Cs as I showed, we had a little loading effect so we didn't quite get as ideal a behavior as Bob Silva showed in his sample. Did I answer your question? I'm not sure.

Q: Well, as you say I don't think most of the measurements were made at pH 5, only cesium and strontium. So I was wondering if you get into the range of everybody else's comparable measurements whether in fact you could expect to get the same kind of behavior between, say, cesium and sodium for sorption sites.

A: As far as we have been able to tell, the answer would be yes for strontium and cesium. Of course, with europium there's a different situation which I'll amplify tomorrow.

Characterization of Minerals (Rock)

Q: I just want to caution everyone that the materials should be characterized. I think that a lot of mineralogists, a lot of metallurgists, and most of the laboratories have very fine characterization staffs and a lot of them will tell you that there are a lot of natural materials that are as pure or purer as anything they can synthesize in the lab--crystographically and elementally. But there are also sources of materials that have the same crystallinity, that have the same crystal structure and that are chemically pure, for example, Lyndy's sapphire. There are companies that produce synthetic AO_2O_3 which is α structure (corrundum structures). So there are materials around and it is not just AO_2O_3. There are a lot of materials around that are chemically what you want and also crystographically what you want and relevant to the geological systems. That was my comment. I spent 5 years on the thesis where I received samples from collectors and they weren't what they supposedly were, and they should be checked. Wards sends students out (every graduate department student has to go out every summer); they handle the rocks; they sell them for Wards; and that is what you get. Wards sells their collections for classroom use. You should be very cautious. All contractors and investigators should be very cautious about not only Wards' material but every source. They label them the best they can with the energy and money available. Even the Smithsonian has problems because they can't control the collections. So just be very cautious about that. And I think everyone is liable for that type of criticism and help because it is just a fact of life that they don't have the energies to do the work in any other way.

C: Bob, just to emphasize Ken's statement, I have two samples of clays. They both have their origins from Wards and they were both collected at the same location and both sold as two similarly related clays.

A: Yes, I don't think that is a problem. The clays that we have used were obtained from the University of Missouri.

Q: Is that the API collection?

A: No. I think it's sponsored by the Clay and Clay Mineral Society. I am not sure if those are API clays or not.

C: No, they are not.

A: I don't think they are. The illite that we got, so far as I know, was about the best natural illite that you can find. Also, relatively fine synthetic clays. We have some synthetic montmorillonite that we obtained, but it is a lot harder to work with because it is synthetic. Montmorillonite is a much lower particle size, by about a factor of 10 over the natural.

Q: The chromographic alumina that you used--did you leach that and look for Na as a leachate?

A: To start with, the alumina is equilibrated with sodium chloride or whatever medium several times until we were sure that all the capacity was taken up by the sodium.

Q: You haven't done it with just deionized water?

A: No.

Q: Was this the same montmorillonite you used in the other studies. I mean with the cobalt and cadmium?

A: It all came from the University of Missouri. This information is, I believe, contained in the annual report.

Nuclide Concentration

Q: How does your Am concentration compare with solubility levels that were suggested by others?

A: The concentration level I have, 10^{-9} and 10^{-10} molar, is low enough that we wouldn't expect precipitation in the bulk solution; but according to other theories there are different properties in the bulk solution and the layer around the mineral surface which would alter the complexation process. So, what we actually observe might be a precipitation effect that could account for the presence of solids but not in the bulk solution.

Q: Those results as I remember could be faulty in that the concentration level is pH dependent with considerably lower concentration at the higher pHs.

A: Lower concentrations were 10^{-10}.

C: I thought it was 10^{-11} or 10^{-12}.

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Sorption-Desorption of Long-Lived Radionuclide Species on Geologic Media

ANNUAL REPORT

October 1, 1979

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NOTICE

Abstract

The influence of time, temperature, pH, Eh, Fe^{+2}, and Tc concentrations on the sorption-desorption of Tc on a basalt, granite, and shale was investigated. Loss of the TcO_4^- anion from the solution phase appears not to be due to sorption of the anion on the solid phase matrix, but rather due to the reduction to a lower oxidation state; probably TcO_2 which is highly water-insoluble. Loss of TcO_4^- increased with time. There appears to be an interaction between the reduction of TcO_4^- and temperature, viz, increasing temperature enhanced the initial reduction rate, but the rate exponentially decayed at high temperatures (72 vs. 22°C). Basalt significantly reduced TcO_4^- faster and in greater quantities than the granite or shale samples. On the order of 10^6 more Tc-99 was retained on anoxic basalt columns than Tc-95m; however, the Sorption Concentration Ratios (0.64 and 3.54 ml/g) were not appreciably different. The additions of Fe^{+2} prior to TcO_4^- additions did not affect TcO_4^- reduction; but, additions of Fe^{+2} to Tc-rock suspensions reduced TcO_4^-. The reduced form of Tc is slowly oxidized to the TcO_4^- under oxic conditions. In Eh-pH monitored stirred suspensions, the single most important variable influencing the loss of TcO_4^- was Eh of the suspension.

Losses of TcO_4^- from basalt suspensions were observed at measured Eh's approximately 0.240 volts higher than those theoretically necessary for the formation of the water-insoluble TcO_2. Pertechnetate ($\mu\underline{M}$) was observed to be stable in the presence of 100 $\mu\underline{M}$ Fe^{+2}, pH 5, and Eh $\sim$ +0.400 volts; even at Fe^{+2}/TcO_4^- ratios $> 10^6$, the pertechnetate was observed to be stable at pH's between 4.5 and 5.5. As the pH was increased to 6.5 and greater the loss of TcO_4^- from solution was directly proportional to the loss of Fe^{+2}. Data indicated that TcO_4^- was reduced

by Fe^{+2} as the pH was increased, and Tc^{+4} was isomorphically substituted into the lattice of $Fe(OH)_3$ because of the similarity in ionic radii (0.65 Å) of Tc^{+4} and Fe^{+3}.

INTRODUCTION

Presented in this report are the data and conclusions derived from sorption-desorption of various long-lived radionuclide species on geologic material being considered as host rocks for a repository of nuclear wastes. The work was supervised and conducted by C. W. Francis and E. A. Bondietti, Environmental Sciences Division, Oak Ridge National Laboratory.

OBJECTIVE OF PROGRAM

The objective of this work is to understand the magnitude of sorption-desorption and processes that control the interactions of long-lived radionuclides with geologic materials. To do this, sorption-desorption is being conducted under various environmental conditions. The most important comparison being sorption-desorption under anaerobic and aerobic environments; as the presence or absence of oxygen will dictate the chemical speciation and hence, the sorption-desorption characteristics of Tc-99 and Np-237, and possibly the U radionuclides. Sorption is being carried out in stirred cells and columns in which the concentration of radionuclides in the aqueous phase is varied from 10^{-6} to 10^{-10} M. The ultimate objective is to identify which long-lived radionuclides and the various environmental conditions in specific geologic media that sorption may be insignificant and that would allow migration from a geologic repository to the earth's surface faster than the physical decay of the radionuclide.

PREVIOUSLY REPORTED PROGRESS

This program was initiated in January 1976 to investigate possible differences in K_d determinations by thin-layer chromatographic techniques and the equilibrium batch methods conventionally used to measure K_d's. The work involved the development of a coupled-equations model to determine K_d values and selectivity coefficients of radionuclides in unsaturated flow along a chromatographic column. Aside from the annual reports presented in the proceedings of the Task 4 Contractor information meeting of the Waste Isolation Safety Assessment Program, a report (Quantitative Analysis of Soil Chromatography I. Water and Radionuclide Transport, ORNL-5337, M. Reeves, C. W. Francis, and J. O. Duguid) was written describing in detail the model used for water and radionuclide transport under conditions of unsaturated flow. Using the coupled-equations model, no significant difference could be detected in the K_d's or selectivity coefficients of Sr-85 and Ni-63 with Conasuaga shale by either of the two techniques, unsaturated flow chromatographic or the equilibrium batch method. The chromatographic technique, however, was superior in detecting the presence of one or more species of a radionuclide.

It became obvious that the K_d of a radionuclide depended on the speciation and oxidation state of the radionuclide. A major difference in the sorption of two long-lived radionuclides (Tc-99 and Np-237) under anoxic conditions would be expected as TcO_4^- and NpO_2^+ are not the stable thermodynamics species in anoxic groundwaters in contact with ferrous bearing igneous rocks. Recent work in Science (Geologic Migration Potentials of Tc-99 and Np-237, E. A. Bondietti, and C. W. Francis, 1979) demonstrated that TcO_4^- and NpO_2^+ are not stable under anoxic conditions in presence of a basalt and a granite. Loss of Tc was considerably greater in stirred cells than in anoxic columns. We also have evidence that U(VI) is reduced to U(IV) under anoxic conditions in the presence of the Sentinel Gap basalt.

PROGRESS

Interaction of TcO_4^- with Rocks

Objectives: The major objectives in this work are as follows:

(1) Determine the influence of Tc concentrations on loss of Tc.

(2) Evaluate the kinetics of Tc sorption on rocks.

(3) Determine the influence of temperature on Tc sorption.

(4) Describe the loss of TcO_4^- from the aqueous phase of rock suspensions in terms of pH, Eh, ratios of solution to solid, and Fe^{+2} concentrations.

To carry out these objectives, Tc sorption was monitored in stirred reactors and columns containing various rocks ranging in particle size. The Tc was added to the solution phase as TcO_4^- in concentrations ranging from 10^{-5} to 10^{-13} M Tc using either Tc-99 or Tc-95m.

Sorption of Tc on Sentinel Gap Basalt in Columns

We had earlier demonstrated that $^{99}TcO_4^-$ at concentrations of 10^{-7} M was easily reduced in anoxic stirred cells (> 99% loss in four days) containing Sentinel Gap basalt; however, in anoxic columns containing $^{99}TcO_4^-$ at 10^{-6} M only 9-10% was removed after five days residence time. The faster rate of loss in stirred cells was thought to be due to the grinding effect producing freshly exposed rocks surfaces in an anaerobic environment. Freshly exposed rock surfaces would not be generated in packed columns, and possible oxygen leakages into tubing and pumps in columnar designs makes the maintenance of anoxic environments more difficult than in N_2 purged stirred cells.

To obtain long residence times in columns, in excess of five days, requires either large columns or very slow pumping rates. For example, at a flow rate of 0.05 ml/min., a column volume of 360 ml would be required. Thus, for a pore volume of 50%, approximately 1 kg of sieved material would be needed (assuming particle density of ca. 3 g/cm^3). For unsaturated flow, effective pore volume (20-10%), the quantity of processed rock would be 2.5 to 5.0 times greater making procurement of the processed rock one of the major constraints of such an experiment. Small to medium size columns conventionally used in the laboratory (50 to 150 cm^3) require flow rates on the order of 50 to 500 μℓ/hr which are difficult to maintain. To avoid the above problems, approximately 60 grams of Sentinel Gap basalt (18-50 mesh, ground in a ceramic pestle and mortar) were placed in a 1.5 x 30 cm column (K-15 Pharmicia). The columns were purged overnight with high purity N_2 gas (scrubbed through alkaline solutions of dithionite and pyrogallic acid). Simulated basalt groundwater (Table 2) containing tracer quantities of HTO and either Tc-95m (4.7×10^{-12} <u>M</u>) or Tc-99 (6.4×10^{-6} <u>M</u>) was also purged overnight to displace any dissolved O_2 before pumping (by negative pressure) into the basalt columns. The simulated groundwater was added at the top of the column, and pumping was discontinued when the wetting front reached the bottom of the packed column. The columns were sealed and after a designated time, fresh, nontagged groundwater was slowly pumped into the columns to displace the original solution. The quantity of original solution added to the column was determined from HTO assay of the effluent. Effluent was collected into liquid scintillation vials in 20 drop aliquots (approximately 0.94 ml). Concentrations of HTO and Tc were calculated from dual channel counting data using a channel ratio technique (Tc-95m concentrations were confirmed by gamma counting in a NaI-detector-multichannel counting facility).

Form of Tc Sorbed: Earlier studies in small columns had indicated that the sorbed Tc was not readily displaced with oxic PNL No. 3 groundwater (Fig. 1). Even 2 N NaCl did not displace significant amounts of the Tc; however, on adding 5% H_2O_2 Tc was rapidly eluted from the column (Fig. 1). Elution of Tc with H_2O_2 indicated that the TcO_4^- had been reduced to a lower oxidation state under the anoxic sorption conditions. It is not clear nor do we have evidence what the lower oxidation state might be. Based on known thermodynamic data, the most likely oxidation state is Tc(IV) either as the oxide (TcO_2) or hydrated oxide [$TcO(OH)_2$]. The elution data illustrated in Figure 1 have revealed that the sorbed Tc is not an easily exchangeable cation or anion, and the release of Tc takes place in the presence of a mild oxidant (weak bromate solutions have also been used to displace the sorbed Tc). Because Tc sorption on igneous rocks under anoxic conditions behaves nonideally with respect to conventions established for the equilibrium distribution coefficient (K_d), we will refrain from using the K_d nomenclature in this report. Instead, we will define sorption in terms of a sorption concentration ratio (S_{CR}), viz, a strict literal interpretation of the concentration of Tc on the solid phase relative to its concentration in the solution phase. Its calculation and its units (ml/g) are identical to those used for K_d.

Effect of Residence Time and Tc Concentrations: For all residence times (1, 3, and 7 days), less than 10% of the Tc-95m was recovered from the columns (> 90% of the Tc-95m retained with the basalt). On the other hand, greater than 10% of the Tc-99 added to the column was recovered for all residence times (25 to 84% of the Tc-99 retained by the basalt, Table 1). In terms of the fraction of Tc added to the column, and in

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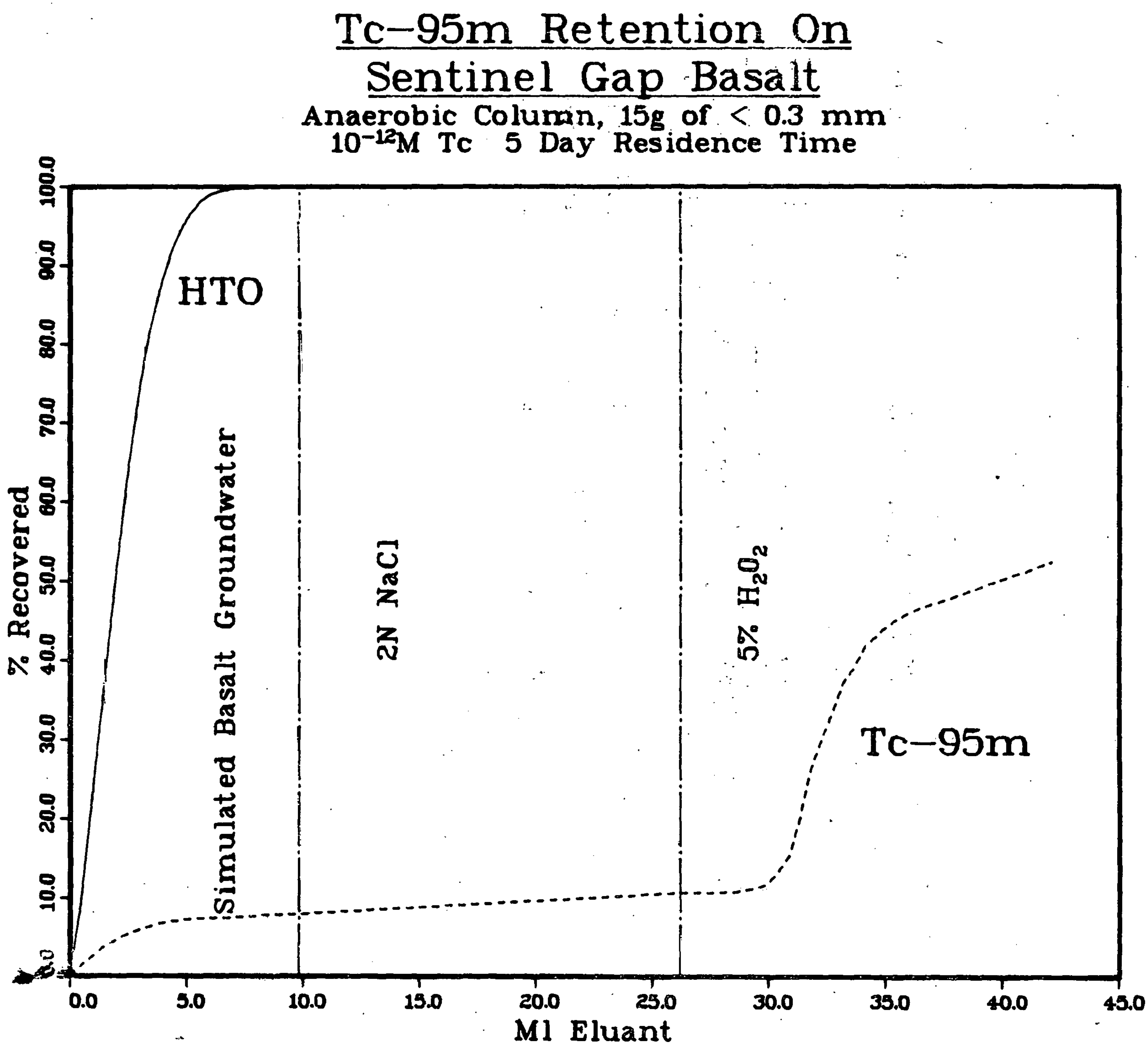

FIG. 1

TABLE 1. Influence of Residence Time and Tc Concentration on Sorption of Tc on Basalt Under Anoxic Conditions

	Tc-99 6.4×10^{-6} M Tc				Tc-95m 4.75×10^{-12} M Tc			
Residence Time Days	Tc Retained %	Tc Retained pM/g	S_{CR} ml/g	Solution/Solid	Tc Retained %	Tc Retained pM/g $\times 10^{-4}$	S_{CR} ml/g	Solution/Solid
1	25.5	178	0.04	0.109	91.9	4.8	1.25	0.110
3	52.7	216	0.07	0.064	94.0	7.0	2.42	0.155
7	83.8	659	0.64	0.123	97.4	4.4	3.54	0.094

pM = picomoles

terms of the S_{CR}, Tc-95m was retained or reduced by the basalt more effectively than Tc-99. However, on the basis of mass of Tc sorbed, approximately 10^6 times more Tc-99 was sorbed than Tc-95m. Sorption of Tc-99 increased as a function of residence time ($Y = 41.1 + 84.5T$, $r^2 = 0.933$, where T is time in days), while sorption of Tc-95m appears to be independent of time after a one day residence time. All S_{CR}'s are very low even when > 97% of the Tc was sorbed to the basalt. This is a result of the very low solution to solid ratios in the columns (0.064 and 0.155). However, desorption D_{CR}'s would be very high, in that it was difficult to detect quantities of Tc in the third and fourth column volumes (> 25 ml of eluant), Figure 2.

In terms of S_{CR}, Tc-95m at initial Tc concentrations of 4.75×10^{-12} $\underline{M}$ was sorbed more effectively than Tc-99 (Tc conc. 6.4×10^{-6} $\underline{M}$); however, significantly greater quantities of Tc in terms of grams of Tc sorbed per gram of basalt was observed with Tc-99. The sorption appears to be a precipitation reaction, probably as a result of the reduction of TcO_4^- to an undefined lower oxidation state that is highly water-insoluble. On the order of 3-5% of the Tc-95m remained in solution, representing a concentration of about 2.4×10^{-13} $\underline{M}$. Based on Tc thermodynamic data (Pourbaix, 1966), Eh's on the order of -180 to -140 mv would be required at pH's 8.5 to 8.0 to maintain this concentration in the solution phase. These Eh values are significantly lower than those measured in our stirred reactors, but at the same time, we have never made Eh measurements at solution to solid ratios of < 0.1. We do know that as the ratio is decreased, the Eh readings are appreciably lower. If 10^{-13} $\underline{M}$ Tc, or for that matter, any other limiting solubility concentration, were taken to be an equilibrium solution phase concentration, then S_{CR}'s are simply a function of the initial Tc concentration. Thus, the

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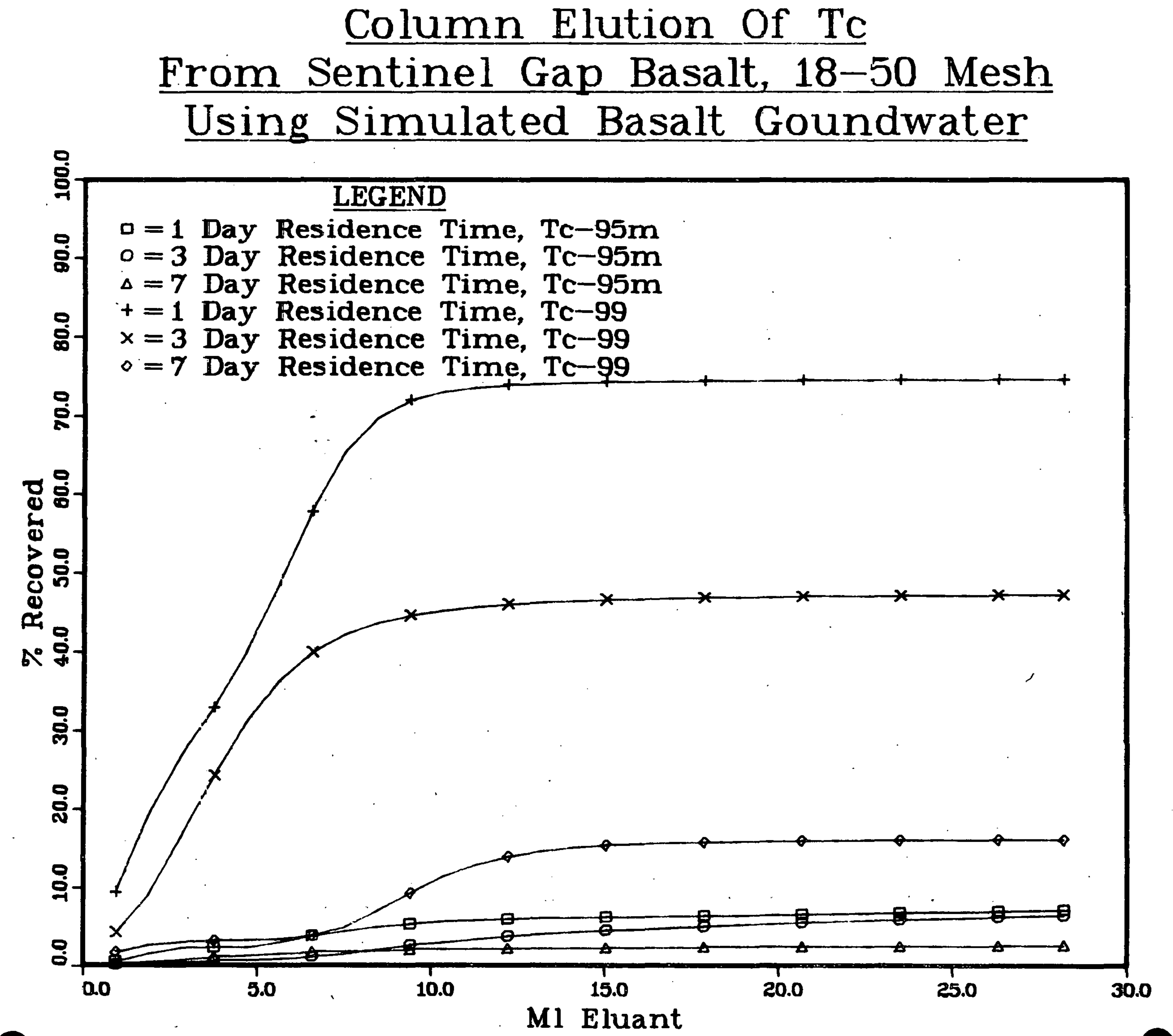

FIG. 2

quantity of TcO_4^- reduced is dependent on the quantity of reductant available, probably Fe^{+2} on the rock surfaces. It is not clear what the parameters are that affects the rate, the influence of temperature is investigated in the next section.

Anoxic Batch Sorption Studies

Anoxic rock (18-50 mesh) suspensions in PNL No. 3 groundwater were carried out in the following manner. In a three neck boiling flask, 200 ml of No. 3 groundwater tagged with Tc were purged overnight with high purity N_2 (< 1 ppm O_2) scrubbed through alkaline solutions of dithionite and pyrogallic acid. Weighed amounts of rock were added to 10 cm^3 plastic syringes with a stainless steel hypodermic needle. The syringes containing the rock sample were purged a few minutes with high purity N_2. A small hole in the back of the syringe was used for exiting N_2, and pushing forward the plunger resulted in a deaerated, anoxic system. The needles were sealed by inserting into No. 00 rubber stoppers. Deaerated No. 3 groundwater was transferred to the syringes via a rubber septum in one of the necks of the boiling flask. The syringes were weighed before and after purging and filling with Tc labeled solutions to determine the quantity of groundwater added. The syringes containing the rock-groundwater suspensions were placed in water baths of 0°, 22° (room temperature), and 72°C. These water baths were purged with 99.997% pure general purpose N_2. Glass vials capped with silicone rubber septa were also used. In this case, the rock sample was purged with N_2 before the addition of deaerated simulated groundwater. Results from vial-septa procedure were comparable to data obtained in the syringes.

<u>Influence of Time and Temperature</u>: Suspensions of Sentinel Gap Basalt

(4 grams in ca. 4 ml of PNL No. 3 groundwater) were used to evaluate the influence of temperature on sorption of Tc-99 (μ M conc. Tc). Sorption was carried out at 0°C (ice bath), 22°C (room temperature), and 72°C (hot water bath). The suspensions were agitated on a daily basis (week-ends excepted).

Initially, there appeared to be an interaction between temperature and time. For example, the initial sorption (one day) tended to be greater at 72°C than at 0 or 22°C, however, at seven (7) days, there was significantly more Tc sorbed at 22°C than at 72°C (Table 2). Increasing time revealed no statistical difference in sorption at 22 and 72°C. On the other hand, there appears that there was a significant increase in sorption at 22 and 72°C over 0°C. The general trend between temperature and time is illustrated in Figure 3. The extreme amount of variability among replicates makes interpretation difficult. The source of variability is not clear. The major source of variability was likely the inability to adequately control the rate at which oxygen contaminated the system. Variability of Tc sorption on unweathered Conasauga shale (Table 3) was considerably less than that observed with Sentinel Gap basalt. Previous work under similar sorption conditions showed that Tc sorption on basalt was on the order 10^5 times greater than sorption on the shale (based on total mass of Tc sorbed). Sorption on basalt thus appears to be more dependent on Eh-pH conditions than sorption on shale. Work presented in the next section shows that Tc sorption on basalt is highly dependent on Eh, as well as pH of the suspension. Thus, work labeled "anoxic sorption" should be viewed with caution, as the degree of anoxicity has a large influence on sorption.

Effect of Tc Concentration: There appeared to be no significant differ-

TABLE 2. ^{99}Tc Sorption (S_{CR}, ml/g) on Basalt from PNL No. 3 Groundwater Under Anoxic Conditions[1]

Temperature °C	Time (Days)				
	1	3	7	15	30
0	0.34 ± 0.10	0.97 ± 0.28	7.72 ± 5.88	2.10 ± 0.86	2.01 ± 1.70
22	1.70 ± 0.51	78.2 ± 98.6	420 ± 197	139 ± 106	312 ± 403
72	2.53 ± 2.48	8.48 ± 9.14	13.7 ± 15.1	146 ± 37	106 ± 61

[1] Data at times less than 15 days represent four or more replicates, while data at 15 and 30 days represent two replicates. Composition of PNL No. 3 groundwater in meq per liter are as follows: $NaHCO_3$, 0.95; Na_2SO_4, 0.35; $MgSO_4$, 0.08; $CaSO_4$, 0.07; $CaCl_2$, 0.26; KCl, 0.20; KF, 0.04.

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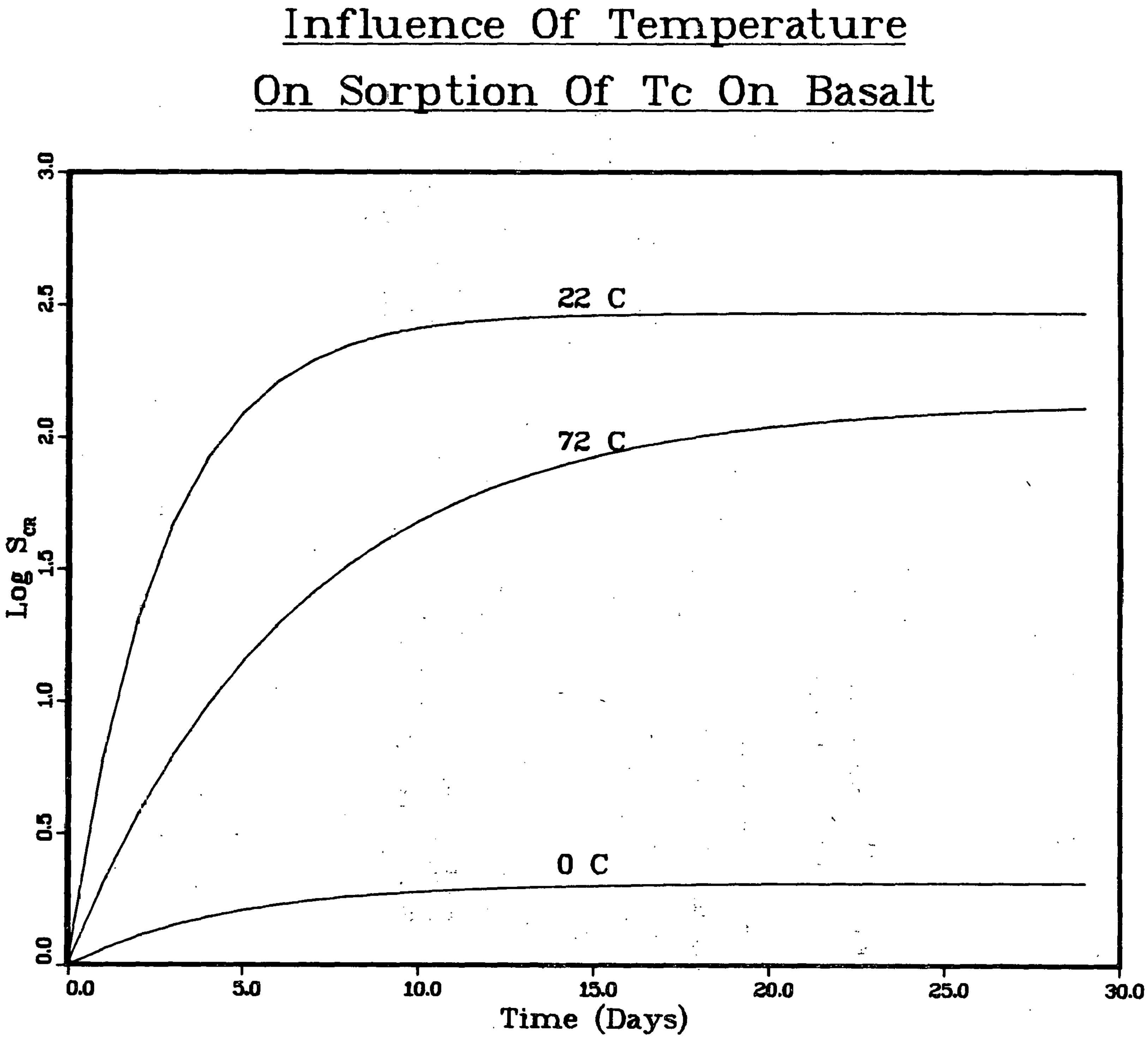

Influence Of Temperature On Sorption Of Tc On Basalt

FIG. 3

TABLE 3. ^{99}Tc Sorption (S_{CR}, ml/g on Unweathered Conasauga Shale (18-50 mesh) from 2 M NaCl Under Anoxic Conditions

Temperature °C	Time (Days)		
	5	12	13
0	0.50 ± 0.03	0.47 ± 0.11	0.58 ± 0.11
22	0.35 ± 0.04	1.09 ± 0.04	0.37 ± 0.03
72	1.38 ± 0.40	1.24 ± 0.11	1.73 ± 0.27

ence in sorption (expressed in terms of S_{CR}) of Tc-99 and Tc-95 on basalt (Table 4), except at 22°C. In this case, higher sorption was observed for Tc-99 (7×10^{-6} $\underline{M}$ Tc) than for Tc-95m (2.1×10^{-12} $\underline{M}$ Tc). Again, it is important to point out that in terms of mass of Tc sorbed, there was $> 10^6$ times more Tc-99 sorbed than Tc-95m, and final risk analysis involving Tc-99 migration from a repository should be directed at ultimate or permissible concentration of soluble Tc in the aqueous phase, rather than an arbitrary nonequilibrium "K_d" value.

Effect of Added Fe^{+2}: The addition of Fe^{+2} (9 μg/ml) to the No. 3 groundwater prior to the addition of Tc-99 did not appreciably change the sorption of Tc-99 on basalt (Table 5). On the other hand, Fe^{+2} additions to suspensions of basalt in No. 3 groundwater containing TcO_4^- effectively removed Tc from the solution phase (next section). The solubility of Fe^{+2} in No. 3 groundwater (pH 8.0, 58 μg HCO_3^-/ml) is considerably less than 1 μg Fe^{+2}/ml (Hem, 1967). Thus, the solubility of siderite may control the TcO_4^- reduction in basalt suspensions.

Effect of Solution:Solid Ratio of the Suspension: Increasing the solution:solid ratio of the suspension appears to significantly lower the S_{CR} of Tc (Table 6). This is probably due to the lower Fe^{+2} concentrations, and the greater probability of Fe^{+2} oxidation by dissolved oxygen in suspensions of larger solution:solid ratios. For example, we know Eh measurements in basalt suspensions decrease as the solution:solid ratio decreases (next section).

Sorption of Tc on Basalt in an Eh-pH Controlled Stirred Reactor

An anoxic stirred reactor was made from a small glass desicator (ID

TABLE 4. The Effect of Tc Concentration on Sorption of Tc on Sentinel Gap Basalt (18-50 mesh)[1]

Time Days	Sorption Concentration Ratio (S_{CR} in ml/g)	
	0°C	
	Tc-95m 2.1×10^{-12} $\underline{M}$ Tc	Tc-99 7×10^{-6} $\underline{M}$ Tc
1	0.37 ± 0.07	0.34 ± 0.10
3	0.68 ± 0.23	0.97 ± 0.28
7	4.83 ± 0.59	7.72 ± 5.88
	22°C	
1	1.31 ± 0.04	1.70 ± 0.51
3	5.98 ± 0.36	78.2 ± 98.6
7	29.1 ± 0.70	420 ± 197
	72°C	
1	3.20 ± 0.37	2.53 ± 2.48
3	14.1 ± 7.20	8.48 ± 9.14
7	30.4 ± 10.8	13.7 ± 15.1

[1] Data for Tc-95m are from two replicates, and for Tc-99 the data represents four replicates except at 72°C which were replicated ten times. Average solution:solid ratio for Tc-95m data was 1.47 ± 0.14 and 0.93 ± 0.05 for the Tc-99 data.

TABLE 5. Influence of Temperature and Fe^{+2} Additions on Tc Sorption on Sentinel Gap Basalt[1]

Time Days	Sorption Concentration Ratio (S_{CR} in ml/g)[2]				All Samples	
	0°C					
	$-Fe^{+2}$		$+Fe^{+2}$			
1	0.35	0.10[2]	1.03	0.57	0.68	0.53
3	0.97	0.28	1.33	0.89	1.18	0.68
7	7.72	5.88	2.17	1.06	4.79	4.91
	22°C					
1	1.70	0.51	3.00	1.53	2.53	1.26
3	78.2	98.6	17.6	16.9	22.6	15.7
7	420	197	51.4	56.3	236	238
	72°C					
1	2.53	2.48	5.48	4.00	3.37	3.14
3	8.48	9.14	22.3	12.6	12.7	11.8
7	13.7	15.1	11.4	10.8	13.0	13.5

[1] Treatment values represent four replicates except for the $-Fe^{+2}$ at 72°C which included ten replicates. Solution to solid ratio 0.96 ± 0.09 (ml/g), initial Tc concentration ca. 7×10^{-6} M.

[2] Ferrous iron (as $FeCl_2$) was added to deaerated simulated groundwater (equivalent to 9 μg Fe^{+2}/ml) prior to the Tc.

TABLE 6. Influence of Solution to Solid Ratio on S_{CR} of Tc-99 on Sentinel Gap Basalt[1]

Time Days	Sorption Concentration Ratio (S_{CR} in ml/g)	
	0°C	
	$\frac{\text{Solution}}{\text{Solid}}$ = 9.80 (mℓ/g)	$\frac{\text{Solution}}{\text{Solid}}$ = 0.96 (mℓ/g)
1	0.29 ± 0.04	0.34 ± 0.10
3	1.82	0.97 ± 0.28
7	0.05 ± 0.38	7.72 ± 5.88
	22°C	
1	0.93 ± 0.49	1.70 ± 0.51
3	3.55 ± 2.33	78.2 ± 98.6
7	4.41 ± 2.69	420 ± 197
	72°C	
1	3.27 ± 0.57	2.53 ± 2.48
3	4.42 ± 4.55	8.48 ± 9.14
7	3.55 ± 4.21	13.7 ± 15.1

[1] Data at solution:solid ratio of 9.8 are from two replications and for solution:solid ratio of 0.96, the data represent four replications except at 72°C which were replicated ten times.

of 16 cm) covered with ∿ 1.2 cm thick plexiglass. Through the plexiglass, two Pt electrodes (wire probe type - Fisher 13-639-115), and a glass combination pH and reference electrode (Ag-AgCl) connected to a Corning Digital 110 pH meter were used to monitor pH and Eh (corrected by adding 200 mv to the meter readings) of the suspension. The pH meter in turn was connected to a Brown strip-chart recorder (0.14 cm/min) that was modified to alternately record either the pH or Eh over 25 sec. intervals. The suspension was deaerated by flowing N_2 (99.997% pure general purpose or zero grade N_2) through a glass fritted diffusor. The solution (1500 ml of No. 3 PNL simulated basalt groundwater) was purged with N_2 at least 24 hours before the basalt (< 50 mesh) was added. After adding the basalt, the pH of the suspension was altered using 0.1 $\underline{N}$ HCl, and was continuously adjusted to the desired pH until the pH was stable overnight; thereafter, Tc (∿ 10^{-6} $\underline{M}$ Tc) was added. The concentration of TcO_4^-, Fe^{+2}, Eh, and pH were monitored over time. Ferrous iron was determined immediately after filtering a 10 ml aliquot through a 0.22 μm Millipore filter, using a modified bath-phenanthroline procedure (Lee and Stumm, 1960).

The objective of this work was to determine how the variables pH, Eh, Fe^{+2}, and solution:solid ratio affected sorption of Tc on Sentinel Gap basalt. Rather than attempting to establish equilibrium conditions (in terms of Tc sorption), emphasis was placed on determining how Eh, pH, Fe^{+2}, and solution:solid ratio affected the rate of Tc sorption. To do this, sorption in terms of S_{CR} was measured over time. For the most part, a linear relationship between S_{CR} and time in days was observed (Fig. 4 and Table 7). The rate of Tc sorbed on basalt in PNL No. 3 groundwater was determined for 25 environmental conditions. Values of pH ranged from 5.5 to 9.2, Eh from -0.140 to 0.625 volts, and solution:

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The Sorption Concentration Ratio S_{CR}
Of Tc On Sentinel Gap Basalt (<50Mesh)
In An Anoxic Stirred Reactor

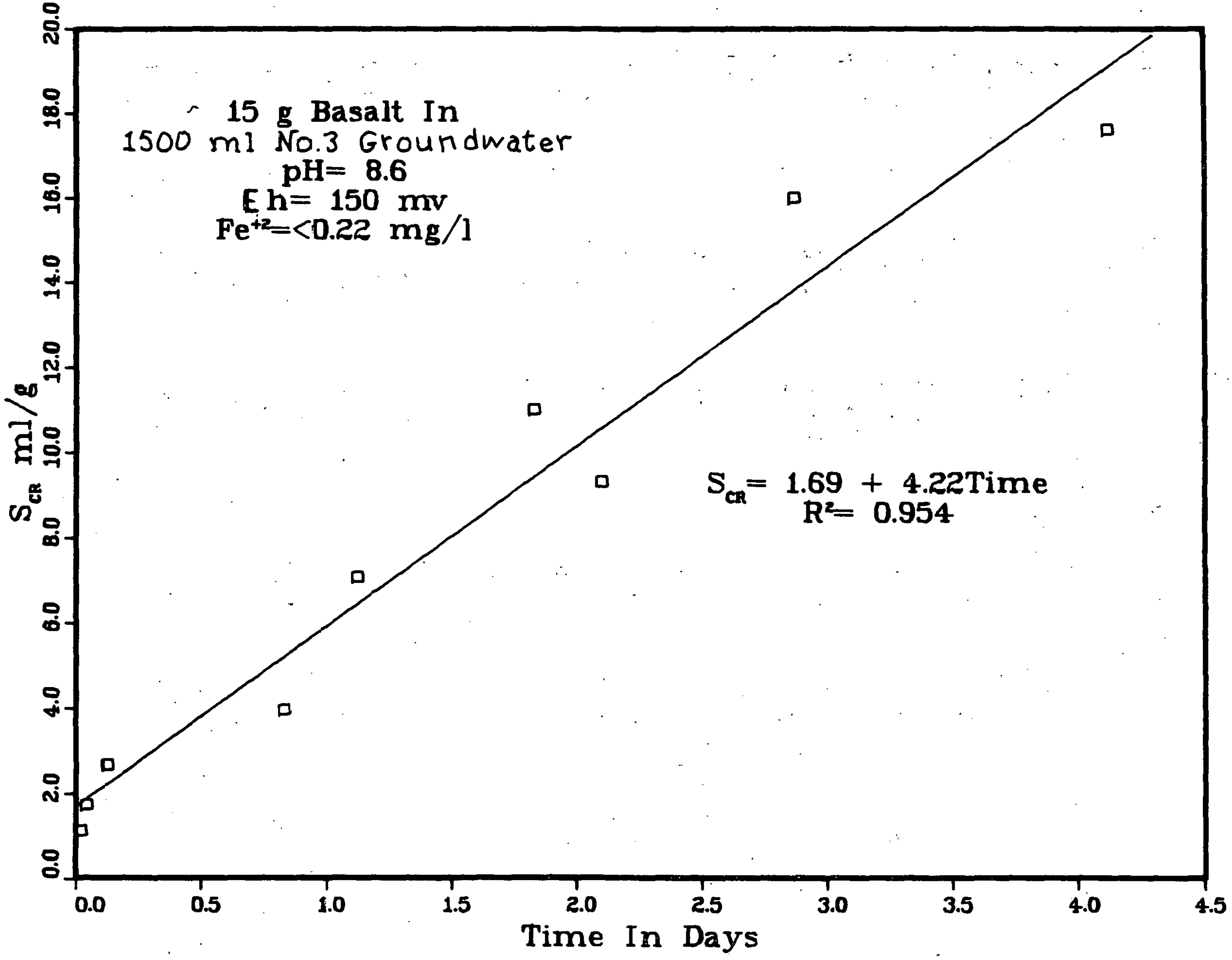

FIG. 4

TABLE 7. Loss Rate of Tc-99 on Basalt (< 50 mesh)

pH	Eh Volts	Solution/Solid	Rate ml/g/day	R^2	N	Time Days	Initial Tc μM
8.6	0.150	100	4.2	0.954	9	4.1	48.0
7.7	0.080	30	66.0	0.949	9	4.0	4.5
6.6	0.150	100	83.0	0.982	7	1.9	4.3
6.6	0.065	10	854.0	0.955	5	2.0	31.0
7.9	-0.037	30	264.0	0.986	7	1.3	4.2
8.1	-0.140	15	378.0*	0.990	6	1.0	6.7
7.5	0.300	50	1.9	0.434	3	2.0	5.6
6.5	0.340	25	7.2	0.980	3	1.7	5.6
5.5	0.420	50	1.8	0.838	3	1.9	5.6
5.5	0.440	25	5.5	0.704	3	1.9	5.6
8.5	0.205	25	7.3	1.000	2	1.0	5.6
9.2	0.410	50	< 0.01	na	3	2.0	5.6
8.9	0.490	25	< 0.01	na	3	2.0	5.6
7.5	0.480	50	< 0.01	na	3	2.0	5.6
7.5	0.475	25	< 0.01	na	3	2.0	5.6
6.5	0.590	50	< 0.01	na	3	2.0	5.6
6.5	0.410	25	< 0.01	na	3	2.0	5.6
5.6	0.625	50	< 0.01	na	3	2.0	5.6
5.6	0.450	25	< 0.01	na	3	2.0	5.6
9.0	0.240	50	0.68	0.472	3	2.0	5.6
8.8	0.220	25	< 0.01	na	3	2.0	5.6
8.8	0.178	15	0.62	0.664	6	5.0	5.6
8.1	0.085	100	< 0.01	na	9	5.0	7.7

*Worn magnetic stirrer exposed.

solid ratio (ml/g) from 15 to 100. The dissolution of Fe(II) from the basalt was monitored in each case, and supplemental ferrous iron was added in some instances. Contrary to some previous thinking, Tc sorption was not directly dependent on Fe^{+2} solution concentrations. The influence of Fe^{+2} on Tc sorption will be addressed in a following section.

Statistical Interpretation: Sorption rates less than 1 ml/g/day were deleted for statistical analyses leaving eleven observations. Multiple linear regression analysis of these data using the rate of sorption of Tc as the dependent variable revealed that Eh_a[1] was the single most important variable (Table 8). Slightly greater than 50% of the variation could be accounted for by the variables Eh and pH. Use of log rate, Eh_a, and log initial [Tc] increased the coefficient of determination (R^2). Thus, from these data we are able to quantitatively predict the loss rate of Tc knowing Eh, pH, Tc concentration, and solution:solid ratio.

Rate of Tc Loss Based on Thermodynamic Data: In the above section, the loss of Tc was found to be highly dependent on Eh_a. If the mechanism for sorption of Tc (loss of Tc from solution) is due to reduction of the TcO_4^- to the TcO_2, then the rate of Tc sorption should be a function of the reducing potential of the system. From Pourbaix (1966), the solubility of TcO_2 is based on the following equation:

$$TcO_2 + 2\ H_2O \rightleftarrows TcO_4^- + 4\ H^+ + 3\ e^-$$

or

$$Eh_c = 0.738 - 0.0788\ pH + 0.0197\ \log\ (TcO_4^-).$$

---

[1] Eh_a = Eh adjusted to pH 7 [Eh_a = 59.1 (pH-7.0) + Eh]

TABLE 8. Multiple Linear Regression Analysis of Tc Sorption Rate as the Dependent Variable

Variables			Coefficient of Determination R^2	F	P^a
Model Rate = f(pH, Eh, Eh_a, LCON, SSR)^b					
Eh_a			0.572	5.36	0.0333
Eh			0.332	4.48	0.0634
SSR			0.195	2.17	0.1740
LCON			0.182	2.00	0.1910
pH			0.001	0.01	0.9760
Eh_a	LCON		0.633	6.91	0.0180
Eh_a	SSR		0.588	5.69	0.0290
Eh_a	pH		0.572	5.36	0.0333
Eh_a	LCON	SSR	0.793	8.92	0.0087
Model LOG RATE = f(pH, Eh, Eh_a, LCON, SSR)					
Eh_a			0.881	67.9	0.0001
Eh			0.693	20.3	0.0015
SSR			0.112	1.1	0.3135
pH			0.039	0.4	0.5604
LCON			0.007	0.1	0.8034
Eh_a	pH		0.909	40.4	0.0001
Eh_a	SSR		0.902	36.9	0.001
Eh_a	LCON		0.883	30.2	0.002
Eh_a	pH	SSR	0.922	27.5	0.0003

[a] P = probability of greater F.

[b] Eh_a = Eh adjusted to pH 7 [Eh_a = 59.1 (pH - 7.0) + Eh]
LCON = log Tc conc.
SSR = solution:solid ratio
Rate = sorption rate of Tc (ml/g/day)

Thus,

$$Ra = f(Eh_c - Eh_m),$$

where Ra is the rate of Tc loss from solution (in our work expressed as ml/g/day), Eh_c is the calculated potential according to Pourbaix (1966), and Eh_m, the potential measured in the stirred reactor. If the loss of Tc is noted at $Eh_c - Eh_m < 0$, then either (1) the loss of Tc from solution is occurring by a mechanism different than precipitation of TcO_2, or (2) the standard free energy of formation value for TcO_2 listed by Pourbaix is incorrect. A likely mechanism is the formation of a compound other than TcO_2 which is being precipitated or sorbed to the basalt, i.e. $TcO(OH)_2$.

Linear regression analysis showed a high correlation between log Ra and $Eh_c - Eh_m$.

$$\log Ra = 2.09 + 6.45\ (Eh_c - Eh_m) \quad R^2 = 0.910$$

Expressed in a non-linear regression of the form (Fig. 5).

$$Eh_c - Eh_m = -0.241 + 0.330\ (1 - e^{-0.0117Ra})$$

When Ra = 0, $Eh_c - Eh_m = -0.241$ volts.

Thus, the Tc sorption data in the stirred reactors imply that the TcO_2 is formed 0.241 volts higher than predicted by Pourbaix (1966) assuming Eh_m values are valid. Another possibility is the formation of the $TcO(OH)_2$ and other reduced forms of Tc which would account for Tc losses observed in our experimental work. Regardless of the actual solid phase formed, TcO_4^- is lost from the solution phase and 'sorbed' on basalt (not necessarily as the TcO_4^-) at significantly higher Eh's than that predicted for TcO_2 (Fig. 6).

<u>Influence of Fe^{+2} on Sorption of Tc on Basalt</u>: In an earlier section,

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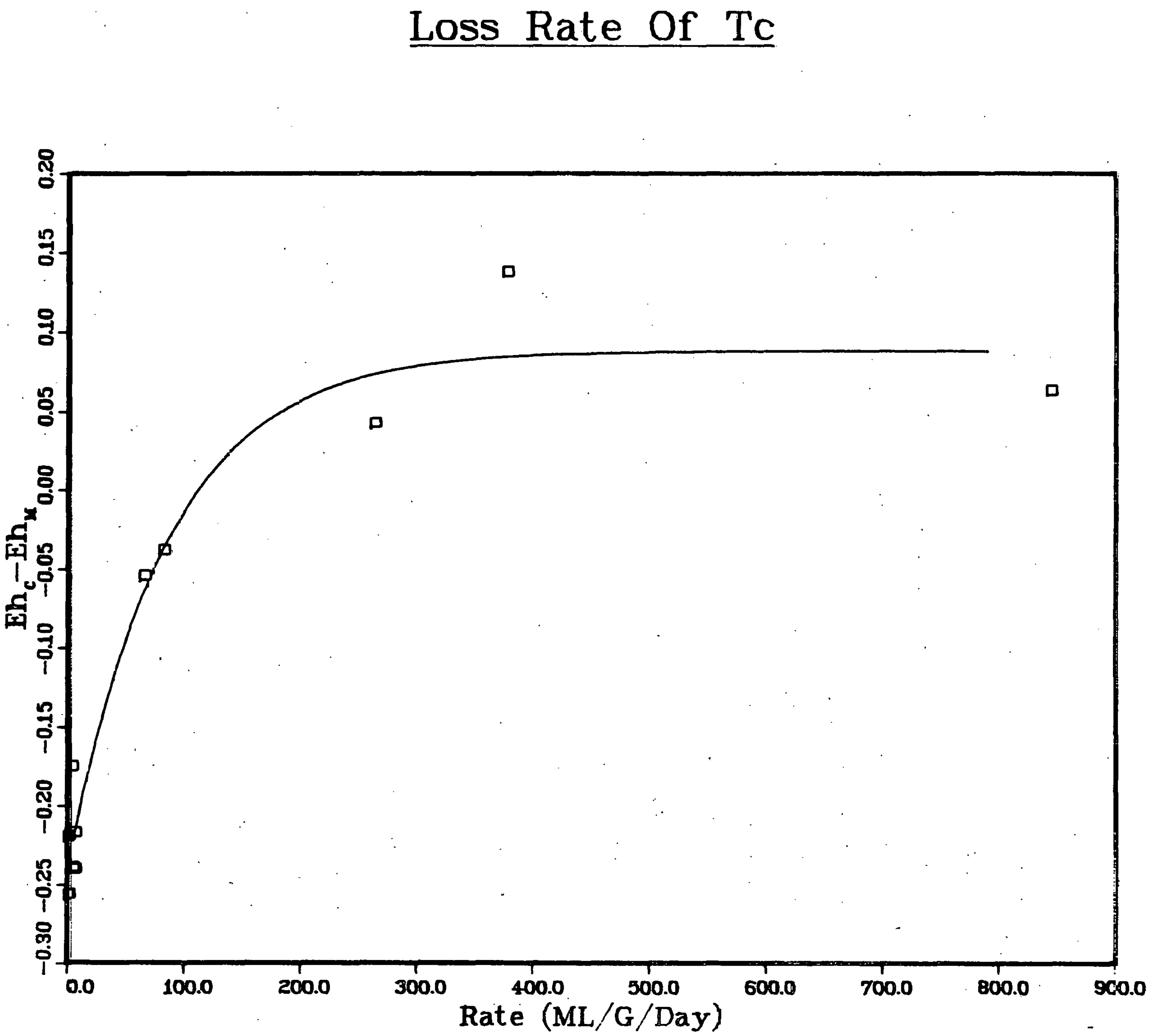

FIG. 5

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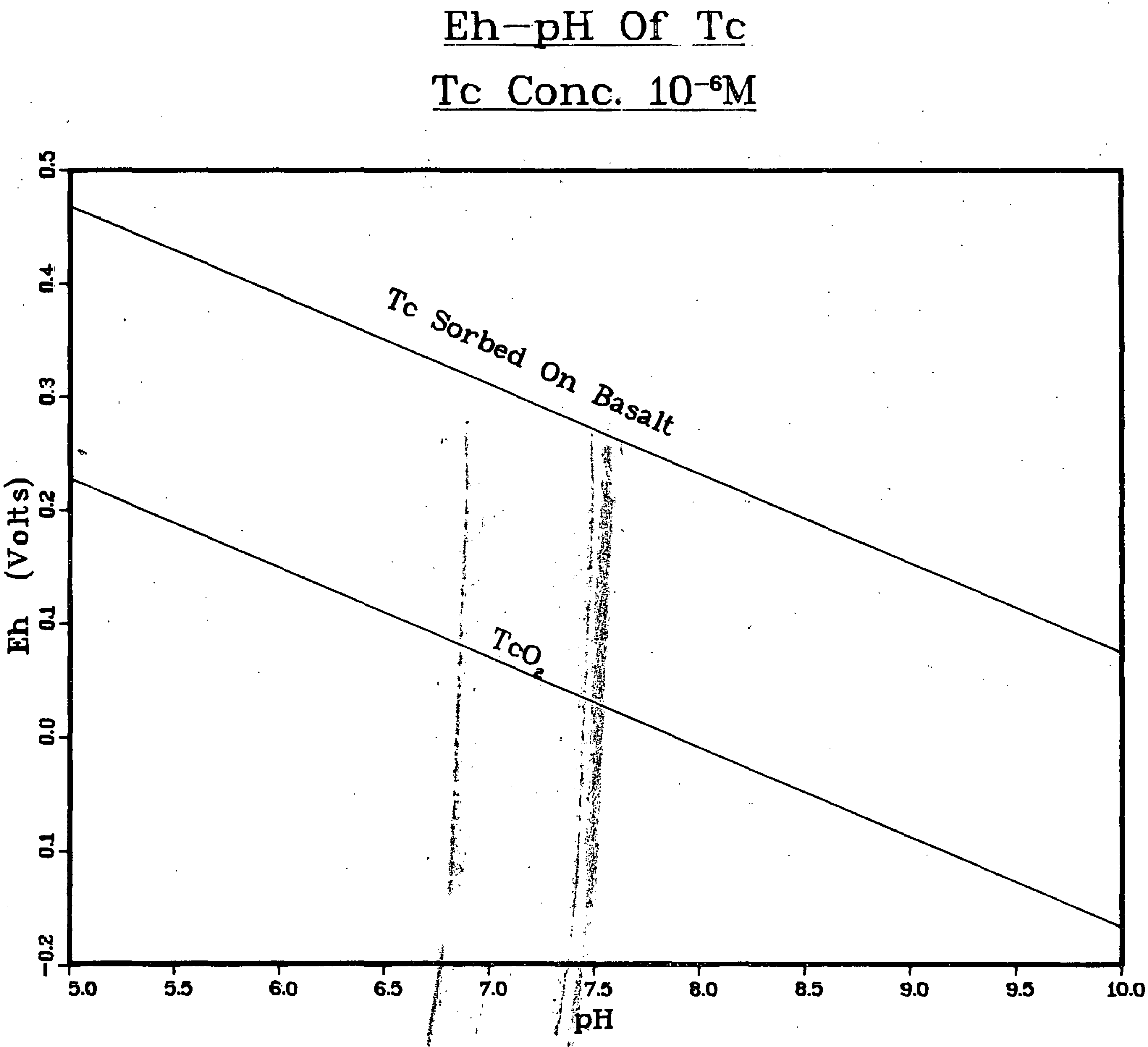
Eh–pH Of Tc
Tc Conc. 10^{-6}M
Eh (Volts)
0.5
0.4
0.3
0.2
0.1
0.0
0.1
−0.2
Tc Sorbed On Basalt
TcO_2
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
pH

FIG. 6

data were presented that showed additions of Fe^{+2} (161 μ M, 9 μg/ml) to PNL No. 3 groundwater did not significantly alter the S_{CR} of Tc on basalt. These data were obtained by adding the TcO_4^- following Fe^{+2} additions. However, if Fe^{+2} is added to an anoxic stirred reactor containing a suspension of basalt to which TcO_4^- had been previously added, the TcO_4^- concentration will rapidly decline. For example, ferrous (eq. 450 μ M or 25 ppm Fe) added to a reactor (15 g basalt in 1500 ml No. 3 groundwater) at an Eh = 140 mv, pH 8.6 containing 41 μ M Tc lowered the Tc concentration to less than 0.5 μ M in approximately one hour (Eh = -100 mv, pH = 8.5). Concentration of Fe^{+2} in the final solution was less than 5 μ M. The implication here is that TcO_4^- is not stable in the presence of ferrous iron; however, the data in Table 9 show that TcO_4^- is stable at concentrations of 3-5 μ M in presence of 30 to 50 μ M of ferrous. This occurs only at low pH values (< 5.5) in the PNL No. 3 groundwater where Fe^{+2} is solubilized from the basalt and soluble carbonates are purged from the suspension as CO_2 by the N_2 purge stream. The point here is that Fe^{+2} concentrations *per se* do not dictate TcO_4^- concentrations.

Loss of Tc from solution can be initiated by either adding ferrous iron or raising the pH (Table 9). Both actions precipitate Tc from solution. Measurements of Eh_m are significantly lower; however, adjusted to pH 7 (Eh_a) the redox potentials are not greatly different. In fact, in Reactor No. 1, Eh_a at pH 6.5 is significantly lower than at 5.9, yet the suspension at pH 6.5 supports approximately ten times the quantity of Tc. Tests confirmed that Tc in solution at pH 5.5 was present as the TcO_4^-, and not a reduced form (i.e., Tc was not precipitated in a solution of $FeCl_3$ adjusted to form a $Fe(OH)_3$ precipitate). These data indicate that Tc is co-precipitated with ferrous iron. Rimshaw (1961) observed

TABLE 9. Influence of pH Adjustment and Ferrous Iron Additions on Sorption of Tc on Basalt[1]

Reactor No. 1						Reactor No. 2					
Time hr	pH	Eh_m Volts	Fe μM	Tc μM	E°	Time hr	pH	Eh_m Volts	Fe μM	Tc μM	E°
72	9.0	0.250	< 6	5.64	1.063	72	8.8	0.350	< 6	5.55	1.147
72	7.5	0.290	< 6	4.55	0.986	72	7.5	0.260	< 6	5.43	0.955
72	6.5	0.225	< 6	5.28	0.841	72	6.5	0.340	< 6	3.83	0.959
72	5.5	0.400	32.6	5.14	0.938	72	5.5	0.400	53.1	3.50	0.941
Added Ferrous						Adjusted pH to 8.5					
2	5.9	0.310	110	0.47	0.900	2	8.5	0.190	4.5	2.71	0.969
32	5.9	0.340	83	0.81	0.925	32	8.5	0.225	1.8	2.59	1.005

[1] Reactor No. 1 contained 24 g of Sentinel Gap Basalt (< 50 mesh), No. 2 contained 48 g. Each reactor contained 1500 ml PNL groundwater. ${}^{99}Tc$ as TcO_4^- was added to each reactor equivalent to 6.25 μM. Ferrous chloride, equivalent to 168 μM, was added in 0.01 N HCl. $E° = Eh_m + 0.0788\ pH - 0.0197 \log Tc$; Average calculated E° = 0.969 ± 0.078.

the same and advocated that TcO_2 is isomorphically substituted into the magnetite lattice. There is no doubt that both Tc and Fe^{+2} are precipitated. It is well known that reduced forms of Tc are carried on $Fe(OH)_3$ precipitation, and it appears that under anoxic conditions Tc is precipitated with $Fe(OH)_3$. Presumably Tc(VII) is reduced to the Tc(IV) during the process; however, loss of Tc occurs at a higher energy potential (E°) than that cited for TcO_2 (Pourbaix, 1966). Calculation of E° ($E° = Eh_{m} + 0.0788\ pH - 0.0197\ \log Tc$) for these 12 observations gives nearly the same value (0.969 ± 0.078 volts) as that determined using the kinetic sorption illustrated in Figure 5 data (0.979 volts).

An experiment was carried out to determine the loss of TcO_4^- from an anoxic solution of the PNL No. 3 groundwater not containing basalt. In this case, the groundwater was acidified to pH less than 6, and additions of ferrous iron were added to evaluate the influence of ferrous iron concentrations on loss of TcO_4^- from solution. Adding Fe^{+2} equivalent to 56 μ M did not significantly reduce the TcO_4^- concentration after 3.5 hours (Table 10). Another equal increment of Fe^{+2} appeared to lower the TcO_4^- concentration, however, loss was relatively small (between 10 to 20%). Technetium was rapidly lost from solution when the pH was elevated to 7.5. For example, greater than 95% of the Tc was lost from the solution phase after 10 minutes (pH = 7.83, Eh = 0.100 volt). According to Pourbaix (1966), approximately 86 m M of TcO_4^- would be stable at this pH and Eh. Thus, as in the basalt suspensions, TcO_4^- is lost from solution at Eh-pH values significantly higher than that predicted by thermodynamic calculations if the mechanism for loss were the precipitation of TcO_2. A requirement for loss of TcO_4^- from solution is an anoxic environment, but the loss coincides with the loss of Fe^{+2} from solution. The mechanisms or the products of precipitation are not

TABLE 10. Influence of pH and Ferrous Iron on Loss of Tc from Solution (PNL #3 Basalt Groundwater)[a]

Time		Eh_m	Eh_c	Fe^{+2}	^{99}Tc	^{99}Tc
hr	pH	Volts		µM		%
	4.87	0.412		< 0.1	4.20	
[b]Added Ferrous Chloride						
0.17	5.55	0.308	0.258	48.3	4.20	100
0.33	5.57	0.300	0.246	46.4	4.10	97.6
1.00	5.65	0.282	0.230	51.0	4.12	98.2
2.00	5.60	0.275	0.239	51.0	3.94	93.6
3.50	5.62	0.282	0.239	44.6	4.16	99.1
29.5	4.83	0.336	0.375	50.7	4.24	101
[b]Added Ferrous Chloride						
0.0	5.48	0.265				
0.17	5.49	0.260	0.243	93.5	4.20	99.9
0.33	5.58	0.245	0.226	94.7	3.50	83.5
1.00	5.62	0.228	0.220	90.6	3.58	85.0
2.00	5.63	0.223	0.221	83.8	3.62	86.1
3.50	5.63	0.222	0.216	100.8	3.62	86.1
27.2	5.00	0.315	0.329	95.4	3.84	91.4
[c]Added Sodium Hydroxide						
0.01	7.48	0.239				
0.17	7.83	0.100	-0.164	66.8	0.20	4.9
0.33	7.54	0.045	-0.116	77.2	0.12	3.1
2.00	7.58	-0.045	-0.123	77.0	0.10	2.6
3.50	7.36	-0.043	-0.085	80.4	0.04	1.0
23.0	6.20	+0.120	+0.123	72.0	0.06	1.7
[d]Added Sodium Bicarbonate						
2.0	8.70	<-0.250	-0.265	8.6	0.04	1.0

[a] Measured, Eh_m, and calculated, Eh_c, values are also presented ($Eh_c = 0.771 + 0.0591 \log \frac{Fe^{+3}}{Fe^{+2}}$, $\log K_{sp}\ Fe(OH)_3 = -38.5$).

[b] Equivalent to 56 µM

[c] Used 0.1 M NaOH to raise pH

[d] Added ∿ 0.3 g solid

clearly defined, i.e., one assumes that loss is via reduction of TcO_4^- to Tc(IV), however, we have no definite proof that the sorbed form is in the reduced state. A likely mechanism is that precipitation of Fe^{+2} to magnetite activates the reduction of TcO_4^- to TcO_2. Because we observed the loss of TcO_4^- in alkaline environments at potentials significantly above the magnetite-hematite line, it is possible the Fe^{+2} is oxidized to Fe^{+3} while reducing TcO_4^- to TcO_2! The alkaline environment makes Fe^{+2} very unstable, and is oxidized to Fe^{+3} by furnishing electrons to the most available receptor (TcO_4^-) in the absence of an adequate supply of O_2. Loss of Tc probably occurs due to co-precipitation of Tc^{+4} with $Fe(OH)_3$. Because of the similarity in ionic radii (0.65 Å) of Tc^{+4} and Fe^{+3}, the precipitation of Tc is likely due to the isomorphic substitution of Tc^{+4} for Fe^{+3} ultimately forming mixed oxides of hematite (Fe_2O_3) or goethite (FeOOH) and TcO_2.

Dissolution of Tc Sorbed on Basalt: The column work presented in the earlier part of this report showed that Tc sorbed on basalt was returned to the solution phase on treatment with 5% H_2O_2 or weak bromate solutions indicating that the reduced form of Tc was reoxidized to TcO_4^-. To test how rapidly sorbed Tc was returned to the aqueous phase under oxic environmental conditions, a suspension of basalt in which Tc had been sorbed under anoxic conditions was purged with air. The aqueous phase was monitored for TcO_4^- over time (pH 7.5 to 7.7). The dissolution rate of Tc sorbed on basalt was on the order of 10^{-2} μ M/day, and presumably represented the oxidation of reduced Tc to the TcO_4^- (Fig. 7). This rate is significantly slower than the rate of sorption (reduction). For example, sorption which was carried out at pH 6.6 and Eh of 0.150 volts (15 g basalt in 1500 ml of PNL No. 3 groundwater) proceeded at 3.8

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Dissolution Of Basalt Sorbed Tc

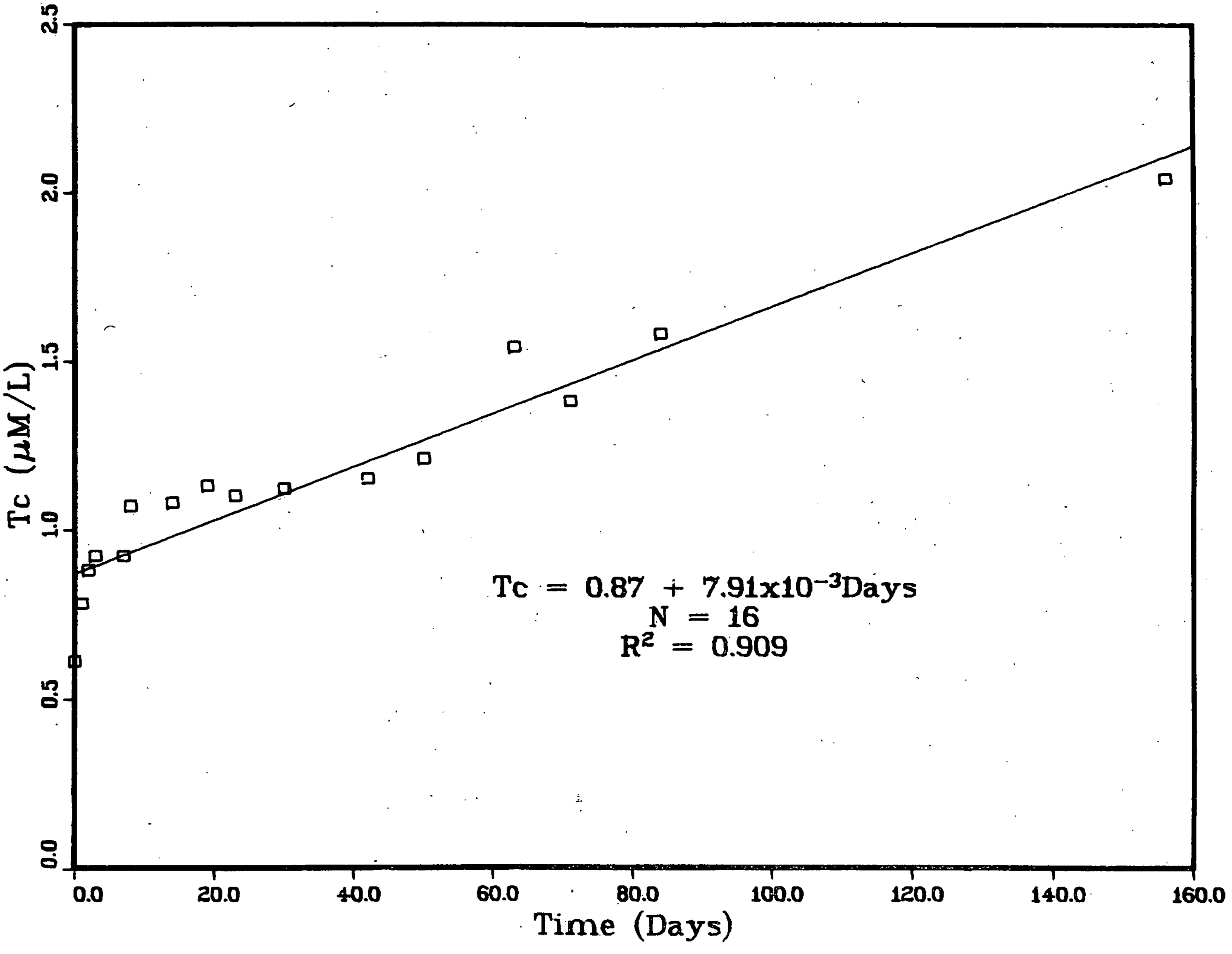

FIG. 7

μ $\underline{M}$/day. Thus, reoxidation of Tc with aerated suspensions is significantly slower than TcO_4^- reduction under anoxic conditions suitable for the formation of TcO_2. However, in terms of geological time, the oxidation rate is sufficiently fast to assure the conversion of any reduced Tc to the TcO_4^-.

To test the influence of pH on the dissolution of precipitated Tc, Tc was precipitated from solution (in the absence of basalt) by adding ferrous iron to a PNL No. 3 groundwater at pH 9.2 (Table 11). Within 1.5 hours, the concentration of Tc was less than 1.5% of the initial concentration. The concentration of Fe^{+2} was less than 2 μ $\underline{M}$ due to the precipitation as Fe hydroxides and carbonates. Lowering the pH to 5.5 - 6.0 released significant amounts of Fe^{+2} and Tc in less than one hour, indicating that under deaerated conditions the dissolution of precipitated Tc is related to the dissolution of iron. The soluble Tc was not tested to confirm if it was the TcO_4^- or a reduced form; however, it was assumed to be TcO_4^-, as we have not observed a reduced form in the aqueous phase except where appreciable quantities of soluble organic matter was also present. These data suggest that on acidification the Tc is reoxidized at the expense of ferric iron! Further work should be continued to confirm such a relationship.

SUMMARY AND CONCLUSIONS

In column studies, increasing residence times increased sorption of Tc on Sentinel Gap basalt (18-50 mesh) at both initial influent Tc concentrations of ca. 10^{-6} and 10^{-12} $\underline{M}$ using ^{99}Tc and ^{95m}Tc respectively. At the lower concentrations (10^{-12} $\underline{M}$) the sorption measured in terms of Sorption Concentration Ratio (S_{CR}, ml/g) ranged from 1.2 to 3.5 ml/g and were slightly higher than those (0.04 to 0.64 ml/g) measured at the

TABLE 11. Dissolution of Tc From an Iron Precipitate Suspension[1]

Time hr	pH	Eh Volts	Tc	Fe^{+2}
			μM	
0[2]	9.23	0.240	4.86	< 2
0.17	8.95	-0.210	0.17	< 2
0.33	9.00	-0.200	0.12	< 2
1.50	9.10	-0.170	0.08	< 2
- - - - - - - - - - Adjusted pH - - - - - - - - - -				
0.17	5.65	0.200	0.65	22
0.42	5.55	0.230	0.63	23
1.00	5.88	0.205	0.76	26
22.8	4.85	0.370	1.17	26
25.9	3.35	0.565	1.46	28

[1] PNL No. 3 groundwater purged with zero grade N_2

[2] Added $FeCl_2$ equivalent to 56 μM

higher influent concentration. However, in terms of actual number of grams of Tc sorbed on the basalt, there were approximately 10^6 times more Tc sorbed using ^{99}Tc at 10^{-6} M, than that observed using ^{95m}Tc at 10^{-12} M. Sorption had not reached equilibrium after seven days. Sorbed Tc was not easily exchangeable with 2 N NaCl, but could be rapidly eluted from the columns using 5% H_2O_2 or weak solutions of HBO_3, indicating the sorbed Tc to be a reduced form likely TcO_2 or its hydrated analog $TcO(OH)_2$.

In batch suspensions (solution:solid ratio of ca. 1) little difference was also noted in S_{CR}'s between initial Tc concentration of 10^{-6} and 10^{-12} M. Sorption increased with time (up to 30 days) and was higher at 22° and 72°C than at 0°C. Increasing the solution:solid ratio appears to have decreased the S_{CR} when using ^{99}Tc at Tc concentrations of 10^{-12} M. The difference was likely due to lower concentrations of Fe^{+2} in the solution phase, and differences in Eh and pH values between the two. However, no significant difference in S_{CR}'s were observed when Fe^{+2} was added to the solution phase before TcO_4^- additions. On the other hand, TcO_4^- was rapidly removed from solution when ferrous iron was added to stirred anoxic suspensions of basalt and TcO_4^-. In the alkaline PNL No. 3 groundwater containing carbonates, the ferrous iron concentrations are rapidly lowered to concentrations less than 6 μ M due to the formation of Fe hydroxides and carbonates ($FeCO_3$, siderite).

Experimental work in Eh-pH controlled stirred reactors revealed that loss of TcO_4^- from the solution phase was highly correlated to the Eh and pH of the suspensions. Initial loss rates (0-5 days) of Tc expressed as S_{CR}'s were found to increase linearly with respect to time. Loss of TcO_4^- from suspensions of basalt were observed over a pH range of 5.5 to 9.2, Eh's from 0.590 to -0.140 volts and solution:solid ratios ranging from 15 to 100. Loss of TcO_4^- from solution was observed at redox potentials significantly higher than those theoretically required to precipitate TcO_4^- as TcO_2. Loss of TcO_4^- appeared to be more dependent on the loss of ferrous iron from solution than any other measured variable. The mechanism of precipitation, or the form of Tc in the precipitate, are not clearly defined. It appears that as the solubility of ferrous iron is exceeded in alkaline pH's, ferrous iron is oxidized by TcO_4^- in the absence of O_2 to form a mixed precipitate of $Fe(OH)_3$ and $TcO(OH)_2$, ultimately forming mixed oxides of hematite (Fe_2O_3), goethite (FeOOH) and possibly magnetite (Fe_3O_4) depending on Eh and TcO_2. The similarity in size of the ionic radii of Tc^{+4} and Fe^{+3} (0.65 Å) suggests that Tc^{+4} isomorphically substitutes for Fe^{+3} during the precipitation of $Fe(OH_3$. At pH 5.0, 2 μ M of Tc was found to be stable in the presence of 100 μ M of ferrous iron. Thus, the mere presence of ferrous iron at these pH's does not dictate that TcO_4^- will be reduced to an insoluble form. Loss of Tc from solution appears to be highly correlated with the simultaneous loss of ferrous iron from the solution phase.

These experiments have shown that loss of TcO_4^- from solution is dependent on the solution chemistry of the system. The major role of the sorbent is providing a source of soluble ferrous iron, or ferrous readily available on the surface of the sorbent, which in alkaline environments in absence of an adequate supply of molecular oxygen, will reduce the TcO_4^- to the insoluble reduced form. Thus, TcO_4^- will not likely be stable in alkaline groundwater depleted in oxygen in contact with rocks rich in reduced forms of iron.

Interaction of U, Np, and Pu with Rocks

The objectives of this work are to (1) evaluate the sorption-desorption of U on basalt under anoxic and oxic conditions, (2) evaluate the sorption-desorption of Pu on rocks at solution concentrations below the solubility of Pu in water, and (3) evaluate sorption of Np(V), U(VI), Pu(V & VI), and Pu(IV) on Rustler formation materials.

Sorption-Desorption of U on Basalt
Anoxic vs. Oxic

Uranium-237 as U(VI) was used to evaluate the sorption of U on S-1 Granite under anoxic and oxic conditions. Simulated groundwater (PNL No. 3) containing ^{237}U was purged overnight with N_2 scrubbed through an alkaline solution of dithionite and pyrogallic acid to remove dissolved oxygen. Approximately four ml of this solution were added to 15 ml glass vials containing four grams of granite (18-50 mesh) which had been purged of O_2 as described in the previous section on batch sorption measurements with TcO_4^- on basalt. Sorption was measured over time at three temperatures (0, 22, and 72°C). Controls, consisting of solutions and rocks which were not purged with N_2, were used to monitor sorption under oxic conditions at the same temperatures.

Granite suspensions purged with N_2 revealed significantly higher S_{CR}'s of U at 72°C than suspensions at the same temperature not purged with N_2 (Table 12). An increase in temperature appeared to have enhanced sorption of U on granite at 72°C compared to sorption at 0 or 22°C. These data suggest that U(VI) may be reduced to U(IV) under anoxic conditions. Interpretation of the data in this manner should be viewed with caution, however, as purging the PNL No. 3 groundwater with N_2 significantly increases the pH of the solution, and may lower the concen-

TABLE 12. ^{237}U Sorption (S_{CR}, ml/g) on S-1 Granite from PNL No. 3 Groundwater

Temperature °C	Time (Days) 15	36
Anoxic		
0	9.28 ± 2.35	5.67 ± 0.56
22	3.86 ± 1.70	5.59 ± 3.88
72	20.3 ± 7.7	32.3 ± 12.5
Oxic		
0	4.35 ± 1.74	3.39 ± 0.01
22	2.28 ± 0.72	5.31 ± 2.16
72	2.88 ± 0.30	7.22 ± 5.21

Anoxic data are averages from four replicates, oxic data are averages from two replicates.

TABLE 13. Desorption of ^{237}U from S-1 Granite[1]

Temperature °C	Sorption Conditions (36 Days) Anoxic	Oxic
	D_{CR}, ml/g	
0	5.01 ± 0.43	3.39 ± 0.72
22	14.2 ± 0.5	15.1 ± 2.7
72	22.1 ± 7.3	27.8 ± 24.5

[1] Desorption under oxic conditions at room temperature ca. 22°C in PNL NO. 3 groundwater after a 5-day equilibrium. Average of two replicates.

tration of CO_3^{-2} available to complex the U(VI). Purging 20 hours with the N_2 stream raises the pH of PNL No. 3 groundwater from approximately 8.0 to 9.0-9.2. It is likely that sufficient CO_3^- remains to complex the U(VI), concentrations on order of 10^{-13} M; thus, the higher S_{CR} observed at 72°C under anoxic conditions may represent reduction of U(VI) to (IV). Subsequent desorption of U sorbed under oxic and anoxic conditions, however, indicated that if U(VI) was reduced to U(IV) under the anoxic sorption conditions, the U(IV) was rapidly oxidized to U(VI), Table 13. Desorption at the higher temperatures (22 and 72°C) was significantly less than at 0°C. Only at 0°C were the sorption-desorption concentration ratios similar indicating equilibrium conditions.

Sorption-Desorption of Pu on Rocks

Very high "K_d's" of Pu are encountered when rock sorption experiments are conducted. This occurs because Pu(IV) is extensively hydrolyzed in neutral solutions and interacts strongly with rock surfaces. In a waste repository, the concentration of Pu leaching from source materials will be low simply because of the low solubility of Pu in water.

In order to evaluate Pu K_d's under realistic conditions, two experiments were conducted. First, Sentinal Gap basalt, Westerly granite, and argillaceous shale were contacted with $^{238}Pu(V)$ in 10^{-3} M $NaHCO_3$. Plutonium-238 was added as Pu(V) to avoid the problems encountered when Pu(IV) is added to neutral solutions from acid Pu stock solutions. If Pu(IV) is added to a neutral solution at concentrations > 10^{-12} M, the aqueous phase is supersaturated with respect to Pu(IV). However, if Pu is added as Pu(V), the added Pu(V) is rapidly reduced to Pu(IV), the quantity depending on the amount of ferrous iron leaching from the rock.

The unreduced Pu(V) is then removed from the rock with two N NaCl washes. Thus, the Pu which subsequently 'desorbs' represents surface-associated Pu(IV). While 99.9% of the added Pu remained with rocks, the concentration of the dissolving Pu [Pu(IV) determined by valence analyses] was low enough to insure that with subsequent dilution in an aquifer, the concentrations were below natural α-emitters like Ra-226. This is illustrated in Table 14.

For this experiment, the desorption K_d's were on the order of 10^4, and the third desorption K_d was not significantly different from the first desorption K_d. The molar Pu concentration ranged between 7.9×10^{-13} and 1.2×10^{-14}. Desorption K_d's are probably more representative than adsorption K_d's, since it is almost impossible to avoid some Pu(V) formation during the spiking of experiments with Pu(IV).

We have then examined what the sorption behavior of 10^{-13} M Pu-238 would be if solution-stable Pu was contacted with basalt and granite chips. Sorption and desorption results are presented in Table 15.

Sorption of Pu-238 (10^{-13} M) in 10^{-3} M $NaHCO_3$ on basalt and granite chips (surface area, approximately 3 to 10 cm^2) showed that Pu-238 concentrations reached a minimum in about 20-30 days. K_d's were on the order of 10 ml/cm^2. Final Pu-238 concentrations were approximately 10^{-14} M and were largely Pu(V). The initial solution contained approximately 10% Pu(V) and 90% Pu(IV), which had been stable with respect to its Pu concentration (10^{-13} M) for six months. Desorption with 10^{-3} and 10^{-2} M $NaHCO_3$ solutions revealed basalt-sorbed Pu was less leachable than granite-sorbed Pu. Carbonate complexes are suggested by the lower K_d's. This experiment does not say much except to point out the importance of valence states in sorption experiments.

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TABLE 14. Successive Desorption "K_d's" (one month intervals) of Pu-238 Initially Added as Pu(V), Followed by Two NaCl Washes[1]

Rock	N	"K_d" x 10^{-4} (ml/g)			Log M of desorbed Pu[2]
		1	2	3	
basalt	4	2.0 ± 1.0	3.0 ± 0.7	2.2 ± 1.2	-12.9 to -12.4
granite	4	2.3 ± 2.3	1.0 ± 0.5	3.3 ± 2.8	-13.0 to -12.1
shale	4	9.9 ± 11.0	30.0 ± 23.0	5.7 ± 2.2	-13.9 to -12.3

[1] Desorption conducted in the presence of synthetic groundwater (PNL #3, see Table 2)

[2] -13.2 is equal to 1 pCi Pu-239/liter

TABLE 15. Surface Area K_d's for Pu-238 (10^{-13} $\underline{M}$, Stable in Solution of 10^{-3} $\underline{M}$ $\mathrm{NaHCO_3}$, pH 8.4 for Six Months)[1]

Time	Granite	Basalt
Sorption		
Days	K_d (ml/cm^2)	
0.75	0.2	0.4
10.0	2.0	3.0
20.0	3.3 ± 0.1	8.0 ± 0.7
40.0	5.6 ± 0.4[2]	9.2 ± 0.9[2]
Desorption		
After 14 Days in		
10^{-3} $\underline{M}$ $\mathrm{NaHCO_3}$	100 ± 50	100 ± 50
10^{-2} $\underline{M}$ $\mathrm{NaHCO_3}$	9 ± 3	46 ± 20
10^{-1} $\underline{M}$ $\mathrm{NaHCO_3}$	1.6 ± 0.2	28 ± 10

[1] Sentinel Gap basalt and Westerly granite chips with estimated surface areas ranging from 3.7 to 8.4 cm^2 in 5 ml of 10^{-3} $\underline{M}$ $\mathrm{NaHCO_3}$, pH 8.4 (S areas geometrically estimated).

[2] Over 90% of the soluble Pu in these final solutions was Pu(V) originally present in the stock solution. A small portion of the Pu(V), between 10-15%, was reduced by the rock chips. The desorption K_d's, however, represent only the loss at Pu(IV) from the rocks surface, thus if the Pu(V) concentrations were subtracted from the soluble Pu, the resulting Kd would be about 100 or close to the desorption Kd in 10^{-3} $\underline{M}$ $\mathrm{NaHCO_3}$.

Neptunium(V), U(VI), Pu(V), and Pu(IV) Sorption on Rustler Formation Materials

Culebra (dolomite) and Magenta (gypsum) materials sent to the WISAP contractors and characterized in PNL-2797 (Ames, 1978) were equilibrated with deionized water and air for one week. The solutions were filtered, evaporated until precipitates formed, and re-filtered. Chemical analysis (Table 16) showed that the Culebra solution is essentially saturated with respect to dolomite (Culebra solution, 14.3 ppm Ca, 8.36 ppm Mg, 69 ppm total CO_2, pH 8.6). The Magenta solution data (6.05 ppm Ca, 3.67 ppm Mg, 17 ppm total CO_2, pH 7.8) would need speciation analysis to ascertain species distribution because of sulfate. However, it is likely near saturation also. The respective solutions were tagged with the respective elements and oxidation states, and except for Pu(IV), all were solution-stable (one month). The Pu(IV)-tagged solutions were immediately added to the rocks. Washed, 20-50 mesh rocks were used, 10 grams to 10 ml of equilibrating solution (Table 16).

Table 17 indicates that K_d's for U(VI) are lower than Np(V) for both rocks. This is due to the stronger carbonate complexes for U(VI). Culebra sorbed both elements more strongly than Magenta. Plutonium was not stable and was reduced as the increasing K_d's of the Pu(V) work suggests. Unpublished work suggests that Np(V) and Pu(V), as well as U(VI) and Pu(VI) should have about the same K_d (i.e., each oxidation state is similar). Based on desorption and added U-233 experiments, the K_d's for Np and U appear to be truly equilibrium values, that is, sorption K_d equals desorption K_d. Not so for Pu(V).

Tetravalent Pu was sorbed more strongly than the other oxidation states, and during the desorption tests, Pu(IV) actually came into solution from the Magenta since the soluble desorption concentration was

TABLE 16. Chemical Analyses of Solutions Equilibrated with Rustler Formation Rocks[1]

	Rock	
Element	Magenta	Culebra
	- - - -μg/ml- - - -	
Ca^{2+}	605	14.3
Mg^{2+}	3.67	8.36
Na^{+}	4.4	1.06
K^{+}	20.0	0.54
SO_4^{2-}	1590	4.45
F^{-}	0.13	0.17
Cl^{-}	10.4	3.24
CO_3^{2-} (total)[2]	17.0	69.0
SiO_2	1.89	11.3
P	0.02	0.014
	- - - -ng/ml- - - -	
Mn	4.4	1.2
Fe	1.9	1.6

[1] Supplied by WISAP

[2] Total alkalinity

TABLE 17. Oxidation States of Np, U, Pu Show Variable Sorption Behavior Towards Rustler Formation Rocks

Both Np(V) and U(VI) show stable valence, and reversible behavior; Pu(V) is reduced to Pu(IV) which shows much higher sorption. Underlined values are assumed to be near equilibrium K_d's. Magenta solution pre-rock equilibrated (pH 7.8; total alkalinity 17 ppm). Culebra solution pre-rock equilibrated (pH 8.6; total alkalinity 69 ppm).

Rock	Time Days	K_d, ml/gram (± S.D.)			
		^{239}Np(V)	^{237}U(VI)	^{236}Pu(V)	^{236}Pu(IV)
Magenta	Sorption				
	0.13	2.2(.8)	1.7(.1)	--	--
	2	4.7(.6)	2.4(.1)	2.6(.2)	--
	7	6.6(.5)	2.2(.1)	103(7)	382(17)
	9	--	--	--	403(7)
	Desorption				
	2	--	3.5(.1)[1]	> 200	
	5	6.5(.3)	2.5(.5)	> 200	
	7	--	--	--	450(5)[3]
Culebra	Sorption				
	0.13	29(.7)	6.9(.3)	--	
	2	127(2)	11.0(.3)	--	
	3	187(3)	12.1(.4)	65(6)	
	5			118(4)	
	7	199(4)	11.1(.4)	148(5)	769(30)
	9				2136(34)
	Desorption				
	2		17.5(.2)[2]	> 200	
	5	199(3)	15.7(.2)	> 200	
	7				3027(20)[4]

[1] U-233 added with re-equilibration solution had K_d = 3.6(.2)

[2] U-233 added with re-equilibration solution had K_d = 14.6(.5)

[3] Pu did come into solution upon contact with fresh solution

[4] Pu continued to be lost from solution (i.e., less found in solution than left with the original aqueous phase not removed to determine adsorption).

larger than the small amount left when the adsorption-phase solution was largely withdrawn. For Culebra, however, the total soluble Pu after seven days of desorption was actually less than the soluble Pu left with the rock when the adsorption phase solution was withdrawn. This data and the suggested reduction of Pu(V) to Pu(IV) by both rocks, indicated that the Pu K_d's are greater than 400 for Magenta and greater than 3000 for Culebra. For Pu, we use "K_d" to compare with the Np and U results; no equilibrium condition was established for this "K_d". These results are interesting because they point out the importance of carbonate in affecting K_d's of Np and U. Granted the proof is not here, but our experience with the two actinide oxidation states indicates this is a valid statement. More definitive work will follow.

QUESTIONS AND ANSWERS

ORNL-II

Residual Time or Kinetics or Nuclide Concentration

Q: Did you do the experiment more than once?

A: No, but I have another one showing the resolution, and the effective time on, say, 1 day, 3 days, and 7 days. At the 1-day residence time, we can recover about 75% of it. Going down to the 3-day residence time, it is approximately 50%, and of course, at the 7-day residence time, which implies that over time adsorption is enhanced. Apparently, more of the pertechnetate is being reduced in the column.

Q: You really say you have an isotope separation process between 95 and 99. I mean the previous one.

A: It is a mass difference, yes. Actually, we would be better off not even putting 99 or 95 m in there. One had a concentration of 10^{-12}. The other had a concentration of 10^{-6}.

Q: I know that Eh is very difficult to measure, but I noticed that, Chet, you had Eh measurements of 0.014 to 0.625 volts measured over a long period of time. What was the drift in those measurements, and were you successful in measuring them accurately?

A: There is certain amount of drift, I'd say for the most part less than 10 or 15%. But that brings up an extremely good point. So many of the presentations or the reports say under anoxic conditions, but what does it really mean? This is very important, because it makes a lot of difference between anoxic at pH 7 and 0.20 volts versus 0.14.

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LABORATORY STUDIES OF Pu-237 SORPTION ON SELECTED MINERALS UNDER ANOXIC CONDITIONS

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C. D. Washburne and W. J. Martin

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INTRODUCTION

An objective of the Waste Isolation Safety Assessment Program (WISAP) is to develop the capabilities needed to assess the post-closure safety of geologic repositories for radioactive waste. In support of this objective, scientifically defensible generic and site specific data necessary for safety assessments must be obtained. The sorption behavior of plutonium was studied as a part of WISAP Task 4 (Sorption/Desorption Analysis) to obtain defensible generic data, and to evaluate the methodology used for measuring sorption Kd values.

Twelve selected minerals and four solutions were used to investigate the sorption behavior of plutonium (Relyea et al. 1979) under ambient atmospheric conditions ($pO_2 \simeq 0.7$). The lack of atmospheric oxygen at depths proposed for geologic repositories presents the possibility of an anoxic environment for waste migration, thus the plutonium behavior study has been replicated under anoxic conditions ($pO_2 \simeq 2.7$).

Sorption of plutonium by a particular mineral, rock or soil can be expressed by the Kd value,

$$Kd = C_A/C_S \qquad (1)$$

where:

C_A = Pu concentration in the adsorbed phase (dpm/g) and
C_S = Pu concentration in the solution phase (dpm/ml)

giving the Kd units of ml/g. Complete sorption of Pu by a mineral yields an infinite Kd value while the other extreme (no mineral adsorption of Pu) gives a Kd value of zero. A zero Kd allows the nuclide to move with the velocity of the ground water. As the Kd increases, nuclide movement is retarded.

METHODS AND MATERIALS

Bulk samples of twelve common minerals were obtained from Ward's Natural Science Establishment Inc. These minerals were characterized chemically, physically and mineralogically (Ames 1979).

The phyllosilicate minerals (kaolinite, montmorillonite, illite, biotite and vermiculite) were separated by sedimentation to obtain the fraction less than 2.0 μm. Kaolinite, illite and montmorillonite were further treated with pH 5 sodium acetate to remove $CaCO_3$ and with 30% H_2O_2 to destroy organic matter. The tektosilicates (quartz, albite, anorthite and microcline) and inosilicates (hornblende, enstatite and augite) were crushed to pass through a No. 140 sieve ($<$106 μm). All twelve minerals were washed with NaCl or $CaCl_2$ (depending upon the solution to be used in the sorption study) to saturate exchange sites. Minerals were weighed in tared polycarbonate centrifuge tubes (0.50 g per tube) and washed three times with one of the four untraced solutions. After the third wash, sample tubes were reweighed to determine the excess solution left by washing.

Synthetic ground waters were prepared using reagent grade chemicals and distilled water. The four solutions used were 1) 5.13 $\underline{N}$ NaCl at pH 7.0, 2) 0.03 $\underline{N}$ $CaCl_2$ at pH 7.0, 3) 0.03 $\underline{N}$ NaCl at pH 7.0, and 4) 0.03 $\underline{N}$ $NaHCO_3$ at pH 8.2. Adjustment of pH prior to tracer addition was made as needed with NaOH or HCl.

A portion of each solution was filtered through a 0.45 m membrane and spiked with ^{237}Pu from an acid stock solution ($\approx$4 $\underline{M}$ HCl). Solutions were allowed to equilibrate for seven days with pH adjustments made as needed. Spiked solutions were filtered again before adding 15 ml aliquots to tubes containing the mineral samples. Blank tubes (15 ml of spiked influent solution with no mineral adsorbent) were used for determination of influent concentration and container wall adsorption.

Samples were shaken at about 60 oscillations per minute in a plexiglass box connected by tygon tubing to a modified Forma® anaerobic chamber. Samples were removed from the shaker for analysis after cumulative shaking periods of 3, 10 and 30 days. Solid and liquid phases were separated by centrifuging sample tubes at 6000 rpm (800 g*) for 20 minutes. Aliquots of 10 ml were placed in plastic liquid scintillation vials for gamma counting in a 5-in. by 5-in. Bicron well type NaI(Tl) crystal. Measurements of pH and Eh were made on the slurry left in the sample tubes before returning the 10 ml counting aliquot for further shaking. Eh measurements were made with a commercial bright Pt electrode versus a calomel reference electrode.

Samples were run in triplicate using the blank-corrected batch method. Calculation of Kd values was carried out using the equation

$$Kd = \left(\frac{rAi - Ae}{Ae}\right)\left(\frac{v + x}{w}\right) \tag{2}$$

where:

r = ratio of spiked solution volume (v) to the total solution volume (v + x).
v = volume of spiked solution added to sample tubes (15 ml).
x = volume of excess solution left after the third cold wash (ml).
Ai = activity in solution from blank tubes (influent, dpm/ml).
Ae = activity in solution from sample tubes (effluent, dpm/ml).
w = mass of mineral used for sorption (0.50 g).

RESULTS AND DISCUSSION

Results from the anoxic Pu adsorption experiment are shown in Tables 1 through 4. Plutonium adsorption distribution coefficients Kd(Pu) under anoxic conditions were generally higher for the phyllosilicates than for either the tektosilicates or inosilicates. Comparison of Kd(Pu) values between ambient and anoxic environments or among solutions in an anoxic

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* $g = 980 \text{ cm/sec}^2$.

TABLE 1. Pu Adsorption in Reduced Oxygen Atmosphere (NaCl 5130 meq/ℓ)

Mineral	3 Days			10 Days			30 Days		
	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	6.5 ±0.2	464 ±76	3090 ±820	7.2 ±0.2	≤0	1420 ±590	6.8 ±0.4	394 ±28	≥1200
Montmorillonite	8.3 ±0.2	738 ±18	694 ±25	8.2 ±0.1	407 ±198	845 ±65	8.1 ±0.4	521 ±17	440 ±105
Vermiculite	8.3 ±0.5	733 ±41	448 ±105	8.5 ±0.1	833 ±94	685 ±147	8.5 ±0.1	560 ±49	>998 ±453
Biotite	8.5 ±0.2	744 ±21	360 ±72	8.3 ±0.1	638 ±33	641 ±47	7.9 ±0.2	533 ±50	>964 ±512
Kaolinite	6.7 ±0.3	464 ±258	967 ±500	6.4 ±0.2	266 ±128	389 ±53	6.0 ±0.4	438 ±109	343 ±216
Quartz	7.0 ±0.5	520 ±189	1060 ±307	6.5 ±0.1	505 ±168	351 ±48	7.1 ±0.3	529 ±96	251 ±157
Albite	8.7 ±0.4	491 ±108	3620 ±2210	8.5 ±0.1	≤0	1175 ±309	8.0 ±0.4	488 ±64	≥1260
Anorthite	8.8 ±0.1	551 ±184	3160 ±3090	8.3 ±0.2	407 ±104	486 ±34	8.2 ±0.4	477 ±53	423 ±197
Microcline	8.7 ±0.8	393 ±403	4670 ±2240	8.2 ±0.3	606 ±38	939 ±407	8.2 ±0.3	530 ±75	≥1170 ±150
Hornblende	8.7 ±0.4	463 ±127	1002 ±175	8.5 ±0.1	621 ±35	949 ±178	8.1 ±0.3	509 ±16	730 ±470
Enstatite	8.6 ±0.3	686 ±60	886 ±163	8.4 ±0.3	335 ±92	497 ±276	7.5 ±1.5	467 ±49	245 ±46
Augite	9.3 ±0.2	571 ±149	1141 ±495	9.1 ±0.2	405 ±205	633 ±117	8.7 ±0.1	541 ±27	≥1260

TABLE 2. Pu Adsorption in Reduced Oxygen Atmosphere ($CaCl_2$ 30 meq/ℓ)

Mineral	3 Days			10 Days			30 Days		
	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	7.3 ±0.4	724 ±8	13,420 ±4,940	7.8 ±0.1	375 ±206	≥9550	7.9 ±0.2	162 ±81	≥1090
Montmorillonite	8.1 ±0.0	785 ±16	5,657 ±644	7.7 ±0.1	622 ±48	≥9550	8.1 ±0.2	398 ±186	≥836 ±492
Vermiculite	8.0 ±0.2	758 ±38	6,770 ±2,140	7.9 ±0.0	109 ±98	≥6020 ±2480	8.2 ±0.2	474 ±47	≥948 ±266
Biotite	8.3 ±0.1	818 ±20	≥2x10^4	7.9 ±0.1	674 ±329	3840 ±1270	8.1 ±0.1	452 ±109	≥974 ±252
Kaolinite	6.9 ±0.0	±693 ±3	4,550 ±1,300	8.2 ±0.1	516 ±116	≥9550	8.3 ±0.2	414 ±51	≥880 ±380
Quartz	8.1 ±0.5	721 ±72	2,690 ±2,040	8.2 ±0.1	416 ±42	1060 ±990	8.2 ±0.1	223 ±34	588 ±383
Albite	9.1 ±0.1	770 ±26	≥2x10^4	8.3 ±0.3	650 ±14	ND	8.3 ±0.2	92 ±39	≥1040 ±110
Anorthite	8.5 ±0.2	748 ±33	≥1.3x10^4 ±0.7x10^4	8.0 ±0.1	12 ±19	1028 ±528	7.8 ±0.6	342 ±97	≥663 ±387
Microcline	9.1 ±0.3	770 ±27	≥1.8x10^4 ±0.4x10^4	8.6 ±0.1	26 44	1603 ±692	8.2 ±0.2	145 ±194	≥855 ±424
Hornblende	8.8 ±0.1	746 ±34	≥1.2x10^4 ±0.7x10^4	8.6 ±0.6	357 ±256	1690 ±289	8.2 ±0.2	172 ±154	≥897 ±386
Enstatite	9.7 ±0.1	768 ±63	9,790 ±4,460	8.7 ±0.2	606 ±40	1393 ±226	8.6 ±0.1	521 ±95	≥970 ±260
Augite	9.4 ±0.3	809 ±30	≥8,500 ±10^4	9.2 ±0.0	ND	1188 ±689	9.3 ±0.1	526 ±38	≥1100

TABLE 3. Pu Adsorption in Reduced Oxygen Atmosphere (NaCl 30 meq/ℓ)

	3 Days			10 Days			30 Days		
Mineral	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	7.5	716	458	8.6	225	406	8.7	504	≥467
	±0.1	±63	±161	±0.1	±22	±50	±0.1	±170	±57
Montmorillonite	9.1	837	601	8.8	481	≥2460	8.7	628	≥575
	±0.2	±26	±97	±0.2	±278		±0.2	±211	
Vermiculite	8.5	797	5800	8.7	436	≥2400	8.8	707	≥500
	±0.2	±60	±2680	±0.1	±70		±0.2	±18	
Biotite	8.7	620	1010	8.5	595	≥2460	8.6	710	≥575
	±0.3	±280	±180	±0.1	±141		±0.1	±19	
Kaolinite	7.4	806	222	8.3	464	216	8.3	743	285
	±0.0	±21	±105	±0.1	±137	±18	±0.3	±65	±172
Quartz	9.1	724	232	8.5	391	157	8.3	518	19
	±0.1	±206	±4	±0.3	±109	±39	±0.2	±198	±18
Albite	9.2	332	216	9.3	246	1120	9.0	535	≥575
	±0.1	±65	±24	±0.2	±229	±800	±0.4	±109	
Anorthite	9.0	661	236	8.6	≤0	417	8.5	595	81
	±0.1	±193	±52	±0.2		±249	±0.3	±167	±39
Microcline	9.7	720	454	9.2	229	409	8.6	534	≥335
	±0.2	±27	±174	±0.2	±128	±370	±0.2	±265	±238
Hornblende	9.2	728	1080	8.8	444	229	8.8	574	333
	±0.5	±22	±396	±0.1	±164	±8	±0.1	±18	±86
Enstatite	9.4	527	898	8.9	415	254	8.8	513	192
	±0.1	±277	±336	±0.1	±285	±109	±0.4	±379	±45
Augite	9.9	716	1400	9.3	103	303	8.9	713	154
	±0.0	±69	±360	±0.2	±21	±249	±0.1	±58	±117

TABLE 4. Pu Adsorption in Reduced Oxygen Atmosphere ($NaHCO_3$ 30 meq/ℓ)

	3 Days			10 Days			30 Days		
Mineral	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	8.5 ±0.2	761 ±34	$1.8x10^4$ $\pm1.0x10^4$	8.8 ±0.1	225 ±50	$3.4x10^4$ $\pm1.3x10^4$	9.5 ±1.0	27 ±33	≥10,860 ±4,070
Montmorillonite	8.7 ±0.1	808 ±36	$2.0x10^4$ $\pm0.6x10^4$	9.2 ±0.1	401 ±74	$1.15x10^4$ $\pm0.10x10^4$	11.2 ±0.9	332 ±33	±4,650 ±1,870
Vermiculite	8.7 ±0.2	803 ±70	8800 ±4450	9.2 ±0.2	412 ±233	7440 ±1160	10.8 ±0.4	490 ±194	≥15,580
Biotite	8.7 ±0.0	706 ±10	5510 ±6820	9.0 ±0.0	448 ±261	6900 ±2260	10.2 ±1.5	116 ±104	4,470 ±660
Kaolinite	8.6 ±0.3	675 ±23	$\geq2.7x10^4$ $0.4x10^4$	9.1 ±0.1	283 ±140	$1.23x10^4$ $\pm0.15x10^4$	9.3 ±0.1	419 ±122	≥8,740 ±7,160
Quartz	7.7 ±0.2	748 ±51	1610+314	9.2 ±0.2	374 ±211	309 ±110	9.7 ±0.4	693 ±9	73 ±26
Albite	9.2 ±0.1	344 ±10	$\geq3x10^4$	9.2 ±0.1	252 ±247	4260 ±1210	9.2 ±1.0	≤0	1,650 ±330
Anorthite	9.1 ±0.0	736 ±17	5360 ±1490	9.3 ±0.1	273 ±173	492 ±428	9.0 ±0.4	199 ±197	367 ±221
Microcline	9.4 ±0.2	532 ±158	5010 ±4210	9.4 ±0.1	126 ±55	6050 ±3570	10.1 ±0.5	163 ±47	288 ±87
Hornblende	8.9 ±0.1	797 ±15	$\geq3x10^4$	9.2 ±0.0	528 ±186	2650 ±990	9.2 ±0.4	638 ±32	1,310 ±1,020
Enstatite	8.9 ±0.1	780 ±49	4090 ±950	9.2 ±0.1	279 ±36	1740 ±850	9.1 ±1.0	602 ±52	1,040 ±110
Augite	9.3 ±0.2	713 ±20	3310 ±1070	9.3 ±0.1	363 ±224	1560 ±1220	10.0 ±1.4	336 ±265	2,070 ±600

environment was difficult because of adsorption of Pu by blank container walls. The blank container correction assumes that blank and sample tube walls adsorb the same amount of radionuclide. When blank tubes adsorb more than sample tubes, the measured value for Ai in Equation 2 is too low and the calculated Kd values are thus conservatively low.

Table 5 compares measured Kd(Pu) values at 30 days for ambient and anoxic environments. Blank wall adsorption of Pu placed upper limits on the measured anoxic Kd(Pu) values of 1000 ml/g in 5.13 N NaCl and 0.03 N NaCl, 500 ml/g in 0.03 N $CaCl_2$ and 1.5 x 10^4 ml/g in 0.03 N $NaHCO_3$. Many Kd(Pu) values were equal to or larger than the upper limits, creating difficulties in the comparison of Kd values between anoxic and ambient conditions or among solutions in the anoxic environment.

A study of the Pu sorption by blank and sample tubes was made to estimate the error introduced by blank corrections. Measured ^{237}Pu activities from anoxic and ambient blank tubes (Ai) were determined after 30 days of shaking time (78 days elapsed time for anoxic and 178 days elapsed time for the ambient blanks). After correction for decay of ^{237}Pu, a comparison was made with the influent activities after three days of shaking. The difference was taken as the amount sorbed by blank tubes and is shown in Table 6. More blank tube sorption occurred under anoxic than ambient conditions in all solutions but the bicarbonate.

One of each of the triplicate samples from the anoxic study was emptied of solid-liquid slurry and counted to determine the amount of ^{237}Pu sorbed by sample tube walls relative to the blank containers. The fraction of the total Pu added to each tube which is adsorbed by a blank tube was designated f and the fraction of the total Pu sorbed by a sample tube was called t. We found that blank tubes always adsorbed more Pu than the sample tubes with the same solution, $f > t$. Most sample tubes adsorbed less than 5% of the amount adsorbed by the blank tubes and none adsorbed more than 20% ($t \leq 0.2$ f). Some activity supposedly adsorbed by sample tubes could be attributed to activity on fine mineral particles adhering to tube walls or precipitates formed during weathering that may plate-out on the container. Thus, values for t would be biased toward the high side by these fines and precipitates.

TABLE 5. Comparison of Measured Kd_m(Pu)(1) Values at 30 Days in Ambient Atmospheric and Anoxic Environments

Mineral	5.13 N NaCl		0.03 N $CaCl_2$		0.03 N NaCl		0.03 N $NaHCO_3$	
	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic
Illite	2,283(2) ±555	≥1,200	3,291 ±696	≥1,090	1,086 ±209	≥467 ±57	12,180 ±9,950	≥10,860 ±4,070
Montmorillonite	918 ±781	440 ±105	5,268 ±3,025	≥836 ±492	6,760 ±4,565	≥575	7,510 ±1,810	4,650 ±1,870
Vermiculite	1,648 ±316	≥998 ±453	4,580 ±2,470	≥948 ±266	2,333 ±731	≥500	6,780** ±864(3)	≥15,580
Biotite	1,048 ±320	≥964 ±512	1,195 ±135	≥974 ±252	1,243 ±101	≥575	2,222** ±376	4,470 ±660
Kaolinite	641 ±146	343 ±216	1,270 ±220	≥880 ±380	1,218** ±301	285 ±172	10,240 ±2,860	≥8,740 ±7,160
Quartz	517 ±235	251 ±157	1,361 ±334	588 ±383	697* ±300	19 ±18	178* ±31	73 ±26
Albite	1,997 ±148	≥1,260	2,732 ±622	≥1,040 ±110	2,875 ±381	≥575	820** ±291	1,650 ±330
Anorthite	984 ±216	423 ±197	1,219 ±71	≥663 ±387	1,219** ±76	81 ±39	1,240* ±145	367 ±221
Microcline	676** ±122	≥1,170 ±150	819 ±135	≥855 ±424	428 ±47	≥335 ±238	458 ±40	288 ±87
Hornblende	969 ±150	730 ±470	1,324 ±284	≥897 ±386	1,160* ±340	333 ±86	1,813 ±382	1,310 ±1,020
Enstatite	755** ±50	245 ±46	1,199 ±108	970 ±260	562** ±71	192 ±45	713 ±166	1,040 ±110
Augite	863** ±130	≥1,260	1,470 ±220	≥1,100	950** ±170	154 ±117	2,660 ±380	2,070 ±600

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(1) Kd(Pu) has units of ml/g.

(2) Each Kd value is reported as the mean ± one standard deviation for three identical samples.

(3) * denotes a significant difference between the anoxic and ambient Kd(Pu) value with 95% confidence while ** denotes greater than 99% confidence.

TABLE 6. Adsorption of ^{237}Pu by Blank Container Walls Under Anoxic (pO_2 = 2.7) and Ambient (pO_2 = 0.7) Conditions

	5.13 N NaCl	0.03 N $CaCl_2$	0.03 N NaCl	0.03 N $NaHCO_3$
Ambient	30%*	0	35%	47%
Anoxic	76%	86%	72%	23%

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* Percent of total ^{237}Pu adsorbed after 30-day shaking time compared to influent activity after 3 days of shaking.

Significant negative correlations (95% confidence) were found between calculated Kd values and t/f in both 0.03 N NaCl and 0.03 N $NaHCO_3$. The same correlation was significant at only 90% confidence in 5.13 N NaCl and no correlation was observed in 0.03 N $CaCl_2$. In general more sample tube adsorption is observed in containers with low Kd minerals such as quartz. Sorption of Pu by a sample tube would effectively lower the effluent activity, Ae, in Equation 2, resulting in a higher Kd value.

The effects of blank and sample container sorption on Kd(Pu) can be studied if f and t are measured. Actual influent and effluent values (as if there were no container sorption) can be calculated from:

$$Aim = Aia\ (1 - f) \tag{3}$$

and

$$Aem = Aea\ (1 - t) \tag{4}$$

where the letter m refers to measured values and a refers to actual values. Substitution of Aia and Aea into Equation 2 gives a corrected value for Kd(Pu):

$$Kd_a = \left[\left(\frac{v}{v + x}\right)\left(\frac{Aim}{1 - f}\right) - \left(\frac{Aem}{1 - t}\right)\right]\left(\frac{1 - t}{Aem}\right)\left(\frac{v + x}{w}\right) \tag{5}$$

which reduces to:

$$Kd_a = \frac{v}{w}\left[\left(\frac{Aim}{Aem}\right)\left(\frac{1 - t}{1 - f}\right) - 1\right] - \frac{x}{w} \tag{6}$$

The values for Kd(Pu) reported in Table 5 are calculated from measured values, defined by Equation 2 as:

$$Kd_m = \frac{v}{w}\left[\frac{Aim}{Aem} - 1\right] - \frac{x}{w} \tag{7}$$

The ratio Kd_m/Kd_a is useful in displaying the effects of blank and sample container sorption of Pu. The ratio of Kd_m/Kd_a obtained from Equations 6 and 7 is given by:

$$\frac{Kd_m}{Kd_a} = \left(1 + \frac{x}{wKd_a}\right)\left(\frac{1 - f}{1 - t}\right) - \frac{v}{wKd_a}\left(\frac{f - t}{1 - t}\right) - \frac{x}{wKd_a} \tag{8}$$

With the condition:

$$0 \leq t \leq f \leq 1$$

we find that as $f \rightarrow 0$ (or $f \rightarrow t$); $Kd_m/Kd_a \rightarrow 1$; the measured and corrected Kd(Pu) values are the same. As f increases, Kd_m decreases relative to Kd_a and conservatively low values for Kd(Pu) are calculated using Equations 2 or 7.

Figures 1 and 2 graphically show the effect of blank tube sorption (f) on measured Kd(Pu) values. For large values of Kd_a, the ratio of Kd_m/Kd_a approaches $(1 - f)/(1 - t)$, thus large values of Kd_m can be corrected (conservatively) by using

$$Kd_a \geq \left(\frac{1 - t}{1 - f}\right) Kd_m \tag{9}$$

For small values of Kd_m, such as that found for quartz in 0.03 N NaCl ($f = 0.72$ and $t = 0.14$), Figures 1 and 2 show that Kd_m is less than zero for an actual Kd value less than 50 ml/g. Figure 3 shows the result of lowering the solution to solid ratio (v/w). Reducing the solution volume relative to

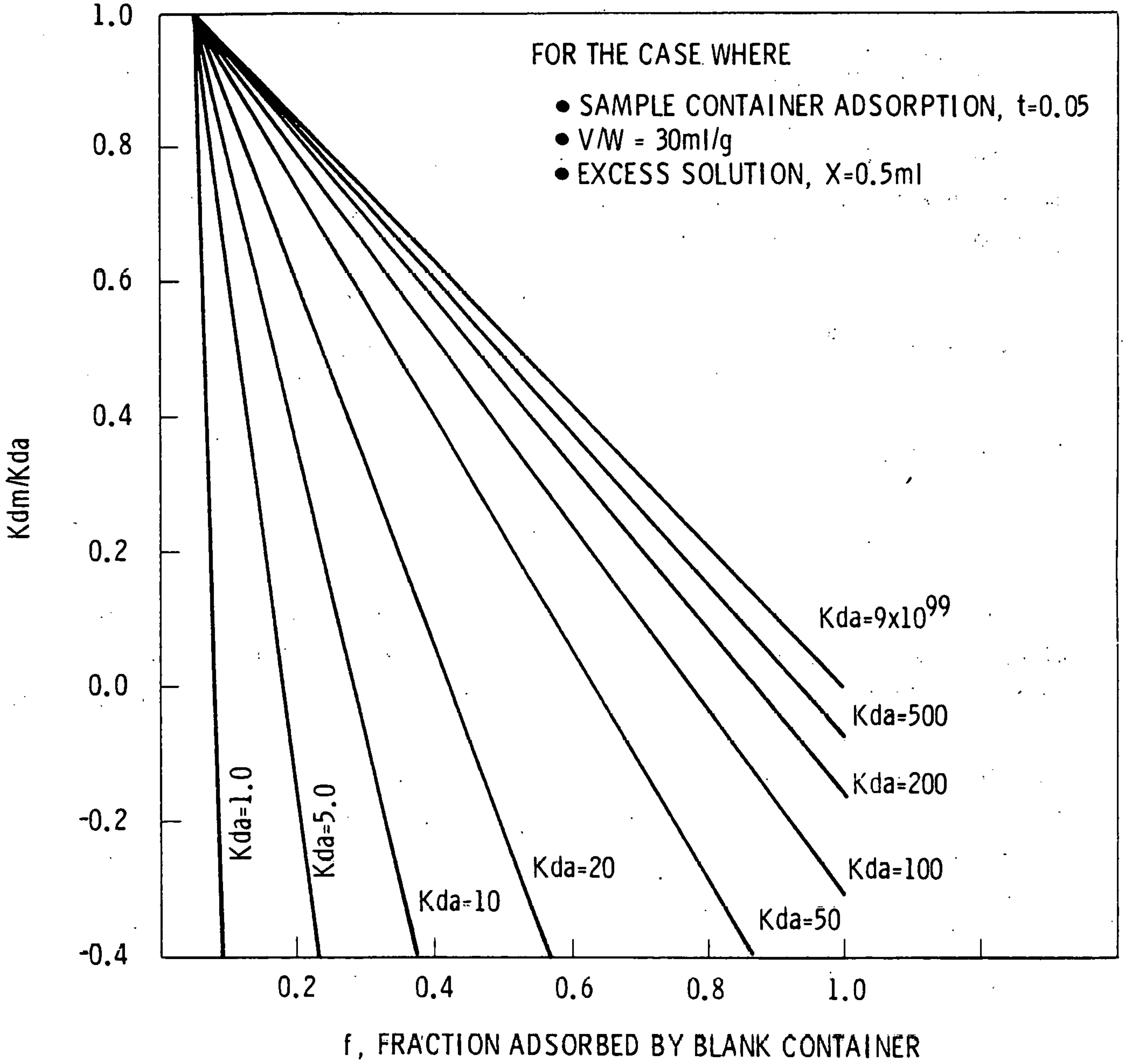

FIGURE 1. Effects of Blank Container Sorption on Calculated Kd_m Versus Corrected Kd_a Values

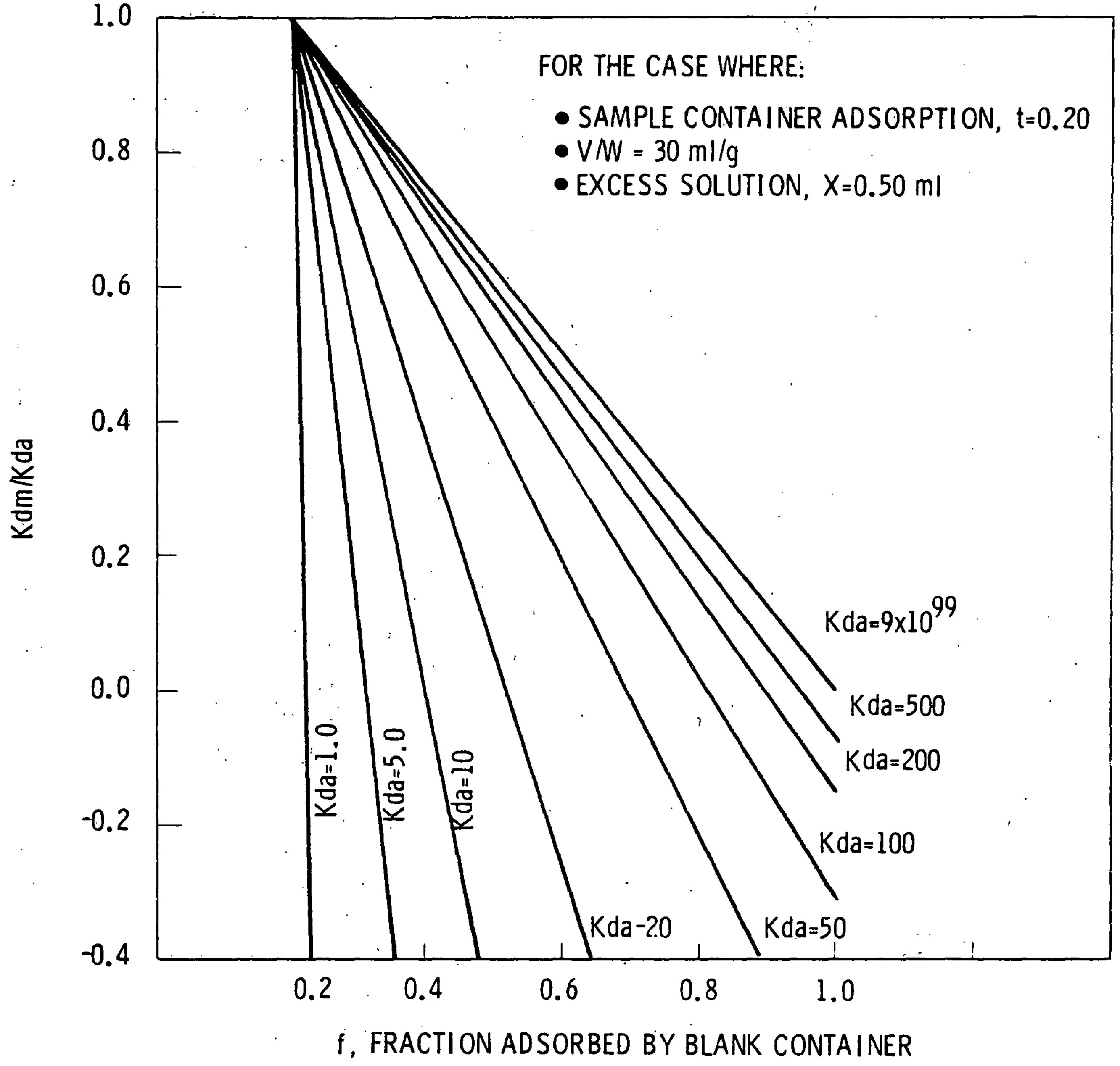

FIGURE 2. Effects of Blank Container Sorption on Calculated Kd_m Versus Corrected Kd_a Values

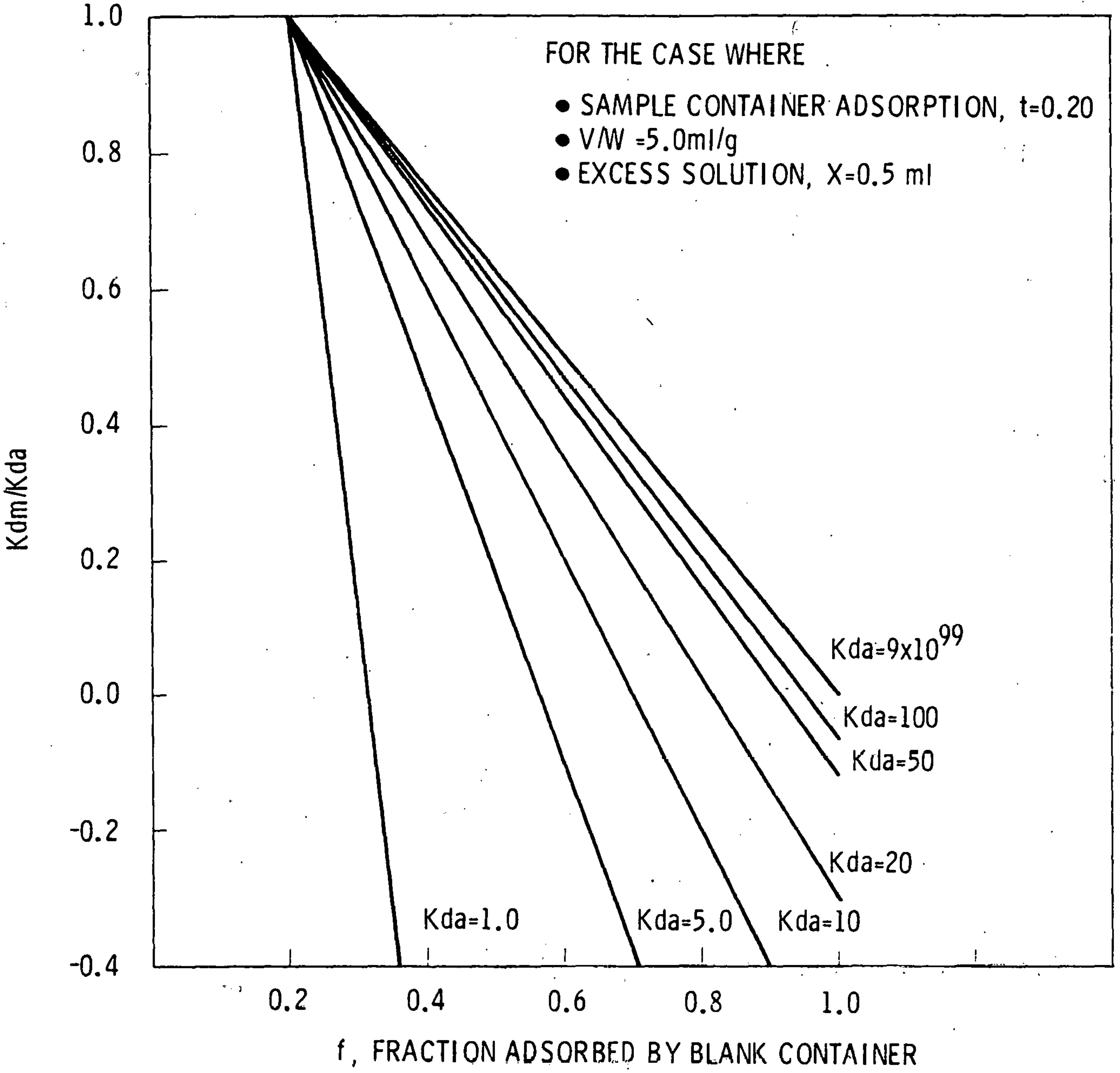

FIGURE 3. Effects of Blank Container Sorption on Calculated Kd_m Versus Corrected Kd_a Values

the solid phase results in a higher Kd_m:Kd_a ratio only for small values of Kd_a. The limit imposed by Equation 9 on large Kd values remains unaffected. Even with v/w reduced from 30 ml/g to 5 ml/g, the effects of blank tube sorption are large for the lower Kd_a region ($0 \leq Kd_a \leq 10$). Nuclides in this region are the most critical as they possess the highest migration potential.

If the excess volume, x, is neglected in Equation 8 (resulting in a still conservatively low estimate of Kd_a), Kd_a is given in terms of Kd_m, f and t as:

$$Kd_a = \left[Kd_m + \frac{v}{w}\left(\frac{f - t}{1 - t}\right)\right]\left(\frac{1 - t}{1 - f}\right) \tag{10}$$

Table 7 shows the corrected Kd_a(Pu) values from Table 5. Because sample tube sorption was not measured after the ambient Pu sorption study, a conservative value of t = 0.2 was used for correction of the ambient Kd(Pu) values.

Before correction Table 5 shows no significant differences between ambient and anoxic Kd_m(Pu) values in 0.03 N $CaCl_2$. Table 7 shows that in this solution, Kd_a(Pu) is generally larger under anoxic than ambient atmospheric conditions. A trend was found for larger Kd_m(Pu) values under ambient than anoxic conditions in 0.03 N NaCl. After correction of the calculated Kd_m values, there were far fewer significant differences and the trend disappeared. Correction of Kd_m(Pu) also showed that Pu sorption from 0.03 N $NaHCO_3$ is lower under anoxic than ambient conditions.

TABLE 7. Comparison of Corrected Kd(Pu)(1) Values at 30 days in Ambient Atmospheric and Anoxic Environments

Mineral	5.13 N NaCl Ambient	 Anoxic	0.03 N $CaCl_2$ Ambient	 Anoxic	0.03 N NaCl Ambient	 Anoxic	0.03 N $NaHCO_3$ Ambient	 Anoxic
Illite	3,076* ±745(2,3)	≥5,100	3,291** ±696	≥7,830	1,567 ±300	≥1,730 ±203	2.1×10^4 $\pm1.7\times10^4$	$\geq1.4\times10^4$ $\pm0.5\times10^4$
Montmorillonite	1,240 ±1,050	1,930 ±439	5,270 ±3,030	5,990 ±3,430	9,680 ±6,530	≥2,120	1.3×10^4* $\pm0.3\times10^4$	6,030 ±2,420
Vermiculite	2,220 ±430	≥4,260 ±1,890	4,580 ±2,470	≥6,770 ±1,850	3,350 ±1.050	≥1,850	1.2×10^4** $\pm0.1\times10^4$	$\geq2.0\times10^4$
Biotite	1,420 ±430	≥3,950 ±1,990	1,200** ±140	≥7,080 ±1,790	1,790* ±150	≥2,120	3,820* ±640	5,780 ±850
Kaolinite	870 ±200	1,500 ±890	1,270* ±220	≥6,360 ±2,680	1,760 ±430	1,070 ±600	1.8×10^4 $\pm0.5\times10^4$	$\geq1.1\times10^4$ $\pm0.9\times10^4$
Quartz	705 ±316	1,110 ±630	1,360 ±330	3,630 ±2.260	1,010* ±430	92 ±69	326** ±53	100 ±32
Albite	2,690** ±200	≥5,310	2,730** ±620	7,400 ±650	4,130 ±550	≥2,100	1,420 ±500	2,120 ±420
Anorthite	1,330 ±290	1,810 ±800	1,220 ±70	≥4,790 ±2,690	1,760** ±110	362 ±138	2,140** ±250	470 ±280
Microcline	920** ±160	≥4,830 ±610	820* ±140	≥6,180 ±2,990	630 ±70	1,250 ±840	800** ±70	365 ±108
Hornblende	1,310 ±200	≥3,030 ±1,890	1,320* ±280	≥6,480 ±2,710	1,680 ±490	1,250 ±300	3,120 ±650	1,660 ±1,290
Enstatite	1,020 ±70	1,080 ±190	1,200** ±110	≥6,870 ±1,790	820 ±100	753 ±157	1,240 ±280	1,350 ±140
Augite	1,170** ±170	≥5,350	1,470** ±220	≥7,900	1,370 ±240	820 ±760	4,560* ±640	2,670 ±770

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(1) Kd(Pu) has units of ml/g.
(2) Each Kd value is reported as the mean ± one standard deviation for three identical samples.
(3) * denotes a significant difference between the anoxic and ambient Kd(Pu) value with 95% confidence while ** denotes greater than 99% confidence.

SUMMARY AND CONCLUSIONS

The blank-corrected batch method is not well suited for measuring low Kd values when the radionuclide under study is sorbed on blank container and sample container walls. Containers which do not adsorb the nuclide should be used, but this may not be possible with nuclides such as Pu and Am.

A method which directly determines the radionuclide activity on the solid phase is more appropriate for low Kd determinations; however, this method is more time consuming than the blank-corrected batch method as it requires twice the counting time. Measurement of the activity sorbed on blank container and sample container walls can be utilized to correct measured Kd values, but this too requires extra counting time.

Corrections have been made for measured Kd values for plutonium under anoxic conditions after 30 days of shaking. Values for Kd(Pu) were highest for the phyllosilicate minerals illite, montmorillonite, vermiculite and biotite. Corrected Kd_a(Pu) values were generally higher under anoxic than ambient atmospheric conditions in both 5.13 N NaCl and 0.03 N $CaCl_2$. Lower values for Kd_a(Pu) were observed in 0.03 N $NaHCO_3$ under anoxic than under ambient conditions.

There were no statistically significant differences in Kd_a(Pu) for the two oxygen conditions for the 0.03 N NaCl solution. Thermodynamic data suggest that Pu sorption would be greater under anoxic conditions as shown in two of the four solutions used. At present there is no explanation for the apparent lack of agreement of the other two solutions. In general Pu adsorption by the minerals was high with the lowest mean value for corrected data being Kd_a(Pu) = 92 for quartz under anoxic conditions. Of the 96 permutations (12 minerals x 4 solutions x 2 oxygen conditions) in only 14 instances did the Kd_a(Pu) fall below 1000 ml/g and in only 5 instances did Kd_a(Pu) fall below 500 ml/g.

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TABLE 1. Pu Adsorption in Reduced Oxygen Atmosphere
(NaCl 5130 meq/ℓ)

	3 Days			10 Days			30 Days		
Mineral	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	6.5 ±0.2	464 ±76	3090 ±820	7.2 ±0.2	≤0	1420 ±590	6.8 ±0.4	394 ±28	≥1200
Montmorillonite	8.3 ±0.2	738 ±18	694 ±25	8.2 ±0.1	407 ±198	845 ±65	8.1 ±0.4	521 ±17	440 ±105
Vermiculite	8.3 ±0.5	733 ±41	448 ±105	8.5 ±0.1	833 ±94	685 ±147	8.5 ±0.1	560 ±49	≥998 ±453
Biotite	8.5 ±0.2	744 ±21	360 ±72	8.3 ±0.1	638 ±33	641 ±47	7.9 ±0.2	533 ±50	≥964 ±512
Kaolinite	6.7 ±0.3	464 ±258	967 ±500	6.4 ±0.2	266 ±128	389 ±53	6.0 ±0.4	438 ±109	343 ±216
Quartz	7.0 ±0.5	520 ±189	1060 ±307	6.5 ±0.1	505 ±168	351 ±48	7.1 ±0.3	529 ±96	251 ±157
Albite	8.7 ±0.4	491 ±108	3620 ±2210	8.5 ±0.1	≤0	1175 ±309	8.0 ±0.4	488 ±64	≥1260
Anorthite	8.8 ±0.1	551 ±184	3160 ±3090	8.3 ±0.2	407 ±104	486 ±34	8.2 ±0.4	477 ±53	423 ±197
Microcline	8.7 ±0.8	393 ±403	4670 ±2240	8.2 ±0.3	606 ±38	939 ±407	8.2 ±0.3	530 ±75	≥1170 ±150
Hornblende	8.7 ±0.4	463 ±127	1002 ±175	8.5 ±0.1	621 ±35	949 ±178	8.1 ±0.3	509 ±16	730 ±470
Enstatite	8.6 ±0.3	686 ±60	886 ±163	8.4 ±0.3	335 ±92	497 ±276	7.5 ±1.5	467 ±49	245 ±46
Augite	9.3 ±0.2	571 ±149	1141 ±495	9.1 ±0.2	405 ±205	633 ±117	8.7 ±0.1	541 ±27	≥1260

TABLE 2. Pu Adsorption in Reduced Oxygen Atmosphere ($CaCl_2$ 30 meq/ℓ)

	3 Days			10 Days			30 Days		
Mineral	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	7.3	724	13,420	7.8	375	≥9550	7.9	162	≥1090
	±0.4	±8	±4,940	±0.1	±206		±0.2	±81	
Montmorillonite	8.1	785	5,657	7.7	622	≥9550	8.1	398	≥836
	±0.0	±16	±644	±0.1	±48		±0.2	±186	±492
Vermiculite	8.0	758	6,770	7.9	109	≥6020	8.2	474	≥948
	±0.2	±38	±2,140	±0.0	±98	±2480	±0.2	±47	±266
Biotite	8.3	818	$\geq 2\times10^4$	7.9	674	3840	8.1	452	≥974
	±0.1	±20		±0.1	±329	±1270	±0.1	±109	±252
Kaolinite	6.9	±693	4,550	8.2	516	≥9550	8.3	414	≥880
	±0.0	±3	±1,300	±0.1	±116		±0.2	±51	±380
Quartz	8.1	721	2,690	8.2	416	1060	8.2	223	588
	±0.5	±72	±2,040	±0.1	±42	±990	±0.1	±34	±383
Albite	9.1	770	$\geq 2\times10^4$	8.3	650	ND	8.3	92	≥1040
	±0.1	±26		±0.3	±14		±0.2	±39	±110
Anorthite	8.5	748	$\geq 1.3\times10^4$	8.0	12	1028	7.8	342	≥663
	±0.2	±33	$\pm 0.7\times10^4$	±0.1	±19	±528	±0.6	±97	±387
Microcline	9.1	770	$\geq 1.8\times10^4$	8.6	26	1603	8.2	145	≥855
	±0.3	±27	$\pm 0.4\times10^4$	±0.1	44	±692	±0.2	±194	±424
Hornblende	8.8	746	$\geq 1.2\times10^4$	8.6	357	1690	8.2	172	≥897
	±0.1	±34	$\pm 0.7\times10^4$	±0.6	±256	±289	±0.2	±154	±386
Enstatite	9.7	768	9,790	8.7	606	1393	8.6	521	≥970
	±0.1	±63	±4,460	±0.2	±40	±226	±0.1	±95	±260
Augite	9.4	809	≥8,500	9.2	ND	1188	9.3	526	≥1100
	±0.3	±30	$\pm 10^4$	±0.0		±689	±0.1	±38	

TABLE 3. Pu Adsorption in Reduced Oxygen Atmosphere (NaCl 30 meq/ℓ)

	3 Days			10 Days			30 Days		
Mineral	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	7.5 ±0.1	716 ±63	458 ±161	8.6 ±0.1	226 ±22	406 ±50	8.7 ±0.1	504 ±170	≥467 ±57
Montmorillonite	9.1 ±0.2	837 ±26	601 ±97	8.8 ±0.2	481 ±278	≥2460	8.7 ±0.2	628 ±211	≥575
Vermiculite	8.5 ±0.2	797 ±60	5800 ±2680	8.7 ±0.1	436 ±70	≥2400	8.8 ±0.2	707 ±18	≥500
Biotite	8.7 ±0.3	620 ±280	1010 ±180	8.5 ±0.1	595 ±141	≥2460	8.6 ±0.1	710 ±19	≥575
Kaolinite	7.4 ±0.0	806 ±21	222 ±105	8.3 ±0.1	464 ±137	216 ±18	8.3 ±0.3	743 ±65	285 ±172
Quartz	9.1 ±0.1	724 ±206	232 ±4	8.5 ±0.3	391 ±109	157 ±39	8.3 ±0.2	518 ±198	19 ±18
Albite	9.2 ±0.1	332 ±65	216 ±24	9.3 ±0.2	246 ±229	1120 ±800	9.0 ±0.4	535 ±109	≥575
Anorthite	9.0 ±0.1	661 ±193	236 ±52	8.6 ±0.2	≤0	417 ±249	8.5 ±0.3	595 ±167	81 ±39
Microcline	9.7 ±0.2	720 ±27	454 ±174	9.2 ±0.2	229 ±128	409 ±370	8.6 ±0.2	534 ±265	≥335 ±238
Hornblende	9.2 ±0.5	728 ±22	1080 ±396	8.8 ±0.1	444 ±164	229 ±8	8.8 ±0.1	574 ±18	333 ±86
Enstatite	9.4 ±0.1	527 ±277	898 ±336	8.9 ±0.1	415 ±285	254 ±109	8.8 ±0.4	513 ±379	192 ±45
Augite	9.9 ±0.0	716 ±69	1400 ±360	9.3 ±0.2	103 ±21	303 ±249	8.9 ±0.1	713 ±58	154 ±117

TABLE 4. Pu Adsorption in Reduced Oxygen Atmosphere ($NaHCO_3$ 30 meq/ℓ)

Mineral	3 Days			10 Days			30 Days		
	pH	Eh	Kd	pH	Eh	Kd	pH	Eh	Kd
Illite	8.5	761	1.8x10^4	8.8	225	3.4x10^4	9.5	27	≥10,860
	±0.2	±34	±1.0x10^4	±0.1	±50	±1.3x10^4	±1.0	±33	±4,070
Montmorillonite	8.7	808	2.0x10^4	9.2	401	1.15x10^4	11.2	332	+4,650
	±0.1	±36	±0.6x10^4	±0.1	±74	±0.10x10^4	±0.9	±33	±1,870
Vermiculite	8.7	803	8800	9.2	412	7440	10.8	490	≥15,580
	±0.2	±70	±4450	±0.2	±233	±1160	±0.4	±194	
Biotite	8.7	706	5510	9.0	448	6900	10.2	116	4,470
	±0.0	±10	±6820	±0.0	±261	±2260	±1.5	±104	±660
Kaolinite	8.6	675	≥2.7x10^4	9.1	283	1.23x10^4	9.3	419	≥8,740
	±0.3	±23	0.4x10^4	±0.1	±140	±0.15x10^4	±0.1	±122	±7,160
Quartz	7.7	748	1610+314	9.2	374	309	9.7	693	73
	±0.2	±51		±0.2	±211	±110	±0.4	±9	±26
Albite	9.2	344	≥3x10^4	9.2	252	4260	9.2	≤0	1,650
	±0.1	±10		±0.1	±247	±1210	±1.0		±330
Anorthite	9.1	736	5360	9.3	273	492	9.0	199	367
	±0.0	±17	±1490	±0.1	±173	±428	±0.4	±197	±221
Microcline	9.4	532	5010	9.4	126	6050	10.1	163	288
	±0.2	±158	±4210	±0.1	±55	±3570	±0.5	±47	±87
Hornblende	8.9	797	≥3x10^4	9.2	528	2650	9.2	638	1,310
	±0.1	±15		±0.0	±186	±990	±0.4	±32	±1,020
Enstatite	8.9	780	4090	9.2	279	1740	9.1	602	1,040
	±0.1	±49	±950	±0.1	±36	±850	±1.0	±52	±110
Augite	9.3	713	3310	9.3	363	1560	10.0	336	2,070
	±0.2	±20	±1070	±0.1	±224	±1220	±1.4	±265	±600

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EFFECTS OF HYDROGEN PEROXIDE PRETREATMENT OF CLAY MINERALS ON THE ADSORPTION OF Sr-85 and Tc-95m UNDER ANOXIC CONDITIONS

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INTRODUCTION

Soil clay minerals purified according to the procedures recommended by Jackson (1956) are often used in studies of the behavior of trace metals from sewage sludge, coal fly ash or radionuclides from nuclear waste. Jackson's procedure was originally a purification technique for soil clays prior to mineralogical analysis. Use of hydrogen peroxide for organic matter removal is implied in numerous references to Jackson (1956) and explicit mention of the hydrogen peroxide (H_2O_2) treatment is found in many others: Huang (1975); Landa, Thorvig and Gast (1977); Shuman (1976); and Weidenfeld and Hossner (1978).

Destruction of organic matter with H_2O_2 has been shown to destroy the amorphous oxides of Fe, Si, Al and Mn, and to lower the soil pH (Lavkulich and Wiens 1970, Douglas 1971). This obviously changes some soil properties but is not thought to greatly change the properties of clay minerals for purposes of mineralogical analysis. However, these purification procedures are often used on clay samples intended for other purposes than mineralogical analysis and important differences between treated (H_2O_2 or NaOCl) and untreated clays may go unnoticed.

Many heavy metals and radionuclides that are potentially hazardous to man have more than one possible oxidation state. Anerobic or anoxic environments would find these elements in a reduced state with a concomitant change in behavior relative to aerobic environments.

Oxidation of clay minerals by H_2O_2 or NaOCl may buffer the redox potential (Eh) of a system at sufficiently high values such that expected changes in oxidation states cannot occur. Bondietti and Francis (1979) found that NaOCl treated basalt could not reduce TcO_4^- in an aerobic environment, but untreated basalt in an anoxic environment did reduce the TcO_4^- to a form bound to the basalt surface. It is though that similar effects may be observed on clay minerals treated with H_2O_2 and utilized to study the sorption behavior of radionuclides in an anoxic environment.

METHODS AND MATERIALS

Bulk samples of kaolinite (Macon, GA), montmorillonite (Chambers, AZ, No. 23) and Vermiculite (ID) were obtained from Wards Natural Science Establishment Inc. Table 1 shows the surface areas (by Ethylene Glycol) and cation exchange capacities (CEC determined by the ^{85}Sr method) for these clays and Table 2 gives their bulk chemical compositions and mineralogies.

In preparation, approximately 200 g of kaolinite and montmorillonite were ground with a ceramic mortar and pestle to pass through a 120 mesh seive (>125 μm). The vermiculite was placled in a blender as a slurry for fifteen minutes and oven dried prior to grinding with mortar and pestle. Samples were washed in 1 M NaCl then distilled water before being split in halves. Approximately one-half of each sample (100 g) was subjected to an H_2O_2 treatment in which a 2 to 1 clay-water suspension was heated to 65° ± 5°C. Small aliquots of 30% H_2O_2 were added over a six hour period. To minimize damage to the clays no acid was added to lower the pH. Treated and untreated clays were then washed once with 1 N NaCl and three times in distilled de-ionized water before being freeze-dried.

Adsorption experiments were carried out in a 3x3x2 factorial design (3 minerials, 3 salt concentrations and 2 H_2O_2 treatments - treated and untreated) with 3 repititions.

Salt concentrations used were 1 to 1, 1 to 10 and 1 to 100 dilutions of WIPP Brine B as shown in Table 3, which are essentially 5.0, 0.5 and 0.05 N NaCl.

One gram samples of each clay were weighed into tared 50 ml Oak Ridge type screw cap polycarbonate centrifuge tubes. Each sample was subsequently washed twice under anoxic conditions with 15 ml of the appropriate solution and reweighed to determine the excess solution remaining. Thirty milliliters of spiked (^{85}Sr and ^{95m}Tc) de-oxygenated solution was then pipetted into each tube.

Tubes were shaken under an anoxic atmosphere (pO_2 = 2.7) and sampled at 10 and 30 days. At each sampling time all tubes were centrifuged at 7000 rpm for 20 min and 10 ml of solution was removed for gamma-ray counting on an ORTEC 25% Ge(Li) detector. Measurements of pH and redox potential (Eh) were also made at these times.

Distribution coefficients (Kd) were calculated using the blank corrected - batch Kd formula:

$$Kd = \left(\frac{rAi - Ae}{Ae}\right)\left(\frac{v+x}{w}\right)$$

where

r = ratio of tracer solution volume to total solution volume = v/(v+x)

v = volume of tracer solution added (30 ml)

x = volume of excess solution left after last wash (ml)

Ai = radionuclide activity in solution from blank container (tracer influent without clay) (cpm in 10 ml)

Ae = radionuclide activity left in solution after contact with clay (effluent) (cpm in 10 ml)

w = mass of clay in sample tubes (1.00 g).

High Kd values represent a small amount of activity in the solution and high sorption on the minerals.

RESULTS AND DISCUSSION

No significant differences were detected for strontium adsorption between treated and untreated clay samples (Tables 4, 5 and 6). Values for strontium distribution coefficients, Kd(Sr), were found to increase as the NaCl concentration decreased. Values for Kd(Sr) were also found to increase as the mineral surface area and CEC increased. Strontium behavior follows ion exchange theory and the H 0 pretreatment effects are insignificant.

No significant differences were detected for ph or Eh values (Tables 7, 8 and 9) on treated and untreated clay sample pairs. Thus, the treatment did not affect clay samples to a measurable extent as far as the pH and Eh were concerned.

Tables 10 and 11 (strontium analysis of variance, ANOVA, for ten and thirty day results) show the significant sources of variation for Sr to be 1) the salt concentration, 2) the mineral type, and 3) the salt concentration - mineral interaction. The relative significance of these is unchanged between ten and thirty days.

Mineral and treatment effects on technetium adsorption (Tables 12 and 13) are significant at both ten and thirty days; however, the mineral effects differ from those found with Sr. Values found for Kd(Tc) do not correlate with the CEC or the surface area as Kd(Sr) values did. Adsorption Kd values for Tc show a tendency to increase with decreasing salt concentration only at thirty days. The salt effects are shown to be significant only in Table 10 (thirty day ANOVA).

At ten days, treatment effects are the most significant source of variation in technetium adsorption. After thirty days treatment effects are still significant, but the order of importance has become: 1) mineral, 2) salt concentration, 3) salt-concentration-mineral interaction, and 4) treatment. The behavior of technetium at thirty days has become more like that of strontium. Effects from the pretreatment of clays with oxidants may not be significant for longer experiments. Values for Kd(Tc) on montmorillonite showed no significant differences between treatments at thirty days (Table 6). At longer times differences between treated and untreated kaolinite and vermiculite may also disappear.

CONCLUSIONS

Treatment of three clay minerals with hydrogen peroxide affects the observed adsorption behavior of technetium relative to untreated clay under anoxic conditions. A possible adsorption mechanism for Tc is the reduction of TcO_4^- to a more positively charged or better adsorbed species. Oxidation of the clay by H_2O_2 would hinder the reduction of TcO_4^- by buffering the clay-water system at a higher Eh value, although a difference in measured Eh value may go undetected.

Sorption of strontium by the clays under the same conditions is not affected by a pretreatment with H_2O_2. The behavior of strontium follows that expected from ion exchange theory.

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TABLE 1. Physical Characterization of Clays

Mineral	Cation Exchange Capacity meq/100 g (^{85}Sr)	Surface Area m^2/g (Ethylene Glycol)
Kaolinite	5.0 ± 0.9	30.7 ± 0.5
Vermiculite	77.0 ± 4.8	312.5 ± 7.8
Montmorillonite	87.4 ± 2.7	722.2 ± 6.9

TABLE 2. Chemical-Mineralogical Characterization of Clays
(Large area electron microprobe chemical analysis)

	Kaolinite wt%	Vermiculite wt%	Montmorillonite wt%
SiO_2	54.8	47.7	64.6
TiO_2	1.5	0.7	0.3
Al_2O_3	43.1	11.7	19.3
FeO	0.1	9.5	3.3
CaO	≤0.1	1.3	8.5
MgO	≤0.1	22.0	3.3
Na_2O	≤0.1	0.5	≤0.1
K_2O	0.4	6.2	≤0.1
	99.9%	99.6%	99.3%
	96% Kaolinite Up to 4% Quartz	70% Vermiculite 30% Biotite	92% Montmorillonite Up to 8% Calcite

TABLE 3. Salt Solution Composition (WIPP Brine B, slightly altered)

CONCENTRATION

Cations	(mg/Liter)	meq/Liter)
Ca^{2+}	900	45.00
Mg^{2+}	10	0.82
Sr^{2+}	1.5	0.03
Na^+	115,000	5000
K^+	15	0.38
Cs^+	1.0	0.01
Anions		
HCO_3^-	10	0.16
SO_4^{2-}	4,190	87.3
Cl^-	175,000	4936
BO_3^{3-}	10	0.51
Br^-	400	5.00

TABLE 4. Adsorption Kd Values for ^{85}Sr and ^{95m}Tc on Kaolinite (ml/g)

Salt Concentration	Adsorption Time (days)	Kd(Sr)		Kd(Tc)	
		Untreated	Treated	Untreated	Treated
5.0 M NaCl	10	1.0 ± 0.8(2)	1.2 ± 3.2	2.7 ± 3.2	2.5 ± 4.6
	30	-1.6 ± 0.6	-2.0 ± 1.0	5.1 ± 0.5	0.3 ± 0.7
0.5 M NaCl	10	-0.8 ± 0.4	0.1 ± 0.7	19 ± 16	1.4 ± 0.5
	30	1.6 ± 2.4	1.0 ± 1.4	66 ± 52	4.5 ± 2.9
0.05 M NaCl	10	11.5 ± 1.5	14.2 ± 0.4	11 ± 6	0.0 ± 0.2
	30	11.6 ± 1.0	15.0 ± 1.9	55 ± 13	3.8 ± 2.2

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(1) untreated clay was not subjected to H_2O_2, treated clay was heated at 60 C with 30% H_2O_2.

(2) mean ± std. dev. (n=3).

TABLE 5. Adsorption Kd Values for ^{85}Sr and ^{95m}Tc on Vermiculite (ml/g)

Salt Concentration	Adsorption Time (days)	Kd(Sr)		Kd(Tc)	
		Untreated	Treated	Untreated	Treated
5.0 M NaCl	10	7.5 ± 6.6(2)	3.3 ± 0.4	21 ± 20	5.6 ± 7.8
	30	9.2 ± 2.1	3.3 ± 0.3	16 ± 6	6.8 ± 5.3
0.5 M NaCl	10	5.5 ± 0.5	7.3 ± 1.9	1.2 ± 1.4	-1.8 ± 2.0
	30	7.0 ± 0.7	8.6 ± 1.1	45 ± 6	-1.9 ± 2.8
0.05 M NaCl	10	152 ± 18	126 ± 20	30 ± 19	8.9 ± 0.4
	30	260 ± 88	194 ± 66	170 ± 46	124 ± 36

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(1) untreated clay was not subjected to H_2O_2, treated clay was heated at 60 C with 30% H_2O_2.

(2) mean ± std. dev. (n=3).

TABLE 6. Adsorption Kd Values for ^{85}Sr and ^{95m}Tc on Montmorillonite (ml/g)

Salt Concentration	Adsorption Time (days)	Kd(Sr) Untreated	Kd(Sr) Treated	Kd(Tc) Untreated	Kd(Tc) Treated
5.0 M NaCl	10	0.9 ± 1.0(2)	0.7 ± 0.6	0.0 ± 1.2	-0.4 ± 0.5
	30	1.9 ± 0.6	1.0 ± 1.7	3.5 ± 2.7	-0.2 ± 1.6
0.5 M NaCl	10	12.3 ± 1.2	14.6 ± 1.1	-0.2 ± 1.1	-2.7 ± 1.0
	30	11.3 ± 0.7	11.2 ± 1.0	5.3 ± 0.8	4.3 ± 1.3
0.05 M NaCl	10	225 ± 40	222 ± 33	4.3 ± 0.4	2.3 ± 0.9
	30	360 ± 90	267 ± 32	4.2 ± 1.0	5.7 ± 2.9

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(1) untreated clay was not subjected to H_2O_2, treated clay was heated at 60 C with 30% H_2O_2.

(2) mean ± std. dev. (n=3).

TABLE 7. Measured pH and Eh Values for Kaolinite Systems

Concentration	Adsorption Time (days)	Untreated pH	Untreated Eh(o)*	H_2O_2 Treated pH	H_2O_2 Treated Eh(o)*
5.0 M NaCl	10	6.9 ± 0.3(1)	640 ± 40(2)	7.1 ± 0.3	540 ± 50
	30	6.5 ± 0.3	610 ± 80	6.4 ± 0.3	520 ± 40
0.5 M NaCl	10	6.9 ± 0.3	650 ± 30	7.0 ± 0.3	660 ± 80
	30	6.2 ± 0.4	610 ± 30	6.2 ± 0.4	630 ± 60
0.05 M NaCl	10	6.6 ± 0.3	660 ± 50	6.8 ± 0.3	680 ± 30
	30	5.8 ± 0.7	660 ± 40	6.0 ± 0.5	660 ± 10

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* Eh(o) = measured Eh (mv) + (pH) (59 mv)

(1) pH = mean ± (std. dev. of 3 measurements + 0.2 pH units meter accuracy)

(2) Eh(o) = mean ± std. dev. of 3 measurements

TABLE 8. Measured pH and Eh Values for Vermiculite Systems

Concentration	Adsorption Time (days)	Untreated		H_2O_2 Treated	
		pH	Eh(o)*	pH	Eh(o)*
5.0 M NaCl	10	7.3 ± 0.3(1)	520 ± 90(2)	7.3 ± 0.3	590 ± 50
	30	7.7 ± 0.3	610 ± 20	7.7 ± 0.3	660 ± 20
0.5 M NaCl	10	7.6 ± 0.2	620 ± 10	7.4 ± 0.3	600 ± 10
	30	8.3 ± 0.3	640 ± 30	7.7 ± 0.3	640 ± 20
0.05 M NaCl	10	7.4 ± 0.3	580 ± 50	7.3 ± 0.3	590 ± 10
	30	7.4 ± 0.4	640 ± 50	7.1 ± 0.3	610 ± 10

---

* Eh(o) = measured Eh (mv) + (pH) (59 mv)
(1) pH = mean ± (std. dev. of 3 measurements + 0.2 pH units meter accuracy)
(2) Eh(o) = mean ± std. dev. of 3 measurements

TABLE 9. Measured pH and Eh values for Montmorillonite Systems

Concentration	Adsorption Time (days)	Untreated		H_2O_2 Treated	
		pH	Eh(o)*	pH	Eh(o)*
5.0 M NaCl	10	7.0 ± 0.3(1)	570 ± 50(2)	6.9 ± 0.3	580 ± 90
	30	6.9 ± 0.3	530 ± 30	7.3 ± 0.5	580 ± 20
0.5 M NaCl	10	7.4 ± 0.3	640 ± 0	7.4 ± 0.2	670 ± 20
	30	7.8 ± 0.3	680 ± 30	7.7 ± 0.4	670 ± 30
0.05 M NaCl	10	7.4 ± 0.2	610 ± 20	7.4 ± 0.3	600 ± 80
	30	7.6 ± 0.3	620 ± 60	7.7 ± 0.3	640 ± 60

---

* Eh(o) = measured Eh (mv) + (pH) (59 mv)
(1) pH = mean ± (std. dev. of 3 measurements + 0.2 pH units meter accuracy)
(2) Eh(o) = mean ± std. dev. of 3 measurements

TABLE 10. Analysis of Variance for Sr Adsorption at Three Salt Concentrations on Peroxide Treated and Untreated Clays

At 10 Days

Source of Variation	Degrees of Freedom	Mean Squares	F-Value	
Treatment (T)	1	104	0.5	ns
Mineral (M)	2	25,534	134	**
Salt Concentration (S)	2	87,510	460	**
T x M	2	153	0.8	ns
T x S	2	127	0.7	ns
M x S	4	21,070	111	**
T x M x S	4	103	0.5	ns
Error	36	190		

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ns - Not Significant
** - Significant at 99% Confidence or Higher

TABLE 11. Analysis of Variance for Sr Adsorption at Three Salt Concentrations on Peroxide Treated and Untreated Clays

At 30 Days

Source of Variation	Degrees of Freedom	Mean Squares	F-Value	
Treatment (T)	1	4,396	3.6	ns
Mineral (M)	2	52,651	43.5	**
Salt Concentration (S)	2	192,289	161.5	**
T x M	2	1,280	1.1	ns
T x S	2	3,923	3.2	ns
M x S	4	45,575	37.7	**
T x M x S	4	1,242	1.0	ns
Error	36	1,209		

---

ns - Not Significant
** - Significant at 99% Confidence or Higher

TABLE 12. Analysis of Variance for Tc Adsorption at Three Salt Concentrations on Peroxide Treated and Untreated Clays

At 10 Days

Source of Variation	Degrees of Freedom	Mean Squares	F-Value
Treatment (T)	1	892	13.9 **
Mineral (M)	2	478	7.4 **
Salt Concentration (S)	2	196	3.0 ns
T x M	2	158	2.5 ns
T x S	2	39	0.6 ns
M x S	4	271	4.2 **
T x M x S	4	103	1.6 ns
Error	36	64	

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ns - Not Significant
** - Significant at 99% Confidence or Higher

TABLE 13. Analysis of Variance for Tc Adsorption at Three Salt Concentrations on Peroxide Treated and Untreated Clays

At 30 Days

Source of Variation	Degrees of Freedom	Mean Squares	F-Value
Treatment (T)	1	8,006	25 **
Mineral (M)	2	15,120	47 **
Salt Concentrations (S)	2	14,463	45 **
T x M	2	1,870	5.8 **
T x S	2	1,157	3.6 *
M x S	4	10,508	33 **
T x M x S	4	423	1.3 ns
Error	36	323	

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ns - Not Significant
* - Significant at 95% Confidence
** - Significant at 99% Confidence or Higher

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SORPTION BEHAVIOR OF ^{85}Sr, ^{137}Cs and ^{95m}Tc UNDER NORMAL ATMOSPHERIC AND REDUCED OXYGEN LEVELS

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SORPTION BEHAVIOR OF ^{85}Sr, ^{137}Cs and ^{95m} Tc UNDER NORMAL ATMOSPHERIC AND REDUCED OXYGEN LEVELS

The objective of this study was to determine whether the sorption-desorption behavior of radionuclides is affected by reducing the oxygen level in a rock-solution system. In order to accomplish the objective, a series of batch adsorption experiments were conducted in an anoxic chamber for comparison with previous results obtained under ambient atmospheric conditions.(1) Oxygen levels were reduced to less than 2000 ppm inside the anoxic chamber (compared to 200,000 ppm in air). Common to both anoxic and ambient studies were four solutions (5.13N NaCl, 0.03N $CaCl_2$, 0.03N NaCl and 0.03N $NaHCO_3$) and twelve minerals, including phyllosilicates (montmorillonite, illite, vermiculite, biotite and kaolinite), tektosilicates (quartz, albite, anorthite and microcline), and inosilicates (hornblende, enstatite and augite).

The minerals were crushed to less than 111 μm; 0.5 gram of each was weighed into an Oak Ridge polycarbonate centrifuge tube. The anoxic samples were each washed three times (twenty-four hours for each wash) using one of the four solutions to equilibrate the minerals with the solution. Radionuclides were added to about 700 ml of cold solution in the anoxic chamber and the pH was adjusted to 8.2 ± 0.1 for 0.03N $NaHCO_3$ and 7.0 ± 0.1 for the other three solutions. Each spiked solution was monitored for a week, with pH adjustment being made as needed before filtering through a 0.45 μm filter. Fifteen ml of the appropriate tagged solution were then pipetted into each sample tube. The tubes were sealed by wrapping the screw top threads with Teflon tape. These were shaken for three days before centrifuging at 7000 rpm for 20 minutes and sampling. All Kd values reported are blank corrected and were determined with a 25% Ge(Li) detector system or a 5 in. x 5 in. NaI (Tl) well-type detector system.

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(1) Serne, R. J. (Chairman), 1979. "Waste Isolation Safety Assessment Program Task 4 Second Contractors Meeting Proceedings," Seattle, Washington, October 1978, Report No. PNL-SA-7352.

Analysis of the minerals for purity was reported at the 1978 Task 4 Meeting.(1) Table 1a shows the mineral chemical compositions and Table 1b shows the surface areas and cation exchange capacities (CEC) for each mineral. The solution chemical compositions prior to and after mineral contact have been determined by inductively coupled argon plasma spectroscopy, atomic adsorption spectroscopy, and ion chromatography. Results are given in Tables 2 through 6.

Since reduced oxygen levels are not expected to change the chemical behavior of Sr^{2+} and Cs^{1+}, Sr and Cs were utilized to determine whether changes occur in the minerals because of a difference in oxygen levels. As Tc is sensitive to the oxidation-reduction potential, Kd differences were expected. An attempt to measure the redox potential (Eh) with Pt electrodes was made to determine the validity of Eh measurements for predicting nuclide Kd values. Values for pH were also measured. All pH, Eh, and Kd measurements were done in triplicate at 3 days, 10 days, and 30 days for adsorption and at 30 days for desorption measurements.

RESULTS AND DISCUSSION

Under anoxic conditions the pH was initially higher for each mineral-solution combination than under ambient condition, but at the 30-day sampling time, only pH values for the 0.03N $NaHCO_3$ were significantly different from those values measured in the ambient system. These values were lower in the anoxic environment than in air. Tc was utilized to determine the effects of reduced O_2 levels on a multivalent radionuclide. The observed Kd values for Sr, Cs, and Tc are reported in Tables 7 to 18.

Analysis of the three dilute effluent solutions (Table 4, 0.03N NaCl; Table 5, 0.03N $CaCl_2$; and Table 6, 0.03N $NaHCO_3$) showed significant differences between the ambient and anoxic cases. Silicon and aluminum concentrations were generally lower in the presence of air. Iron and silicon in the effluents increased over initial concentrations in the bicarbonate solution under both anoxic and ambient conditions. Iron concentrations were lowest in 0.03N $CaCl_2$ effluents. Bicarbonate and carbonate concentrations in 0.03N NaCl and 0.03N $CaCl_2$ were higher in the anoxic effluent than solutions in the ambient 0.03N $NaHCO_3$ effluent. The differences in solution compositions indicate that the minerals are not in the same physico-chemical state under ambient atmospheric and lowered oxygen levels.

Values for Kd(Sr)(2) in the 5.13N NaCl brine were found to increase by a factor of 100 on illite and vermiculite when compared to values obtained in an ambient environment. Comparisons of the 30-day Kd values for Sr, Cs and Tc under anoxic and ambient conditions are given in Tables 19, 20 and 21. The Kd(Sr) value on biotite was reduced by a factor of two in the anoxic environment while values for the other nine minerals contacting the brine remained unchanged. While some values for Kd(Sr) changed with time in 0.03N $CaCl_2$, only three significant differences (95% confidence level) were found between ambient and conditions at the end of 30 days of mineral-solution

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(2) Kd(Sr) is the Kd value for strontium, Sr, defined in this study as the ratio of the Sr concentration on the solid phase to the Sr concentration in solution with units of ml/g.

contact. In 0.03N NaCl, Kd(Sr) under anoxic conditions is higher for illite than the ambient value, but smaller on the four remaining phyllosilicates under anoxic conditions.

Values for Kd(Sr) after the 30-day desorption period are generally higher than the 30-day adsorption Kd(Sr) values. An analysis of solutions resulting from contact with the minerals and 0.03N NaCl for 30 days show that both Ca^{2+} and natural Sr^{2+} are released into solution by weathering of the minerals. Natural strontium concentrations ranged from less than 6×10^{-7}M up to 3×10^{-6}M, and calcium concentrations from 4×10^{-5}M to 8×10^{-4}M were found. The observed decrease in Kd(Sr) with time may be due to increasing competition for sorption sites between tracer ^{85}Sr and the Ca and Sr released from the minerals. Analysis of solutions after desorption was not done; however, the Ca^{2+} and Sr^{2+} released during adsorption studies were removed with the original solution before addition of cold 0.03N NaCl for desorption. Since the most easily weathered Ca^{2+} and Sr^{2+} were released during the adsorption study, it is possible that Ca and Sr concentrations after the 30-day desorption study were lower than they were after the 30-day adsorption tests. Less competition with naturally occurring Sr and Cs would account for the higher desorption Kd values.

Values for Kd(Sr) were highest in bicarbonate solution (0.03N $NaHCO_3$). Kd(Sr) was lowest in 5.13N NaCl and 0.03N $CaCl_2$. An increase of Kd(Sr) with time was observed in the bicarbonate solution on all tektosilicates, inosilicates, and on kaolinite; however, Kd(Sr) was found to decrease with time on the remaining phyllosilicates.

In general, Kd(Sr) values were lower in an anoxic environment than in an ambient one. The difference in the two environments was overshadowed by the time dependence of many Kd(Sr) values which indicates that equilibrium had not been attained.

Adsorption of cesium from the 5.13N NaCl brine was generally lower under anoxic conditions than in an ambient environment. Vermiculite was the only mineral to show higher Kd(Cs) values in an anoxic environment. The values for Kd(Cs) on montmorillonite, albite, anorthite and hornblende were significantly lower under reduced oxygen levels, while the rest were statistically unchanged.

Cesium adsorption from 0.03N $CaCl_2$ by the 2:1 layer phyllosilicates remained as high under anoxic conditions as in an ambient environment. Significant increases in Kd(Cs) under anoxic conditions were observed on montmorillonite and anorthite compared to ambient conditions. The remaining minerals (tektosilicates and inosilicates) showed decreases in Kd(Cs) ranging from a factor of four on microcline to an order of magnitude for kaolinite, albite, hornblende and enstatite under anoxic conditions compared to ambient conditions. Adsorption of cesium from 0.03N NaCl and the bicarbonate solution was generally lower or unchanged under anoxic conditions than in an ambient environment. Values for Kd(Cs) in the diluted brine (0.03N NaCl) and in 0.03N $NaHCO_3$ were generally lower or unchanged under anoxic conditions compared under ambient conditions.

Sorption Kd values for cesium under anoxic conditions were generally lower in all solutions compared to results obtained in the ambient environment. The 2:1 layer phyllosilicates were least affected by reduced oxygen levels, which may indicate more weathering of the primary minerals under anoxic conditions.

The sorption of technetium in a reduced oxygen environment contrasted sharply with the sorption of strontium and cesium. In the four solutions, with twelve minerals common to studies for all three nuclides, no significant decreases in technetium Kd values were observed under anoxic conditions. The variability between replicates in Kd(Tc) was large (standard deviation sometimes greater than 50% of the mean Kd value). Technetium sorption also exhibited erratic behavior with time as Kd values increased or decreased by one or two orders of magnitude between sampling times.

The anticipated correlation between observed Kd(Tc) values and the redox potential (measured with commercial Pt electrodes) is not apparent at this time. However, the removal of oxygen from mineral-solution systems has generally increased the sorption of technetium.

Adsorption of Tc is greatest on the inosilicates and tektosilicates for all times and solutions studied. Illite was the only phyllosilicate to show any consistent sorption of Tc. Analysis of solutions in contact with illite found significant quantities of SO_4^{-2} and lowered pHs which may have been caused by oxidation of FeS_2 (pyrite). The pertechnetate anion, TcO_4^-, could have been reduced in this reaction and readily adsorbed. Biotite and vermiculite also adsorbed Tc from 0.03N $CaCl_2$ and 5.13N NaCl, respectively. Generally, phyllosilicates sorbed Tc poorly compared to the "hard rock" minerals (inosilicates and tektosilicates). Bondietti(1) reported finding chunks of metal in rock samples distributed for the controlled sample program.(3) These were probably introduced in the grinding process from the metal plates used to crush the rock samples. Oxidation of metallic Fe to Fe^{2+} and Fe^{3+} would reduce TcO_4^- to the easily adsorbed Tc^{4+}. Thus, the key to increased Tc sorption may be found in understanding the environmental iron system.

After completion of anoxic desorption experiments, the sample and blank correction tubes were emptied and analyzed for activity sorbed by containers. Very little activity was sorbed by the blank containers. No significant adsorption of Sr by the blank tube walls was observed in any of the anoxic solutions. Cesium adsorption by the walls was less than 1% in three anoxic solutions and less than 2% in 0.03N $CaCl_2$. Technetium was not adsorbed by the tube containing 0.03N $NaHCO_3$. Less than 2% was adsorbed from the NaCl brine or the 0.03N NaCl solution. Significant adsorption of Tc by the blank tube was observed only in 0.03N $CaCl_2$ where 2 to 10% of the total Tc activity was removed from solution by the polycarbonate tube walls. A portion of the activity left in sample tubes seemed to be associated with coatings of fine mineral particles (or precipitates of weathering products) adhering to the tube walls.

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(3) Relyea, J. F. and R. J. Serne, 1979. Controlled Sample Program Publication Number 2: Interlaboratory Comparison of Batch Kds, PNL-2872.

SUMMARY AND CONCLUSIONS

Identical mineral samples and simulated groundwaters were used in a study of the sorption of technetium, strontium and cesium under anoxic conditions for comparison with sorption results under ambient atmospheric conditions.

Results from these experiments show that the anoxic sorption of strontium and cesium is generally unchanged or lower than sorption under ambient conditions. The sorption of both Cs and Sr is inhibited by the presence of high NaCl concentrations (brines), and Sr sorption is reduced by the presence of Ca^{2+} in solution. Values for Kd(Cs) and Kd(Sr) often change with time, as both the mineral properties and solution chemical composition change due to weathering of the minerals. In these instances equilibrium has not been attained; differences between ambient and anoxic Kd values found at short contact times may disappear at equilibrium.

Both Kd values and their variability were increased for technetium under anoxic conditions. Technetium adsorption is greatest on the "hard rock" minerals (tektosilicates and inosilicates) which may be influenced by small chunks of metal from the apparatus used to grind the minerals to power form.

TABLE 1a. Mineral Compositions (percent by weight)

	Phyllosilicates				
	Illite	Montmorillonite	Vermiculite	Kaolinite	Biotite
SiO_2	67.1	64.6	47.7	54.8	43.9
TiO_2	0.8	0.3	0.7	1.5	1.9
Al_2O_3	20.1	19.3	11.7	43.1	11.3
FeO	5.1	3.3	9.5	0.1	16.9
CaO	--	8.5	1.3	--	0.5
MgO	--	3.3	22.0	--	14.1
Na_2O	--	--	0.5	--	--
K_2O	6.1	--	6.2	0.4	11.1
	99.3	99.3	99.6	99.9	99.7

	Tektosilicates			
	Quartz	Albite	Anorthite	Microcline
SiO_2	99.8	60.5	64.2	67.5
TiO_2	--	--	--	--
Al_2O_3	--	20.5	21.0	17.1
FeO	0.2	9.0	1.2	1.8
CaO	--	5.2	5.6	0.1
MgO	--	--	--	--
Na_2O	--	3.6	6.2	--
K_2O	--	1.3	1.2	13.6
	100.0	100.1	99.4	100.1

	Inosilicates		
	Hornblende	Enstatite	Augite
SiO_2	50.5	58.6	55.7
TiO_2	1.4	--	5.0
Al_2O_3	10.0	--	--
FeO	14.5	8.8	6.1
CaO	--	0.5	24.4
MgO	9.3	30.9	9.0
Na_2O	--	--	--
K_2O	0.5	--	--
	99.0	98.8	100.2

TABLE 1b. Mineral and Rock Physical Characterization

Mineral Rock	Cation Exchange Capacity meq/100 g	Surface Area
Illite	13.8 ± .8	165.3 ± 3.3
Kaolinite	5.0 ± .9	30.7 ± .5
Montmorillonite	87.4 ± 2.7	722.2 ± 6.9
Vermiculite	77.0 ± 4.8	312.5 ± 7.8
Biotite	15.3 ± 1.1	68.8 ± .8
Quartz	0.15 ± .07	2.8 ± .2
Albite	1.5 ± .3	8.4 ± 3.7
Anorthite	1.8 ± .4	9.2 ± 1.3
Microcline	1.2 ± .2	5.1 ± 1.0
Hornblende	2.9 ± .5	4.3 ± .8
Enstatite	1.9 ± .3	15.7 ± 1.0
Augite	4.5 ± .6	7.1 ± .4

TABLE 2. Solution Chemical Compositions from Batch Kd Experiments Initial Solution Concentrations (ppm)(1)

Solution (2)	(3)	(4)	CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Blank	A	O	0	11(5) ±5(6)	183,000 ±7,000	36 ±33	≤10	≤20	≤10	≤500	≤5	121,000 ±7,000	≤5	≤10
Blank	A	N	0	11 ±5	193,000 ±2,000	36 ±33	≤10	≤20	≤10	≤500	≤5	121,000 ±7,000	≤5	≤10
Blank	B	O	0	11 ±10	916 ±105	≤0.1	≤0.1	537 ±75	≤0.1	9 ±6	1.4 ±0.2	4 ±2	≤0.05	≤0.1
Blank	B	N	0	11 ±10	916 ±105	≤0.1	≤0.1	537 ±75	≤0.1	9 ±6	1.4 ±0.2	4 ±2	≤0.05	≤0.1
Blank	C	O	0	14 ±10	1100 ±11	≤0.1	≤0.1	0.2 ±0.2	≤0.1	14 ±3	0.05 ±0.05	672 ±45	≤0.05	≤0.1
Blank	C	N	0	14 ±10	1100 ±11	≤0.1	≤0.1	0.2 ±0.2	≤0.1	14 ±3	0.05 ±0.05	672 ±45	≤0.05	≤0.1
Blank	D	O	264 ±84	1216 ±223	43 ±22	≤0.1	≤0.1	0.2 ±0.2	≤0.1	≤5	≤0.05	652 ±37	≤0.05	≤0.1
Blank	D	N	264 ±84	1216 ±223	43 ±22	≤0.1	≤0.1	0.2 ±0.2	≤0.1	≤5	≤0.05	652 ±37	≤0.05	≤0.1

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(1) Results from nonradioactive solution contacting sample minerals for 30 days.

(2) Blank = no mineral in contact with solution, following tables three letter abbreviations for minerals are Ill = illite, Mon = montmorillonite, Ver = vermiculite, Bio = biotite, Kao = kaolinite, Qtz = quartz, Alb = albite, Anr = anorthite, Mic = microcline, Hor = hornblende, Ens = enstatite, Aug = augite.

(3) Initial solutions; A = 5.13N NaCl, B = 0.03N $CaCl_2$, C = 0.03N NaCl, D = 0.03N $NaHCO_3$.

(4) Atmosphere used for test; N = anoxic, O = oxic.

(5) Mean value of duplicate samples for each ground water, except when no difference between oxic and anoxic treatments are found, then each concentration is the mean of 4 analyses. Numbers without error estimate are results of single run or below detection limit.

(6) Error is given as one standard deviation from the mean.

TABLE 3. Solution Chemical Compositions from Batch Kd Experiments Initial Solution Concentrations (ppm) from Initial 5.13N CaCl(1)

Solution (2)	(3)	(4)	CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Ill	A	0	0	15.6(5)	182,440	99	<10	<20	<10	<500	<5	111,300	<5	<10
Ill	A	N	0	37.1	197,120	<150	<10	<20	<10	<500	<5	122,600	<5	<10
Mon	A	0	0	49	179,210	74	<10	20	<10	<500	<5	113,400	<5	<10
Mon	A	N	0	76	194,919	<150	<10	30	<10	<500	<5	124,500	<5	<10
Ver	A	0	0	55	179,210	112	<10	20	<10	<500	<5	116,500	<5	<10
Ver	A	N	0	82	193,820	<150	<10	20	<10	<500	<5	112,700	<5	<10
Bio	A	0	0	63	180,280	<100	<10	20	<10	<500	<5	113,000	<5	<10
Bio	A	N	24	36	195,470	<150	<10	20	<10	<500	<5	122,700	<5	<10
Kao	A	0	0	2	178,670	95	<10	<20	<10	<500	<5	109,500	<5	<10
Kao	A	N	0	12	194,920	<150	<10	<20	<10	<500	<5	123,200	<5	<10
Qtz	A	0	0	4	179,210	116	<10	<20	<10	<500	<5	111,500	<5	<10
Qtz	A	N	0	14	194,920	<150	<10	<20	<10	<500	<5	115,600	<5	<10
Alb	A	0	0	18	179,210	<100	<10	10	<10	<500	<5	109,900	<5	<10
Alb	A	N	0	49	195,470	<150	<10	20	<10	<500	<5	119,300	<5	<10
Anr	A	0	0	59	179,750	<100	<10	20	<10	<500	<5	114,100	<5	<10
Anr	A	N	0	63	196,570	<150	<10	20	<10	<500	<5	114,100	<5	<10
Mic	A	0	0	8	176,520	143	<10	<20	<10	<500	<5	109,500	<5	<10
Mic	A	N	0	23	195,470	<150	<10	<20	<10	<500	<5	129,400	<5	<10
Hor	A	0	0	57	178,130	30	<10	20	<10	<500	<5	106,600	<5	<10
Hor	A	N	0	70	194,920	<150	<10	20	<10	<500	<5	117,600	<5	<10
Ens	A	0	0	31	178,130	97	<10	<20	<10	<500	<5	119,100	<5	<10
Ens	A	N	0	47	194,370	<150	<10	<20	<10	<500	<5	118,000	<5	<10
Aug	A	0	12	59	177,050	<100	<10	30	<10	<500	<5	113,200	<5	<10
Aug	A	N	29	32	194,920	<150	<10	30	<10	<500	<5	120,900	<5	<10

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(1) Results from nonradioactive solution contacting sample minerals for 30 days.

(2) Blank = no mineral in contact with solution, following tables three letter abbreviations for minerals are Ill = illite, Mor = montmorillonite, Ver = vermiculite, Bio = biotite, Kao = kaolinite, Qtz = quartz, Alb = albite, Anr = anorthite, Mic = microcline, Hor = hornblende, Ens = enstatite, Aug = augite.

(3) Initial solutions; A = 5.13N NaCl, B = 0.03N $CaCl_2$, C = 0.03N NaCl, D = 0.03N $NaHCO_3$.

(4) Atmosphere used for test; N = anoxic, 0 = oxic.

(5) No duplication or brine samples.

TABLE 4. Solution Chemical Compositions(1) from Batch Kd Experiments Mineral-Solution Concentrations (ppm) from Initial 0.03N $CaCl_2$

Solution			CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
(2)	(3)	(4)												
Ill	B	O	0	22	937(5) ±92(6)	22 ±6	≤0.2	567 ±61	≤0.1	39 ±19	15 ±12	5 ±2	0.2 ±0.3	2.8 ±1.0
Ill	B	N	0	39	937 ±92	22 ±6	0.3 ±0.3	567 ±61	≤0.1	39 ±19	15 ±12	5 ±2	0.2 ±0.3	2.8 ±1.0
Mon	B	O	0	14	934 ±93	2.4 ±1.0	≤0.1	547 ±66	≤0.1	25 ±19	6 ±2	8 ±7	1.2 ±0.4	8.3 ±4.3
Mon	B	N	0	6	934 ±93	2.4 ±1.0	≤0.1	547 ±66	≤0.1	25 ±19	6 ±2	8 ±7	1.2 ±0.4	8.3 ±4.3
Ver	B	O	0	16	930 ±95	0.4 ±0.2	0.2 ±0.2	501 ±60	0.3 ±0.4	63 ±15	5.0 ±1.8	19 ±13	0.7 ±0.7	2.5 ±0.1
Ver	B	N	0	20	930 ±95	0.4 ±0.2	0.5 ±0.5	501 ±60	1.1 ±0.1	63 ±15	7.2 ±1.3	31 ±17	0.7 ±0.7	3.5 ±0.6
Bio	B	O	0	18	927 ±99	0.4 ±0.4	≤0.1	552 ±53	0.2 ±0.2	27 ±26	4.9 ±2.1	4 ±2	≤0.05	1.7 ±0.9
Bio	B	N	0	29	927 ±99	≤0.1	≤0.1	552 ±53	0.7 ±0.8	27 ±26	4.9 ±2.1	12 ±8	≤0.05	1.7 ±0.9
Kao	B	O	0	4	920 ±117	0.3 ±0.3	≤0.1	559 ±60	≤0.1	20 ±14	1.4 0.4	4 ±2	≤0.05	2.1 ±1.8
Kao	B	N	0	6	920 ±117	≤0.1	0.7 ±0.7	559 ±60	≤0.1	20 ±14	1.4 ±0.4	4 ±2	≤0.05	2.1 ±1.8
Qtz	B	O	0	≤0.1	945 ±88	≤0.1	≤0.1	558 ±67	0.10 ±0.05	20 ±3	1.4 ±0.4	13 ±12	≤0.05	10 ±8
Qtz	B	N	0	6	945 ±88	≤0.1	≤0.1	558 ±67	0.4 ±0.2	20 ±3	1.4 ±0.4	13 ±12	≤0.05	10 ±8
Alb	B	O	0	14	934 ±92	0.8 ±0.5	0.2 ±0.1	546 ±63	<0.1	26 ±16	1.5 ±0.5	11 ±4	0.1 ±0.2	2.6 ±1.6
Alb	B	N	0	23	934 ±92	0.8 ±0.5	0.2 ±0.1	546 ±63	<0.1	26 ±16	1.5 ±0.5	11 ±4	0.1 ±0.2	2.6 ±1.6

TABLE 4. (contd)

Solution			CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Anr	B	O	0	18	940 ±90	0.4 ±0.5	0.6 ±0.3	554 ±71	<0.1	18 ±11	1.7 ±0.8	12 ±9	0.25 ±0.22	2.9 ±1.0
Anr	B	N	0	27	940 ±90	0.4 ±0.5	0.6 ±0.3	554 ±71	0.11 ±0.13	18 ±11	1.7 ±0.8	12 ±9	0.25 ±0.22	2.9 ±1.0
Mic	B	O	0	12	950 ±93	0.5 ±0.7	≤0.1	529 ±80	<0.1	22 ±6	1.4 ±0.4	9 ±2	≤0.05	4.2 ±1.7
Mic	B	N	0	12	950 ±93	0.5 ±0.7	0.3 ±0.3	529 ±80	0.2 ±0.2	22 ±6	1.4 ±0.4	9 ±2	≤0.05	4.2 ±1.7
Hor	B	O	0	8	948 ±93	0.7 ±0.7	≤0.1	547 ±66	0.1 ±0.1	28 ±3	7.4 ±2.7	8 ±5	≤0.05	3.3 ±1.3
Hor	B	N	0	18	948 ±93	0.7 ±0.7	≤0.1	547 ±66	0.5 ±0.5	28 ±3	7.4 ±2.7	8 ±5	≤0.05	3.3 ±1.3
Ens	B	O	6	2	936 ±89	0.4 ±0.4	≤0.1	542 ±64	≤0.1	24 ±16	13 ±4	9 ±7	≤0.05	16 ±12
Ens	B	N	0	25	936 ±89	0.4 ±0.4	≤0.1	542 ±64	0.4 ±0.4	24 ±16	13 ±4	9 ±7	≤0.05	16 ±12
Aug	B	O	0	14	951 ±94	0.5 ±0.5	≤0.1	548 ±69	0.1 ±0.1	15 ±9	9.1 1.0	10 ±6	≤0.05	22 ±11
Aug	B	N	10	45	951 ±94	0.8 ±0.8	≤0.1	548 ±69	0.3 ±0.3	15 ±9	7.0 ±0.3	10 ±6	≤0.05	22 ±11

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(1) Results from nonradioactive solution contacting sample minerals for 30 days.
(2) Blank = no mineral in contact with solution, following tables three letter abbreviations for minerals are Ill = illite, Mon = montmorillonite, Ver = vermiculite, Bio = biotite, Kao = kaolinite, Qtz = quartz, Alb = albite, Anr = anorthite, Mic = microcline, Hor = hornblende, Ens = enstatite, Aug = augite.
(3) Initial solutions; A = 5.13N NaCl, B = 0.03N $CaCl_2$, C = 0.03N NaCl, D = 0.03N $NaHCO_3$.
(4) Atmosphere used for test; N = anoxic, O = oxic.
(5) Mean value of duplicate samples for each ground water, except when no difference between oxic and anoxic treatments are found, then each concentration is the mean of 4 analyses. Numbers without error estimate are results of single run or below detection limit.
(6) Error is given as one standard deviation from the mean.

TABLE 5. Solution Chemical Compositions from Batch Kd Experiments Mineral-Solution Concentrations (ppm) from Initial 0.03N NaCl(1)

Solution (2)	(3)	(4)	CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Ill	C	O	0	32	1098(5) ±18(6)	42 ±14	≤0.1	32 ±10	≤0.1	24 ±8	3.9 ±1.1	668 ±32	0.21 ±0.05	2.1 ±0.1
Ill	C	N	0	70 ±20	1098 ±18	42 ±14	≤0.1	32 ±10	≤0.1	24 ±8	3.9 ±1.1	668 ±32	0.21 ±0.05	2.1 ±0.1
Mon	C	O	0	25	1114 ±51	3.2 ±1.3	≤0.1	26 ±17	0.1 ±0.1	19 ±15	1.2 ±0.3	710 ±59	0.23 ±0.17	5.0 ±1.3
Mon	C	N	0	33	1114 ±51	3.2 ±1.3	≤0.1	26 ±17	≤0.1	19 ±15	1.2 ±0.3	710 ±59	0.23 ±0.17	5.3 ±1.3
Ver	C	O	0	27	1126 ±64	≤0.1	0.25 ±0.07	7.7 ±2.1	0.3 ±0.3	34 ±5	1.8 ±0.4	716 ±50	0.05 ±0.05	2.4 ±0.6
Ver	C	N	0	33	1126 ±64	≤0.1	0.25 ±0.07	7.7 ±2.1	0.3 ±0.3	41 ±9	2.2 ±0.4	716 ±50	0.05 ±0.05	2.8 ±0.6
Bio	C	O	0	41	1124 ±59	≤0.1	0.1 ±0.05	17 ±7	≤0.1	15 ±6	2.2 ±1.6	724 ±42	≤0.05	1.9 ±1.7
Bio	C	N	0	43	1124 ±59	≤0.1	0.1 ±0.05	17 ±7	0.20 ±0.14	15 ±6	2.2 ±1.6	724 ±42	≤0.05	1.9 ±1.7
Kao	C	O	0	10	1122 ±57	≤0.1	≤0.1	1.6 ±1.6	≤0.1	13 ±3	0.5 ±0.5	719 ±43	≤0.05	1.7 ±1.6
Kao	C	N	0	4	1122 ±57	≤0.1	0.3 ±0.3	1.6 ±1.6	≤0.1	13 ±3	0.5 ±0.5	719 ±43	≤0.05	1.7 ±1.6
Qtz	C	O	0	5	1167 ±124	≤0.1	≤0.1	2.1 ±2.1	≤0.1	24 ±19	0.5 ±0.5	749 ±87	≤0.05	6.5 ±5.0
Qtz	C	N	0	12	1167 ±124	≤0.1	≤0.1	2.1 ±2.1	≤0.1	24 ±19	0.5 ±0.5	749 ±87	≤0.05	6.5 ±5.0
Alb	C	O	0	33	1093 ±3	0.4 ±0.5	1.1 ±1.1	12 ±3	≤0.1	15 ±14	0.6 ±0.5	742 ±55	≤0.5	2.3 ±0.7
Alb	C	N	0	39	1275 ±22	0.4 ±0.5	1.1 ±1.1	12 ±3	≤0.1	15 ±14	0.6 ±0.5	742 ±55	0.5 ±0.5	2.3 ±0.7

TABLE 5. (contd)

Solution			CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Anr	C	O	0	35	1178 ±172	≤0.1	0.9 ±0.7	14 ±5	≤0.1	15 ±8	0.7 ±0.7	756 ±117	0.24 ±0.07	2.6 ±0.5
Anr	C	N	0	45	1178 ±172	≤0.1	0.9 ±0.7	18 ±2	0.1 ±0.1	15 ±8	0.7 ±0.7	756 ±117	0.24 ±0.07	2.6 ±0.5
Mic	C	O	0	12	1150 ±74	0.5 ±0.5	0.5 ±0.5	2.5 ±2.0	0.5 ±0.5	24 ±8	≤0.1	724 ±63	≤0.05	3.9 ±2.8
Mic	C	N	0	16	1150 ±74	0.5 ±0.5	0.5 ±0.5	2.5 ±2.0	0.5 ±0.5	24 ±8	≤0.1	724 ±63	≤0.05	3.9 ±2.8
Hor	C	O	0	41	1176 ±94	1.0 ±1.0	0.9 ±0.6	12 ±3	0.6 ±1.1	23 ±8	4 ±3	749 ±71	≤0.05	6.6 ±4.4
Hor	C	N	0	20	1176 ±94	0.6 ±0.6	0.5 ±0.5	12 ±3	0.6 ±1.1	23 ±8	4 ±3	749 ±71	≤0.05	6.6 ±4.4
Ens	C	O	0	31	1180 ±160	≤0.1	≤0.1	4.5 ±1.8	1.2 ±1.7	14 ±1	8 ±5	757 ±109	≤0.05	13 ±12
Ens	C	N	0	33	1180 ±160	≤0.1	≤0.1	4.5 ±1.8	1.2 ±1.7	14 ±1	8 ±5	757 ±109	0.50 ±0.50	13 ±12
Aug	C	O	0	68	1136 ±61	0.1 ±0.1	0.1 ±0.1	22 ±1	1.1 ±1.2	40 ±25	4 ±3	723 ±52	≤0.05	31 ±14
Aug	C	N	8 ±4	44	1136 ±61	0.7 ±0.5	0.1 ±0.1	22 ±1	1.1 ±1.2	40 ±25	4 ±3	723 ±52	≤0.05	31 ±14

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(1) Results from norradioactive solution contacting sample minerals for 30 days.
(2) Blank = no mineral in contact with solution, following tables three letter abbreviations for minerals are Ill = illite, Mon = montmorillonite, Ver = vermiculite, Bio = biotite, Kao = kaolinite, Qtz = quartz, Alb = albite, Anr = anorthite, Mic = microcline, Hor = hornblende, Ens = enstatite, Aug = augite.
(3) Initial solutions; A = 5.13N NaCl, B = 0.03N $CaCl_2$, C = 0.03N NaCl, D = 0.03N $NaHCO_3$.
(4) Atmosphere used for test; N = anoxic, O = oxic.
(5) Mean value of duplicate samples for each ground water, except when no difference between oxic and anoxic treatments are found, then each concentration is the mean of 4 analyses. Numbers without error estimate are results of single run or below detection limit.
(6) Error is given as one standard deviation from the mean.

TABLE 6. Solution Chemical Compositions from Batch Kd Experiments Mineral-Solution Concentrations (ppm) from Initial 0.03N $NaHCO_3$ (1)

Solution (2)	(3)	(4)	CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Ill	D	O	66(5) ±93(6)	1136 ±135	24 ±7	32 ±12	3.8 ±3.5	2.8 ±1.4	0.8 ±0.7	8 ±6	1.5 ±1.1	695 ±55	0.08 ±0.05	12 ±11
Ill	D	N	145 ±37	1498 ±125	41 ±3	32 ±12	3.8 ±3.5	2.8 ±1.4	0.8 ±0.7	8 ±6	1.5 ±1.1	695 ±55	≤0.05	12 ±11
Mon	D	O	127 ±90	1263 ±270	14 ±7	2.1 ±0.6	1.4 ±1.8	2.3 ±1.1	0.4 ±0.4	7 ±7	0.8 ±0.1	587 ±63	≤0.05	8.7 ±0.4
Mon	D	N	127 ±90	1263 ±270	64 ±43	1.7 ±2.4	1.4 ±1.8	3.1 ±1.5	0.4 ±0.4	7 ±7	1.4 ±0.1	587 ±63	≤0.05	12 ±4
Ver	D	O	168 ±83	1438 ±134	12 ±7	0.7 ±0.8	0.4 ±0.1	3.3 ±1.0	0.9 ±0.3	24 ±4	2.8 ±0.2	673 ±22	≤0.05	3.9 ±0.6
Ver	D	N	168 ±83	1438 ±134	34 ±1	0.7 ±0.8	1.9 ±0.1	2.6 ±1.0	2.8 ±0.1	24 ±4	5.6 ±0.4	673 ±22	≤0.05	9.2 ±2.0
Bio	D	O	151 ±69	1539 ±161	19 ±11	1.5 ±1.8	1.6 ±1.7	3.1 ±2.8	0.3 ±0.1	6 ±4	3 ±4	693 ±37	≤0.05	0.8 ±0.1
Bio	D	N	269 ±52	1292 ±64	19 ±11	1.5 ±1.8	1.6 ±1.7	3.1 ±2.8	0.3 ±0.1	6 ±4	3 ±4	693 ±37	≤0.05	0.8 ±0.1
Kao	D	O	101 ±50	1350 ±177	20 ±1	1.6 ±2.4	0.2 ±0.1	1.5 ±1.4	≤0.1	7 ±5	0.4 ±0.4	694 ±24	≤0.05	1.2 ±1.7
Kao	D	N	279 ±19	1350 ±177	35 ±4	1.6 2.4	0.2 ±0.1	1.5 ±1.4	0.1 ±0.1	7 ±5	0.4 ±0.4	694 ±24	≤0.05	1.2 ±1.7
Qtz	D	O	209 ±121	1243 ±330	28 ±14	1.6 ±1.6	≤0.1	3.3 ±2.9	1.5 ±0.6	7 ±2	0.9 ±1.0	714 ±39	≤0.05	6 ±3
Qtz	D	N	209 ±121	1243 ±330	59 ±37	1.6 ±1.6	≤0.1	3.3 ±2.9	1.5 ±0.6	7 ±2	0.9 ±1.0	714 ±39	≤0.05	6 ±3
Alb	D	O	152 ±49	1530 ±84	18 ±1	0.4 ±0.4	1.8 ±1.8	2.7 ±1.6	0.5 ±0.6	≤5	0.6 ±0.6	677 ±43	≤0.05	8 ±6
Alb	D	N	267 ±82	1281 ±129	37 ±8	0.4 ±0.4	1.8 ±1.8	2.7 ±1.6	0.5 ±0.6	≤5	0.6 ±0.6	677 ±43	≤0.05	8 ±6

TABLE 6. (contd)

Solution			CO_3	HCO_3	Cl	SO_4	Al	Ca	Fe	K	Mg	Na	Sr	Si
Anr	D	O	146 ±21	1574 ±170	20 ±5	0.6 ±0.6	1.7 ±0.8	2.5 ±1.4	1.4 ±1.5	6 ±1	0.5 ±0.6	696 ±49	0.07 ±0.05	5 ±3
Anr	D	N	276 ±110	1303 ±148	32 ±2	0.6 ±0.6	1.7 ±0.8	2.5 ±1.4	1.4 ±1.5	6 ±1	0.5 ±0.6	696 ±49	≤0.05	5 ±3
Mic	D	O	123 ±68	1529 ±60	15 ±7	0.6 ±0.4	0.6 ±0.2	2.3 ±1.9	1.1 ±1.2	12 ±6	0.6 ±0.7	659 ±38	≤0.05	5 ±3
Mic	D	N	297 ±142	1294 ±177	32	0.6 ±0.4	0.6 ±0.2	2.3 ±1.9	1.1 ±1.2	12 ±6	0.6 ±0.7	659 ±38	≤0.05	5 ±3
Hor	D	O	192 ±24	1338 ±286	23 ±8	1.4 ±1.1	0.5 ±0.2	1.3 ±0.3	0.1 ±0.05	9 ±8	4.1 ±2.4	672 ±28	≤0.05	3.3 ±1.2
Hor	D	N	293 ±107	1222 ±234	47 ±12	≤0.1	0.5 ±0.2	1.3 ±0.3	0.3 ±0.05	9 ±8	4.1 ±2.4	672 ±28	≤0.05	3.3 ±1.2
Ens	D	O	203 ±50	1479 ±151	16 ±2	1.6 ±1.7	≤0.05	3.6 ±3.0	0.5 ±0.4	5 ±5	16 ±3	700 ±23	≤0.05	32 ±5
Ens	D	N	314 ±61	1303 ±136	46 ±21	1.6 ±1.7	≤0.05	3.6 ±0.3	0.5 ±0.4	5 ±5	11 ±2	700 ±23	≤0.05	10 ±2
Aug	D	O	209 ±42	1489 ±119	22 ±3	0.6 ±0.7	≤0.1	2.2 ±1.7	0.2 ±0.1	10 ±5	13 ±1	686 ±49	≤0.05	30 ±9
Aug	D	N	357 ±6	1202 ±81	51 ±29	0.6 ±0.7	≤0.1	2.2 ±1.7	0.2 ±0.1	10 ±5	10 ±2	686 ±49	≤0.05	30 ±9

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(1) Results from nonradioactive solution contacting sample minerals for 30 days.

(2) Blank = no mineral in contact with solution, following tables three letter abbreviations for minerals are Ill = illite, Mon = montmorillonite, Ver = vermiculite, Bio = biotite, Kao = kaolinite, Qtz = quartz, Alb = albite, Anr = anorthite, Mic = microcline, Hor = hornblende, Ens = enstatite, Aug = augite.

(3) Initial solutions; A = 5.13N NaCl, B = 0.03N $CaCl_2$, C = 0.03N NaCl, D = 0.03N $NaHCO_3$.

(4) Atmosphere used for test; N = anoxic, O = oxic.

(5) Mean value of duplicate samples for each ground water, except when no difference between oxic and anoxic treatments are found, then each concentration is the mean of 4 analyses. Numbers without error estimate are results of single run or below detection limit.

(6) Error is given as one standard deviation from the mean.

TABLE 7. Sr Sorption from 5.13N NaCl Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Sr)(2)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)
Illite	410(3) ±37	7.4 ±0.1	-2.5 ±2.4	570 ±39	7.2 ±0.2	135 ±9	432 ±68	6.4 ±0.2	135 ±2	533 ±49	6.4 ±0.1	ND
Montmorillonite	697 ±65	8.4 ±0.1	0.5 ±0.7	677 ±6	8.3 ±0.1	1.7 ±0.3	564 ±138	7.9 ±0.1	2.9 ±1.3	728 ±51	8.5 ±0.0	3.9 ±14.5
Vermiculite	701 ±13	8.7 ±0.2	-1.9 ±0.8	632 ±16	8.2 ±0.1	136 ±6	416 ±55	8.1 ±0.1	127 ±7	706 ±23	8.1 ±0.3	ND
Biotite	695 ±27	8.8 ±0.3	2.1 ±1.8	709 ±11	8.3 ±0.1	0.3 ±0.7	690 ±41	8.2 ±0.1	1.8 ±1.1	720 ±63	8.6 ±0.1	≤0
Kaolinite	683 ±55	7.2 ±0.2	1.2 ±0.9	675 ±25	6.8 ±0.1	0.8 ±2.2	690 ±37	6.5 ±0.1	9.6 ±17.1	412 ±83	6.8 ±0.3	163 ±272
Quartz	511 ±198	7.3 ±0.2	-0.7 ±1.3	654 ±31	6.8 ±0.6	1.3 ±1.4	689 ±51	6.7 ±0.1	-2.2 ±1.8	739 ±38	7.3 ±0.6	≤0
Albite	366 ±87	8.6 ±0.2	5.9 ±1.4	386 ±100	7.8 ±0.2	5.8 ±1.7	600 ±116	7.6 ±0.3	5.5 ±2.4	553 ±178	7.0 ±0.1	12.3 ±13.4
Anorthite	485 ±41	8.3 ±0.3	6.0 ±2.0	718 ±28	8.0 ±0.0	2.7 ±1.0	664 ±77	7.6 ±0.1	2.3 ±1.1	627 ±144	8.2 ±0.0	9.6 ±8.3
Microcline	470 ±160	7.7 ±0.5	4.5 ±0.5	693 ±4	7.0 ±0.1	3.5 ±3.0	698 ±18	6.5 ±0.6	5.0 ±6.2	471 ±157	7.5 ±0.7	41 ±70
Hornblende	681 ±19	8.9 ±0.2	0.9 ±1.2	695 ±34	8.1 ±0.1	-0.5 ±0.9	693 ±6	8.1 ±0.1	8.7 ±12.7	742 ±8	8.3 ±0.1	2.5 ±4.4
Enstatite	510 ±280	8.9 ±0.3	3.4 ±1.1	718 ±11	8.1 ±0.1	0.4 ±1.3	593 ±171	8.0 ±0.1	1.6 ±0.8	700 ±11	8.0 ±0.1	-1.0 ±1.7
Augite	467 ±127	9.5 ±0.3	4.3 ±1.4	720 ±21	8.8 ±0.1	6.8 ±2.1	586 ±70	8.2 ±0.0	3.9 ±0.2	671 ±31	8.6 ±0.1	0.6 ±1.1

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 8. Sr Sorption from 0.03N $CaCl_2$ Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Sr)(2)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)
Illite	510(3) ±42	7.3 ±0.2	5.0 ±0.7	382 ±151	7.1 ±0.0	6.8 ±1.8	187 ±28	7.2 ±0.1	6.1 ±2.1	352 ±148	6.7 ±0.1	1.0 ±1.7
Montmorillonite	667 ±31	8.0 ±0.0	32 ±2	645 ±35	7.8 ±0.0	32 ±1	234 ±132	7.7 ±0.0	38 ±3	679 ±43	8.1 ±0.1	45 ±8
Vermiculite	614 ±64	7.9 +0.2	30 ±3	548 ±111	7.6 ±0.0	29 ±6	173 ±43	7.7 ±0.2	25.8 ±0.4	420 ±88	8.2 ±0.1	28 ±9
Biotite	534 ±346	8.2 ±0.1	13 ±1	388 ±154	7.7 ±0.1	7.8 ±3.5	434 ±148	7.7 ±0.1	9.0 ±0.4	249 ±142	8.0 ±0.4	12 ±11
Kaolinite	517 ±289	7.0 ±0.1	-0.7 ±0.2	481 ±168	6.1 ±0.1	1.9 ±0.8	175 ±25	6.4 ±0.1	2.1 ±3.3	607 ±96	6.8 ±0.3	15 ±25
Quartz	495 ±231	7.0 ±0.1	-0.5 ±0.4	511 ±92	6.7 ±0.3	0.7 ±2.8	296 ±127	7.4 ±0.3	-0.1 ±1.6	728 ±36	6.7 ±0.3	≈0
Albite	177 ±106	8.9 ±0.1	2.5 ±1.2	435 ±45	7.8 ±0.0	3.4 ±0.4	446 ±232	7.7 ±0.1	8.9 ±1.0	369 ±198	8.2 ±0.5	13 ±10
Anorthite	293 ±254	8.8 ±0.5	1.7 ±0.5	668 ±28	8.2 ±0.2	6.4 ±1.7	475 ±174	7.7 ±0.1	4.7 ±2.7	507 ±87	8.2 ±0.1	7 ±13
Microcline	227 ±103	8.6 ±0.3	2.9 ±1.0	630 ±78	7.6 ±0.0	7.8 ±4.8	393 ±254	7.2 ±0.4	5.4 ±4.3	743 ±10	8.1 ±0.1	3 ±3
Hornblende	579 ±90	8.8 ±0.3	0.3 ±0.7	521 ±240	7.8 ±0.2	3.1 ±1.6		7.7 ±0.0	3.7 ±1.3	752 ±52	8.2 ±0.1	66 ±92
Enstatite	514 ±161	9.0 ±0.1	-0.3 ±0.3	718 ±11	8.1 ±0.1	2.0 ±3.2	293 ±134	7.8 ±0.2	2.6 ±2.3	549 ±83	8.2 ±0.2	1.7 ±2.9
Augite	528 ±164	9.7 ±0.0	0.8 ±0.4	671 ±79	8.9 ±0.1	3.3 ±1.8	638 ±19	8.2 ±0.3	2.5 ±3.7	544 ±264	8.3 ±0.1	≈0

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 9. Sr Sorption from 0.03N NaCl Under Anoxic Conditions (pO_2 = 2.7)

	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
Mineral	Eh(1)	pH	Kd(Sr)(2)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)
Illite	124(3)	7.3	182	250	7.4	103	341	7.6	65	448	7.3	77
	±58	±0.2	±6	±114	±0.1	±1	±253	±0.2	±6	±249	±0.5	±14
Montmorillonite	429	9.3	1000	568	8.9	499	227	8.4	456	439	8.6	753
	±226	±0.1	±102	±62	±0.1	±63	±24	±0.0	±71	±122	±0.1	±148
Vermiculite	528	8.7	747	613	8.0	475	262	8.0	365	317	8.5	632
	±269	±0.1	±97	±77	±0.0	±54	±140	±0.2	±69	±192	±0.4	±26
Biotite	574	9.0	220	708	8.3	74	204	8.0	38	673	8.4	94
	±163	±0.0	±5	±12	±0.0	±3	±8	±0.1	±6	±19	±0.2	±16
Kaolinite	682	7.2	64	464	6.2	36	253	9.0	35	491	6.4	53
	±55	±0.2	±2	±34	±0.2	±5	±38	±0.1	±5	±144	±0.1	±9
Quartz	193	7.3	121	251	6.5	6.1	424	6.8	-1.7	242	7.4	≈0
	±215	±0.4	±23	±156	±0.5	±4.1	±277	±0.4	±1.4	±150	±0.2	
Albite	249	9.6	135	551	8.4	110	690	8.1	88	454	8.2	245
	±114	±0.2	±35	±116	±0.5	±15	±52	±0.1	±35	±279	±0.2	±37
Anorthite	432	9.2	99	643	8.6	46	474	8.1	30	445	8.7	78
	±263	±0.3	±1	±37	±0.1	±11	±236	±0.1	±8	±40	±0.1	±17
Microcline	162	8.4	331	542	7.6	172	441	7.6	53	497	7.9	164
	±87	±0.1	±32	±153	±0.0	±59	±219	±0.2	±4	±319	±0.3	±43
Hornblende	709	9.3	81	539	8.7	53	332	8.5	43	283	8.8	107
	±20	±0.1	±7	±34	±0.1	±6	±174	±0.0	±7	±24	±0.1	±26
Enstatite	327	9.3	70	656	8.6	58	650	8.6	45	417	9.1	118
	±177	±0.1	±18	±36	±0.0	±11	±38	±0.1	±7	±261	±0.3	±57
Augite	399	9.5	82	416	8.7	42	557	8.6	35	543	8.6	107
	±264	±0.1	±3	±256	±0.2	±11	±183	±0.2	±16	±98	±0.1	±48

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 10. Sr Sorption from 0.03N $NaHCO_3$ Under Anoxic Conditions (pO_2 = 2.7)

	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
Mineral	Eh(1)	pH	Kd(Sr)(2)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)	Eh	pH	Kd(Sr)
Illite	436(3) ±154	8.7 ±0.2	483 ±15	331 ±51	9.1 ±0.2	437 ±58	148 ±7	8.6 ±0.1	168 ±30	479 ±223	9.0 ±0.2	558 ±38
Montmorillonite	524 ±239	9.0 ±0.1	1,300 ±130	551 ±169	9.5 ±0.0	886 ±60	256 ±62	9.1 ±0.1	899 ±343	428 ±164	9.6 ±0.0	753 ±174
Vermiculite	630 ±50	9.2 ±0.2	1,150 ±170	671 ±35	9.1 ±0.0	807 ±57	343 ±180	9.0 ±0.1	977 ±360	466 ±253	9.2 ±0.1	ND
Biotite	615 ±75	8.5 ±0.0	568 ±51	556 ±260	9.2 ±0.2	504 ±156	714 ±10	9.1 ±0.1	334 125	449 ±180	9.7 ±0.0	391 ±119
Kaolinite	392 ±305	8.9 ±0.1	121 ±23	686 ±39	9.4 ±0.1	197 ±2	253 ±38	9.0 ±0.1	252 ±29	521 ±229	9.1 ±0.1	515 ±42
Quartz	368 ±335	9.3 ±0.2	51 ±14	706 ±14	9.1 ±0.2	250 ±53	701 ±29	9.3 ±0.1	266 ±17	660 ±44	9.3 ±0.2	386 ±242
Albite	243 ±140	9.7 ±0.1	105 ±6	356 ±122	9.4 ±0.1	3,620 ±2,730	391 ±226	9.4 ±0.2	$\geq 10^4$	569 ±230	9.7 ±0.2	ND
Anorthite	406 ±238	8.9 ±0.0	134 ±8	692 ±19	9.4 ±0.1	290 ±42	302 ±140	9.1 ±0.2	308 ±26	704 ±50	9.6 ±0.0	347 ±185
Microcline	447 ±116	9.0 ±0.0	67 ±26	583 ±101	9.1 ±0.1	506 ±125	675 ±10	9.2 ±0.1	688 ±69	605 ±197	9.6 ±0.1	ND
Hornblende	497 ±297	9.0 ±0.0	189 ±14	701 ±11	9.4 ±0.0	335 ±37	596 ±30	9.3 ±0.3	466 ±187	580 ±120	9.5 ±0.1	549 ±95
Enstatite	460 ±337	9.1 ±0.2	134 ±7	665 ±41	9.2 ±0.1	176 ±17	556 ±45	9.3 ±0.1	197 ±47	426 ±244	9.8 ±0.5	238 ±108
Augite	175 ±110	9.1 ±0.2	334 ±35	475 ±173	9.3 ±0.1	425 ±25	477 ±166	9.2 ±0.2	438 ±102	584 ±128	9.7 ±0.1	722 ±138

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 11. Cs Sorption from 5.13N NaCl Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Cs)(2)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)
Illite	410(3) ±37	7.4 ±0.1	441 ±21	570 ±39	7.2 ±0.2	517 271	432 ±68	6.4 ±0.2	455 ±211	533 ±49	6.4 ±0.1	405 ±48
Montmorillonite	697 ±65	8.4 ±0.1	13 ±1	677 ±6	8.3 ±0.1	14.6 ±0.5	564 ±138	7.9 ±0.1	15.9 ±2.3	728 ±51	8.5 ±0.0	21.3 ±4.0
Vermiculite	701 ±18	8.7 +0.2	98 ±7	632 ±16	8.2 ±0.1	131 ±6	416 ±55	8.1 ±0.1	116 ±5	706 ±23	8.1 ±0.3	107 ±13
Biotite	695 ±27	8.8 ±0.3	647 ±36	709 ±11	8.3 ±0.1	949 ±41	690 ±41	8.2 ±0.1	1143 ±478	720 ±63	8.6 ±0.1	1840 ±237
Kaolinite	683 ±55	7.2 ±0.2	2.1 ±0.7	675 ±25	6.8 ±0.1	3.2 ±2.2	690 ±37	6.5 ±0.1	15 ±17	412 ±83	6.8 ±0.3	60 ±71
Quartz	511 ±198	7.3 ±0.2	-0.4 ±1.4	654 ±31	6.8 ±0.6	1.0 ±0.4	689 ±51	6.7 ±0.1	-2.3 ±3.2	739 ±38	7.3 ±0.6	∿0
Albite	366 ±87	8.6 ±0.2	2.3 ±0.4	386 ±100	7.8 ±0.2	3.2 ±0.8	600 ±116	7.6 ±0.3	5.3 ±0.7	553 ±178	7.0 ±0.1	17 ±6
Anorthite	485 ±41	8.3 ±0.3	6.6 ±1.7	718 ±28	8.0 ±0.0	7.8 ±2.6	664 ±77	7.6 ±0.1	8.8 ±0.9	627 ±144	8.2 ±0.0	21 ±10
Microcline	470 ±160	7.7 ±0.5	0.3 ±0.1	693 ±4	7.0 ±0.1	2.9 ±2.6	698 ±18	6.5 ±0.6	5.2 ±5.4	471 ±157	7.5 ±0.7	41 ±72
Hornblende	681 ±19	8.9 ±0.2	3.5 ±1.1	695 ±34	8.1 ±0.1	3.0 ±1.3	693 ±6	8.1 ±0.1	5.8 ±0.4	742 ±8	8.3 ±0.1	4.2 ±3.0
Enstatite	510 ±280	8.9 ±0.3	1.6 ±0.7	718 ±11	8.1 ±0.1	1.0 ±0.7	593 ±171	8.0 ±0.1	0.6 ±0.3	700 ±11	8.0 ±0.1	∿0
Augite	467 ±127	9.5 ±0.3	1.8 ±1.4	720 ±21	8.8 ±0.1	5.3 ±1.1	586 ±70	8.2 ±0.0	1.3 ±1.0	671 ±31	8.6 ±0.1	38 ±66

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 12. Cs Sorption from 0.03N $CaCl_2$ Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Cs)(2)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)
Illite	510(3) ±42	7.3 ±0.2	8380 ±2080	382 ±151	7.1 ±0.0	5920 ±520	187 ±28	7.2 ±0.1	8800 ±1250	352 ±148	6.7 ±0.1	1.2×10^4 $\pm 0.2 \times 10^4$
Montmorillonite	667 ±31	8.0 ±0.0	228 ±2	645 ±35	7.8 ±0.0	296 ±25	234 ±132	7.7 ±0.0	462 ±109	679 ±43	8.1 ±0.1	758 137
Vermiculite	614 ±64	7.9 +0.2	7500 ±2600	548 ±111	7.6 ±0.0	4990 ±500	173 ±43	7.7 ±0.2	1.8×10^4 $\pm 1.7 \times 10^4$	420 ±88	8.2 ±0.1	28 ±9
Biotite	534 ±346	8.2 ±0.1	5.9×10^4 $\pm 3.0 \times 10^4$	388 ±154	7.7 ±0.1	1.3×10^4 $\pm 1.2 \times 10^4$	434 ±148	7.7 ±0.1	≥105	249 ±142	8.0 ±0.4	1.6×10^4 $\pm 1 \times 10^4$
Kaolinite	517 ±289	7.0 ±0.1	44 ±10	481 ±168	6.1 ±0.1	80 ±19	175 ±25	6.4 ±0.1	180 ±58	607 ±96	6.8 ±0.3	2210 ±830
Quartz	495 ±231	7.0 ±0.1	1.9 ±1.0	511 ±92	6.7 ±0.3	4.2 ±4.3	296 ±127	7.4 ±0.3	5.0 ±2.0	728 ±36	6.7 ±0.3	75 ±37
Albite	177 ±106	8.9 ±0.1	79 ±6	435 ±45	7.8 ±0.0	59 ±7	446 ±232	7.7 ±0.1	88 ±16	369 ±198	8.2 ±0.5	628 ±116
Anorthite	293 ±254	8.8 ±0.5	333 ±5	668 ±28	8.2 ±0.2	1890 ±1140	475 ±174	7.7 ±0.1	4230 ±1300	507 ±87	8.2 ±0.1	6690 ±433
Microcline	227 ±103	8.6 ±0.3	88 ±7	630 ±78	7.6 ±0.0	65 ±13	393 ±254	7.2 ±0.4	61 21	743 ±10	8.1 ±0.1	253 ±93
Hornblende	579 ±90	8.8 ±0.3	137 ±3	521 ±240	7.8 ±0.2	117 ±12		7.7 ±0.0	171 ±77	752 ±52	8.2 ±0.1	1155 ±420
Enstatite	514 ±161	9.0 ±0.1	47 ±0	718 ±11	8.1 ±0.1	29 ±4	293 ±134	7.8 ±0.2	22 ±1	649 ±83	8.2 ±0.2	1853 ±3037
Augite	528 ±164	9.7 ±0.0	88 ±4	671 ±79	8.9 ±0.1	96 ±50	638 ±19	8.2 ±0.3	77 ±22	544 ±264	8.3 ±0.1	233 ±57

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(1) Eh's measured in mv and corrected to pH 0.
(2) Kd's measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 13. Cs Sorption from 0.03N NaCl Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Cs)(2)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)
Illite	124(3) ±58	7.3 ±0.2	11,000 ±2,000	250 ±114	7.4 ±0.1	9210 ±1330	341 ±253	7.6 ±0.2	9719 ±602	448 ±249	7.3 ±0.5	9850 ±2800
Montmorillonite	429 ±226	9.3 ±0.1	881 ±30	568 ±62	8.9 ±0.1	848 ±108	227 ±24	8.4 ±0.0	763 ±122	439 ±122	8.6 ±0.1	1036 ±125
Vermiculite	528 ±269	8.7 ±0.1	7740 ±420	613 ±77	8.0 ±0.0	6440 ±550	262 ±140	8.0 ±0.2	2.8×10^4 $\pm 3.4 \times 10^4$	317 ±192	8.5 ±0.4	2.1×10^4 $\pm 2.2 \times 10^4$
Biotite	574 ±163	9.0 ±0.0	16,000 ±3,000	708 ±12	8.3 ±0.0	5700 ±1620	204 ±8	8.0 ±0.1	1.0×10^4 $\pm 0.7 \times 10^4$	673 ±19	8.4 ±0.2	2.0×10^4 $\pm 1.3 \times 10^4$
Kaolinite	682 ±55	7.2 ±0.2	100 ±2	464 ±34	6.2 ±0.2	99 ±18	253 ±38	9.0 ±0.1	278 ±198	491 ±144	6.4 ±0.1	968 ±397
Quartz	193 ±215	7.3 ±0.4	98 ±18	251 ±156	6.5 ±0.5	7.3 ±3.1	424 ±277	6.8 ±0.4	8.5 ±4.5	242 ±150	7.4 ±0.2	122 ±146
Albite	249 ±114	9.6 ±0.2	112 ±2	551 ±116	8.4 ±0.5	89 ±21	690 ±52	8.1 ±0.1	310 ±360	454 ±279	8.2 ±0.2	467 ±110
Anorthite	432 ±263	9.2 ±0.3	298 ±41	643 ±37	8.6 ±0.1	2570 ±1150	474 ±236	8.1 ±0.1	1279 ±177	445 ±40	8.7 ±0.1	4650 ±1690
Microcline	162 ±87	8.4 ±0.1	135 ±29	542 ±153	7.6 ±0.0	187 ±53	441 ±219	7.6 ±0.2	137 ±18	497 ±319	7.9 ±0.3	492 ±106
Hornblende	709 ±20	9.3 ±0.1	285 ±18	539 ±34	8.7 ±0.1	427 ±106	332 ±174	8.5 ±0.0	441 ±156	283 ±24	8.8 ±0.1	833 ±25
Enstatite	327 ±177	9.3 ±0.1	58 ±8	656 ±36	8.6 ±0.0	41 ±10	650 ±38	8.6 ±0.1	31 ±13	417 ±261	9.1 ±0.3	139 ±70
Augite	399 ±264	9.5 ±0.1	100 ±13	416 ±256	8.7 ±0.2	101 ±12	557 ±183	8.6 ±0.2	91 ±5	543 ±98	8.6 ±0.1	219 ±32

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 14. Cs Sorption from 0.03N $NaHCO_3$ Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Cs)(2)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)	Eh	pH	Kd(Cs)
Illite	436(3) ±154	8.7 ±0.2	7,520 ±770	331 ±51	9.1 ±0.2	7,080 ±1,290	148 ±7	8.6 ±0.1	437 ±72	479 ±223	9.0 ±0.2	2,900 ±1,690
Montmorillonite	524 ±239	9.0 ±0.1	1,067 ±68	551 ±169	9.5 ±0.0	933 ±83	256 ±62	9.1 ±0.1	985 ±125	428 ±164	9.6 ±0.0	1,180 ±300
Vermiculite	630 ±50	9.2 ±0.2	5,830 ±2,030	671 ±35	9.1 ±0.0	3,855 ±385	343 ±180	9.0 ±0.1	4.6×10^4 $\pm 3.4 \times 10^4$	466 ±253	9.2 ±0.1	ND
Biotite	615 ±75	8.5 ±0.0	3,410 ±2,010	556 ±260	9.2 ±0.2	2,580 ±820	714 ±10	9.1 ±0.1	3,150 ±2,560	449 ±180	9.7 ±0.0	2,020 ±241
Kaolinite	392 ±305	8.9 ±0.1	98 ±18	686 ±39	9.4 ±0.1	109 ±9	253 ±38	9.0 ±0.1	164 ±84	521 ±229	9.1 ±0.1	677 ±419
Quartz	368 ±335	9.3 ±0.2	4.9 ±0.5	706 ±14	9.1 ±0.2	8.8 ±2.6	701 ±29	9.3 ±0.1	11.4 ±2.8	660 ±44	9.3 ±0.2	45 ±16
Albite	243 ±140	9.7 ±0.1	108 ±5	356 ±122	9.4 ±0.1	106 ±30	391 ±226	9.4 ±0.2	167 ±12	569 ±230	9.7 ±0.2	508 ±72
Anorthite	406 ±238	8.9 ±0.0	490 ±70	692 ±19	9.4 ±0.1	659 ±132	302 ±140	9.1 ±0.2	1,670 ±1,440	704 ±50	9.6 ±0.0	1,830 ±1,840
Microcline	447 ±116	9.0 ±0.0	90 ±17	583 ±101	9.1 ±0.1	82 ±37	675 ±10	9.2 ±0.1	118 ±41	605 ±197	9.6 ±0.1	414 ±26
Hornblende	497 ±297	9.0 ±0.0	303 ±25	701 ±11	9.4 ±0.0	459 ±118	596 ±30	9.3 ±0.3	610 ±270	580 ±120	9.5 ±0.1	778 ±278
Enstatite	460 ±337	9.1 ±0.2	75 ±4	665 ±41	9.2 ±0.1	50 ±17	556 ±45	9.3 ±0.1	38 ±6	426 ±244	9.8 ±0.5	129 ±12
Augite	175 ±110	9.1 ±0.2	88 ±4	475 ±173	9.3 ±0.1	75 ±20	477 ±166	9.2 ±0.2	113 ±9	584 ±128	9.7 ±0.1	239 ±97

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 15. Tc Sorption from 5.13N NaCl Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Tc)(2)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)
Illite	410(3) ±37	7.4 ±0.1	885 ±39	570 ±39	7.2 ±0.2	1490 ±160	432 ±68	6.4 ±0.2	2960 ±380	533 ±49	6.4 ±0.1	ND
Montmorillonite	697 ±65	8.4 ±0.1	0.6 ±0.9	677 ±6	8.3 ±0.1	-0.1 ±0.1	564 ±138	7.9 ±0.1	0.5 ±1.8	728 ±51	8.5 ±0.0	≤0
Vermiculite	701 ±18	8.7 +0.2	-1.3 ±1.3	632 ±16	8.2 ±0.1	354 ±22	416 ±55	8.1 ±0.1	371 ±20	706 ±23	8.1 ±0.3	ND
Biotite	695 ±27	8.8 ±0.3	1.9 ±2.2	709 ±11	8.3 ±0.1	-2.7 ±0.2	690 ±41	8.2 ±0.1	-1.2 ±0.9	720 ±63	8.6 ±0.1	≤0
Kaolinite	683 ±55	7.2 ±0.2	-3.6 ±0.6	675 ±25	6.8 ±0.1	-0.3 ±2.0	690 ±37	6.5 ±0.1	10.0 ±15.5	412 ±83	6.8 ±0.3	62 ±86
Quartz	511 ±198	7.3 ±0.2	267 ±119	654 ±31	6.8 ±0.6	12.8 ±2.9	689 ±51	6.7 ±0.1	6.2 ±4.1	739 ±38	7.3 ±0.6	45 ±44
Albite	366 ±87	8.6 ±0.2	≥760	386 ±100	7.8 ±0.2	6120 ±2950	600 ±116	7.6 ±0.3	581 ±226	553 ±178	7.0 ±0.1	1307 ±315
Anorthite	485 ±41	8.3 ±0.3	≥490	718 ±28	8.0 ±0.0	2700 ±4100	664 ±77	7.6 ±0.1	4700 ±7500	627 ±144	8.2 ±0.0	1283 ±296
Microcline	470 ±160	7.7 ±0.5	3770 ±3600	693 ±4	7.0 ±0.1	50 ±45	698 ±18	6.5 ±0.6	38 ±25	471 ±157	7.5 ±0.7	533 ±315
Hornblende	681 ±19	8.9 ±0.2	≥2490	695 ±34	8.1 ±0.1	593 ±250	693 ±6	8.1 ±0.1	348 ±75	742 ±8	8.3 ±0.1	1107 ±164
Enstatite	510 ±280	8.9 ±0.3	860 ±1250	718 ±11	8.1 ±0.1	270 ±240	593 ±171	8.0 ±0.1	135 ±83	700 ±11	8.0 ±0.1	555 ±169
Augite	467 ±127	9.5 ±0.3	≥4600	720 ±21	8.8 ±0.1	813 ±115	586 ±70	8.2 ±0.0	469 ±231	671 ±31	8.6 ±0.1	548 ±95

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 16. Tc Sorption from 0.03N $CaCl_2$ Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Tc)(2)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)
Illite	510(3) ±42	7.3 ±0.2	1150 ±560	382 ±151	7.1 ±0.0	6.6 ±5.4	187 ±28	7.2 ±0.1	112 ±10	352 ±148	6.7 ±0.1	34 ±11
Montmorillonite	667 ±31	8.0 ±0.0	-3.9 ±2.1	645 ±35	7.8 ±0.0	-1.2 ±0.9	234 ±132	7.7 ±0.0	4.1 ±0.7	679 ±43	8.1 ±0.1	14 ±1
Vermiculite	614 ±64	7.9 +0.2	-3.4 ±2.8	548 ±111	7.6 ±0.0	3.8 ±2.6	173 ±43	7.7 ±0.2	7.8 ±3.5	420 ±88	8.2 ±0.1	36 ±16
Biotite	534 ±346	8.2 ±0.1	-3.2 ±3.3	388 ±154	7.7 ±0.1	-0.8 ±0.1	434 ±148	7.7 ±0.1	204 ±364	249 ±142	8.0 ±0.4	ND
Kaolinite	517 ±289	7.0 ±0.1	-3.0 ±2.5	481 ±168	6.1 ±0.1	2.6 ±2.5	175 ±25	6.4 ±0.1	26 ±14	607 ±96	6.8 ±0.3	169 ±25
Quartz	495 ±231	7.0 ±0.1	3.1 ±1.6	511 ±92	6.7 ±0.3	1.3 ±2.7	296 ±127	7.4 ±0.3	6.7 ±3.6	728 ±36	6.7 ±0.3	8 ±16
Albite	177 ±106	8.9 ±0.1	≥2500	435 ±45	7.8 ±0.0	9900 ±7200	446 ±232	7.7 ±0.1	667 ±262	369 ±198	8.2 ±0.5	830 ±247
Anorthite	293 ±254	8.8 ±0.5	≥2500	668 ±28	8.2 ±0.2	196 ±58	475 ±174	7.7 ±0.1	425 ±197	507 ±87	8.2 ±0.1	605 ±42
Microcline	227 ±103	8.6 ±0.3	≥2500	630 ±78	7.6 ±0.0	678 ±361	393 ±254	7.2 ±0.4	211 ±138	743 ±10	8.1 ±0.1	465 ±25
Hornblende	579 ±90	8.8 ±0.3	≥2500	521 ±240	7.8 ±0.2	50 ±5		7.7 ±0.0	586 ±271	752 ±52	8.2 ±0.1	756 ±81
Enstatite	514 ±161	9.0 ±0.1	52 ±14	718 ±11	8.1 ±0.1	18 ±17	293 ±134	7.8 ±0.2	1418 ±277	649 ±83	8.2 ±0.2	337 ±124
Augite	528 ±164	9.7 ±0.0	≥1700	671 ±79	8.9 ±0.1	8.9 ±6.9	638 ±19	8.2 ±0.3	1300 ±2300	544 ±264	8.3 ±0.1	261 ±285

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 17. Sr Sorption from 0.03N NaCl Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Tc)(2)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)
Illite	124(3) ±58	7.3 ±0.2	≥900	250 ±114	7.4 ±0.1	1.7×10^4 $\pm 1.0 \times 10^4$	341 ±253	7.6 ±0.2	606 ±19	448 ±249	7.3 ±0.5	277 ±14
Montmorillonite	429 ±226	9.3 ±0.1	≤0	568 ±62	8.9 ±0.1	-2.3 ±1.7	227 ±24	8.4 ±0.0	-1.0 ±0.7	439 ±122	8.6 ±0.1	0
Vermiculite	528 ±269	8.7 ±0.1	≤0	613 ±77	8.0 ±0.0	1.8 ±2.3	262 ±140	8.0 ±0.2	2.4 ±1.9	317 ±192	8.5 ±0.4	12 ±12
Biotite	574 ±163	9.0 ±0.0	≤0	708 ±12	8.3 ±0.0	-1.4 ±1.6	204 ±8	8.0 ±0.1	1.5 ±4.3	673 ±19	8.4 ±0.2	27 ±47
Kaolinite	682 ±55	7.2 ±0.2	≤0	464 ±34	6.2 ±0.2	-2.9 ±0.8	253 ±38	9.0 ±0.1	5.4 ±5.1	491 ±144	6.4 ±0.1	63 ±77
Quartz	193 ±215	7.3 ±0.4	≤0	251 ±156	6.5 ±0.5	1.7 ±6.2	424 ±277	6.8 ±0.4	27 ±13	242 ±150	7.4 ±0.2	87 ±68
Albite	249 ±114	9.6 ±0.2	≥900	551 ±116	8.4 ±0.5	5380 ±4050	690 ±52	8.1 ±0.1	427 ±50	454 ±279	8.2 ±0.2	819 ±194
Anorthite	432 ±263	9.2 ±0.3	≥900	643 ±37	8.6 ±0.1	1090 ±920	474 ±236	8.1 ±0.1	601 ±355	445 ±40	8.7 ±0.1	406 ±97
Microcline	162 ±87	8.4 ±0.1	≥900	542 ±153	7.6 ±0.0	8.2 ±7.9	441 ±219	7.6 ±0.2	16.8 8.1	497 ±319	7.9 ±0.3	163 ±72
Hornblende	709 ±20	9.3 ±0.1	≥360	539 ±34	8.7 ±0.1	8.1 ±1.7	332 ±174	8.5 ±0.0	370 ±279	283 ±24	8.8 ±0.1	448 ±325
Enstatite	327 ±177	9.3 ±0.1	≥510	656 ±36	8.6 ±0.0	10.8 ±2.6	650 ±38	8.6 ±0.1	47 ±43	417 ±261	9.1 ±0.3	255 ±169
Augite	399 ±264	9.5 ±0.1	≥900	416 ±256	8.7 ±0.2	1600 ±1700	557 ±183	8.6 ±0.2	523 ±262	543 ±98	8.6 ±0.1	553 ±334

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 18. Tc Sorption from 0.03N $NaHCO_3$ Under Anoxic Conditions (pO_2 = 2.7)

Mineral	3-day Adsorption			10-day Adsorption			30-day Adsorption			30-day Desorption		
	Eh(1)	pH	Kd(Tc)(2)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)	Eh	pH	Kd(Tc)
Illite	436(3)	8.7	204	331	9.1	7.2	148	8.6	28.5	479	9.0	32
	±154	±0.2	±8	±51	±0.2	±1.9	±7	±0.1	±5.2	±223	±0.2	±11
Montmorillonite	524	9.0	4.9	551	9.5	0.4	256	9.1	1.1	428	9.6	10
	±239	±0.1	±9.8	±169	±0.0	±1.7	±62	±0.1	±1.9	±164	±0.0	±9
Vermiculite	630	9.2	2.8	671	9.1	0.5	343	9.0	2.6	466	9.2	19
	±50	±0.2	±2.1	±35	±0.0	±1.5	±180	±0.1	±1.5	±253	±0.1	±15
Biotite	615	8.5	140	556	9.2	5.0	714	9.1	3.6	449	9.7	43
	±75	±0.0	±236	±260	±0.2	±3.0	±10	±0.1	±4.9	±180	±0.0	±64
Kaolinite	392	8.9	-2.7	686	9.4	0.6	253	9.0	-0.6	521	9.1	0
	±305	±0.1	±0.8	±39	±0.1	±1.8	±38	±0.1	±1.0	±229	±0.1	
Quartz	368	9.3	≥2500	706	9.1	83	701	9.3	61	660	9.3	220
	±335	±0.2		±14	±0.2	±83	±29	±0.1	±28	±44	±0.2	±56
Albite	243	9.7	≥2500	356	9.4	7,791	391	9.4	1550	569	9.7	ND
	±140	±0.1		±122	±0.1	±7,846	±226	±0.2	±1120	±230	±0.2	
Anorthite	406	8.9	1100	692	9.4	111	302	9.1	100	704	9.6	260
	±238	±0.0	±210	±19	±0.1	±142	±140	±0.2	±52	±50	±0.0	±56
Microcline	447	9.0	≥2500	583	9.1	1146	675	9.2	342	605	9.6	520
	±116	±0.0		±101	±0.1	±407	±10	±0.1	±72	±197	±0.1	±116
Hornblende	497	9.0	1065	701	9.4	76	596	9.3	43	580	9.5	236
	±297	±0.0	±284	±11	±0.0	±52	±30	±0.3	±34	±120	±0.1	±87
Enstatite	460	9.1	≥2500	665	9.2	281	556	9.3	60	426	9.8	204
	±337	±0.2		±41	±0.1	±119	±45	±0.1	±16	±244	±0.5	±20
Augite	175	9.1	2870	475	9.3	450	477	9.2	496	584	9.7	388
	±110	±0.2	±2470	±173	±0.1	±140	±166	±0.2	±105	±128	±0.1	±135

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(1) Eh is measured in mv and corrected to pH 0.
(2) Kd is measured in ml/g.
(3) All values are means of 3 repetitions ± 1 standard deviation.

TABLE 19. Comparison of Kd(Sr) Under Anoxic and Ambient Atmospheric Conditions (30-day Contact Time)

Mineral	5.13N NaCl		0.03N $CaCl_2$		0.03N NaCl		0.03N $NaHCO_3$	
	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic
Illite	1.2(2) ±0.5	135 ** ±2	6.2 ±1.5	6.1 ns ±2.1	37 ±1	65 ** ±6	298 ±84	168 ns ±30
Montmorillonite	1.4 ±0.6	2.9 ns ±1.3	27.7 ±0.6	38 ** ±3	1074 ±91	456 ** ±71	1353 ±330	899 ns ±343
Vermiculite	1.9 ±1.1	127 ** ±7	24 ±1	25.8 ns ±0.4	760 ±19	365 ** ±69	1041 ±103	977 ns ±360
Biotite(1)	4.2 ±0.6	1.8 * ±1.1	12.7 ±0.4	9.0 ** ±0.4	149 ±6	38 ** ±6	613 ±61	334 * ±125
Kaolinite	0.2 ±0.9	9.6 ns ±17.1	0.6 ±0.2	2.1 ns ±3.3	77 ±3	35 ** ±5	284 ±107	252 ns ±29
Quartz	1.1 ±0.4	-2.2 * ±1.8	-0.2 ±1.1	-0.1 ns ±1.6	9.0 ±1.6	1.7 ** ±1.4	348 ±70	266 ns ±17
Albite	5.2 ±1.0	5.5 ns ±2.4	4.1 ±0.4	8.9 ** ±1.0	105 ±2	88 ns ±35	545 ±48	≥10^4 ns
Anorthite	5.0 ±1.3	2.3 ns ±1.1	3.0 ±0.3	4.7 ns ±2.7	51 ±3	30 * ±8	459 ±58	308 * ±26
Microcline	4.1 ±1.1	5.0 ns ±6.2	3.6 ±0.9	5.4 ns ±4.3	159 ±7	53 ** ±4	461 ±26	688 ** ±69
Hornblende(1)	1.7 ±0.3	8.7 ns ±12.7	3.6 ±1.5	3.7 ns ±1.3	43.6 ±0.3	43 ns ±7	298 ±4	466 ns ±187
Enstatite(1)	2.2 ±0.5	1.6 ns ±0.8	2.2 ±0.6	2.6 ns ±2.3	50.7 ±0.6	45 ns ±7	132 ±10	197 ns ±47
Augite(1)	6.4 ±0.8	3.9 ** ±0.2	4.6 ±0.6	2.5 ns ±3.7	64 ±6	35 * ±16	625 ±41	438 * ±102

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(1) Ambient Kd values were determined at 20 days.
(2) All Kd values are given in ml/g as the mean ± standard deviation.

TABLE 20. Comparison of Kd(Cs) Under Anoxic and Ambient Atmospheric Conditions (30-day Contact Time)

	5.13N NaCl		0.03N CaCl$_2$		0.03N NaCl		0.03N NaHCO$_3$	
Mineral	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic
Illite	564(2) $\pm$35	455 ns $\pm$211	6960 $\pm$4670	8800 ns $\pm$1250	1.3×10^4 $\pm0.6\times10^4$	9719 ns $\pm$602	1.0×10^4 $\pm0.4\times10^4$	437 * $\pm$72
Montmorillonite	33 $\pm$2	16 ** $\pm$2	218 $\pm$5	462 * $\pm$109	1120 $\pm$81	763 $\pm$122 *	1557 $\pm$370	985 ns $\pm$125
Vermiculite	93 $\pm$9	116 * $\pm$5	8.2×10^4 $\pm6.6\times10^4$	1.8×10^4 ns $\pm1.7\times10^4$	5.9×10^4 $\pm7.1\times10^4$	2.8×10^4 ns $\pm3.4\times10^4$	2.0×10^4 $\pm1.5\times10^4$	4.6×10^4 ns $\pm3.4\times10^4$
Biotite(1)	1485 $\pm$349	1143 ns $\pm$478	7.0×10^4 $\pm8.2\times10^4$	$\geq10^5$ ns	6.0×10^4 $\pm8.7\times10^4$	1.0×10^4 ns $\pm0.7\times10^4$	4211 $\pm$1153	3150 $\pm$2560
Kaolinite	7.3 $\pm$0.8	15 ns $\pm$17	4.6×10^4 $\pm6.7\times10^4$	180 ns $\pm$58	909 $\pm$215	278 * $\pm$198	863 $\pm$37	164 ** $\pm$84
Quartz	2.2 $\pm$0.8	-2.3 ns $\pm$3.2	34 $\pm$14	5 * $\pm$2	58 $\pm$8	8.5 ** $\pm$4.5	37 $\pm$5	11.4 ** $\pm$2.8
Albite	20 $\pm$2	5.3 ** $\pm$0.7	821 $\pm$123	88 ** $\pm$16	519 $\pm$11	310 ns $\pm$360	528 $\pm$10	167 ** $\pm$12
Anorthite	22 $\pm$1	8.8 ** $\pm$0.9	774 $\pm$48	4230 ** $\pm$1300	440 $\pm$35	1279 ** $\pm$177	608 $\pm$36	1670 ns $\pm$1440
Microcline	7 $\pm$2	5.2 ns $\pm$5.4	222 $\pm$76	61 * $\pm$21	391 $\pm$18	137 ** $\pm$18	343 $\pm$21	118 ** $\pm$41
Hornblende(1)	11 $\pm$1	5.8 ** $\pm$0.4	2155 $\pm$116	171 ** $\pm$77	835 $\pm$66	441 * $\pm$156	1097 $\pm$138	610 * $\pm$270
Enstatite(1)	2.5 $\pm$0.6	0.6 ** $\pm$0.3	188 $\pm$18	22 ** $\pm$1	100 $\pm$9	31 ** $\pm$13	134 $\pm$8	38 ** $\pm$6
Augite(1)	3.7 $\pm$0.7	1.3 * $\pm$1.0	450 $\pm$72	77 ** $\pm$22	215 $\pm$29	91 ** $\pm$5	293 $\pm$1	113 ** $\pm$9

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(1) Ambient Kd values were determined at 20 days.

(2) Kd values are listed as the mean ± standard deviation.

TABLE 21. Comparison of Kd(Tc) Under Anoxic and Ambient Atmospheric Conditions (30-day Contact Time)

Mineral	5.13N NaCl		0.03N $CaCl_2$		0.03N NaCl		0.03N $NaHCO_3$	
	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic	Ambient	Anoxic
Illite	4.7(2) ±0.5	2960 ** ±380	0.5 ±0.5	112 ** ±10	10.2 ±1.1	606 ** ±19	-0.9 ±0.4	29 ** ±5
Montmorillonite	0.2 ±0.5	0.5 ns ±1.8	-0.7 ±0.1	4.1 ** ±0.7	-0.6 ±0.4	-1.0 ns ±0.7	-1.5 ±0.3	1.1 ns ±1.9
Vermiculite	0.6 ±0.7	371 ** ±20	-0.8 ±0.3	7.8 * ±3.5	0.4 ±1.0	2.4 ns ±1.9	0.0 ±0.2	2.6 * ±1.5
Biotite(1)	-0.3 ±0.4	-1.2 ns ±0.9	-0.5 ±0.6	204 ns ±364	-0.1 ±0.1	1.5 ns ±4.3	-1.0 ±0.5	3.6 ns ±4.9
Kaolinite	0.4 ±1.0	10.0 ns ±15.5	3.0 ±5.3	26 ns ±14	-0.4 ±0.6	5.4 ns ±5.1	-0.2 ±0.9	-0.6 ns ±1.0
Quartz	1.6 ±0.9	6.2 ns ±4.1	0.7 ±1.0	6.7 * ±3.6	1.4 ±1.5	27 * ±13	-0.4 ±0.3	61 * ±28
Albite	18.0 ±3.3	581 * ±226	2.8 ±1.3	667 * ±262	0.7 ±0.5	427 ** ±50	-0.4 ±0.7	1550 ns ±1120
Anorthite	4.4 ±1.0	4700 ns ±7500	0.5 ±0.7	425 * ±197	1.8 ±1.0	601 * ±355	-0.1 ±0.1	100 * ±52
Microcline	15.5 ±4.0	38 ns ±25	0.1 ±0.4	211 ns ±138	5.8 ±1.2	17 ns ±8	0.6 ±0.1	342 ** ±72
Hornblende(1)	1.6 ±0.5	348 ** ±75	0.4 ±1.1	586 * ±271	0.2 ±0.1	370 ns ±279	-0.8 ±0.5	43 ns ±43
Estatite(1)	0.1 ±0.5	135 * ±83	0.7 ±0.6	1418 ** ±277	0.0 ±0.4	47 ns ±43	-1.8 ±0.4	60 ** ±16
Augite(1)	1.7 ±0.9	469 * ±231	1.1 ±0.8	1300 ns ±2300	1.3 ±1.2	523 * ±262	-1.0 ±0.2	2196 ** ±105

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(1) Ambient Kd values were determined at 20 days.
(2) Kd values are listed as the mean ± standard deviation.

QUESTIONS AND ANSWERS

PNL

Peroxide Pretreatment

Q: In your first study with montmorillonite, vermiculite and kaolinite, did you incorporate the individual cation exchange capacities and surface areas in the statistical analysis or were they combined?

A: No, we didn't include that information in the analysis of variance. The analysis was done with the Kd values obtained from a 3 x 3 x 2 factorial experiment on three minerals with three solution concentrations and two mineral treatments.

Q: You got very high correlation or significance with respect to mineral type, but that may not be the principal parameter. It might in fact be the surface area, cation exchange capacity or the specific cation exchange capacity.

A: It might be for strontium, but the data for technetium show that technetium Kds on kaolinite were higher than on montmorillonite and the Kds on vermiculite were largest. That order doesn't follow the surface area or exchange capacity trend for the minerals.

C: Yes, but in the case of technetium you might have a different mechanism, say precipitation, taking place.

Q: Did you measure the organic matter content of your clays?

A: No, we didn't. There was no visible organic matter but there probably was some that may have affected sorption. The point of the experiment was to determine whether or not there was an effect of peroxide treatment on technetium sorption.

Material Characterization

Q: I have a question about your analysis by X-ray diffraction and electron excitation. You don't show a water component, but it still sums up to 99 or 100%.

A: We neglected any adsorbed water. They were bulk chemical analyses of elements heavier than sodium. I don't think the microprobe can detect anything below that.

C: So that was your criteria. Minerals like kaolinite can have 5 or 10% hydroxyl groups.

A: True, but X-ray and microprobe won't detect the light elements.

C: But they still can't come to 100% structurally.

C: I guess that was my question. It would be better to sum them when you do the X-ray intensity analysis to account for adsorption of the water group as well. Then you would get a sum that is less than 100%.

A: Notice the mineralogy didn't include carbonates either. That can be done by X-ray diffraction but not by electron microprobe. The microprobe is good for doing most elemental mapping because you get a quantitative picture of the heavier elements. You can look at the phases and get more of a quantitative feel for the mineralogy than with X-ray diffraction.

Plutonium Sorption

Q: I see you got high Pu Kds for vermiculite, biotite and montmorillonite but not kaolonite.

A: The large Kds were on the 2:1 clays, not the 1:1 clay kaolinite.

Q: From this should we infer that Pu exchange sites are located in the inner layer positions?

A: It could be. It might be due to surface area or iron content since kaolinite has the lowest Fe content of the phyllosilicates studied.

Pu Oxidation State

Q: I'm wondering if your Pu oxidation state isn't suspect since your solutions were evaporated in air on a sandbath. You might have a couple of oxidation states when you bring it into the box. It's not clear whether you've put the Pu in solution before it's brought into the box.

A: What we try to do is equilibrate the solution with the atmosphere in the box. It sits for about a week in the box until some equilibrium is established in solution.

Q: I would suggest that the equilibrium is already established when you evaporate it in air. Taking the Pu up in solution and putting it in the box probably won't make any difference. You may also have different mixtures of Pu(IV) and Pu(VI) in each of your Pu samples.

A: We could.

Q: Well, it would seem the whole solution should have been made up in the box.

A: Our problem with space in the box is probably the same as with other investigators. We are not allowed to have tracer stock solutions in the box. It's an anaerobic or anoxic box, not a glove box, so the solutions have to be made up in a fume hood.

Q: This may be a question to you or the audience. Isn't it possible to determine the Pu oxidation states before and after equilibration by using a carrying experiment? Is there anything against doing that?

A: We could and it would terminate the experiment by removing a good part of the solution.

Q: I agree with that. You could take out a small sample at the start and end and run a carrier experiment on it. It wasn't really clear as to what oxidation state you were starting with.

A: Yes, I'm not sure what oxidation states we were dealing with.

C: But we could remove one of the uncertainties; we have too many as it is.

A: Yes.

Tracer Concentrations

Q: Have you tried to vary your Tc, Sr and Pu concentrations over a very wide range to see the effects?

A: Not at PNL. Others are doing that. We have been looking at a wide variety of minerals and solutions to find differences in adsorption due to structure or interaction between structure and solution.

Q: But you also have some rather gross concentration effects that might affect interpretation of data.

A: Nuclide or salt concentration?

Q: Concentration of the nuclide.

A: I don't think so. Not with ^{237}Pu. It was below 10^{-11} or 10^{-12} molar and even with Pu that is probably a tracer level. We tried to start with about 10^{-11} molar Pu, but usually 90% precipitated when it was put in solution and filtered. Then 50 to 60% sorbed out onto the blank tube walls so we were down an order of magnitude from where we started.

Blank Correction Versus Direct Counting Methods

Q: May I conclude from your tube adsorption difficulties that you and others have found, that one really shouldn't measure the distribution coefficients by difference in supernatant; that you should just analyze the equilibrated supernatant and the solid phase rather than go through these complicated treatments?

A: No matter which method you use, if you count each tube to see how much was lost that way or if you measure the solid phase Pu, the counting time doubles.

Q: Yes, but you still get something you can rely on. You may only get half as many experiments done.

A: That was the point of this paper, to show that measuring by difference doesn't work with Pu. We have data with Np in the reduced or anoxic atmosphere. Instead of having Kds between 50 and 100 like they are under atmospheric conditions, the Kds are in the thousands. But adsorption on the tube walls is negligible to slight. It's nowhere near 90%. It's not even 10%.

C: Counting the solids and solutions separately doubles the number of samples, not the counting time. Since most of the activity is on the solid, they need short counting times.

C: Counting the solids isn't an easy process because there are several mechanisms to consider such as self-adsorption of X-rays or γ-rays by the rock, geometry of the sample and whether your rock sample is representative if you take a subsample from the container. You have to know what you're doing.

Q: This is the third year this problem has come up. Are we going to come up with a recommended procedure so we don't have to do this again?

A: I don't think we decided but more people are counting solution and solids separately. Not every lab is set up or capable of doing that. We need to make sure that the procedure is reported as to how you correct your blank correction or if you counted the solid phase.

Solid to Solution Ratio Used

Q: In your experiments, did you have your solution volumes constant?

A: Yes. The solution volumes were 30 ml and mineral weights were 1 g. When we took it out for counting it was centrifuged and pipetted into a plastic liquid scintillation vial. After counting, the solution was returned to the tube -- all but a drop or two.

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<u>Waste/Rock Interactions Technology</u>

INTERACTIONS OF PLUTONYL (VI) WITH SOIL MINERALS

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INTERACTION OF PLUTONYL(VI) WITH SOIL MINERALS

Dhanpat Rai, R. J. Serne, and D. A. Moore

ABSTRACT

Plutonium-239 adsorption by different minerals from aerated 0.005 M $CaCl_2$ solutions containing 7.3×10^{-9} M Pu(VI) was studied. When carried out at pH 4, adsorption by the selected minerals differed significantly, with adsorption increasing in the following order: gibbsite < kaolinite < montmorillonite < nontronite ≃ hematite < vermiculite ≃ biotite. When carried out at pH 7, the adsorption on these minerals did not differ significantly and exceeded 93% in all cases.

Several mechanisms that contributed to Pu adsorption were identified. These included ion exchange, specific adsorption, reduction of Pu(VI), and Pu(VI) hydrolysis.

Vermiculite, biotite, and hematite contain relatively large amounts of structural Fe(II) and were found to reduce Pu(VI) to Pu(IV) and/or Pu(III) even in the well aerated suspensions.

The initial ^{239}Pu concentration added to the mineral suspensions was approximately 22 times the maximum permissible concentration (MPC) of ^{239}Pu in unregulated water as established by the U.S. Nuclear Regulatory Commission. However, the ^{239}Pu concentration in equilibrated solutions at pH 7 that contacted the selected minerals were near or lower than the MPC. This was also true for vermiculite, biotite, and hematite at pH 4. A very small percentage of the adsorbed Pu was released when the minerals were contacted with 1 M NaCl. These results combined with the fact that most geomedia at deep repository sites are expected to be alkaline and more reducing than the present experimental conditions indicate that Pu in general and Pu(VI) specifically would be relatively immobile in geomedia that do not contain significant quantities of complexing ligands.

Additional Index Words: plutonium, Pu(VI), adsorption, clay minerals, mechanisms of adsorption.

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INTRODUCTION

The future of nuclear energy depends largely upon the safe disposal of nuclear wastes. To assess the safety of the nuclear waste disposal, the interaction of the waste elements with the geologic media needs to be understood. Because of its long half life, toxicity, and significant concentration in high level nuclear waste, Pu behavior must be determined in order to predict the safe disposal of nuclear waste.

Plutonium can exist in solution in several oxidation states [Pu(III), Pu(IV), Pu(V), Pu(VI)] (Cleveland, 1970). The Pu oxidation state affects the ionic charge and the ability to form complexes with different ligands (Cleveland 1970); thus various oxidation states would be expected to have differing affinities for geologic media. For complete understanding of Pu behavior in the environment, data on free energies of formation of all expected Pu species and their interaction with geomedia are needed.

The available Pu thermodynamic data of environmental concern have been discussed (Rai and Serne, 1977; Cleveland, 1979; Rai et al., 1980a; Rai et al., 1980b). Ames and Rai (1978) did a comprehensive review on soil/sediment interaction with Pu. More recently, extensive data on the adsorption of reduced Pu predominantly Pu(IV) by selected rocks, secondary minerals (clay minerals) and primary rock forming minerals have been reported (Relyea et al., 1979; Relyea and Serne, 1979). However, most of the available data on soil/sediment/rock interaction with Pu (Ames and Rai, 1978; Relyea et al., 1979; Relyea and Serne, 1979) are of an empirical nature such that they are not adequate to predict Pu behavior in the environment. Thus, there is a general lack of information on the mechanisms of Pu adsorption and the adsorption of oxidized Pu [Pu(V) and Pu(VI)] by different minerals. Therefore, the Pu(VI) adsorption studies reported in this paper were conducted. When this study was nearly complete, Rai et al. (1980a) reported evidence suggesting that Pu(V) may be the dominant solution species in oxidizing environments. Although Pu(VI) can: 1) be expected to be much more similar in adsorption to Pu(V) than to Pu(III) or Pu(IV), and 2) under appropriate redox potentials change readily to Pu(V), studies on Pu(V) adsorption, similar to the ones reported here, will also be conducted.

METHODS AND MATERIALS

Clays and Rocks Used for This Study

The samples used in the study were: kaolinite from Macon, Georgia; montmorillonite number 23 from Chambers, Arizona; nontronite number 33A from Garfield, Washington; vermiculite; biotite from Bancroft, Ontario; hematite from Ironton, Minnesota; gibbsite from Minas Gerais, Brazil; and vesicular basalt from Chaffee County, Colorado. The samples were obtained from Ward's Natural Science Establishment, Monterey, California.

Kaolinite, montmorillonite, and nontronite were treated with pH 5 sodium acetate buffer and hydrogen peroxide to remove calcium carbonate and organic matter (Jackson 1956). Less than 2 m size fractions of the clays (kaolinite, montmorillonite, nontronite, vermiculite, biotite) were separated by sedimentation and centifugation techniques for use in this study. Hematite, gibbsite, and vesicular basalt were crushed to pass through a 105 μm sieve. All the samples were saturated with calcium by treating the bulk samples with 1 N $CaCl_2$ and washing the samples free of excess calcium with distilled water.

Pu(VI) Stock Solution

The Pu(VI) stock solution was prepared by oxidizing a concentrated solution of Pu(IV) at 95°C for approximately 16 hr at constant acidity (0.5 M HNO_3) (Cleveland, 1970). The HNO_3 concentration of the Pu(VI) stock solution was then increased to 8 M. Oxidation state analyses of this stock solution have shown it to be >97% Pu(VI) and stable for over a year.

Experimental Technique

One gram of mineral sample was added to a teflon cell containing 34 ml of 0.005 M $CaCl_2$ solution. The mineral suspension was adjusted to either pH 4 or pH 7 and was continuously stirred overnight. Then 0.02 ml of ^{239}Pu(VI) stock solution in 8 M HNO_3 containing 8115 ± 80 dpm was added to the mineral suspension. The final concentration of the added Pu (7.3×10^{-9} M) in the suspension was below the solubility limit for precipitation of $Pu(OH)_4$

(amorphous) (Rai et al., 1980b). The pH of the mineral suspension was then readjusted to the starting pH. Several times during the course of an experiment the stirring was stopped for 5 min and the suspensions were allowed to settle. A sample of the supernatant was withdrawn, filtered through 0.015 m filter, and used for total plutonium and oxidation state analysis. Duplicate tests were conducted.

At the end of a selected sorption period, the suspensions were centrifuged and the supernatant discarded. Desorption of Pu was then carried out using 1 M NaCl solutions at the pH values used for the adsorption studies.

Analytical Methods

For the determination of total Pu in filtered solutions, all Pu in the solutions was: 1) made 1 M in HNO_3 and reduced to Pu(III) with $NH_2OH \cdot HCl$, 2) oxidized to Pu(IV) with $NaNO_2$, 3) extracted with 0.5 M thenoyltrifluoroacetone (TTA) in xylene, and 4) back extracted from TTA with 10 M HNO_3. A portion of the final solution was then dried on stainless steel planchets for total alpha counting (Moore and Hudgens, 1957).

The Pu oxidation state analyses were run using solvent extraction techniques. The test solutions were made 1 M in HNO_3 treated with 0.5 M TTA in xylene to extract Pu(III and IV). Following the Pu(III) and Pu(IV) extraction, the aqueous phase was made 3.5 M in HNO_3 and 0.01 M $KBrO_3$ and contacted with TBP or DBBP to extract Pu(V) and Pu(VI) .

Weight percentages of Fe(II) and Fe(III) in the mineral samples were determined by Dr. J. W. Stucki (University of Illinois, Urbana, Illinois) using his recently developed method.

Surface areas were determined by the ethylene glycol method (Bower and Goestzen, 1959) as modified by Rai and Franklin (1978).

Cation exchange capacities of the samples were done by a ^{85}Sr column method (Routson et al., 1973).

Magnesium and potassium saturated clays were prepared for x-ray diffraction analyses by smearing the clay on petrographic slides (Theisen and Harward, 1962). The following characterization treatments were used for x-ray analysis: Mg saturated, 54% relative humidity; Mg saturated, ethylene glycol; K saturated, 105C, dry air; K saturated, 54% relative humidity; and K saturated, 550C, dry air. Diffractograms were obtained with Cu Kα radiation and a Geiger Muller tube equipped with a monochromatizing crystal. Brown (1961) was used as a reference for clay mineral identification criteria.

RESULTS AND DISCUSSION

Monomineralic samples are needed to determine the contribution of different minerals to total Pu adsorption by different geomedia and to facilitate the interpretation of Pu adsorption data. X-ray diffraction patterns were obtained to determine the crystalline components of these samples. The tracings a part of the of X-ray diffraction patterns of 1:1 and 2:1 clay minerals are given in Figure 1. Montmorillonite, nontronite and biotite were found to be free of detectable amounts of crystalline impurities. The kaolinite sample contained a small amount of mica. The vermiculite sample was found to contain a small amount of interstratified vermiculite-mica. X-ray diffraction data for hematite and gibbsite are not included in this paper, but hematite and gibbsite were found to contain small amounts of quartz. Thus any Pu adsorption can be considered to be specifically due to the given mineral and its properties.

In addition to mineral samples, a rock sample (vesicular basalt) was also included in the study. The mineralogy of a powder sample of this vesicular basalt was determined by X-ray diffraction and petrographic microscopy. The sample has a fine-grained, black, glassy matrix which consists primarily of intersertal glass and plagioclase feldspar. The matrix also contains minor amounts of iron oxide and possibly a pyroxene. The basalt also contains a large proportion of millimeter-size vesicles which were coated or filled with secondary mineralization. These secondary minerals were tentatively identified as a hydrated iron oxide, calcite, and zeolite.

At pH values of approximately 4, the percent of the total ^{239}Pu added which was adsorbed by the different minerals is plotted against time in Figure 2. In general the adsorption increases with time. Pu adsorption by biotite and vermiculite differ substantially from that of the rest of the minerals. Biotite and vermiculite showed high adsorption (>97%) within an hour, then subsequently remained constant with time. The minerals and rocks can be arranged in an increasing order of Pu(VI) adsorption as follows: gibbsite < kaolinite < vesicular basalt < montmorillonite < nontronite ≃ hematite < vermiculite ≃ biotite.

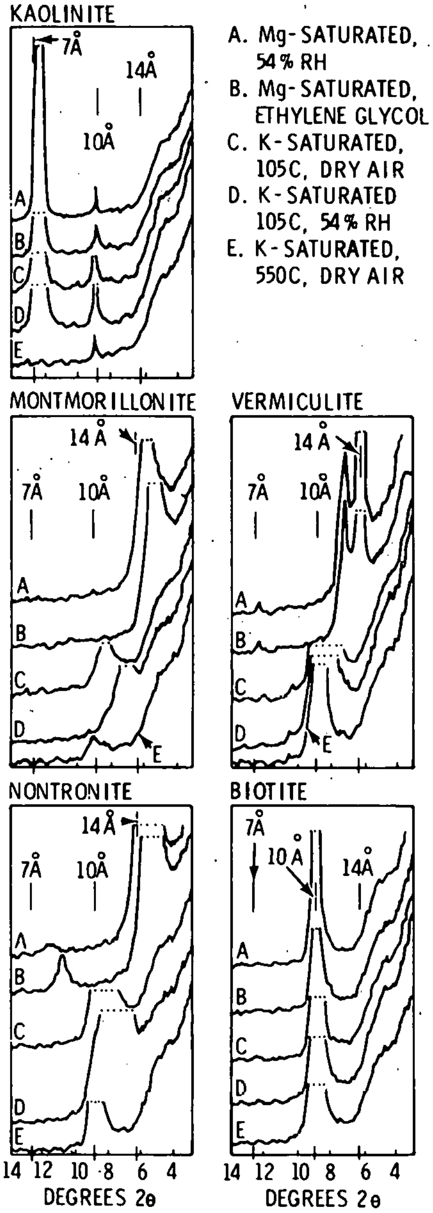

FIGURE 1. Tracings of X-Ray Diffractograms of Clay Samples

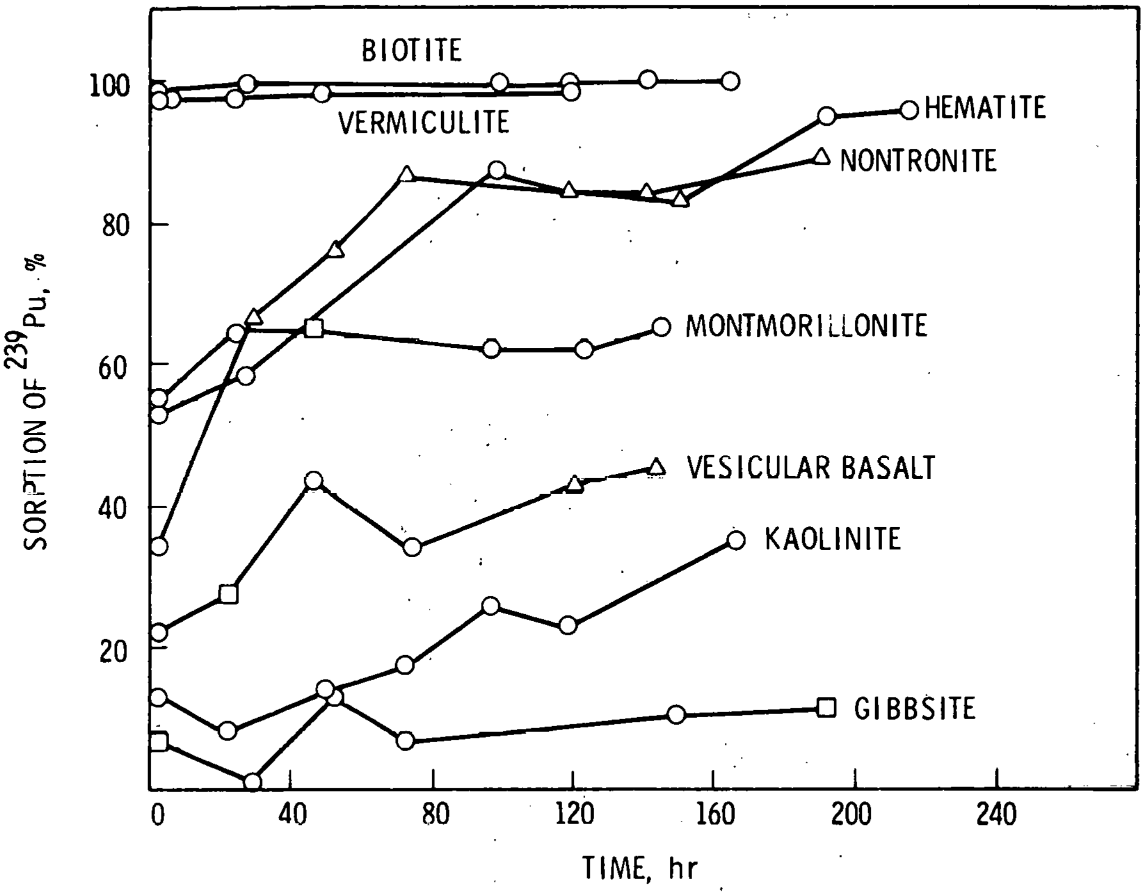

FIGURE 2. Adsorption of ^{239}Pu(VI) by Aerated Mineral Suspensions at pH 4. Averages of Duplicate Samples are Plotted. (O = <7%, □ = 7-15%, and Δ = 15-30% difference between the replicates).

The reasons for differences in Pu adsorption of Pu by different geomedia should be understood before one attempts to predict Pu behavior in the environment. Therefore, several adsorption mechanisms or factors that control Pu adsorption behavior were investigated.

In order to determine the contribution of exchangeable Pu to the total Pu adsorbed, cation exchange capacities of minerals and desorption experiments on the adsorbed Pu were carried out (Table 1). The exchangeable Pu in all the minerals studied varied from 1 to 32.3% of the total adsorbed. Therefore, ion exchange does not appear to be the dominant mechanism for the adsorption of Pu. Regardless of amount, the exchangeable Pu did not correlate with either the cation exchange capacity or the surface area of the minerals (Table 1). Montmorillonite, nontronite, and vermiculite have nearly the same cation exchange capacity but they differ significantly from each other in Pu adsorption (Fig. 2) and show 32.2, 1.4, and 9.0% (of the total adsorbed) exchangeable Pu, respectively. On the other hand, biotite, which has a much lower CEC than montmorillonite, nontronite, or vermiculite, is similar in its percentage adsorption and exchangeable Pu to vermiculite. In general 2:1 type clays (montmorillonite, nontronite, vermiculite, biotite) showed higher adsorption than the 1:1 (kaolinite) type clay, although no such pattern was obvious in exchangeable Pu.

In a further effort to understand the difference in adsorption behavior of minerals, the oxidation state of Pu in solutions in equilibrium with different minerals was studied (Table 2). These results show that essentially all solution Pu is in the oxidized state (plutonyl). However, the presence of oxidized Pu is no guarantee that the adsorbed Pu is also oxidized, because the reduced Pu [Pu(III) and Pu(IV)] has very high adsorption affinity for geomedia compared with the oxidized Pu. Therefore, if a portion of oxidized Pu were reduced, the reduced Pu would be readily adsorbed by the minerals, leaving behind the oxidized Pu.

Ozone is a strong oxidant and can oxidize all Pu to Pu(VI) and can also oxidize the exposed surfaces of minerals. Vermiculite and biotite, at pH 4, showed considerably less adsorption ($<50\%$) when the adsorption was carried out in the presence of ozone (Figure 3). Ozone made little difference in the

TABLE 1. Exchangeable Pu and Selected Properties of Minerals and Rocks

Sample	CEC	Surface Area	Fe Content (Weight %) Fe(II)	Fe(III)[†]	Fe(total)	Desorbed or Exchangeable Pu[‡]
	meq/100 g	m^2/g	%	%	%	%
Kaolinite	5.0 ± 0.9	37 ± 3	0.15	0.21	0.35	17.2
Montmorillonite	87.4 ± 2.7	767 ± 39	0.07	2.45	2.52	32.2
Nontronite	95.0 ± 3.0	888 ± 45	0.15	23.67	23.82	1.4
Vermiculite	77.0 ± 4.8	317 ± 8	1.08	5.67	6.75	9.0
Biotite	15.3 ± 1.1	71 ± 3	11.46	2.29	13.75	4.8
Hematite	ND[δ]	ND[δ]	1.25	11.18	12.43	1
Gibbsite	ND[δ]	12 ± 1	0.00	0.79	0.79	ND
Vesicular Basalt	4.0 ± 1.4	72 ± 4	1.24	3.82	5.06	28.1

[†] Fe(III) was calculated by subtracting Fe(II) from Fe(total)

[‡] At the end of sorption (at pH 4) period noted in Fig. 2, the exchangeable Pu at pH 4 was determined with 1 N NaCl (except in vesicular basalt where 0.01 N $CaCl_2$ was used).

[δ] The results are presented as percentage of the total Pu originally sorbed.

ND = not determined.

TABLE 2. Plutonium-239 Oxidation State Distribution in Solutions Contacting Different Minerals at pH 4

Sample	Contact Time	Pu(V) and/or Pu(VI)
	hr	%
Kaolinite	22	99
		94
	95	95
		98
Montmorillonite	23	94
		95
	121	99
		86
Nontronite	189	95
Gibbsite	49	84
		88
	192	ND†
		ND†
Vesicular Basalt	22	95
	143	99

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† ND = not determined.

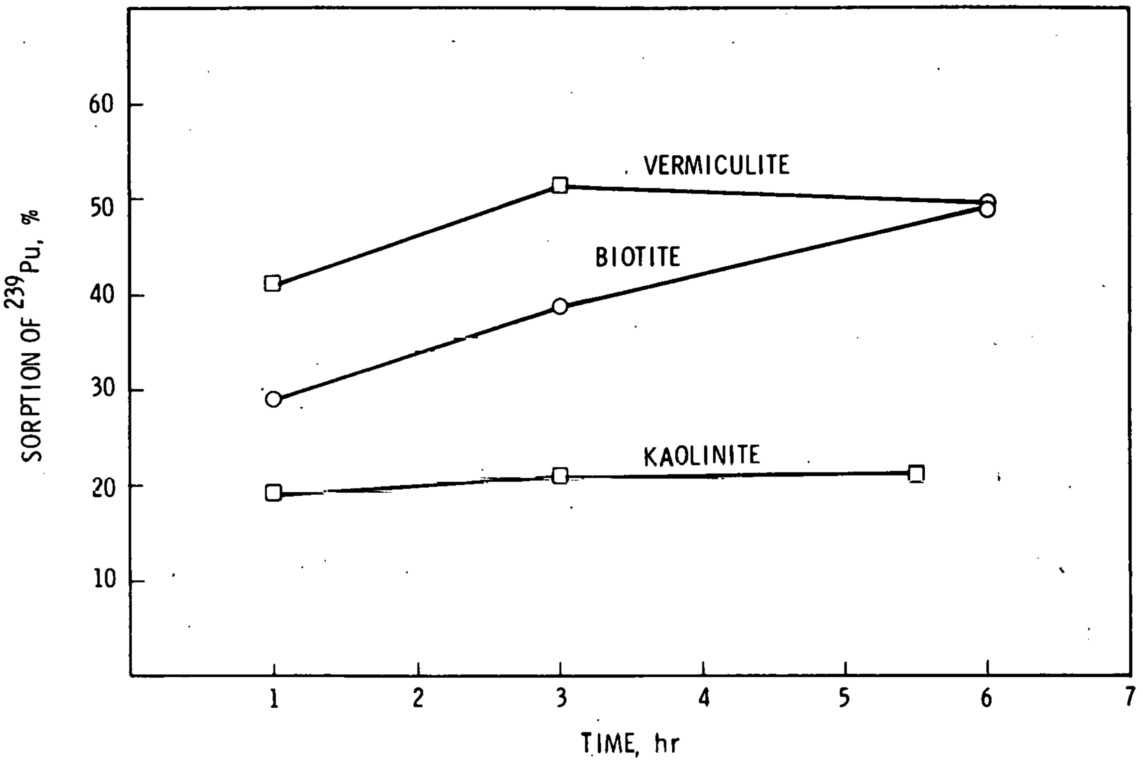

FIGURE 3. Adsorption of Pu in the Presence of Ozone at pH of Approximately 4. Averages of duplicate samples are plotted. (O = <4% and □ = 9-15% difference between the replicates).

adsorption of Pu by kaolinite. These results strongly suggest that a large amount of Pu adsorption by vermiculite and biotite is due to reduction of plutonyl ions, whereas the predominant amount of adsorption by kaolinite is not due to the reduction of plutonyl. Bondietti and Francis (1979) showed that some of the aerated water equilibrated rocks had an ability to reduce NpO_2^+ and TcO_4^-. Therefore, it is not surprising to note that some of these aerated water equilibrated samples possess reduction capacities.

Vermiculite and biotite are known to contain Fe(II) in their structure and the Fe(II) is known to be a strong reductant for plutonyl ions (Cleveland, 1970). In order to check whether the amount of Fe(II) in the minerals could explain the reducing nature of the minerals and the differences in their adsorption behavior (Figure 2), the minerals were analyzed for Fe(II) and Fe(III). The results show that the concentration of Fe(II) in the minerals varied from undetectable to 11.46 weight percent (Table 1). All the minerals (vermiculite, biotite, and hematite) that had high concentrations of Fe(II) (Table 1) also showed very high Pu(VI) adsorption (Figure 2). On the contrary, one of the rock samples (vesicular basalt) that had a high concentration of Fe(II) did not show high adsorption. The reasons for this anomalous behavior of vesicular basalt are not known. Kaolinite and gibbsite had relatively low concentrations of Fe(II) and also showed the low adsorption. Montmorillonite and nontronite are similar in structure and have similar chemical properties except that the octahedral layer in montmorillonite consists predominantly of aluminum where as the octahedral layer in nontronite consists mainly of iron. Montmorillonite has a very low amount of Fe(II), relatively high exchangeable Pu (Table 1) and intermediate adsorption. Thus, the adsorption by montmorillonite may be specifically related to the structure and the properties of this mineral. Nontronite, on the other hand, has only slightly more Fe(II) (0.15%) than montmorillonite (0.07%) but exhibited very low exchangeable Pu and relatively high adsorption. This suggests that the differences in adsorption between nontronite and montmorillonite may be due to the higher reduction of plutonyl in nontronite.

The adsorption of Pu under acidic conditions, such as pH 4, was expected to be lower than under alkaline conditions but was studied to determine the extent of adsorption of Pu(VI) under conditions more favorable to its mobilization. Most of the geomedia under consideration as deep geologic repository sites for radioactive wastes are alkaline (pH >7). Therefore, adsorption of Pu(VI) by different minerals was also studied at pH 7 (Table 3). The results show that the minerals did not differ significantly from each other in their adsorption capacities and that all the minerals exhibited very high adsorption (>93%). Relative to other minerals at pH 4, kaolinite and montmorillonite had fairly high desorption of Pu (Table 1). The percentage of desorption from kaolinite and montmorillonite decreased to <8 at pH 7 (Table 3). Compared with approximately 17 and 32%, respectively, at pH 4 (Table 1).

Specific adsorption, ion exchange, and reduction of plutonyl were discussed as some of the mechanisms that controlled Pu adsorption at pH 4. In addition to these mechanisms, it would appear that the hydrolysis of plutonyl (VI) ions and their subsequent adsorption may contribute significantly to the adsorption of Pu at pH 7 since the minerals (kaolinite, gibbsite) that showed very low adsorption at pH 4 showed very high adsorption under alkaline conditions.

Different radioactive waste disposal sites are expected to contain the minerals used in this study. Thus, to determine the practical usefulness of these results, the concentrations of Pu in the solutions contacting different mineral were compared with the maximum permissible concentrations (MPC) of ^{239}Pu in the waters (3.37×10^{-10} M), at the boundary of the restricted areas, as established by the U.S. Nuclear Regulatory Commission (1979). The initial concentration of ^{239}Pu(VI) (7.3×10^{-9} M) added to the suspensions was approximately 22 times the MPC. Greater than 95.4% adsorption values in this study correspond to ^{239}Pu concentrations less than the MPC. Thus, the results show that ^{239}Pu concentrations in equilbrated solutions at pH 7 that contacted the selected minerals were near or lower than the MPC (Table 3). This was also true for vermiculite, biotite, and hematite at pH 4 (Figure 2).

TABLE 3. Adsorption and Desorption of ^{239}Pu(VI) by Different Minerals at pH 7

Sample	Sorption Time	^{239}Pu Sorption	Desorption of ^{239}Pu†
	hr	%	%
Kaolinite	2.5	88.9 ± 1.5	
	96.0	93.8 ± 2.3	8.1 ± 3.8
Montmorillonite	2.5	92.9 ± 1.6	
	96.0	97.7 ± 0.4	4.9 ± 0.1
Vermiculite	3.5	99.7 ± 0.2	
	22.0	99.8 ± 0.2	ND‡
Gibbsite	3.5	93.6 ± 1.2	
	48.0	95.7 ± 1.3	ND‡

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†At the end of sorption period, desorption was carried out with pH 7 1 M NaCl. The results are present as percent of the total Pu adsorbed. Subsequent to NaCl desorption, approximately 35% Pu was desorbed with 1 M HNO_3 at the end of 1 hr.

‡ND = not determined.

A very small percentage of the adsorbed Pu was released when the minerals were contacted with 1 M NaCl (Tables 1 and 3). Minerals used in the present study were also used by Relyea et al. (1979). Under ambient and anoxic conditions they observed very large adsorption coefficients (adsorption >97%) from 30 meq/l $CaCl_2$, NaCl, and $NaHCO_3$ solutions spiked with ^{237}Pu [considered to be predominantly Pu(IV)][(a)] at concentrations ($<5 \times 10^{-13}$ M) much lower than the MPC. These results combined with the fact that most geomedia at potential deep repository sites are expected to be alkaline and more reducing than the present experimental conditions indicate that Pu in general and Pu(VI) specifically would be relatively immobile in geomedia that do not contain significant quantities of complexing ligands. However, the presence of organic and inorganic ligands that complex Pu, may increase the mobility of Pu.

(a) Subsequent analyses of air-equilibrated stock solutions showed large amounts of oxidized Pu in addition to reduced Pu.

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Waste/Rock Interaction Technology

SOLUBILITY OF PLUTONIUM COMPOUNDS AND THEIR BEHAVIOR IN SOILS

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SOLUBILITY OF PLUTONIUM COMPOUNDS AND THEIR BEHAVIOR IN SOILS

Dhanpat Rai, R. J. Serne and D. A. Moore

ABSTRACT

The solubilities of $^{239}PuO_2(c)$ and $^{239}Pu(OH)_4(am)$ under natural environmental conditions were determined. These data were then used to predict the 1) nature of the solid phases present in contaminated soils, and 2) total concentration of Pu that can be expected in soil solutions when these Pu solids are present.

Based upon solubility measurements, an estimated value of the log K^c (equilibrium constant at room temperature and an approximate ionic strength of 0.0045) for the dissolution of $^{239}PuO_2(c)$ [$PuO_2(c) \leftrightharpoons PuO_2^{+} + e^-$] was found to be -14.8. The estimated value of the log K^c for the dissolution of $^{239}Pu(OH)_4(am)$ [$Pu(OH)_4(am) \leftrightharpoons PuO_2^{+} + 2\ H_2O + e^-$] was found to be -12.8.

Comparison of Pu concentration in equilibrium solutions of contaminated Hanford soils with the $PuO_2(c)$ and $Pu(OH)_4(am)$ solubility lines suggested that $Pu(OH)_4(am)$ was absent from all the samples and that two of the samples contained $PuO_2(c)$. The presence of $PuO_2(c)$ was also confirmed by X-ray diffraction of Pu particles isolated from one of the samples.

Additional Index Words: solubility of $PuO_2(c)$, solubility of $Pu(OH)_4(am)$, equilibrium constant, plutonyl (V), oxidation-reduction, redox potential.

INTRODUCTION

The solid compounds of Pu that may be present in soils have a specific solubility at equilibrium in a given weathering environment and could control the final concentration of Pu in the soil solution. The final concentration could, in turn, largely control the distribution of Pu in the environment. Therefore, knowledge of Pu compounds present in the soil and their solubility are necessary in order to predict the behavior or fate of Pu in soil.

Reliable data on the solubility of crystalline Pu oxide [PuO_2(c)] and amorphous Pu hydroxide [$Pu(OH)_4$(am)], the compounds most likely to form in soils at environmental pH and redox potentials, are lacking (Rai and Serne 1977). Based upon thermodynamic data reported in the literature, an uncertainty of at least five orders of magnitude in the solubility of these compounds is expected (Rai and Serne 1978). An extensive review (Ames and Rai 1978; Ames, Rai and Serne 1976) of the actinides indicate that numerous workers have studied Pu concentrations and distribution with depth in soils around nuclear installations. However, with the exception of Price and Ames (1975), none have made any attempt to identify the solid phases of Pu present in soils. Price and Ames (1975) isolated plutonium particles from contaminated soils and analyzed them with electron microprobe and X-ray diffraction. They were able to isolate and identify discrete particles of Pu as PuO_2(c), but were not able to identify the nature of other Pu compounds associated with soil silicates. The results of Price and Ames (1975) are consistent with the theoretical calculations of Rai and Serne (1977) who predicted that the PuO_2(c) would be comparatively stable in the pH and redox potential ranges found in terrestrial environments.

Clearly more information is needed regarding the solubility of various Pu compounds and the nature of the solid compounds that may be present in the soils. The objectives of this study were to: 1) determine Pu concentrations in equilibrium with PuO_2(c) and $Pu(OH)_4$(am) under environmental conditions, 2) identify Pu compounds in contaminated soils, and 3) provide guidelines for selecting concentrations of Pu for adsorption experiments to assure that Pu precipitation would be negligible or absent.

METHODS AND MATERIALS

The $^{239}Pu(IV)$ hydroxide used in this study was prepared by rapid neutralization of a pure $^{239}Pu(IV)$ nitrate solution ($8\underline{M}$ HNO_3) with NaOH (Cleveland 1970). The precipitate was washed with distilled water. The Pu(IV) hydroxide thus prepared is represented in this study as $Pu(OH)_4(am)$. As expected, the X-ray diffraction pattern of $Pu(OH)_4(am)$ indicated it to be an amorphous compound (Table 2). The crystalline $^{239}PuO_2(c)$ (99.1% enriched in ^{239}Pu) microspheres were obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee. A nearly perfect match of the sample's d spacings with the values reported in American Society for Testing and Materials (1966) indicated that the $PuO_2(c)$ sample used for this study was indeed crystalline (Table 1). In order to determine solubility, approximately 8 mg of these ^{239}Pu solids were suspended in 20 ml of $0.0015\underline{M}$ $CaCl_2$ solution. The samples were adjusted to different pH values with HCl or NaOH. The suspensions were equilibrated with air and shaken for various lengths of time. The pH of the suspensions was periodically readjusted (approximately every fifth day) for the first 3 weeks of the experiment. The pH was measured using a glass electrode. The redox potential (E_m) was measured with a platinum electrode (versus standard calomel electrode corrected to standard hydrogen electrode).

In order to determine the nature of the plutonium compounds present in contaminated soils, three contaminated soil samples (Z9-4-5A; Z9-4-11A; Z12-1D) from two Hanford waste disposal cribs (Z9 and Z12) were used. The samples were washed once with distilled water to remove soluble salts and then equilibrated with $0.0015\underline{M}$ $CaCl_2$ solution in duplicate. Equilibrations were also carried out with soil only and soil plus 5 mg $PuO_2(c)$. As in the case of Pu compounds, the suspensions were equilibrated with air and shaken for various lengths of time.

At various times, the suspensions containing Pu compounds and contaminated soils were centrifuged at 6000 g for 40 min and a small aliquot of the supernate was withdrawn for Pu analyses. A preliminary analysis of these solutions

TABLE 1. X-ray Diffraction Data for Pu Samples

Standard $PuO_2(c)$	d(A°) From Different Pu Samples† Pu Used in Study $PuO_2(c)$	 $Pu(OH)_4(am)$	Filtered Pu	Soil Pu
3.08	3.118	A	3.13	3.13
2.67	2.696	A	2.71	
1.894	1.909	A	1.919	1.888
1.617	1.627	A	1.631	1.623
1.548	1.559	A		1.552
1.234	1.239	A		1.235
1.203	1.208	A		1.204
1.199	1.103	A		1.098

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† Standard $PuO_2(c)$ data ASTM (1966); A = amorphous; Filtered Pu = Pu retained by 0.1 m membrane used to filter $PuO_2(c)$ suspension No. 20 equilibrated for 90 days (Table 1); Soil Pu = Pu separated from contaminated soil Z9-4-11A (Ames, 1974).

indicated a wide variation (as high as 30 fold in some cases) in Pu concentrations of duplicate aliquots withdrawn from a sample. This variation was later found to be due to the inability of centrifugation to completely separate the solid particles from the solution. Filtration through (0.1 and/or 0.015 μm) Nuclepore® filters gave consistent analyses of duplicate aliquots and thus presumably removed the fine solid particles. The Pu activity in solutions was determined by alpha counting in a 2π geometry.

The crystallinity of the Pu samples was determined from X-ray diffraction patterns obtained by using Cu Kα.

TABLE 2. Concentration of Pu in 0.0015M $CaCl_2$ Solution after Contact with $^{239}PuO_2(c)$ and $^{239}Pu(OH)_4(am)$ for Approximately 90 Days

Sample		Log Pu (moles/l) in Solution[†]		
			Filtered Through	
No.	pH	Unfiltered	0.1 m	0.015 µm
		Solutions Contacting $PuO_2(c)$[‡]		
13	3.80	-6.14	-6.17	-6.12
14	3.80	-6.09	-6.08	-6.05
15	4.30	-6.42	-6.60	-6.57
16	4.30	-6.43	-6.43	-6.44
18	5.40	-5.69	-7.28	-7.29
17	5.45	-6.15	-7.46	-7.47
19	7.30	-6.33	-8.70	-8.55
20	7.30	-5.62	-8.71	-8.78
		Solutions Contacting $Pu(OH)_4(am)$[‡]		
21	3.95	-4.40	-4.44	-4.46
22	4.00	-4.54	-4.54	-4.52
5	4.00	-3.90	-4.31	ND
6	4.00	-3.39	-4.22	ND
24	5.00	-5.26	-5.25	-5.25
23	5.05	-5.43	-5.44	-5.47
8	5.25	-4.99	-5.17	ND
7	5.30	-5.19	-5.31	ND
26	6.60	-6.51	-6.77	-6.79
25	6.70	-6.56	-6.83	-6.98
10	6.80	-5.18	-6.63	ND
9	6.83	-5.71	-6.73	ND
27	7.50	-7.43	-7.54	-7.58
28	7.70	-7.19	-7.77	-7.79
12	7.85	-5.21	-7.11	ND

[†] All solutions were centrifuged at 6000 g for 40 min; ND = not determined; the average values of three subsamples counted from each sample are given and the error (one standard deviation) in all the samples was <±0.06, except in unfiltered $PuO_2(c)$ samples 19 and 20 and $Pu(OH)_4(am)$ samples 7 and 9 where the error varied from ±0.13 to ±0.18.

[‡] Approximately 8 mg of crystalline PuO_2 or amorphous $Pu(OH)_4(c)$ was shaken with 20 ml of 0.0015M $CaCl_2$.

RESULTS AND DISCUSSION

SOLUBILITY OF Pu COMPOUNDS

The concentration of Pu in unfiltered and filtered solutions after contact with $^{239}PuO_2(c)$ and $^{239}Pu(OH)_4(am)$ for 90 days is given in Table 2. The samples passed through 0.1 and 0.015 μm filters do not differ significantly from each other, indicating that discrete Pu particles >0.015 μm and <0.1 μm are absent from solutions. The Pu concentrations in unfiltered samples were generally close to those in the filtered solutions except in a few relatively high pH samples where the concentration in unfiltered solutions was up to three orders of magnitude higher than in the filtered solutions. Discrete particles of Pu were found when several filters employed in filtration were examined with a scanning electron microscope and an electron microprobe. X-ray diffraction patterns of the Pu retained on a 0.1 μm membrane (Table 1) used to filter a $PuO_2(c)$ sample indicated it to be a crystalline $PuO_2(c)$. Thus, the difference in Pu concentration between the unfiltered and filtered solutions can be attributed to the incomplete separation of Pu particles from the unfiltered solutions. Therefore, all subsequent samples were filtered before analysis. At the end of the 90 day equilibration, the X-ray diffraction patterns showed that the $PuO_2(c)$ samples were crystalline and $Pu(OH)_4(am)$ samples were amorphous, as was the case at the beginning of the experiment. Thermodynamic prediction (13) and literature data (Lloyd and Haire 1973) indicate that with time $Pu(OH)_4(am)$ will crystallize and change to $PuO_2(c)$. However, the equilibration period employed in this study apparently was not long enough for this change to occur to any measurable extent.

Plutonium concentrations in solution in contact with $PuO_2(c)$ and $Pu(OH)_{4}(am)$ for 90, 130, and approximately 250 days are plotted against pH in Figures 1 and 2. Values for 90, 130, and 250 days are similar, suggesting that equilibrium had been reached after 90 days. The pH of the solutions was observed to continuously decrease with time (Figures 1 and 2) presumably due to radiolysis of water caused by alpha decay. With this decrease in pH the concentration of Pu has increased proportionally again suggesting that the Pu

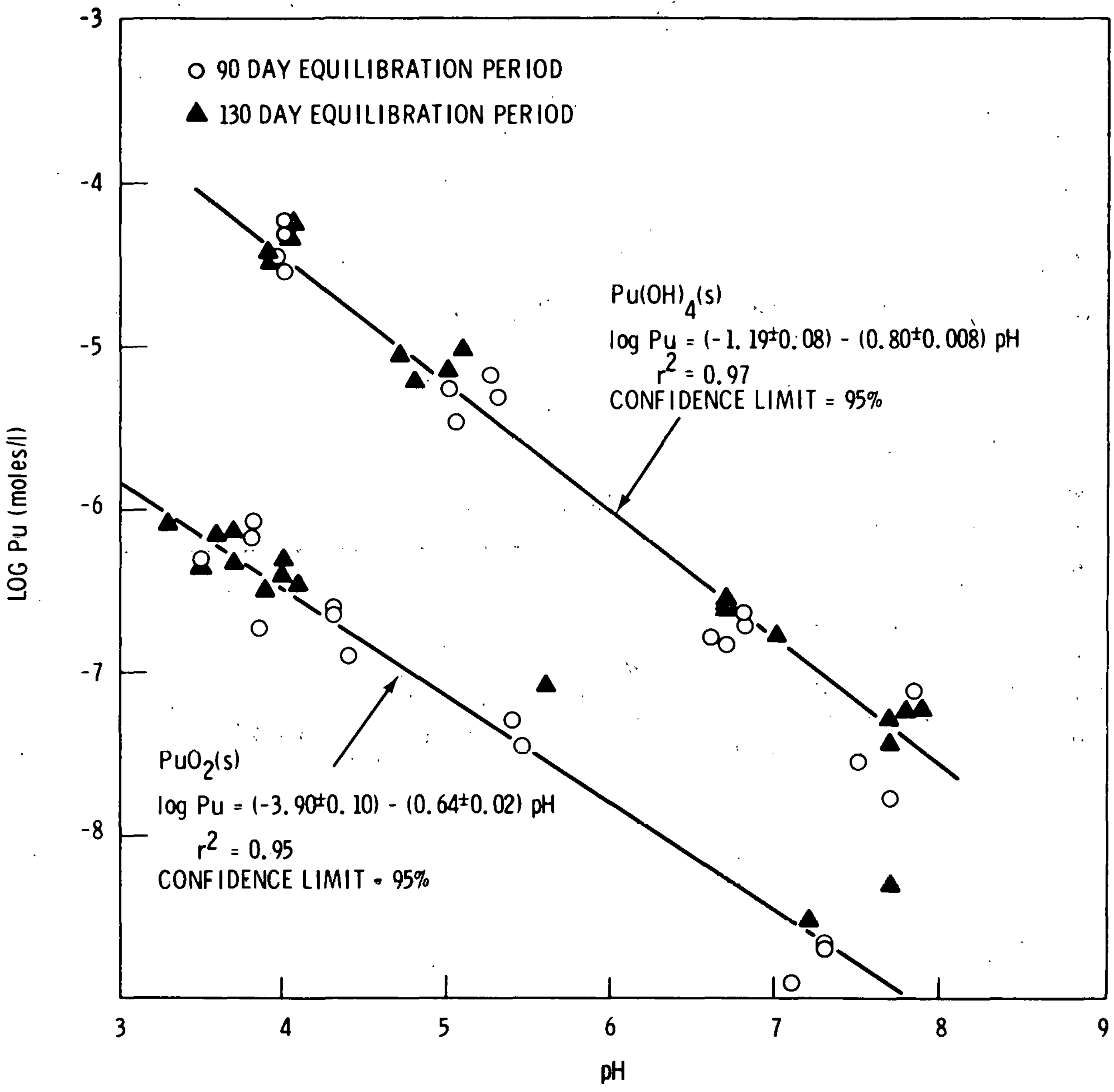

FIGURE 1. Concentration of Pu in Filtered (0.1 μm) Solutions Contacting $^{239}PuO_2(s)$ and $^{239}Pu(OH)_4(s)$

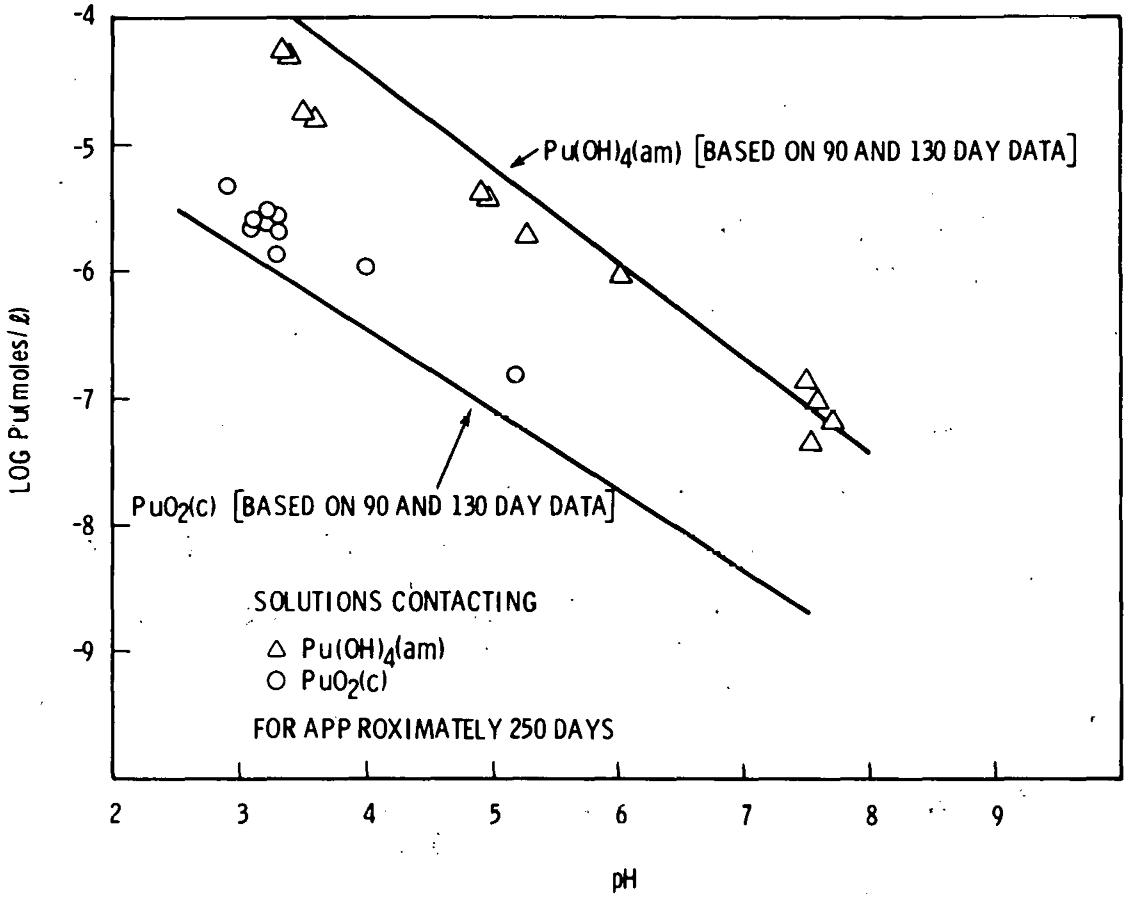

FIGURE 2. Relationship of Electrochemical Potential (Eh), with Respect to Standard Hydrogen Electrode, and pH of Solutions Contacting Different ^{239}Pu Solids

concentrations have reached equilibrium values at all of the measured pH values. As expected (Rai and Serne 1977), $Pu(OH)_4$(am) maintains a higher Pu concentration in solution at environmental pH values than does PuO_2(c). The solubilities of both PuO_2(c) and $Pu(OH)_4$(am) decrease with increasing pH. Linear relationships exist between the pH and total Pu concentration in solution in equilibrium with the different Pu compounds. Theserelationships for PuO_2(c) [Eq. (1)] and for $Pu(OH)_4$(am) [Eq. (2)] are:

$$\log (Pu_{total}) = (-3.90 \pm 0.10) - (0.64 \pm 0.02)\ pH \qquad (1)$$

$$\log (Pu_{total}) = (-1.19 \pm 0.08) - (0.80 \pm 0.01)\ pH \qquad (2)$$

where Pu_{total} is in moles/l. The measured redox potentials (E_m in volts) and pH of PuO_2(c) and $Pu(OH)_4$(am) suspensions (Figure 3) also exhibited a linear correlation as shown in Eq. (3).

$$E_m = (0.727 \pm 0.011) - (0.0545 \pm 0.0008)\ pH \qquad (3)$$

Rai et al. (1980) have shown that the solutions in equilibrium with $Pu(OH)_4$(am) contain mainly Pu(V). Their results also strongly suggest the presence of Pu(V) in solutions contacting PuO_2(c). Pu(V) would be expected to be present predominantly as PuO_2^+ in these solutions because: 1) the relative tendency of Pu ions to form complexes is Pu(IV) > Pu(III) > Pu(VI) > Pu(V) (Coleman 1965), 2) the only anion present in these solutions in significant amounts is Cl^-, which does not form significant complexes with PuO_2^+ (Rai and Serne 1977), and 3) the species PuO_2^+ remains without further hydrolysis between pH zero and pH of approximately 8 (Baes and Mesmer 1976, Rai and Serne 1977). Therefore, the Pu_{total} in Eq. (1) and (2) can be replaced with PuO_2^+. Thus, Eq. (1) and (2) can now be written as Eq. (4) and (5), respectively.

$$\log (PuO_2^+) = (-3.90 \pm 0.10) - (0.64 \pm 0.02)\ pH \qquad (4)$$

$$\log (PuO_2^+) = (-1.19 \pm 0.08) - (0.80 \pm 0.01)\ pH \qquad (5)$$

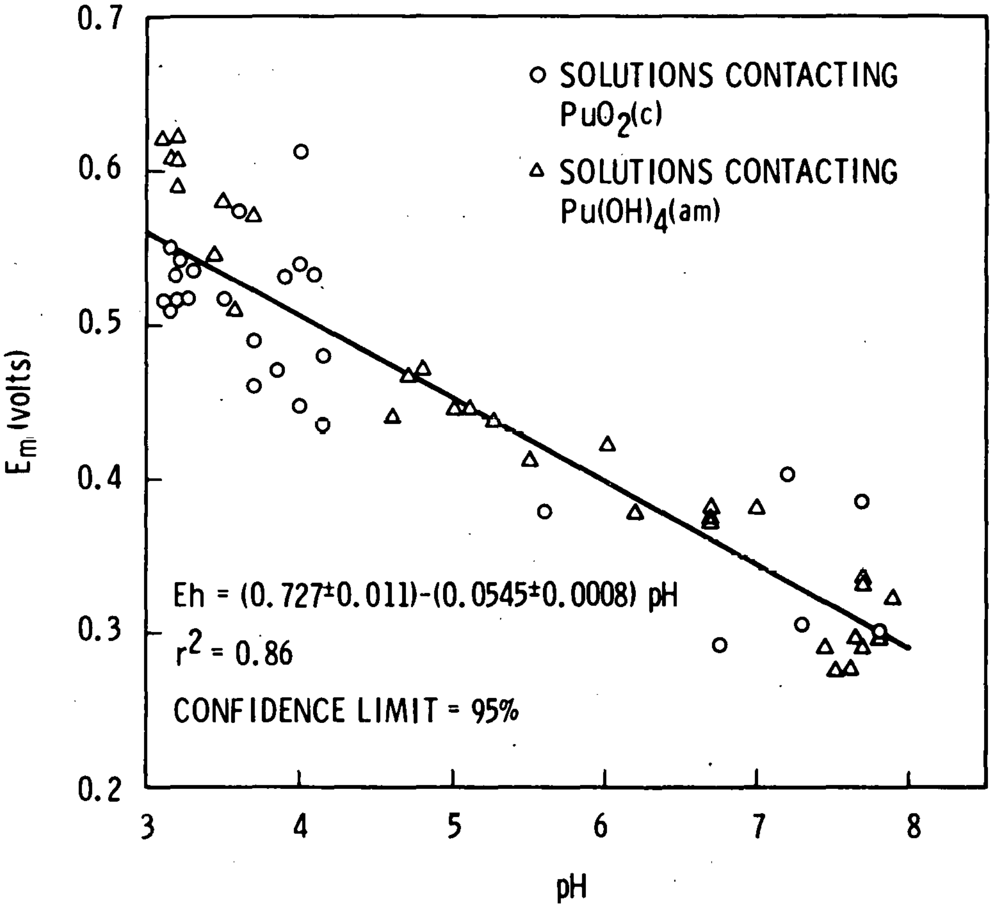

FIGURE 3. Concentration of Pu in Filtered (0.1 μm) Solutions Contacting Contaminated Hanford Soils with Different Treatments

ESTIMATION OF EQUILIBRIUM CONSTANTS

The solubility of $PuO_2(c)$ and $Pu(OH)_4(am)$ is written [Eq. (6) and (7) in terms of PuO_2^+], because the PuO_2^+ is shown to be the solution species in equilibrium with these compounds (Rai, Serne and Swanson 1980).

$$PuO_2(c) \leftrightharpoons PuO_2^+ + e^- \qquad (6)$$

$$Pu(OH)_4(am) \leftrightharpoons PuO_2^+ + e^- + 2H_2O \qquad (7)$$

The products and reactants in Eq. (6) and (7) are related to the equilibrium constant (K°) as follows:

$$\log K = \log [PuO_2^+] - pe \qquad (8)$$

where ( ) around PuO_2^+ denotes activity and the pe refers to the negative log of the electron activity. The pe is related to (Stumm and Morgan 1970) the electrochemical potential (Eh in volts) by

$$pe = 16.9\ Eh \qquad (9)$$

For reasons discussed later in this paper, it is inferred that the E_m values are similar to Eh values. Therefore, pe can be calculated from Eq. (9) for its use in estimating the equilibrium constants. Substituting the value of E_m [Eq. (3)] into Eq. (9)

$$pe = (16.9)\ [(0.727 \pm 0.011) - (0.0545 \pm 0.0008)\ pH] \qquad (10)$$

Substituting Eq. (4) or (5) and Eq. (10) into Eq. (8) and simplifying, the log of the equilibrium concentration constant ($\log K^c$) at room temperature and low ionic strength (≈0.0045) for the dissolution of $PuO_2(c)$ according to Eq. (6) can be written as

$$\log K^c = (-16.19 \pm 0.21) + (0.28 \pm 0.02)\ pH \qquad (11)$$

and the log K^c for the dissolution of $Pu(OH)_4(am)$ according to Eq. (7) can be written as:

$$\log K^c = (-13.48 \pm 0.20) + (0.12 \pm 0.02)\ pH \qquad (12)$$

Equations (11) and (12) hold for a pH range of approximately 4 to 8 (Figure 1). The errors quoted in Eq. (11) and (12) were calculated using a propagation of errors method described by Mandel (1976). Log K^c, at fixed ionic strength and temperature, by definition is a constant. However, log K^c in Eq. (11) and (12) shows a dependence upon pH (approximately 2% deviation per pH unit). This dependence on pH is likely due to experimental errors in measuring PuO_2, pH, and E_m.

The estimated value of log K^c for

$$PuO_2(c) \quad PuO_2 + e^-$$

at the average pH (4.8) value of solutions contacting $PuO_2(c)$ is -14.8. The estimated value of log K^c for

$$Pu(OH)_4(am) \leftrightarrows PuO_2 + 2H_2O + e^-$$

at the average value of pH (5.8) of solutions contacting $Pu(OH)_4(am)$ is -12.8. It should be mentioned that the solutions are of low ionic strength (≈0.005) and thus the concentration equilibrium constant (K^c) is approximately equal to the thermodynamic equilibrium constant (K°).

A literature review was done in order to compare the equilibrium constants determined in this study with the reported values. A log K° for

$$Pu(OH)_4(am) \leftrightarrows Pu^{4+} + 4\ OH^- \qquad (13)$$

based upon solubility measurements in solutions of $pH < 3.5$ is reported by Perez-Bustamante (1965) to vary from -47.3 to -56.3. Baes and Mesmer (1976) reported log K for Eq. (13) to vary from -52.0 to -56.0. Smith and Martell (1976) selected a value of -47.3 which they believed best represents the log K° for this reaction. Clearly, there is wide variation and disagreement in reported values for the solubility product of $Pu(OH)_4(am)$. Based upon the results obtained in the present study, the log K° for the solubility product of $Pu(OH)_4(am)$ Eq. (13) can be estimated in the following manner:

	log K°	Reference
$Pu(OH)_4(am) \leftrightarrows PuO_2^+ + 2\,H_2O + e^-$	-12.8	Present Study
$PuO_2^+ + 4\,H^+ + e^- \leftrightarrows Pu^{4+} + 2\,H_2O$	18.6	Fuger and Oetting 1976
$4\,H_2O \leftrightarrows 4\,H^+ + 4\,OH^-$	-56.0	Sillen and Martell 1964
$Pu(OH)_4(am) \leftrightarrows Pu^{4+} + 4\,OH^-$	-50.2	Rai and Serne 1977

Assuming the thermodynamic data used in the above equations is correct, an estimated log K of -50.2 for the solubility product of $Pu(OH)_4(am)$ is obtained. We prefer to represent the solubility of $Pu(OH)_4(am)$ as described by Eq. (7) rather than Eq. (13), because there is a large possibility of error in the thermodynamic data used to derive Eq. (13). Nevertheless, the estimated solubility product of $Pu(OH)_4(am)$ obtained in this study is certainly within the range of values reported.

There are no data available in the literature for the measured solubility constant of $PuO_2(c)$ for comparison with this study. Baes and Mesmer (1976) calculated the solubility of $PuO_2(c)$ based upon the thermodynamic data and compared it with the reported log K° values (-52 to -56) of the solubility product of $Pu(OH)_4(am)$ and found a great difference (approximately 12 log units) between them. They report that such great differences between the precipitated hydrous oxide and the oxide are unusual and suggested that the reported values for $PuO_2(c)$ and/or $Pu(OH)_4(am)$ are probably in error by several log units. The difference (2 log units) between the log K^c of $PuO_2(c)$ and $Pu(OH)_4(am)$ found in the present study is low as predicted by Baes and Mesmer (Rai, Serne and Swanson 1980) but is considerably smaller than their estimated difference (8 log units) based upon the extrapolation of log K° versus the reciprocal of the lattice parameters of the actinide dioxides.

Making meaningful redox measurements, hence pe, in unpoised solutions with a platinum electrode is difficult. If reliable values of the equilibrium constant and the PuO_2^+ activity in solution were available, accurate values of pe and/or redox potential could then be calculated from Eq. (8). The values of redox potential thus calculated for PuO_2(c) and $Pu(OH)_4$(am) suspensions should be similar to each other, as was the case in measured redox potentials (Figure 3), because the study was conducted using the same isotope of Pu and under similar experimental conditions. Plutonyl (PuO_2^+) concentrations measured in this study were all greater than 1.0×10^{-9} M, where accurate measurements of Pu concentration can be made. Baes and Mesmer (1976) estimated the log K° value of -6.5 for the dissolution of PuO_2(c) [Eq. (14)].

$$PuO_2(c) + 4H^+ \leftrightharpoons Pu^{4+} + 2H_2O \qquad (14)$$

Perez-Bustamante (1965) reported the log K° for the solubility product of $Pu(OH)_4$(am) [Eq. (13)] to vary from -47.3 to -56.3. Assuming these reported log K values are correct, redox potentials were calculated using these log K values and the measured PuO_2 concentrations in Eq. (8) and (9). The redox potential thus calculated, E_c, for PuO_2(c) reaction [Eq. (8)] was approximately 0.61V higher than the E_m. The calculated E_c for $Pu(OH)_4$(am) suspension was found to vary approximately from 0.17V lower to 0.36V higher than the E_m. We conclude from these data that the reported value (1976) for PuO_2(c) solubility is in error and that the measured E_m may truly represent the equilibrium potential of our suspensions which supports usage of our calculated log K^c values as true equilibrium constants. The specific reasons for this conclusion are: 1) the measured E_m for PuO_2(c) and $Pu(OH)_4$(am) suspensions are similar (Figure 3) as expected, whereas the E_c for PuO_2(c) and $Pu(OH)_4$(am) are significantly different, 2) the E_m for $Pu(OH)_4$(am) suspension falls within the range of E_c, 3) the E_c of PuO_2(c) suspensions fall outside the water stability region, and, 4) the E_c of PuO_2(c) falls in the PuO_2^{2+} stability region, whereas the Pu species in solution were inferred to be PuO_2^+ (Rai and Serne 1977). The measured redox potentials (Figure 3) appear to be poised. This poising is hypothesized to be due to relatively high concentrations of Pu in the low pH region and/or radiolysis products of water caused by alpha decay. Further studies with the use of redox buffers and solid compounds of different alpha emitting isotopes have been initiated to check these hypotheses.

IDENTIFICATION OF Pu COMPOUNDS FROM CONTAMINATED SOILS

The presence of Pu compounds in sediments implies that the concentration of Pu in solution will be governed by the solubility of the Pu compounds. Thus, it is important to determine the nature of the solid compounds that may be present in sediments. If no Pu solid compounds are present, sorption reactions alone may govern the concentration of plutonium in solutions.

Large quantities of Pu solids would not be expected to be present in sediments. Therefore, it would be difficult to physically isolate, for identification, the trace amounts of Pu solids that may be present in sediments. It was decided to compare the plutonium concentrations in soil solutions with the experimental solubility of the solid compounds as a means of possibly identifying the plutonium solids that may be present in the sediments.

The soil solution data are plotted in Figure 4 where experimental solubility lines for $PuO_2(c)$ and $Pu(OH)_4(am)$ are also traced for reference. Soil solution points for soils Z9-4-11A and Z9-4-5A fell very near the $PuO_2(c)$ solubility line; however, the solution points for soil Z12-1D fell considerably below the $PuO_2(c)$ solubility line. When $PuO_2(c)$ was added to these suspensions the solution concentration for Z9-4-11A and Z9-4-5A did not change appreciably. The solution concentration for Z12-1D soil increased considerably and approached that of the $PuO_2(c)$ solubility line. Thus, soils Z9-4-11A and Z9-4-5A appear to contain $PuO_2(c)$ since the soil solution points fell close to the $PuO_2(c)$ solubility line and the soil solution concentration did not change appreciably with the addition of $PuO_2(c)$. The presence of crystalline $PuO_2(c)$ in Z9-4-11A sample, inferred from the solubility data, was confirmed by X-ray diffraction analysis of Pu particles isolated from this sample (Table 1). Concentrations of Pu in solutions contacting soil Z12-1D indicate that this soil does not contain $PuO_2(c)$.

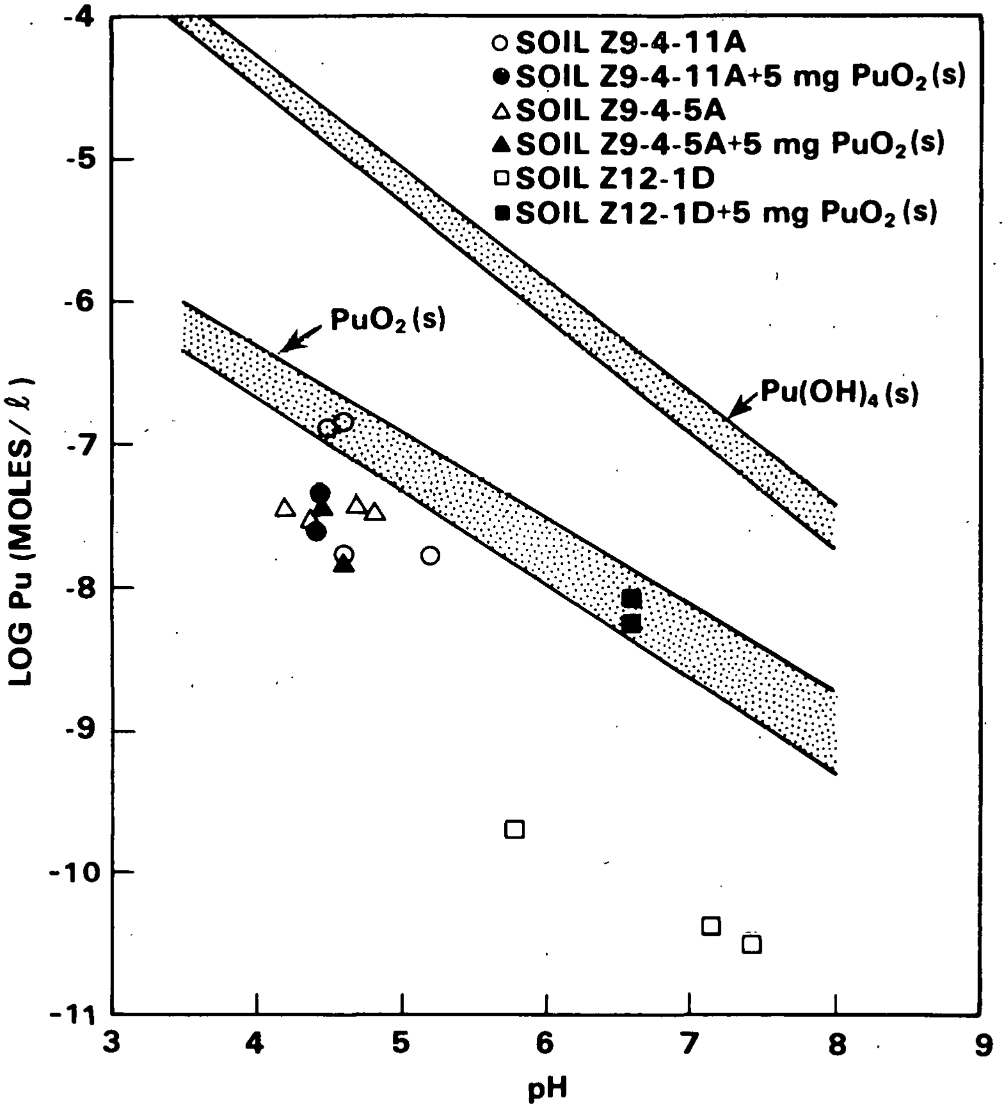
○ SOIL Z9-4-11A
● SOIL Z9-4-11A+5 mg $PuO_2(s)$
△ SOIL Z9-4-5A
▲ SOIL Z9-4-5A+5 mg $PuO_2(s)$
□ SOIL Z12-1D
■ SOIL Z12-1D+5 mg $PuO_2(s)$
$PuO_2(s)$
$Pu(OH)_4(s)$
LOG Pu (MOLES/ℓ)
-4
-5
-6
-7
-8
-9
-10
-11
3
4
5
6
7
8
9
pH

FIGURE 4.

The Pu concentration in all the soil solutions studied were much lower than the $Pu(OH)_4$(am) solubility line, indicating that the soils do not contain this compound.

The results presented above help demonstrate the ability of solid compounds to control the solution concentrations. If leaching occurs from Z9-4-11A and Z9-4-5A soils and the leachate percolates into the soils containing no PuO_2(c), the concentration of Pu in solution would be lower than the PuO_2(c) solubility line and would be governed by sorption reactions. On the other hand, Pu concentrations in solutions percolating through PuO_2(c) contaminated sediments would be expected to be similar to the concentrations predicted from the PuO_2(c) solubility line (Figure 1). Such an event might occur in the immediate vicinity of stored wastes. It is also evident that for the determination of meaningful equilibrium distribution coefficients (Kd), in an oxidizing environment, the Pu concentrations must be below the $Pu(OH)_4$(am) solubility line (and preferably below the PuO_2(c) solubility line) (Figure 1).

Two of the soil samples studied (Z9-4-11A and Z9-4-5A) in this report had received a complex waste with significant amounts of organic ligands with strong potential for forming soluble Pu complexes. However, the observed Pu concentrations are not significantly different than the concentrations present in a dilute PuO_2(c) suspension devoid of organic ligands. It is inferred that the organic ligands originally disposed into these soils have degraded over the period when the wastes were first disposed (approximately 20 yr). This inference is supported by the results of Cleveland (J. M. Cleveland, Chief, Transuranium Research Project, USGS, Denver, Colorado, Personal Communication, September 1977) who did not find detectable amounts of organics in Rocky Flats soil that had been contaminated by lathe cooling oil.

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QUESTIONS AND ANSWERS

D. RAI

Species and Redox (Eh) Control

Q: In your series of experiments for sorption of plutonyl by vermiculite and biotite in the presence of oxidants (ozone), you saw a reduction in the amount that was sorbed. Have you run, or are you planning to run, a series of experiments under the same type of conditions to see how much they can desorb?

A: We did do some experiments and found that we can desorb more in the presence of ozone than with sodium chloride alone.

Solubility

Q: In the beginning of your talk, didn't you refer to papers that stated the plutonium continued to dissolve?

A: Yes. That was a reference to Patterson's work at Los Alamos.

C: But I think the context in which that work was done presumes that plutonium oxide was put in the environment in an open system, not in a test tube. Presumably we're not going to saturate sea water with plutonium.

A: As I recall Patterson's data, their test tubes weren't much different from my test tubes. They were done in the test tube only. Referring to the statement, "they continued to dissolve", I understand that in the context of placing this into the environment in an open system.

Q: You also calculated a log K for the solubility of $Pu(OH)_4$ in terms of PuO_2^+ and then you summed up with water and other reactions and came up with solubility product.

Eh Control Measurements

Q: Implicit in that calculation is a use of some kind of potential. What potential did you use to calculate?

A: We measured the potential with a platinum electrode and then converted these potentials to pe for use in calculations. We recognize that there is a problem about measuring the Eh with platinum electrodes, but we know of no other method better than what we used.

C: Well, I'm not questioning the measurement, you actually took a measurement off the electrode and plugged it in and it came out close to the actual value. Now, I had the same situation in a much different context where I happened to take an electrode reading and the number came out right. Do you believe the electrode reading because the final answer is correct, or do you assume the common accepted belief that these measurements aren't any good.

A: Whether the measurements are good or not depends upon a particular system. If the measurements represent a particular reaction, then they would be right; however, in soils what one most often measures is a mixed potential which may be difficult to interpret. It would also be difficult to make measurements in an unpoised system. The concentration of Pu in the solutions is such that our system appears to be poised. In addition to Pu species the only other species present are the radiolysis products of water. Since our system appears to be poised, the redox values we measure may be fairly close to the actual values.

Q: You say that the plutonium is poising the electrodes.

A: Yes, it would appear that Pu is poising the electrode since the concentration of PuO_2^+, where it was definitely identified, in solution was greater than 10^{-5} M. Systems are most often considered poised if the concentration of the electroactive species is greater than 10^{-5} M.

Solubility

Q: Regarding solubility, you discussed the difference in solubility of what you called $PuOH_4$ and PuO_2. I think what you are seeing is a difference in rate. And whether you've achieved equilibrium may be when the two lines overlap, which they did tend to do there the longer you went. I think that's a rate you're looking at and not a thermodynamic.

A: I would disagree because there is a difference in starting materials. In $Pu(OH)_4$ case it is amorphous whereas PuO_2 is crystalline. Based upon thermodynamics, one would predict that $Pu(OH)_4$ would change into PuO_2. The concentration of Pu in equilibrium with $Pu(OH)_4$ to begin with was approximately 2 log units higher than PuO_2. However, after two years of equilibration, we are seeing some evidence of decrease in concentration of Pu in solution contacting $Pu(OH)_4$, suggesting the conversion of $Pu(OH)_4$ into a more stable crystalline form.

Q: Did you ever vary the pH after what you considered equilibrium dissolutions? Had you done some at pH 2; did you then raise some to pH 7 and having contact with the solid to see if they would fall back?

C: One of the things you've got to do with solubility is you have to approach it from both sides. You cannot just go from one side and then assume...

A: I recognize that and it is nearly impossible to do in the case of plutonium oxide, but we probably could have done it in the case of plutonium hydroxide. It is a question about whether we reached an equilibrium or not. We have data of almost 2 yr. The pH's of the solutions have continually been decreasing because of the radiolysis of water. In response to this decrease in pH, the concentration of plutonium has continuously been increasing. However, it is important to note that increase in Pu concentration has been proportional to the decrease in pH. This fact, in addition to 2 yr data, indicates that equilibrium has been reached.

Q: There was some doubt expressed as to your Eh measurement. How do your Eh and pH measurements coincide with your estimated PO_2? Or can you estimate it?

A: Oxygen acts as a much weaker oxidant than what one calculates based upon the oxygen partial pressures using H_2O/O_2 couple. Therefore, the measured values never coincide with the theoretical values. I do not know of any one method of measuring Eh that would be applicable in the whole Eh range. A recent publication (Cherry et al. 1979; submitted to Journal of Hydrology) discusses various methods (carbon, sulfur, iron, nitrogen, arsenic couples, and platinum) and gives the ranges in which they are suitable. The values measured in our study are in the range where these authors indicate that platinum electrode can be used. At a pH value of approximately 4.5, we definitely identified the Pu species in solution as Pu(V). At these pH values the measured Eh values are close to the calculated Pu(V) stability field.

Q: So it's anoxic then? Is that right?

A: No, I wouldn't say so. The measurements that we made show Eh of 0.72 volts at pH 0. But most of our work was in equilibrium with the air. But if you take the oxygen path at pressure and back-calculate Eh, it doesn't give the same value as we measured.

Q: What if the plutonium sorbs on the electrode surface? That is, if it sits on the electrode surface, and that gets reduced to plus three states on the surface itself.

A: I don't know. I haven't figured that.

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Distribution Category -4

THE KINETICS AND REVERSIBILITY OF RADIONUCLIDE SORPTION REACTIONS WITH ROCKS

Progress Report for Fiscal Year 1979

G. Scott Barney
Glenda E. Brown

Chemical Sciences Group
Research Department

September 1979

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THE KINETICS AND REVERSIBILITY OF RADIONUCLIDE SORPTION REACTION WITH ROCKS--PROGRESS REPORT FOR FISCAL YEAR 1979

G. S. Barney
G. E. Brown

ABSTRACT

Observations of sorption-desorption reactions of cesium, strontium, neptunium, americium, and plutonium on basalt, granite, and argillite were extended to 218 days. Equilibrium concentrations of radionuclides in batch experiments were not reached for most radionuclides even after this lengthy equilibration time. In addition, reactions of the crushed rock with groundwaters (dissolution, hydrolysis, precipitation, etc.) did not reach equilibrium after 150 days. The dissolution of basalt is accompanied by the formation of colloidal particles which contain silicon, iron, calcium, and aluminum. These colloids sorb cesium, strontium, americium, and plutonium during equilibration experiments. Some of the colloids pass through 0.3-μm filters (some are not retained even on 0.01-μm filters) and, therefore, cause calculated K_d values to be too low. Additional experiments were performed to measure the reversibility of radionuclide sorption and the rate of desorption.

Samples of crushed basalt, granite, and argillite were artificially "weathered" by continuous leaching with distilled water for 6 months. The leaching was performed both in air and in an oxygen-free stream of nitrogen gas. The "weathered" rock was then characterized to determine surface area, surface structure, cation exchange capacity, and composition of weathered surface on the rock. Comparisons were made of radionuclide sorption (after 14 days) on fresh rock, rock weathered in air, and rock weathered in N_2. Although there are some exceptions, sorption on rocks weathered in N_2 is less than on rock weathered in air. This is possibly due to the lack of an $Fe(OH)_3$ coating on the rock weathered in N_2. The $Fe(OH)_3$ is known to scavence cations and silica from solution. Sorption of cesium, americium, and plutonium is strongly affected by weathering basalt and argillite. However, the cation exchange capacity is changed very little. This suggests that ion exchange plays a minor role in sorption of these radionuclides.

INTRODUCTION

The work described in this report was supported by the Waste Isolation Safety Assessment Program (WISAP) managed by the Pacific Northwest Laboratory for the Office of Nuclear Waste Isolation (ONWI). This is the third annual progress report of a study begun in March 1977 (Barney and Grutzeck 1977 and Barney and Anderson 1978). Progress for FY 79 is reported herein.

The objectives of this study are to determine the effects of sorption kinetics and irreversible sorption reactions on the measurement of radionuclide distribution between geologic media and groundwater. Distribution ratio (K_d) values will control the rate of migration of radionuclides in groundwater flow from the nuclear waste repository to the biosphere. This information is, therefore, essential for assessment of the safety of radioactive waste disposal in rock formations.

Distribution ratios measured in the laboratory are used to model radionuclide migration in various rock formations proposed as repository sites. Reliable estimates of K_d values must take into account all significant parameters which control K_d under conditions found in the pathway of radionuclide-contaminated groundwater from the repository to the biosphere. Several of these parameters are difficult to control experimentally and/or are poorly understood. Information obtained from this study of two of these parameters (sorption kinetics and reversibility of sorption) will help define a specific method for K_d measurement and will provide insight into the mechanism of sorption reactions.

Rates of tracer sorption on fresh silicate rock surfaces are initially rapid due to fast ion exchange or precipitation reactions. However, there are also very slow sorption reactions occurring which may involve alteration of the rock surfaces due to reaction with groundwater, or diffusion of the tracer into micropores in the rock surface. These slow reactions can greatly affect K_d values over equilibration periods normally used for measuring them in the laboratory. They will also have a significant effect in the actual rock formations near the repository.

Irreversible sorption reactions will also affect K_d measurements. Since "fixed" radionuclides will not appreciably exchange with ions in the aqueous phase, K_d values will likely be more sensitive to the total amount of radionuclides present in the experiment than if sorption were reversible.

It was concluded from prior work (Barney and Anderson 1978) that sorption of radionuclides on basalt, granite, and argillite is strongly affected by reactions of the rock surfaces with groundwater. These reactions (hydrolysis, dissolution, and mineral transformation) are slow under the conditions required for radionuclide distribution measurements. Significant sorption-desorption reactions continue for many months after contacting these silicate rocks with radionuclide-spiked groundwaters. Because of these slow reactions, measurement of equilibrium K_d values for these rocks is probably not practical. Radionuclide distribution must be measured as a function of time for rocks that react slowly with groundwater.

Attempts were made to speed the rock-groundwater reaction by artificially weathering crushed rock with hot, distilled water. Basalt and argillite appear to be more easily weathered than granite. Radionuclide sorption measurements were made on those "weathered" rocks and compared to fresh rock surfaces. Weathering basalt greatly increased the sorption capacity for each radionuclide. Weathered argillite sorbs cesium, plutonium, and americium more strongly than fresh argillite. Weathering granite had no observable effect on sorption.

Several irreversible sorption reactions were identified. Cesium is irreversibly sorbed on granite, and ruthenium is irreversibly sorbed on each of the three rock types. Strontium and neptunium sorption is reversible for each rock type.

MATERIALS AND METHODS

ROCKS

Five crushed rock samples were selected for study, each representing a rock formation at Hanford and the Nevada Test Site which are proposed locations for nuclear waste repositories. The sampling locations and geologic formations from which the samples were taken are given in Table 1.

TABLE 1. Source of Rock Samples

Rock Types	Sampling Location	Geologic Formation
Basalt A	Sentinel Gap, Washington Outcropping	Umtanum Flow
Basalt B	Sentinel Gap, Washington Washington State Hwy 243 Outcropping	Umtanum Flow
Granite A*	Nevada Test Site Sample UE15e7	Climax Stock
Granite B*	Nevada Test Site Sample N901, 147E677.016 (1,367 feet below collar of shaft 1501)	Climax Stock
Argillite	Nevada Test Site Sample UE17e (2,200 feet)	Eleana

*More correctly, a quartz monzonite porphyry.

The bulk elemental compositions, mineral compositions, surface areas, and cation exchange capacities (CEC) of those samples were measured and are given in the Results and Discussion section. The particle sizes of the crushed rocks were: <0.5 mm for Basalt A, Granite A, and Argillite; and 0.3 to 0.9 mm for Basalt B and Granite B.

GROUNDWATERS

Groundwater analyses were obtained for the three geologic formations listed in Table 1. Synthetic groundwaters with compositions approximating those of the above sites were prepared. A thoroughly analyzed water from a well near Paterson, Washington (Pearson 1973) was selected as representative of Hanford basalt aquifers. It is a sodium bicarbonate water with a pH of 8.2. Two groundwater types found beneath the Nevada Test Site (NTS) were chosen for experiments with granite and Eleana argillite. These are, respectively, a sodium-calcium-sulfate water (Walker 1962) and a calcium-magnesium-bicarbonate water (Borg et al. 1976). The compositions of the synthetic groundwaters are given in Table 2.

TABLE 2. Composition of Synthetic Groundwaters (As Prepared)

Basalt	Granite	Argillite
295 mg/ℓ $NaHCO_3$	620 mg/ℓ $CaSO_4 \cdot 2H_2O$ 302 mg/ℓ $NaHCO_3$	112 mg/ℓ $CaCO_3$ 76 mg/ℓ $MgCO_3$ 135 mg/ℓ $NaHCO_3$

RADIONUCLIDE TRACERS

The radionuclides included in this study were: ^{137}Cs, ^{85}Sr, ^{99}Tc, ^{237}Np, ^{241}Am, and plutonium (a mixture of isotopes ^{238} through ^{241}). The purity of each tracer was checked by either gamma or alpha energy analysis.

Methods

Kinetics Experiments

All kinetics experiments and equilibrations were performed at room temperature (23 ± 2°C). Twenty grams of crushed rock and 300 mℓ of the appropriate groundwater were added to sealed, pretared, 16-ounce polyethylene bottles and the mixtures were shaken overnight to pre-equilibrate. The crushed rock was allowed to settle for 24 hours and the supernates were decanted onto 0.3-μm Millipore filters to retain any suspended solids. The solids on the filters were washed into the bottles, and the pre-equilibration procedure was repeated. The bottles were weighed to measure the volume of residual groundwater solution after decanting. Three hundred milliliters of groundwater solution were again added to each bottle. The tracers were added and time was recorded. One bottle for each rock type was not spiked so that the concentration of inert (nonradioactive) groundwater components could be measured as a function of time. The bottles were shaken continuously and the groundwaters were sampled (∿5 mℓ) and filtered with either a 0.3-μm filter or a 0.01-μm filter. Tracer and metal ion concentrations were determined in the filtered samples. Samples were taken over a period of 218 days. After this length of time, the volume of groundwater solution was not sufficient to sample and the experiments were terminated.

Reversibility Experiments

The reversibility of radionuclide sorption reactions was measured by attempting to desorb radionuclides from crushed rocks. Radionuclides were previously sorbed onto the rocks from spiked groundwater solutions. Forty-five grams of crushed rock were pre-equilibrated twice with 300 mℓ of the appropriate groundwater as above. Spiked groundwater solutions were then prepared by pipetting stock tracer solutions into small polyethylene vials, evaporating the solutions in the vials under a heat lamp and adding the dried tracers to the groundwaters. The tracers were allowed to dissolve for 48 hours, during which time the groundwater solutions were shaken continuously. The spiked solutions were then filtered through 0.3-μm Millipore filters. Three hundred milliliters of the spiked groundwaters were added to the pre-equilibrated rocks and the mixture was shaken for 14 days. Samples of the loaded, crushed rock were separated from the mixtures by filtering through 0.3-μm filters. These were kept wet until desorption experiments could be started. Five grams of the loaded rock were contacted for 14 days with 30 mℓ of the appropriate groundwater solution containing various concentrations of CsCl, $Sr(NO_3)_2$, HNO_3, or Na_2H_2(EDTA). The mixtures were centrifuged (the basalt samples were filtered with Amicon CF50A ultrafilters) and the concentration of tracer in the solution was measured.

The kinetics of radionuclide desorption was studied by adding 300 mℓ of unspiked groundwaters to 10 g of the loaded, crushed rock in 16-ounce polyethylene bottles. The bottles were shaken continuously and the solutions sampled weekly for tracer analysis. The solutions were filtered with Amicon CF50A ultrafilters before analysis. Blank kinetics experiments were run using unspiked groundwater for each rock type. Solutions from these experiments were sampled weekly and analyzed for sodium, calcium, magnesium, manganese, zinc, silicon, potassium, strontium, iron, aluminum, boron and phosphorus.

Sorption on Weathered Rock

Artificial weathering of crushed rock under oxygen-free nitrogen gas was accomplished by placing 100 g each of crushed Umtanum basalt (0.5 to 1.0 mm), NTS granite (<1.0 mm), and NTS argillite (<1.0 mm) in separate soxhlet extractors. The gas inlet and exit ports of the extractors were connected in series to a pure N_2 tank with two gas washing bottles between the tank and the extractors. The first bottle was filled with a caustic pyrogallol solution to remove any oxygen present in the N_2 and the second was filled with distilled water to prevent any entrained pyrogallol solution from entering the extractors. The rocks were leached with hot, distilled water for 6 months in flowing N_2 and then air dried.

Radionuclide K_d values for sorption on the weathered rocks were measured as follows.

Five-gram samples of each weathered rock type were added to polycarbonate centrifuge tubes. The rocks were pre-equilibrated twice with the appropriate groundwater type and the tubes centrifuged, decanted, and weighed. Thirty milliliters of spiked groundwater were added to each tube and the mixtures were shaken in the presence of air for 14 days. Tubes containing granite or argillite were centrifuged after this time and the solution and rocks analyzed for tracers. Tubes containing basalt-groundwater mixtures were centrifuged and the solutions filtered through Amicon 50A ultrafilters to remove any colloidal particles present before tracer analysis.

Measurement of CEC, Surface Area, and Surface Analysis

Measurement of CEC: 2-g samples of crushed rock were placed in fritted disk sealing tubes (Corning 39570). A buffered $1.0\underline{N}$ Sr^{2+} solution at pH 5 was passed through the tube to remove any carbonates from the sample. A second 1.0N Sr^{2+} solution at pH 7 was passed through the tube to saturate exchange sites with Sr^{2+}. A 0.05N Sr^{2+} solution at pH 7 spiked with ^{85}Sr was then passed through the tubes and the entrained solution was removed with vacuum. The tubes were then washed with solutions of Magnifloc 905 in distilled water and methanol. The tubes were counted and the CEC calculated.

Surface areas of the crushed rocks were measured using both the BET method and a glycerol sorption method (Madsen 1977). The glycerol sorption method was found to be unsuitable for basalt and granite because of their small surface areas. However, since argillite is largely composed of clay materials, the surface area was large enough to be measured by this method. Comparison of the results obtained for argillite by the two methods illustrates the very large interanl surface area measured by the glycerol method.

The surfaces of artificially weathered and fresh rock surfaces were analyzed using a JEOL-JSM-3 scanning electron microscope with an energy dispersive x-ray analyzer (Princeton-Gamma-Tech) attached to the column. Both surface structure and chemical composition of the surface phases were determined. The effects of weathering were observed by comparing fresh and artificially weathered surfaces mounted in polished sections.

Solution Analyses

Tracer concentrations in solution were determined by standard gamma, alpha, and beta counting techniques. Amounts of tracer in the crushed rock samples were measured for use in K_d calculations using standard gamma counting techniques. Analyses of elemental concentrations in groundwater solutions were accomplished using an inductively coupled argon plasma source spectrometer (Applied Research Laboratories).

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE ROCKS

Each of the rock samples used in these sorption experiments was characterized as follows: (1) bulk elemental analysis, (2) qualitative mineralogy, (3) surface area, and (4) cation exchange capacity. Thorough characterization was necessary so that effects of sample characteristics on sorption measurements could be evaluated. The procedures used for these measurements are given in the Methods section.

The oxide compositions of the rock sample are given in Table 3. Averages of at least three analyses are given. Carbonate and water were not determined. The mineral content of each rock type was determined using x-ray diffraction and scanning electron microscope-microprobe techniques.

TABLE 3. Chemical Composition of Basalt, Granite, and Argillite.

Oxide	Chemical Composition, wt%				
	Basalt A	Basalt B*	Granite A	Granite B*	Argillite
SiO_2	56.7	54.0	68.4	68.4	57.3
Al_2O_3	12.0	13.9	15.9	16.4	20.7
FeO**	11.2	12.3	2.62	2.45	5.62
MgO	3.55	4.37	0.86	1.05	2.33
CaO	6.73	8.39	3.37	3.72	1.41
Na_2O	3.19	3.39	3.37	3.55	0.92
K_2O	1.69	1.19	3.61	3.91	1.29
TiO_2	1.53	1.95	0.29	0.37	0.79
BaO	0.06	--	0.09	--	0.02
P_2O_5	0.47	0.31	0.23	0.10	0.30
Total	97.12	99.80	98.74	99.95	90.36

*Ames 1978.

**Only ferrous iron is assumed to be present.

The following minerals were identified in these rock samples:

Basalt A	Basalt B*	Granite A	Granite B*	Argillite
Labradorite	Laboradorite	Plagioclase	Plagioclase	Quartz
Augite	Augite	Quartz	Quartz	Chlorite
Ilmenite	Andesine	Albite	Microcline or Orthoclase	Calcite
	Ilmenite	Orthoclase	Magnetite	Orthoclase
	Nontronite	Magnetite	Biotite	TiO_2
	Magnetite	Biotite	Titanite	
		Titanite	Apatite	
		Apatite	Hematite	
			Hastingsite	

The basalt is fine-grained (crystals are 1 to 200 μm) with a large amount of glassy or very fine crystalline groundmass. The relatively weak diffraction lines for the basalt indicate a large amount of amorphous material is present. Ilmenite exists as dendrites throughout the matrix. The "granite" (actually a quartz monzonite porphyry) is very coarse grained with some crystals as large as a few centimeters long. There appears to be very little amorphous material present. PHotomicrographs of argillite show crystals of quartz, orthoclase, TiO_2, and calcite scattered throughout a clay matrix (the principal clay mineral is chlorite as determined by x-ray diffraction). The lamellar structure of the clay is apparent from the photomicrographs.

Surface areas of the crushed rocks were measured using both the BET method and a glycerol sorption method (Madsen 1977). The results of duplicate measurements are given in Table 4. The glycerol sorption method was found to be unsuitable for basalt and granite because of their small surface areas. However, since argillite is largely composed of clay minerals, the surface area was large enough to be measured by this method. Comparison of the results obtained for argillite by the two methods illustrates the very large internal surface area measured by the glycerol method. Also, it appears that artificially weathering the argillite opens up the layered structure of the clay component and greatly increases the surface area.

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*Ames 1978.

TABLE 4. Surface Area Measurements

Rock Type	BET, m^2/g	Glycerol, m^2/g
Basalt A	5.1	--
Basalt B*	2.5	10.3
Granite A	0.9	--
Granite B*	0.08	3.9
Argillite	5.4	266
Weathered Argillite (in air)	--	426

*Ames 1978.

Cation exchange capabities of fresh rock and rock weathered in air are shown in Table 5. Artificially weathering basalt appears to slightly lower the CEC. The CEC of argillite is slightly increased after weathering. No change is observed in the CEC for granite after weathering.

TABLE 5. CEC of Fresh and Weathered Rock

Rock Type	CEC, meq/100 g
Umtanum Basalt A:	
Fresh (<0.05 mm)	3.82
Fresh (0.5 to 1.0 mm)	3.97
Weathered in air (0.5 to 1.0 mm)	3.11
Umtanum Basalt B:	
Fresh (20 to 50 mesh)*	4.7±0.2
Climax Stock Granite A:	
Fresh (<1.0 mm)	4.61
Weathered in air (<1.0 mm)	4.63
Climate Stock Granite B:	
Fresh (20 to 50 mesh)*	0.85±0.19
Eleana Argillite:	
Fresh (<1.0 mm)	9.92
Weathered in air (<1.0 mm)	11.9

*Ames 1978.

Kinetics of Radionuclide Sorption-Desorption

In the previous annual report (Barney and Anderson 1978), both short- and long-term kinetic data for the sorption of radionuclides on crushed basalt, granite, and argillite were presented. These data showed that sorption is rapid initially due to fast ion exchange reactions or physical sorption on the surface of the fresh rock. There are also very slow sorption-desorption reactions which take place over a much longer period of time. Sorption curves covering a period of 91 days showed that equilibrium concentration of radionuclides were not achieved in batch equilibration during that time. These long-term sorption-desorption reactions are a result of slow changes in the composition of the rock surface and bulk solution. The rock slowly reacts with the groundwater by hydrolysis, dissolution, oxidation, or mineral transformation of the components of the rock. The products of these reactions influence radionuclide sorption.

The kinetic observations were extended to 218 days. Sorption curves for cesium, strontium, neptunium, plutonium, and americium for this time period are given in Figures 1 through 4. Sorption curves for ^{137}Cs sorption on basalt, granite, and argillite are given in Figure 1. The basalt curve appears to be relatively flat, except for the time from 100 to 150 days. The peak observed in this time range is due to colloidal particles contaminated with ^{137}Cs which pass through the 0.3-μm filter. After 150 days, the solutions were filtered with 0.01-μm filters which apparently retained these colloidal particles. Filtering solutions from granite and argillite experiments with the 0.01-μm filters did not affect the analytical results. Therefore, no colloids were formed during equilibration. The curve for argillite does not level off even after 218 days. The granite curve, however, appears to reach a constant value after about 190 days.

Curves for ^{85}Sr sorption are given in Figure 2. The basalt curve appears to be fairly flat after about 80 days except for the peak due to colloid formation (at 100 to 150 days). Sorption of ^{85}Sr on granite appears to be almost a linear function of time over the 218 days. The argillite curve continues upward, indicating that a desorption reaction is occurring which has not reached equilibrium.

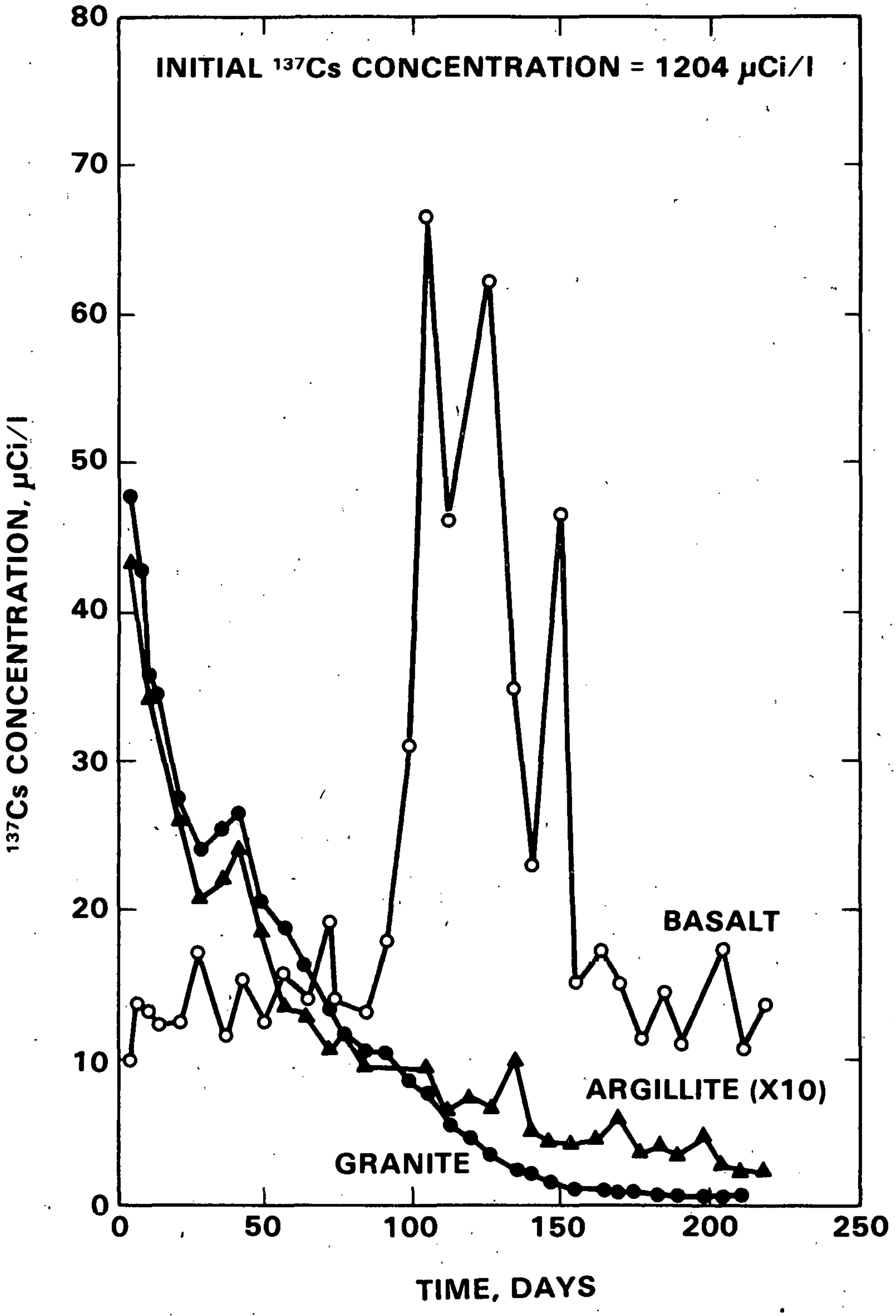


FIGURE 1. Sorption of ^{137}Cs on Basalt, Granite, and Argillite Over a 218-Day Period.

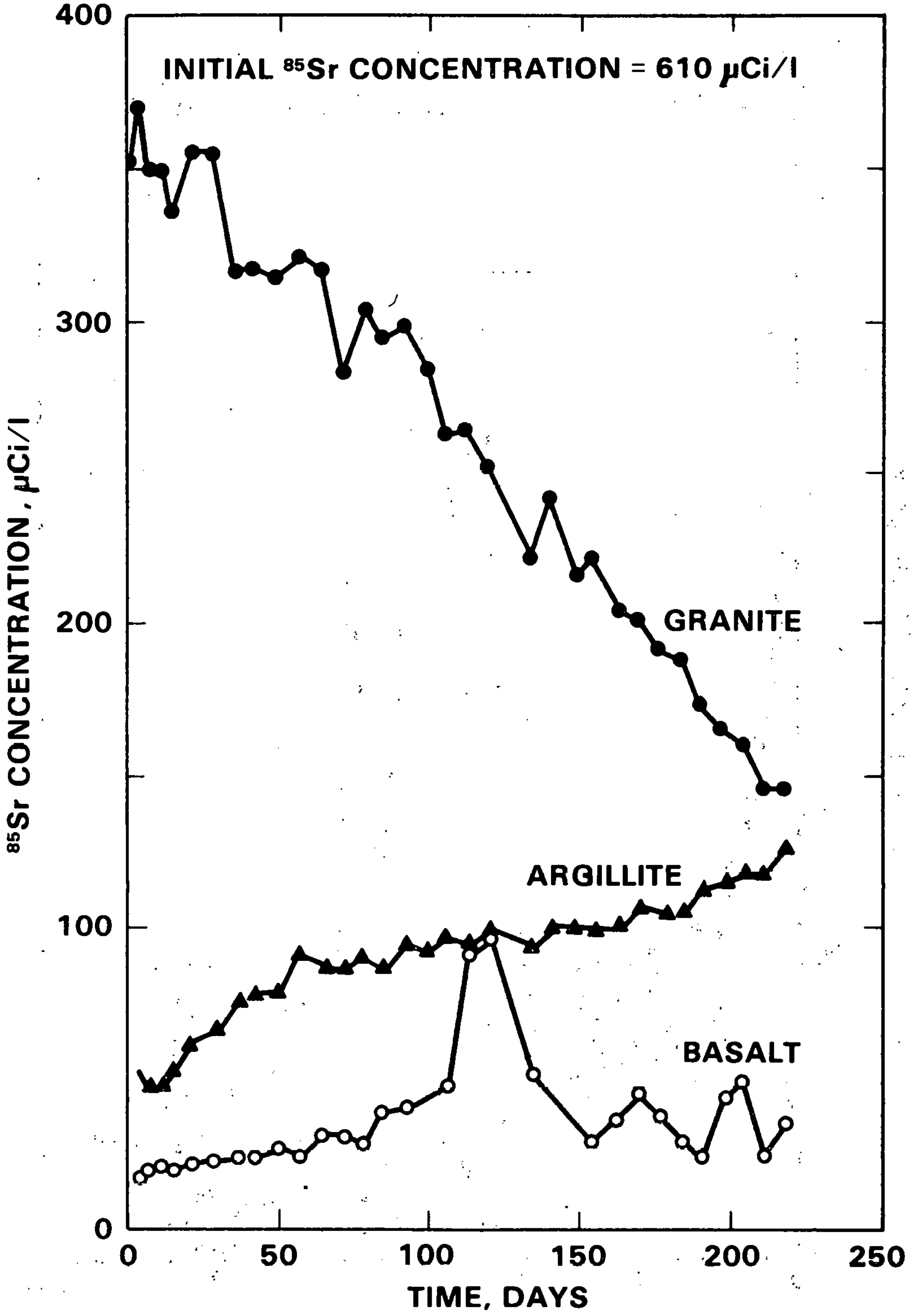


FIGURE 2. Sorption of ^{85}Sr on Basalt, Granite, and Argillite Over a 218-Day Period.

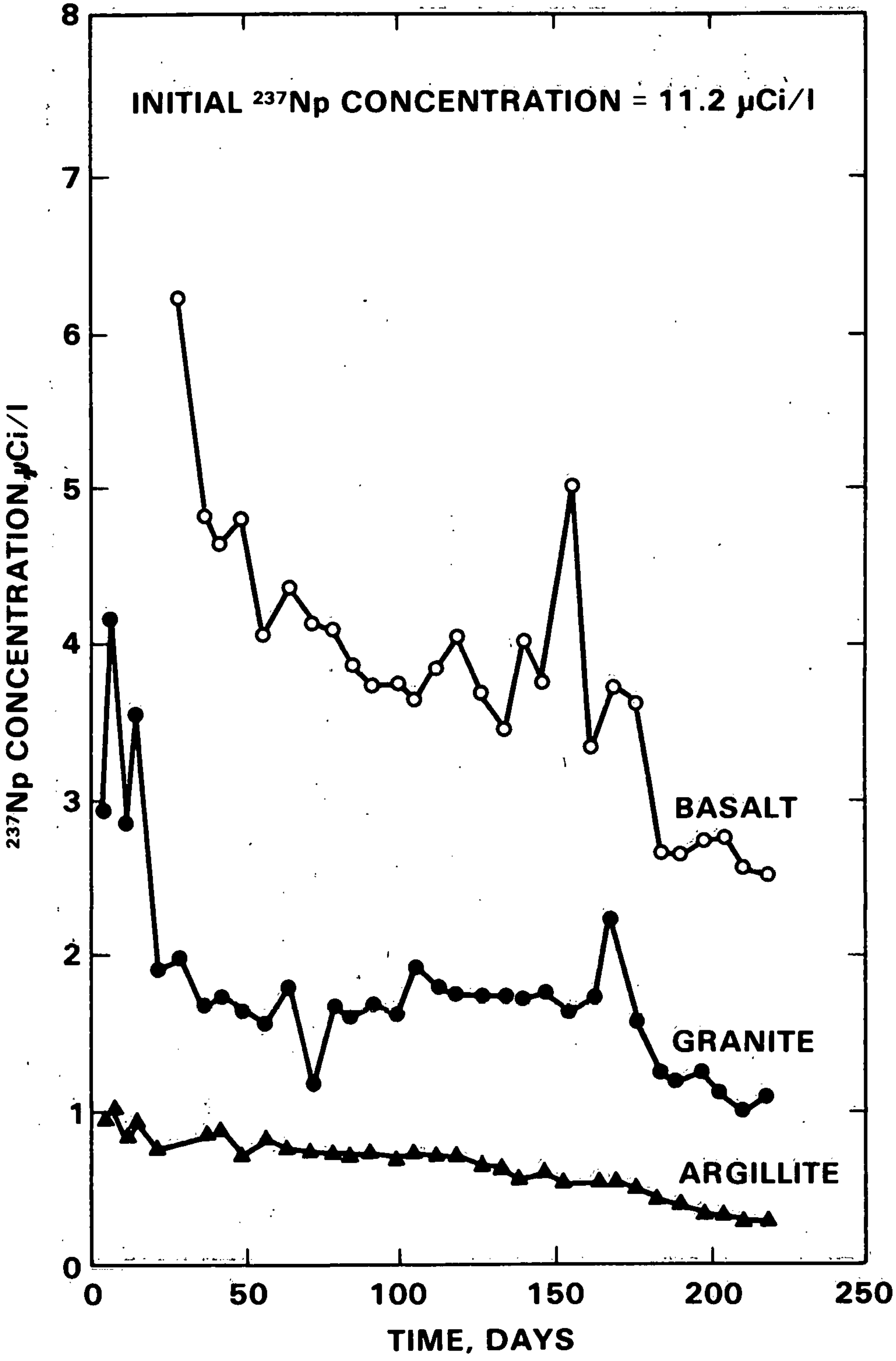


FIGURE 3. Sorption of ^{237}Np on Basalt, Granite, and Argillite Over a 218-Day Period.

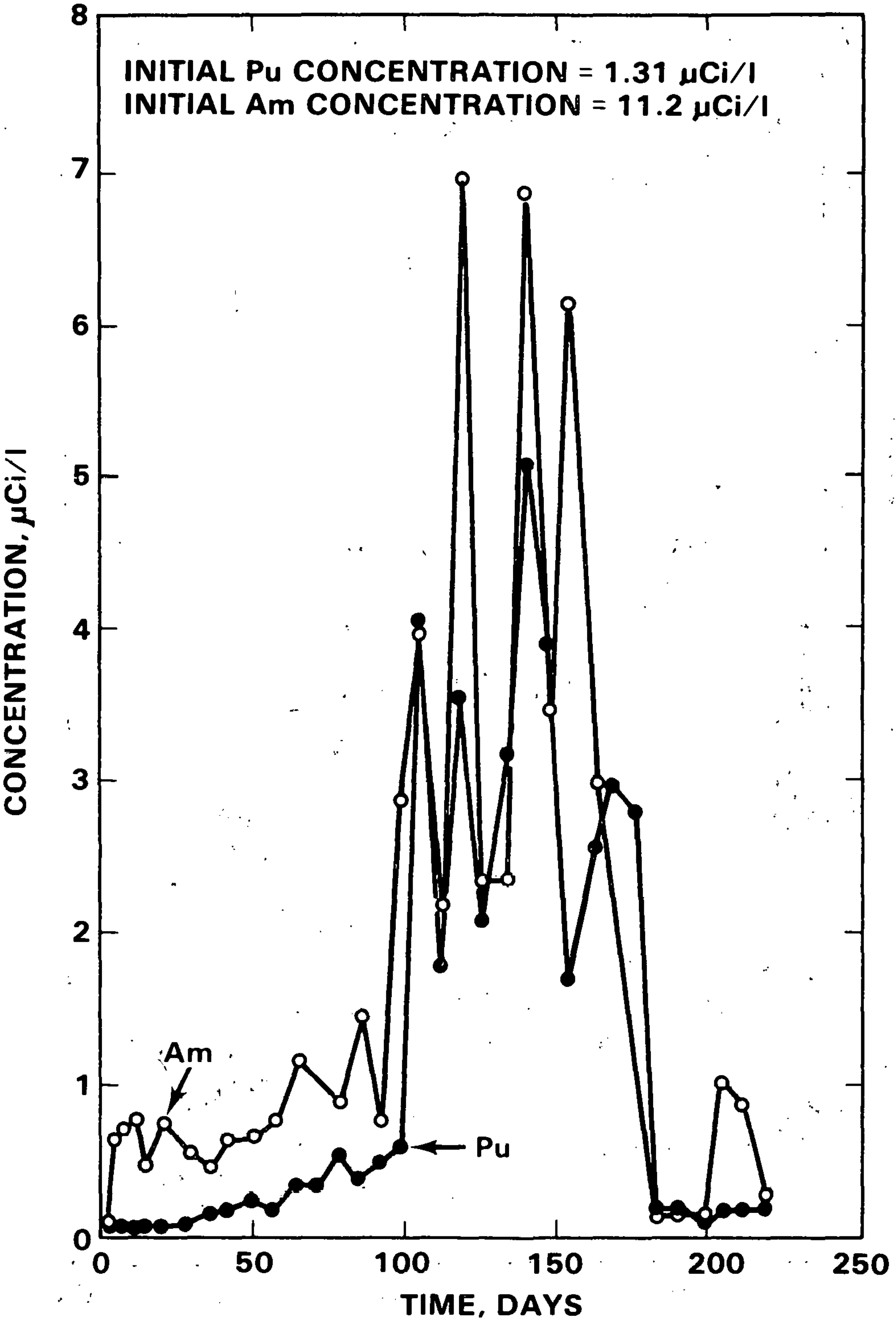


FIGURE 4. Sorption of Plutonium and Americium on Basalt Over a 218-Day Period.

Figure 3 shows that ^{237}Np continues to sorb even after 218 days of equilibration with each of the rock types. The increasing concentrations of plutonium and ^{241}Am in solutions equilibrated with basalt appear to be due to sorption of these actinides on colloids which pass through 0.3-μm filters. Figure 4 shows that when 0.01-μm filters are used (after 180 days) the concentrations of plutonium and ^{241}Am are dramatically reduced. Plots of plutonium and ^{241}Am sorption on granite and argillite show much scatter of the data and no significant trends can be observed.

The results of measurements of the rate of radionuclide sorption on fresh rock surfaces for rock-groundwater-radionuclide systems show that equilibrium is rarely attained even after many months of equilibration. The only sorption reactions that appeared to reach equilibrium before 218 days were ^{137}Cs sorption on basalt and granite, ^{85}Sr sorption on basalt, and plutonium and ^{241}Am sorption on basalt. The surfaces of the rocks are being chemically altered by groundwater, thus changing the sorption characteristics of the rock. Also, the compositions of the groundwater are changing. Ions which compete for sorption sites are being introduced into the solutions. Since these hydrolysis reactions are very slow, the changes in radionuclide sorption are also very slow.

Because of the very slow approach to equilibrium, K_d values based on short equilibration times are of limited value unless the K_d is given as a function of time. This is true for all silicate rocks and minerals which can undergo slow hydrolysis reactions.

Dissolution and precipitation reactions of major components of the three groundwater-rock systems were measured over an extended period of time (154 days). Concentrations of sodium, potassium, calcium, magnesium, barium, zinc, curium, aluminum, iron, silicon, and chromium were determined in groundwaters equilibrated with curshed basalt, granite, and argillite. The results are shown in Figures 5, 6, and 7. Only those elements with significant concentrations (>1 ppm) are plotted. The pH was constant for each groundwater over the 154 days. Values of pH for basalt, granite, and argillite averaged 8.8, 8.4, and 8.8, respectively.

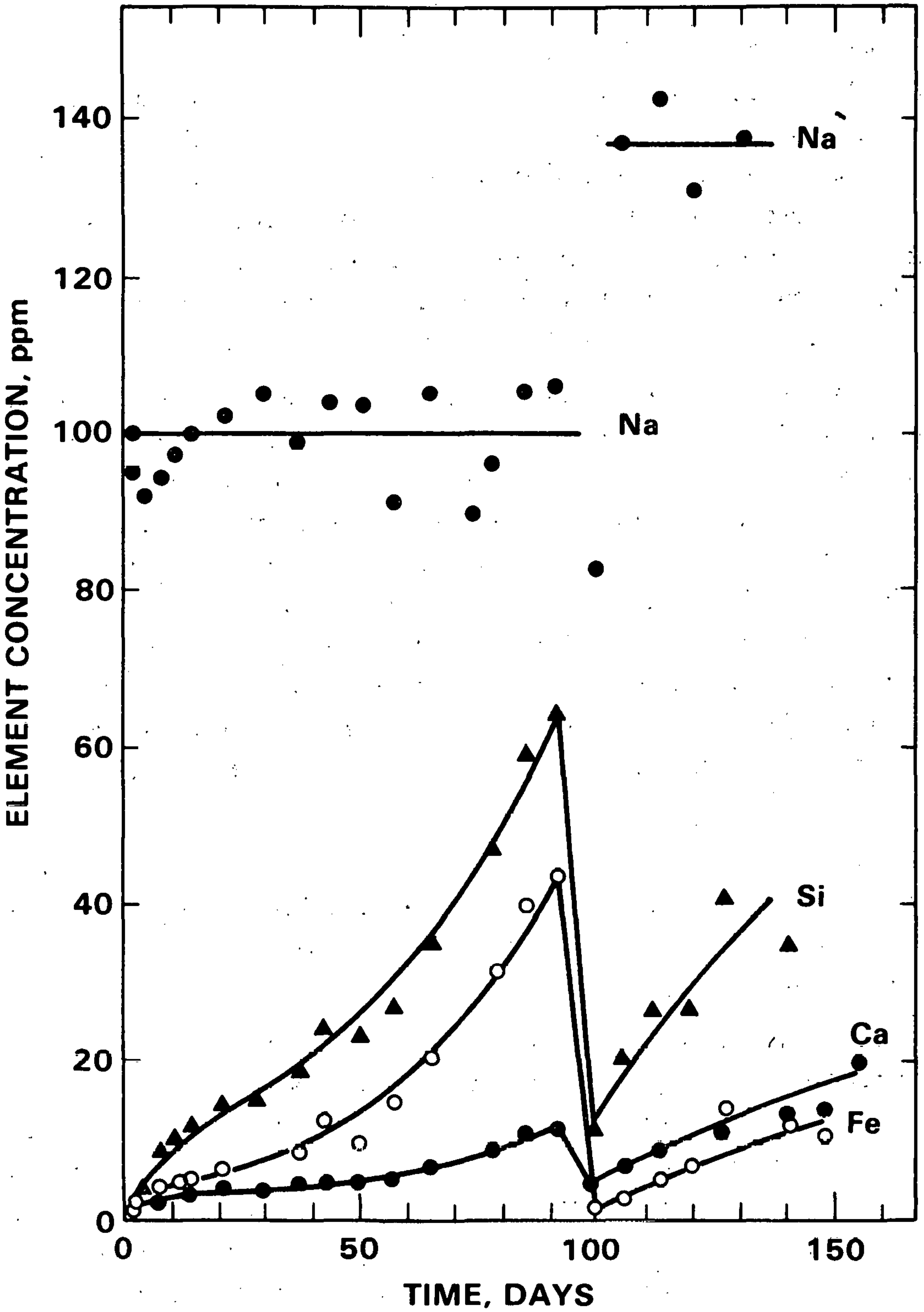


FIGURE 5. Dissolution Curves for Elemental Components of Basalt in Groundwater.

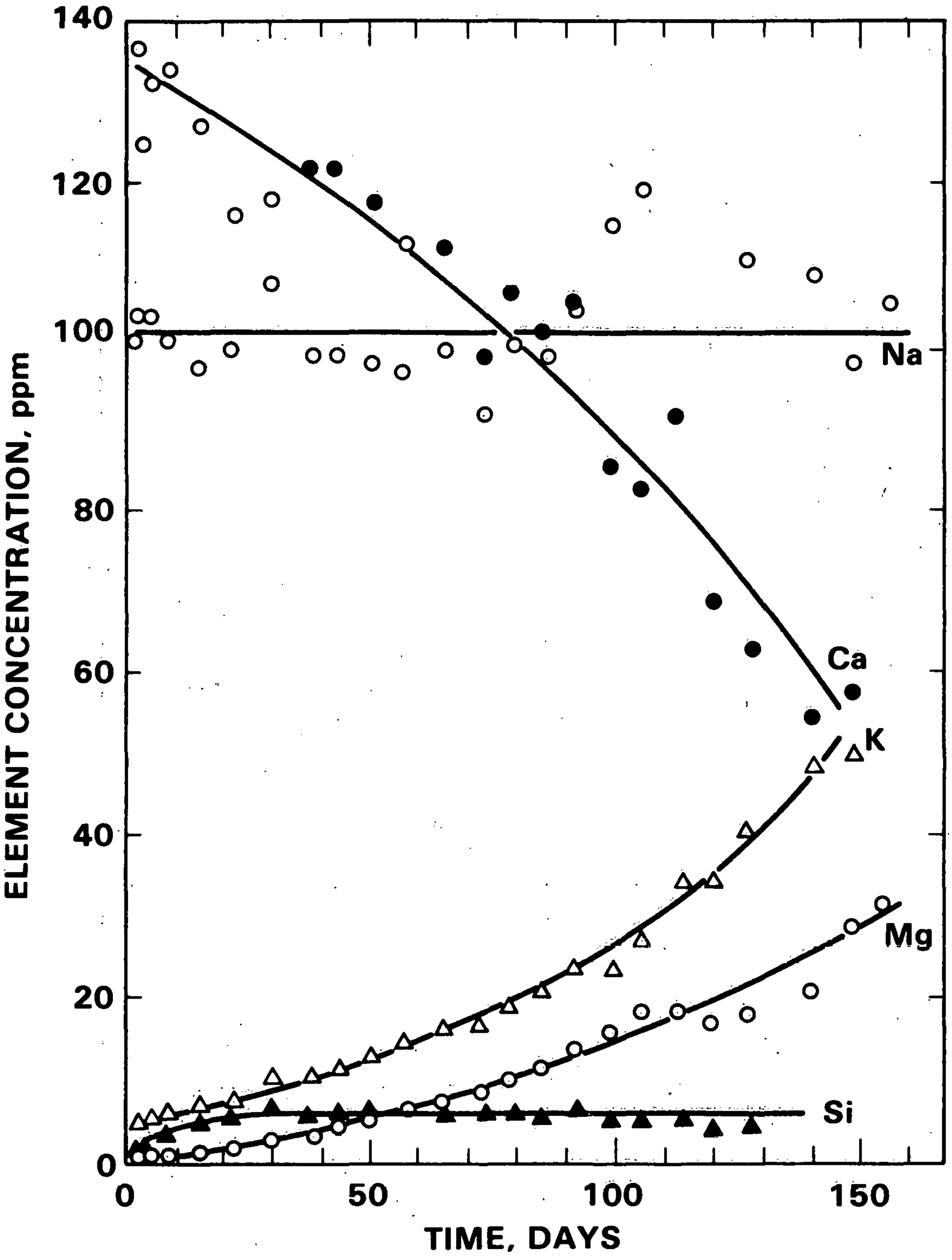


FIGURE 6. Dissolution Curves for Elemental Components of Granite in Groundwater.

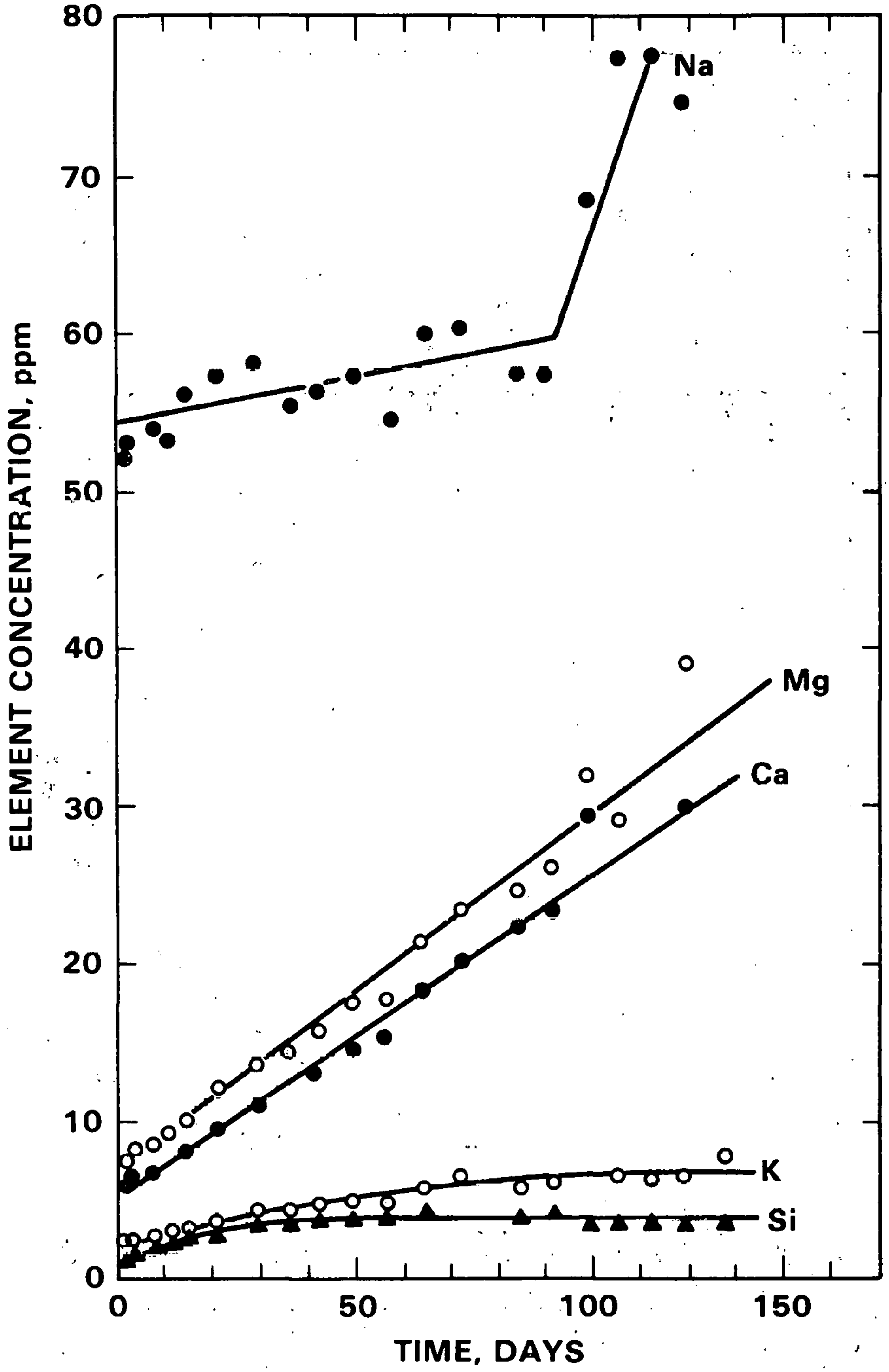


FIGURE 7. Dissolution Curves for Elemental Components of Argillite in Groundwater.

Figure 5 shows dissolution of silicon, iron, and calcium from basalt in the $NaHCO_3$ groundwater. This is most likely due to dissolution and hydrolysis of the glassy phase of the basalt. The concentrations of silicon and iron exceed the solubilities of $SiO_2 \cdot xH_2O$ and must be present in solution as colloids which pass through 0.3-µm filters. The discontinuities in the silicon, iron, and calcium curves at 98 days are a result of filtering the solutions with 0.01-µm filters. Most of the colloidal particles containing these elements must be larger than 0.01 µm. The sudden increase in sodium concentration is not understood.

Figure 6 shows dissolution of potassium and magnesium from granite and precipitation of calcium as a function of time. Silicon and aluminum concentrations reach equilibrium concentrations after approximately 30 days. Calcium ion appears to be replacing K^+ and Mg^{2+} either by ion exchange or mineral replacement reactions. The number of equivalents of Ca^{2+} precipitated (0.0040 eq.) is approximately equal to the total equivalents of K^+ (0.0014 eq.) plus Mg^{2+} (0.0025 eq.) released.

$$Ca^{2+} + R(K,Mg) = R(Ca) + K^+ + Mg^{2+}$$

R = mineral substrate

Both silicon and aluminum appear to be in equilibrium with products of the reaction between groundwater and granite. Filtering the granite groundwater with 0.01-µm filters did not affect the dissolution curves. Therefore, it appears that no measureable amounts of colloids are produced by dissolution of granite.

Both magnesium and calcium are dissolved from argillite. The rate of dissolution of these elements is nearly constant throughout the 154 days. Silicon reaches a constant concentration after about 50 days. Potassium is very gradually dissolved by the groundwater.

Dissolution of elemental components of basalt, granite, and argillite in synthetic groundwaters continues even after 150 days of equilibration. The dissolution of basalt is accomplished by formation of colloidal solids which contain silicon, iron, calcium, and aluminum. These colloids are probably products of hydrolysis of the glassy phase of basalt. This amorphous phase is the most susceptible to leaching with water as shown by SEM photomicrographs of leached basalt surfaces.

Components of granite dissolve incongruently with time. This suggests that a new solid phase (or phases) forms on the granite surface with time. Calcium ions appear to replace K^+ and Mg^{2+} in the granite since equivalent amounts of Ca^{2+} and $K^+ + Mg^{2+}$ are precipitated and dissolved, respectively. Apparently, trace amounts of Sr^{2+} also participate in this replacement reaction since ^{85}Sr has a precipitation curve similar to Ca^{2+}.

Magnesium, calcium, and potassium are dissolved when argillite is equilibrated with groundwater. Small amounts of sodium are also dissolved. Since these ions are not replaced by other cations from solution, anions must be going into solution to balance the charge. Hydroxyl ion is ruled out since the pH is constant. The anions are likely CO_3^{2-} or HCO_3^- since a significant amount of carbonate was previously found in the argillite. Some magnesium and calcium are rapidly precipitated on addition of argillite to the groundwater. The initial concentrations of these ions are larger than those found after 1 day of contact with argillite.

In general, the rock surfaces undergo reactions of the type: [Rock + H_2O + M = dissolved species + solid products], where M is a general chemical species originally present in the groundwater. The solid products may be deposited on the rock surfaces as a continuous layer or, as in the case with feldspars (Berner and Holdren 1979), as discrete crystalline deposits. With basalt, the solid products form colloidal-sized particles which are dispersed in the groundwater. In each case, the above reaction influences the sorption of radionuclides since the reaction products have different affinities for the radionuclides than the original rock surface. In addition, the dissolved species can affect sorption by competing with the radionuclide for sorption sites or by changing the chemical identify of the radionuclide (by complexing, redox reactions, etc.).

REVERSIBILITY OF RADIONUCLIDE SORPTION

Experiments to determine the reversibility of several radionuclide sorption reactions were continued in FY 79. Improvements in the design of the reversibility experiments were as follows:

- Longer equilibration times were used for both sorption and desorption experiments.
- Lower concentrations of tracers were used to prevent precipitation.
- Dried tracers were added to the groundwater to prevent alteration of the groundwater composition due to addition of tracer solution.
- Spiked groundwaters were filtered through 0.3-μm filters to remove any undissolved tracer.

The rock loaded with tracer was equilibrated with several different solutions and the amount of tracer desorbed was measured. Rates of radionuclide desorption into unspiked groundwater were measured over a period of 5 weeks. The results for cesium desorption into solutions of various CsCl concentrations are shown in Figure 8. Radioactive cesium desorbs from each rock type when contacted with relatively high concentrations of CsCl solution. However, the granite curve levels off after saturation of sorption sites (as determined by CEC) is completed. If exchange of cesium on the rock is rapid and reversible,

$$\frac{[R^*Cs]}{[RCs]} = \frac{[^*Cs^+]}{[Cs^+]}$$

where [RCs] is the concentration of cesium sorbed on the rock and $[^*Cs^+]$ is the concentration of radioactive tracer. Since the rock is saturated,

$$[R^*Cs] + [RCs] = C$$

where C is a constant. Since,

$$[RCs] >> [R^*Cs]$$

$$[RCs] = C$$

and $$[Cs^+] = C\,\frac{[{}^*Cs^+]}{[R{}^*Cs]}$$

Therefore, as the concentration of total cesium increases the percent cesium desorbed should increase if the reaction is reversible.

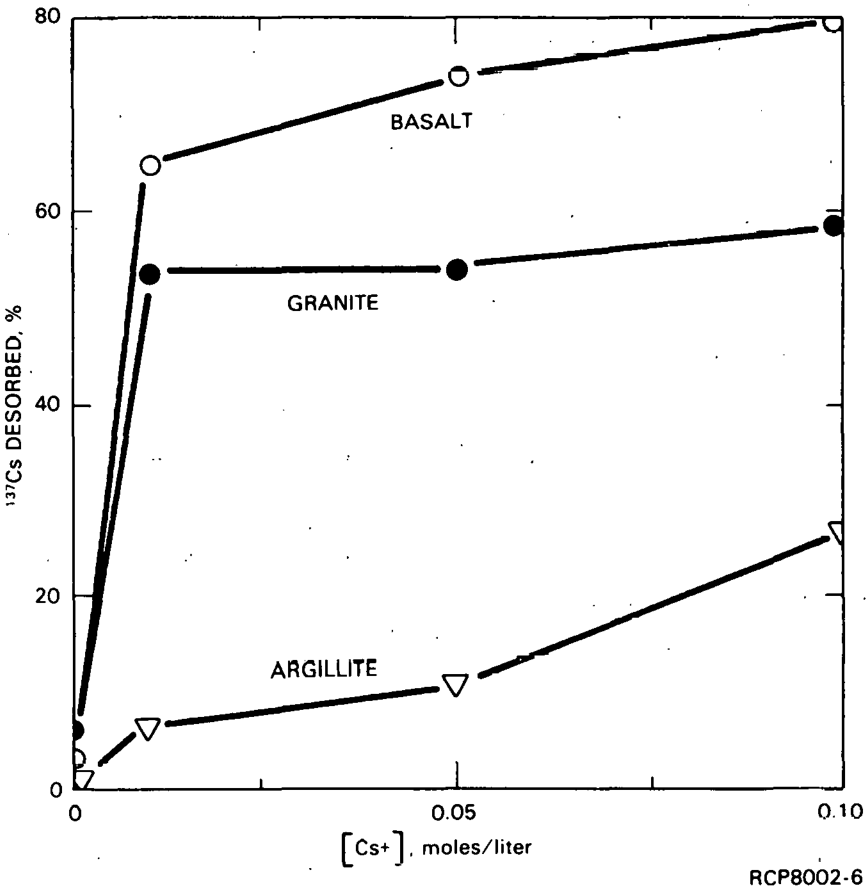


FIGURE 8. Desorption of ^{137}Cs (After 14 Days) From Basalt, Granite, and Argillite Into Groundwater Solutions Containing Various Concentrations of CsCl.

If the reaction is irreversible or if desorption is slow compared to sorption,

$$\frac{[R^*Cs]}{[RCs]} > \frac{[^*Cs]}{[Cs^+]}$$

and

$$[Cs^+] > C\,\frac{[^*Cs^+]}{[R^*Cs]}$$

Therefore, the slopes of the curves (percent ^{137}Cs desorbed versus Cs^+ concentration) should decrease if the sorption is irreversible. The slope of the granite curve is almost zero after the initial desorption of ∿50% of the ^{137}Cs, indicating partial irreversible sorption of cesium on granite.

If a radionuclide sorption reaction is truly reversible, the equilibrium K_d value should be approached by either sorption or desorption of the radionuclide. In other words, K_d (sorption) = K_d (desorption). For this to be true, the rates of sorption and desorption must not be widely different and all other factors which affect K_d must remain the same. Since some sorption isotherms are not linear, it is important that total radionuclide concentration be considered when comparing sorption and desorption K_d values. The results of desorption of cesium, strontium, and neptunium from basalt, granite, and argillite into their respective unspiked groundwaters are shown in Figures 9, 10, and 11.

Desorption K_d values over a 5-week period for basalt are shown in Figure 9. Sorption K_d values for 2-week equilibrations are given for comparison. The desorption K_d values are larger than sorption K_d values for each radionuclide. However, the desorption K_d values are gradually decreasing with time and may eventually approach sorption K_d values. From these data, it appears that the desorption reactions are slower than the sorption reactions. The reactions do, however, appear to be reversible.

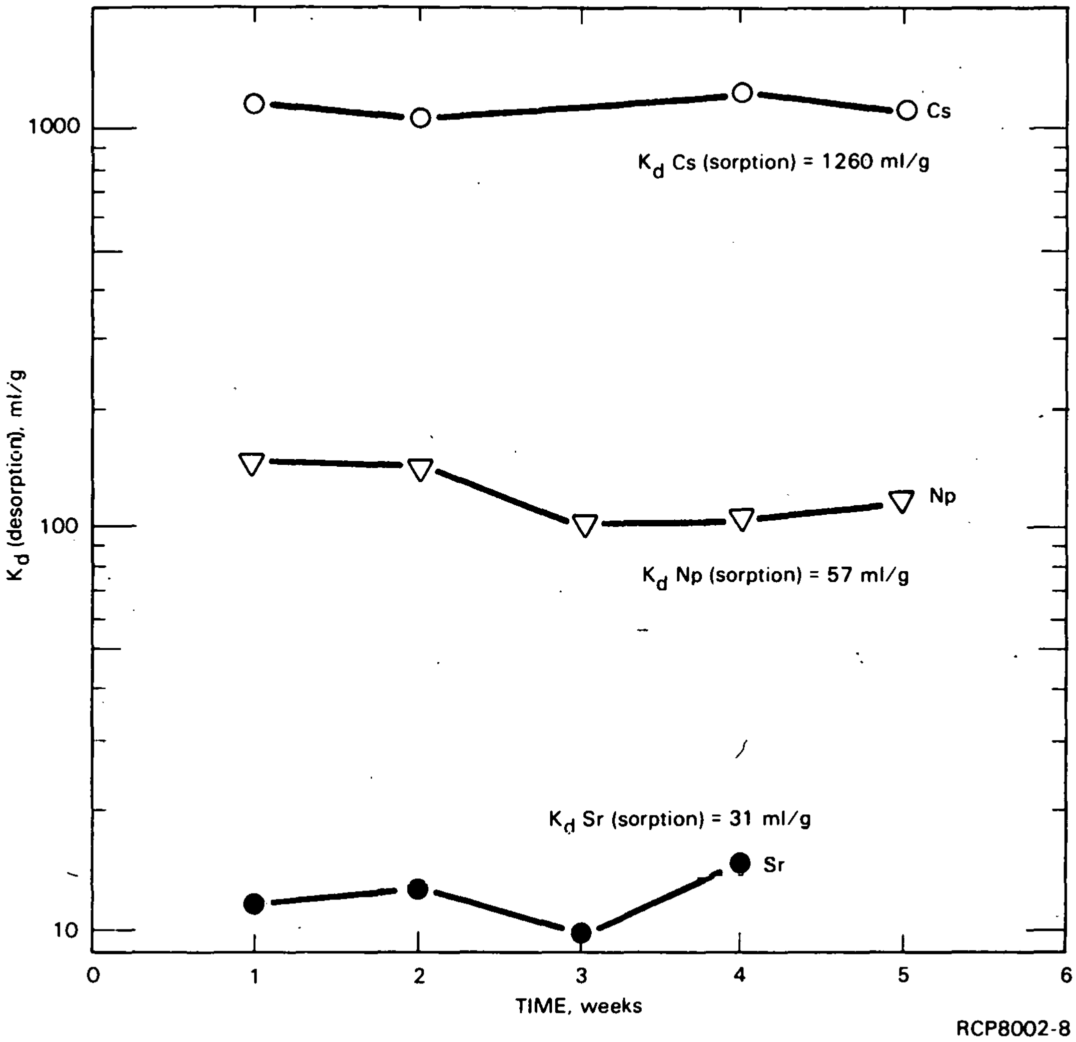


FIGURE 9. Values of K_d for Desorption of Cesium, Strontium, and Neptunium From Basalt Into Unspiked Groundwater Over a 5-Week Period. (14-day sorption K_d values are shown for comparison.)

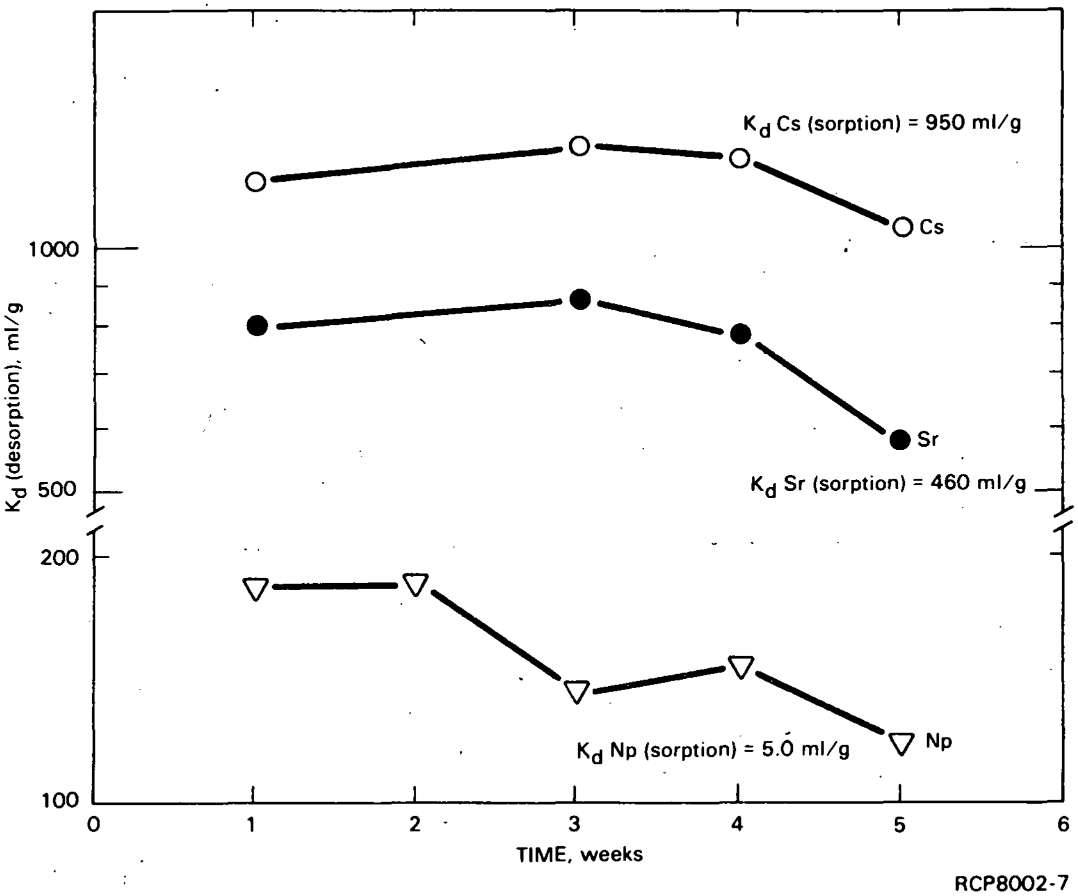


FIGURE 10. Values of K_d for Desorption of Cesium, Strontium, and Neptunium From Granite Into Unspiked Groundwater Over a 5-Week Period. (14-day sorption K_d values are shown for comparison.)

The sorption of cesium, strontium, and neptunium on granite (Figure 10) appears to be reversible. However, longer term desorption measurements show that cesium and neptunium are gradually resorbed onto the granite. This behavior can be explained by assuming at least two types of sorption sites on the granite - one that binds the tracer strongly and one that binds the tracer weakly. When the loaded granite is placed in unspiked groundwater, weakly-bound tracer is quickly released into solution. This released tracer is then slowly sorbed at the sites which strongly bind the tracer. This process continues until almost all the tracer is strongly bound.

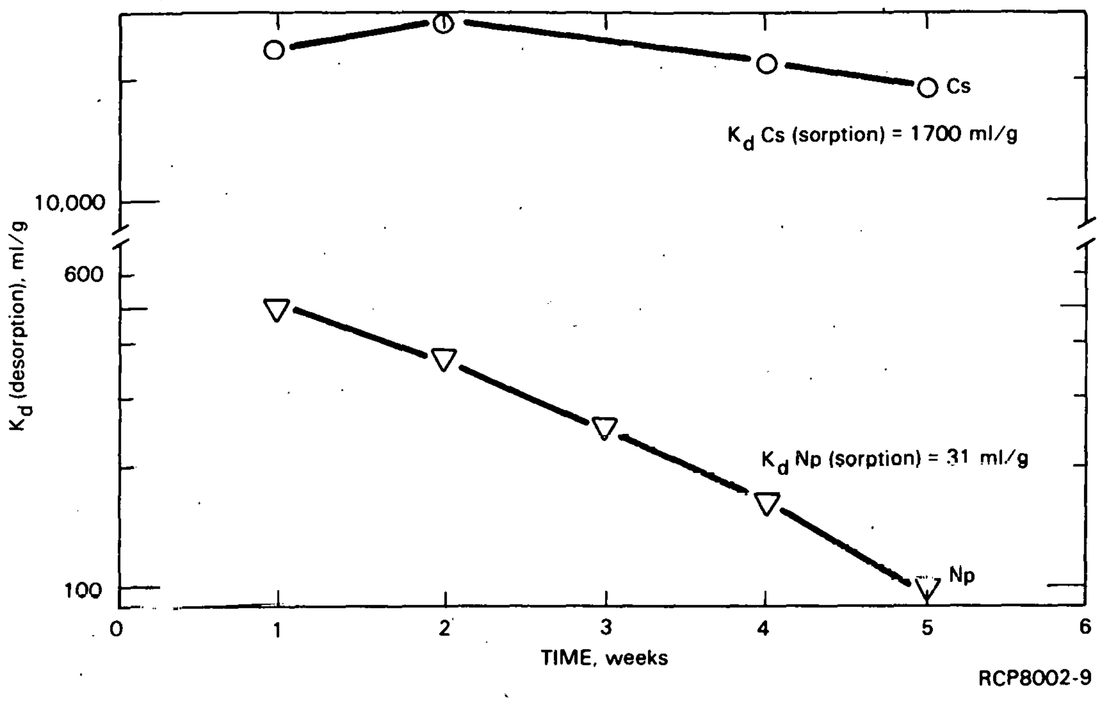


FIGURE 11. Values of K_d for Desorption of Cesium and Neptunium From Argillite Into Unspiked Groundwater Over A 5-Week Period. (14-day sorption K_d values are shown for comparison.)

Desorption K_d values for cesium on argillite (Figure 11) are about one order of magnitude larger than sorption K_d values. This reaction appears to be irreversible (or the sorption rate is much faster than the desorption rate). The same is true for neptunium.

ROCK WEATHERING

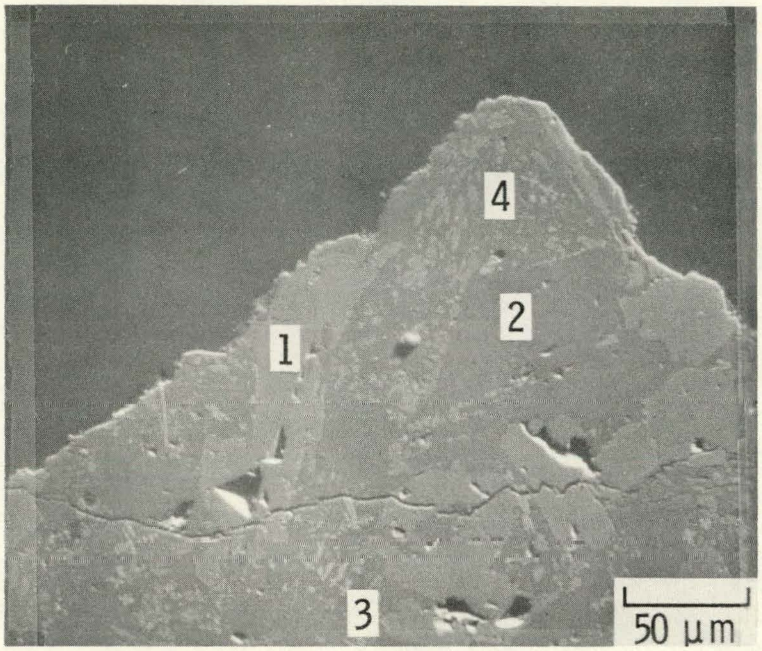
Contaminated groundwater from a waste repository will contact both weathered and fresh rock surfaces in the repository environment. These weathered rock surfaces will be composed of layers of alteration products from the parent rock, such as clay minerals, oxides, and hydroxides. The alteration products will, of course, have different sorption characteristics than the parent rock. To determine the effect of weathering on radionuclide sorption, samples of crushed basalt, granite, and argillite were artificially weathered. Sorption experiments were then performed using the weathered rocks. Scanning electron microscope analysis of the rocks identified changes caused by weathering which affect the sorption properties.

The rock samples were artificially weathered by leaching with hot distilled water in a soxhlet extractor. After 6 months of leaching in air, the basalt developed a brown crust due to formation of ferric hydroxide. A brown layer also formed on the granite sample. Also, a white colloidal suspension (probably $SiO_2 \cdot xH_2O$) was abundant in the basalt and argillite boiling flasks, with a smaller amount present in the granite boiling flask. In an oxygen-free atmosphere, no ferric hydroxide crusts formed, but the colloidal suspension was seen.

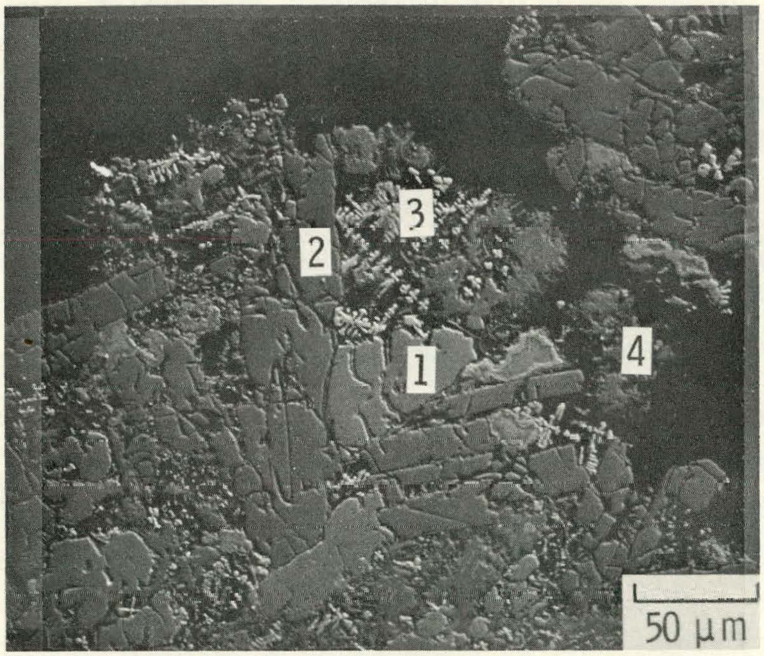
Scanning electron photomicrographs of the rocks before and after weathering show that the surface structure of the basalt is altered significantly by weathering. The relatively smooth surface of fractured, fresh basalt contrasts with the rough, detailed surface of the weathered basalt. It appears that the glassy matrix of the basalt has been leached away, leaving the more persistent crystalline phases behind. No obvious changes were found in the microstructure of granite or argillite after weathering as observed from SEM photomicrographs of the rough, unpolished surfaces of the rocks. However, the layered structure of the argillite did expand during weathering. This is indicated by the large increase in internal surface area.

Scanning electron photomicrographs of polished sections of basalt, granite, and argillite showed additional changes due to weathering. Energy dispersive x-ray analysis was used for phase identification. Comparisons were made for unweathered rocks and rocks weathered in a N_2 atmosphere.

Four phases were found in the basalt samples. Augite, plagioclase, ilmenite and groundmass areas are labelled in Figure 12. This figure also shows the differences between weathered and unweathered basalt surfaces. The weathered basalt has an altered layer about 100 μm into the surface (Figure 13). In this altered layer, the groundmass has partially dissolved away, leaving a fine, web-like framework. On some of the augite grains, 2- to 5-μm crusts of iron oxide ($Fe_2O_3 \cdot xH_2O$) have formed (Figure 14). The x-ray spectra in Figure 14 show the change in relative amounts of aluminum, silicon, and iron between the crust and inner area of the grain. Some of the other augite grains are cracked. The plagioclase grains are also cracked, and beginning to break into smaller pieces. No changes were noticed for the ilmenite grains.



A. UNWEATHERED BASALT



B. WEATHERED BASALT

1. AUGITE
2. PLAGIOCLASE
3. ILMENITE
4. GROUNDMASS

FIGURE 12. Comparison of Unweathered and Weathered Basalt.

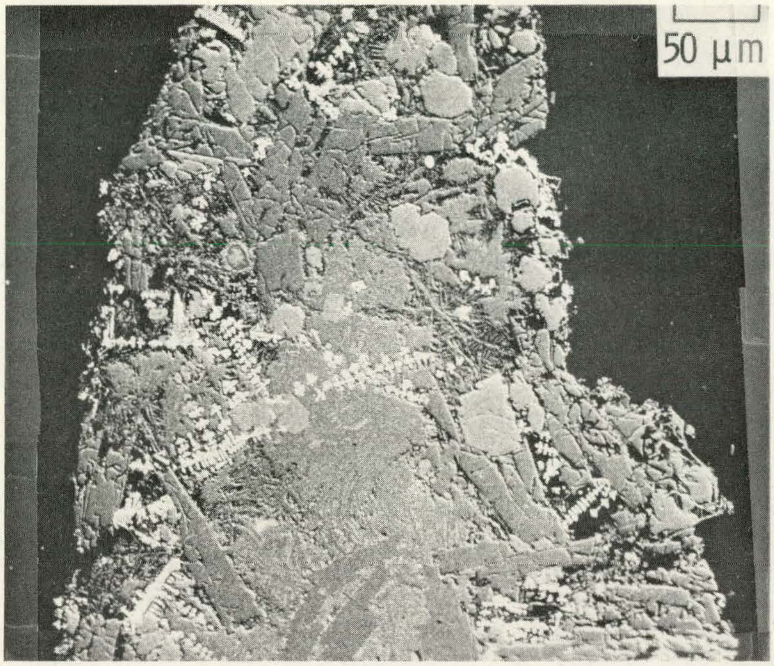
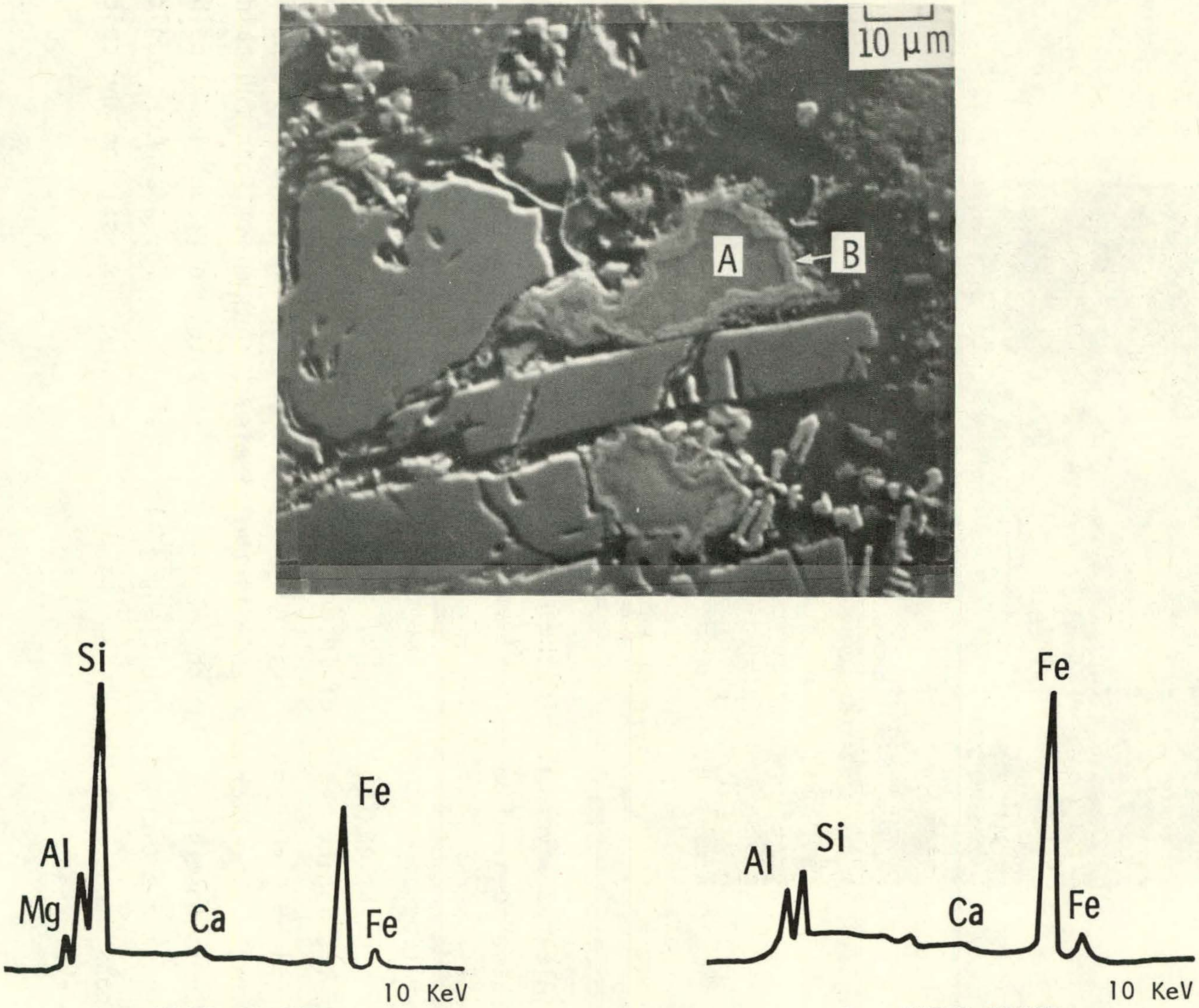


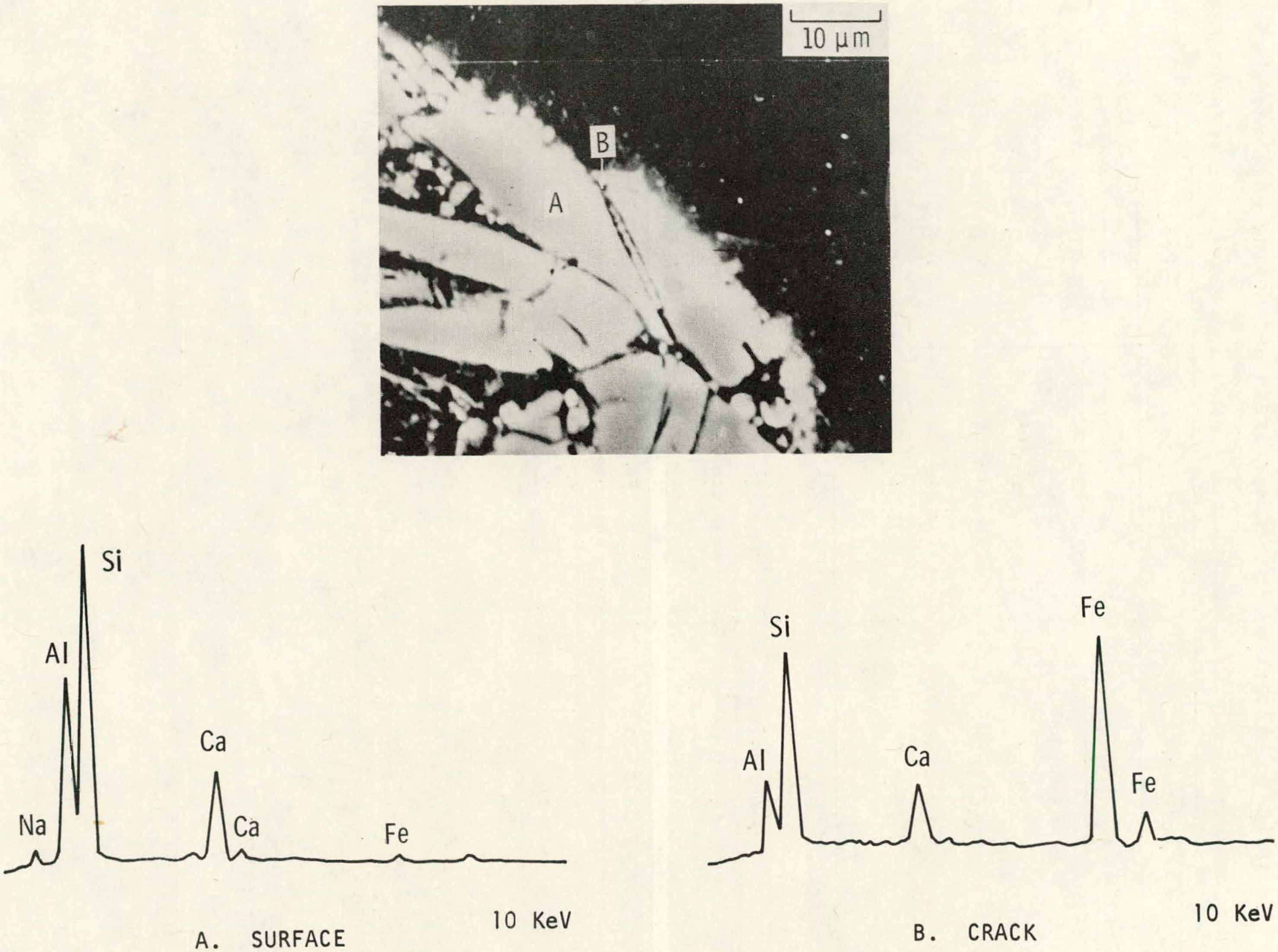
FIGURE 13. Weathered Basalt.

Altered layers within the cracks in the plagioclase and augite grains were also seen. Figure 15 shows a cracked plagioclase grain, and x-ray spectra for the surface and the alteration product in the crack. The relative ratios of elements in the two areas are given in Table 6. Table 6 also gives the ratios for a cracked augite grain and alteration layer. Figure 16 shows the augite region of interest and corresponding x-ray spectra. The plagioclase elemental ratios indicate that an iron oxide layer has formed in the crack. The lack of change in the aluminum, sodium, silicon and calcium ratios is most likely due to the x-ray analysis volume (about 1 μm) being larger than the crack. The changed elemental ratios for weathered augite are consistent with dissolution of magnesium, aluminum, silicon and calcium from the phase.



A. INNER SURFACE B. OUTER CRUST

FIGURE 14. Weathered Augite.



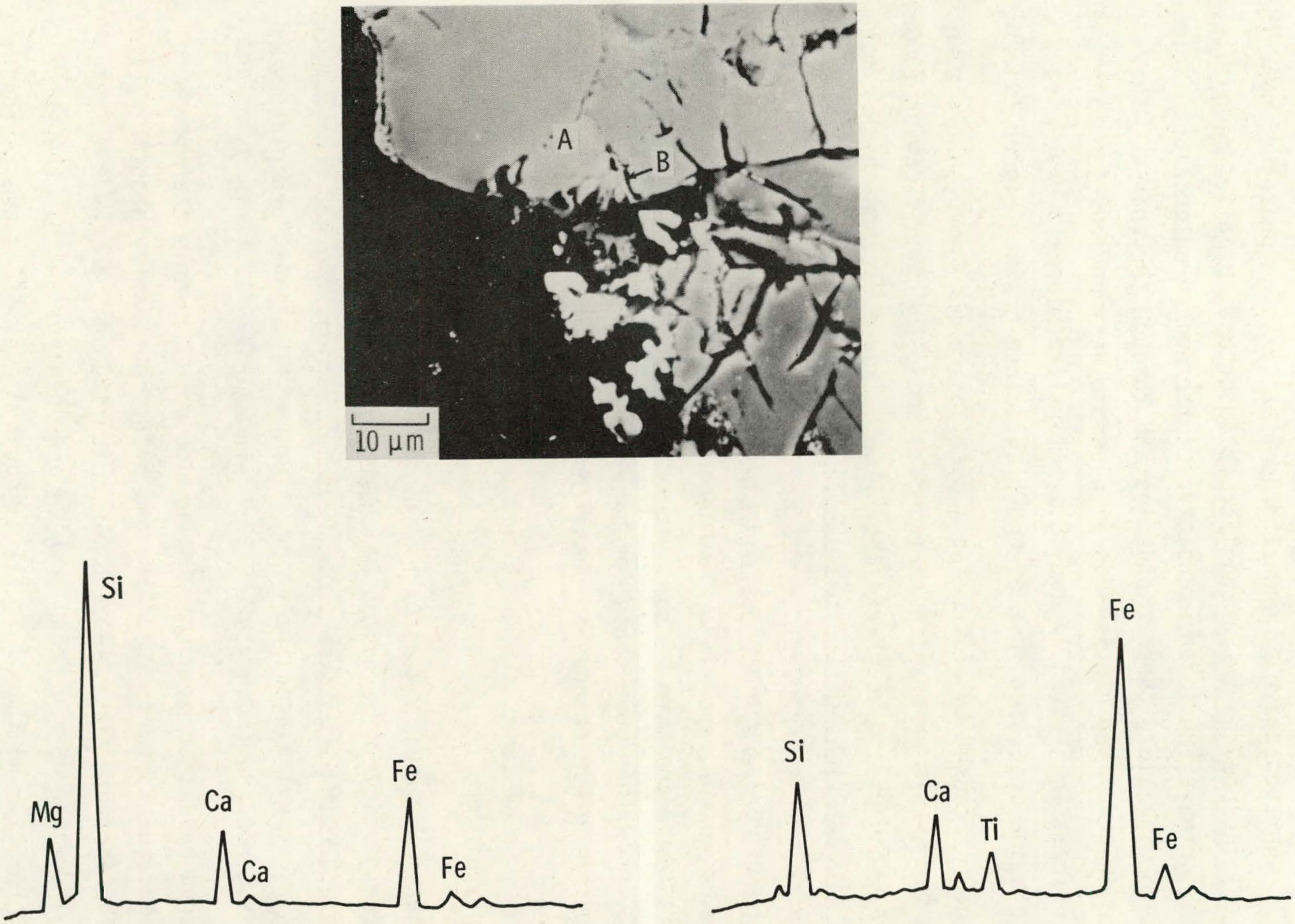
A. SURFACE

B. CRACK

FIGURE 15. Weathered Plagioclase.

TABLE 6. Elemental Ratios for Fresh and Weathered Plagioclase and Augite Surfaces

Element	Surface	Crack
Plagioclase		
Aluminum	1.0	1.0
Sodium	0.10	0.103
Silicon	1.910	1.917
Calcium	0.468	0.632
Iron	0.062	2.046
Augite		
Iron	1.0	1.0
Magnesium	0.718	0.055
Aluminum	0.257	0.105
Silicon	3.527	0.461
Calcium	0.756	0.339



A. SURFACE

B. CRACK

FIGURE 16. Weathered Pyroxene.

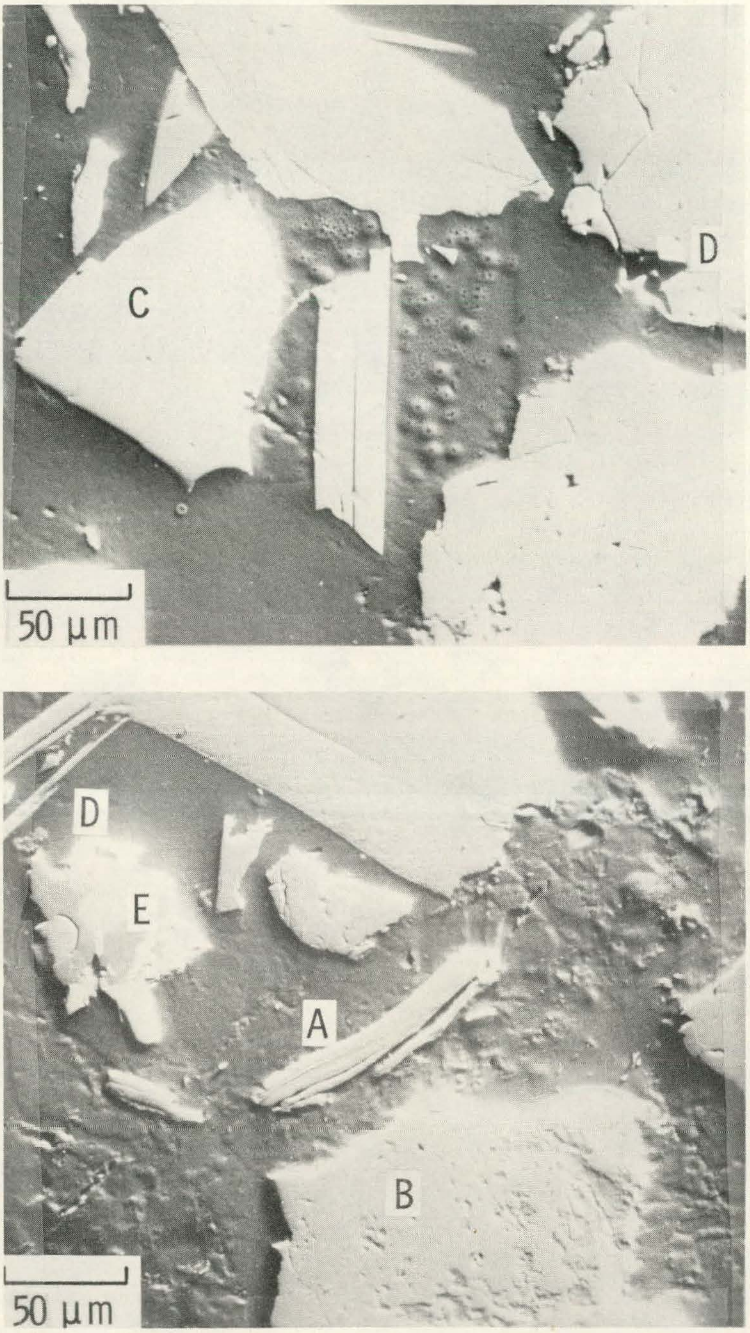
Weathered granite also shows changes due to the weathering process. Figure 17 is representative of unweathered granite. The phases present (not all labelled) include quartz, orthoclase, plagioclase, biotite, magnetite, and apatite. Figure 18 is representative of the weathered granite. Note the cracks forming along phase boundaries and through the phases. The layered structure of the biotite has also become very obvious (compare the two biotite areas in Figures 17 and 18). Clay-like minerals have also formed within the cracks on some of the plagioclase grains (Figure 19).

The changes caused by weathering argillite are much more subtle than those seen for basalt or granite. Figure 20 shows low magnification (300x) views of unweathered and weathered argillite. Figure 21 shows higher magnification (1000x) views of the two samples. Phases identified in the unweathered argillite included quartz, apatite, calcite, chlorite, pyrite, orthoclase, and pyroxene. The phases identified in the weathered argillite were quartz, pyroxene, and clay. The weathered argillite shows more small (<5 μm) particles, and more of the "matrix" clay-like material. The holes in Figure 20 show that some phase (probably calcite) has completely dissolved away. No other changes in phase compositions due to the weathering were noticed.

SORPTION ON WEATHERED ROCK

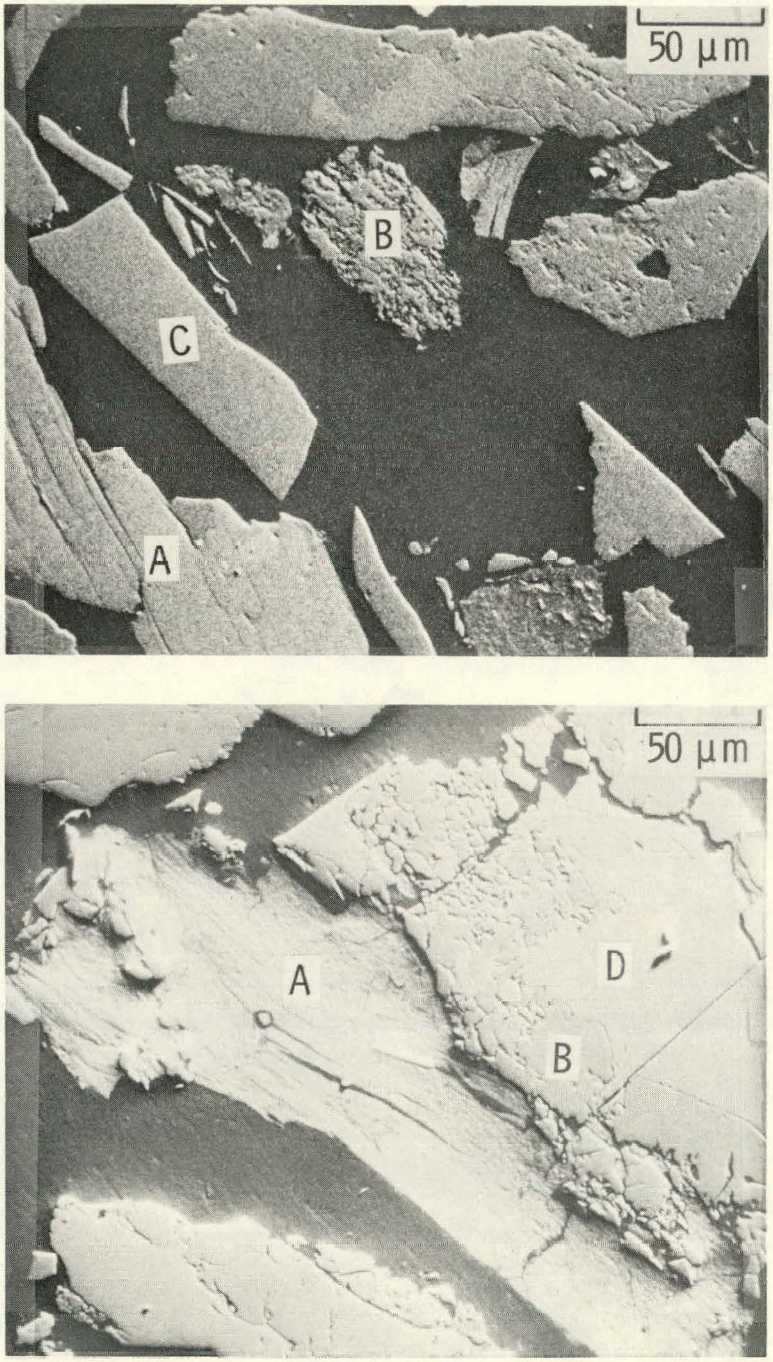
Sorption measurements were made using the weathered and fresh rock samples. The particle size of the weathered and fresh rock samples were the same, since both were taken from the same original crushed rock sample. Values of K_d were calculated for ^{137}Cs, ^{85}Sr, ^{237}Np, ^{241}Am, and plutonium for both weathered and fresh rock. These are compared in Table 7.

Weathered basalt sorbs each radionuclide more strongly than fresh basalt. Values of K_d for ^{137}Cs, ^{85}Sr and ^{237}Np increase by about a factor of five. The increase for ^{241}Am and plutonium is even greater. Sorption properties of weathered and fresh granite are identical within the error of the experiments. Weathered argillite sorbs ^{137}Cs, ^{85}Sr, and plutonium more strongly than fresh argillite. However, the opposite is true for ^{85}Sr and ^{237}Np.



A. BIOTITE
B. PLAGIOCLASE
C. QUARTZ
D. MAGNETITE
E. APATITE

FIGURE 17. Unweathered Granite.



A. BIOTITE

B. PLAGIOCLASE

C. QUARTZ

D. ORTHOCLASE

FIGURE 18. Weathered Granite.

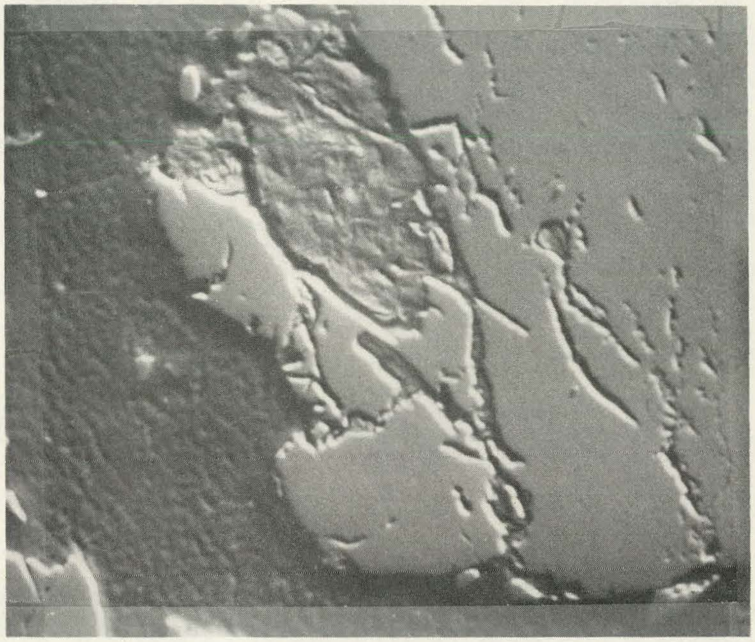
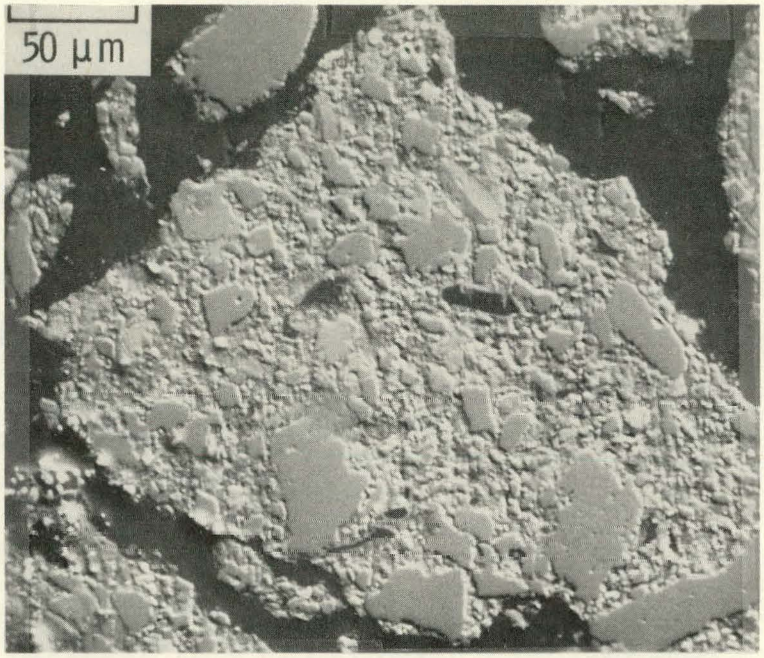
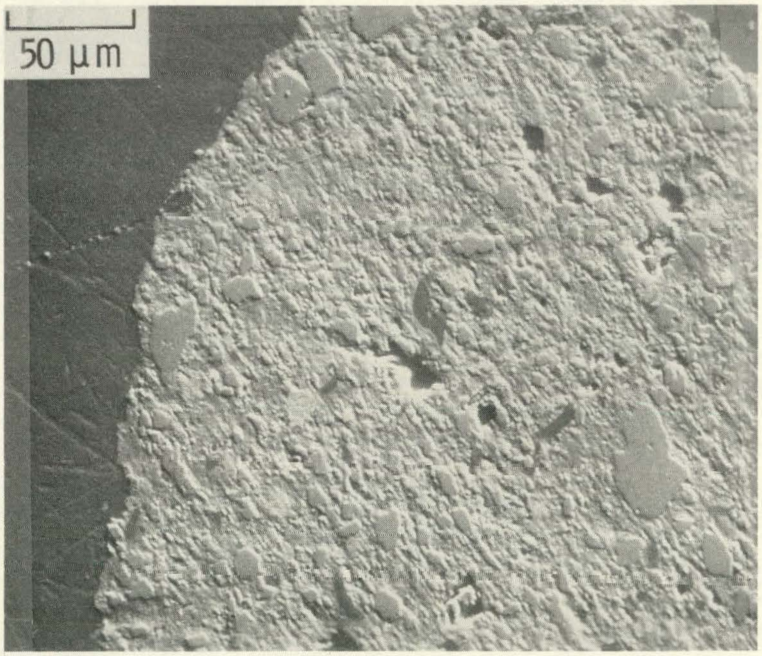


FIGURE 19. Weathered Granite With Alteration Products.



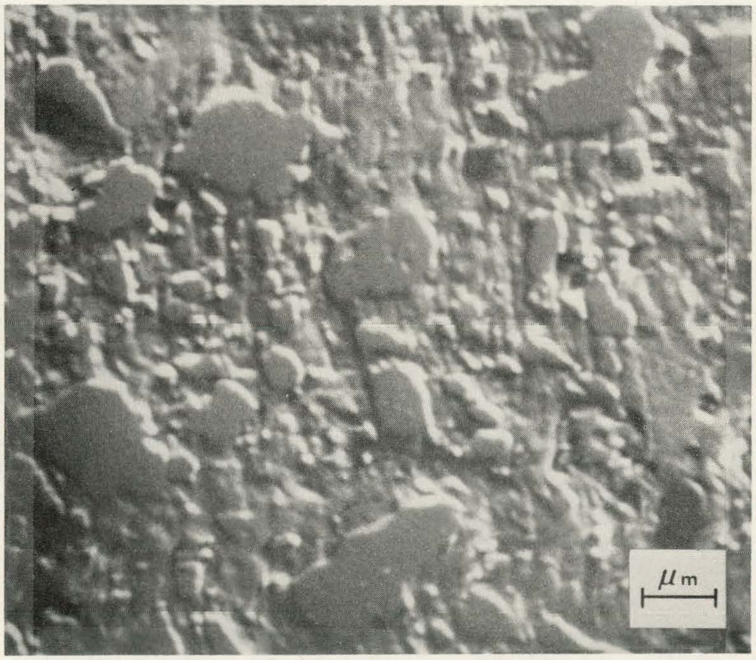
A. UNWEATHERED ARGILLITE



B. WEATHERED ARGILLITE

FIGURE 20. Argillite.

A. UNWEATHERED ARGILLITE



B. WEATHERED ARGILLITE

FIGURE 21. Comparison of Unweathered and Weathered Argillite.

TABLE 7. Comparison of Radionuclide Distribution Ratios for Fresh Rock and Rock Weathered in Air and N_2

Rock Type	K_d*, mℓ/g for				
	Cesium	Strontium	Neptunium	Americium	Plutonium
Basalt:					
Fresh	350 ± 40	108 ± 20	10 ± 1	6.2 ± 2.3	18 ± 2
Weathered in air	1500 ± 300	500 ± 100	49 ± 16	18,000 ± 17,000	2000 ± 200
Weathered in N_2	1420 ± 150	34 ± 2	37 ± 4	>116,000	11,000 ± 500
Granite:					
Fresh	1100 ± 200	6.2 ± 0.5	45 ± 2	27,000 ± 12,000	12,000 ± 10,000
Weathered in air	1100 ± 300	6.4 ± 0.8	39 ± 3	21,000 ± 5000	12,000 ± 7000
Weathered in N_2	1070 ± 70	3.9 ± 0.2	3.4 ± 2.2	35,000 ± 18,000	1940 ± 90
Argillite:					
Fresh	2400 ± 400	108 ± 5	79 ± 10	22,000 ± 14,000	15,000 ± 5000
Weathered in air	13,000 ± 2000	78 ± 6	56 ± 16	65,000 ± 44,000	29,000 ± 18,000
Weathered in N_2	39,000 ± 8000	41 ± 2	17 ± 2	6100 ± 700	870 ± 120

*14-day equilibration, mean of three replicate experiments. Error shown is 1σ.

The large increase in distribution ratios for basalt may be due to the large increase in surface area caused by weathering. The lack of change in distribution ratios for granite is consistent with the SEM data. Only minor changes (biotite layering, beginning of cracking and clay formation) between the unweathered and weathered granite samples were found.

The increase in distribution ratios for ^{137}Cs, ^{241}Am and plutonium with weathered argillite may also be due to increased surface area. It may also be due to an iron oxide coating on the argillite surface. Strontium and neptunium are probably sorbed by an ion exchange mechanism. Very little increase in CEC (Table 5) is seen for weathered rock, so no large changes should be seen in K_d if sorption is dominated by ideal cation exchange.

In general, the change in sorption properties after weathering is not due to changes in CEC. The CEC of each rock type changes very little after weathering. This suggests that ion exchange plays a minor role in sorption of cesium, americium and plutonium, but may be more important for strontium and neptunium sorption.

Changes in K_d for rocks weathered in air and in N_2 are pronounced. The principal difference between weathering basalt, granite, or argillite in air or under anoxic conditions is oxidation of the Fe^{2+} in each of these iron-containing rocks. According to Siever and Woodford (1979), dissolution of basalt, obsidian, fayalite, and hypersthene is slowed in the presence of oxygen due to the armoring effect of $Fe(OH)_3$ which precipitates on the surface. This $Fe(OH)_3$ coating not only slows dissolution, but scavenges cations and silica from solution. Therefore, we should observe different sorption properties for rocks weathered in air compared to those weathered in N_2. Although there are some exceptions, sorption on rock weathered in N_2 is less than that weathered in air. This might be due to the lack of an $Fe(OH)_3$ coating on the rock weathered in N_2. However, for basalt, weathering under N_2 generally increases sorption compared to fresh rock surfaces. This increase may be due to a surface area phenomenon.

The radionuclides are sorbing via different mechanisms. For strontium and neptunium sorption on argillite, ion exchange may be important. In other cases, distribution ratios may depend on surface area. For others, reaction between the radionuclide, groundwater, and rock determines the distribution ratios.

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QUESTIONS AND ANSWERS

RHO

Q: What particle sizes did you use?

A: We started with <0.5 mm.

Colloid Formation by Rock Weathering

Q: There must be a reason the colloids suddenly appeared at that particular moment? (100 days)

A: That is a good question. I think there is probably a continuous formation of colloids. I don't know why at 100 days all of a sudden we started seeing this very strong sorption of cesium on colloids passing through 0.3 μm filters.

Q: At what point did you change your filter types?

A: At 150 days; that is why we get the large decrease in the apparent concentration of americium and plutonium.

Weathering Products

Q: Is that discontinuity with sodium for real?

A: I really don't know where that sodium comes from. The only explanation that I can see is that it came from the filters.

Q: What is the material that has been used in the filters?

A: I am not really sure what the filter material was composed of. It doesn't seem likely that the sodium came from the filters, but I can't think of any other explanation. We have used ultrafilters in some recent experiments to try to eliminate these colloids, and we still have a problem. We are using 0.003 micron ultrafilters and we are still getting colloids passing through those filters, so I don't know what else we can do. Kd sorption on basalt is experimentally not very easy.

Ground Water

Q: What did you use for ground water for the climax stock? You implied that you have made it up from an aquifer close by, but there really isn't any aquifer in climax stock.

A: No, there's none in climax stock but there are aquifers nearby.

Q: But in the granite?

A: Not in the granite.

Colloid Formation or Solid-Solution Separation

Q: Are there any special techniques in using these super fine pore-size filters? I have never used one, and I know I have trouble with even 1/10 micron.

A: We found a very good filter to use for these particular filtrations. It is a cone ultrafilter that can be used in a centrifuge, and it works out very nicely.

Q: So you spin it?

A: You spin it and the solution goes through the filter.

Rock Weathering

Q: Something implicit in what you are saying is that the radionuclides you are monitoring as a function of time may simply be sitting in solution waiting for the rock to alter. In other words the rock is changing composition, perhaps forming more hydrated minerals on the surface as the adsorption site density increases; then the cesium goes onto the surface of the rock. However, what you are monitoring in actuality is a rock alteration phenomena and not necessarily a reaction rate of the radionuclide.

A: That's right. Well, there's another possibility, diffusion of the radionuclides into the pores of the rock.

Q: Have you looked at these colloids that you have filtered out in terms of the activity that's on them or are you hypothesizing that that's where the nuclides are?

A: Well, it seems reasonable to assume that the radionuclides are sorbed on the colloids because when we remove the colloids the radioactivity disappears from the solution.

Q: You counted the filters; they're on the filters?

A: No, we didn't count the filter. We counted the solutions after filtration.

Colloids

Q: Did you have any colloid problems with granites?

A: No. We used 0.01 to 0.3 micron filters and saw no difference at all.

Q: Only with iron rich rocks did you have colloid problems?

A: Well, only with basalt. I suspect what we're seeing is dissolution of the glassy phases of basalt and then precipitation of iron and silicon and calcium to form the colloid.

Weathering Products

Q: Do you prewash the ultrafilters to remove anything that was in them? You had to have sodium--higher concentrates of sodium--when you changed over the filters.

A: Well, we haven't shown the working of the ultrafilters here. We used the 0.01 micron filter. I haven't gotten all the data yet.

Q: I found quite fascinating your simultaneous measurement of all of the major solution components that were coming from the other end of rock columns as well as the measurements of the nuclides. The fact that you saw such changes in the water composition...what does this imply about the so-called pre-equilibration of water with rock before the experiment starts?

A: That's a question that I have myself. Pre-equilibrated water or rock-equilibrated water seems to me like it's going to be very important how long you pre-equilibrate them. You can have a whole range of concentrations of ions depending on what length of pre-equilibration.

C: I have one thing to say about that. The tuff waters that we have pre-equilibrated, waters have equilibrated with tuff, we have them ranging from a few weeks to about a year, really hasn't changed much at all. (The major ions that are in solution are constant.)

A: Right.

C: We see the same thing on the granites and argillites -- the same material you're talking about. Some of those ions are already present and the concentrations don't change fast -- particularly with the granite.

C: Maybe the real question is that you should look at an equilibrated rock with the ground water. It would seem to me that the volume of ground water and its composition are not going to be affected by the rock. That will stay the same. What will be affected are the fractures in the rocks and the alteration products, and eventually maybe the alteration products within the fractures -- especially in hard rocks like basalts and in granite. That's going to govern much of the solubility and a lot of the adsorption of nuclides when the canister and backfill materials have been breached.

C: In the laboratory, maybe, but maybe not necessarily in the field where the rock-to-fluid ratio may be very high.

C: Yes, but you're still going to have an influx of ground water as we keep flushing the system, you have solubility of product precipitates, along with fractures and so on, and it's a more complicated system than just putting in a certain water and watching what's coming out.

C: Hopefully, you wouldn't put a repository where you'd have the Mississippi River flowing through the rock.

C: That's true. But we're looking at the worst-case where there is a breach.

C: In Scott's experiment he agitated the materials so that there was a constant abrasion of the material against itself so that any hydrolysis that went on at the surface would soon be removed and the process be allowed to continue. I don't think it's going to be possible in Scott's experiment to understand what's going on until those solids are characterized. I doubt exceedingly that we'll understand the process so long as we're continually renewing the surface and allowing that process to go forward. In the case of basalt, several people have been making simple assumptions it's the iron that's involved. My own perception of that would be that it is hydrolysis of the plagioclase which is increasing the pH to the point that the OH^- concentration precipitates the iron which then adsorbs the radionuclide.

C: You could carry that particular process to its conclusion by essentially equilibrating your rock, by grinding the rock in the water -- grinding, mechanically pulverizing it -- and then you would probably reach a very high pH.

C: Quite so. In the case of the so-called ultra-grinder for muscovite, for example, you can grind the muscovite to the place where you no longer get an X-ray diffraction pattern, and the material is a virtual base. And the same way you can grind carbonates to the point that they no longer have crystallinity. The continuous agitation is no longer related to any of the simple long-range structures we call minerals. It's a surface and colloids and other material which must be highly sorptive. (And you have to look at that solid phase.) You have to characterize it. I don't understand that at three years into this program how it's possible to conceive of an experiment as a straight chemical one without any characterization of the phases.

C: I think tomorrow we'll get more into the characterization. We've seen some of the work.

C: But you see in that dynamic experiment, you're continually grinding and continually making an array of fresh surfaces, altered material, material in between. You're getting adsorption on the whole array.

Q: Well, the argument before about the renewing of the surface increasing the basicity of the rock or otherwise disturbing the whole process and making it inapplicable to the real situation points out something we've been advocating for a long time -- use intact rock, and then you don't have this problem of introducing activated surfaces.

C: I think the more basic generalization than that is to use the same phase throughout (the same phases) at least throughout the experiment.

Rock Weathering

Q: The pyroxines in basalts are very generally zoned. Have you looked for zoning in these pyroxines before you weathered them? In other words, interior cores being of a different composition than the exterior portions of the single mineral?

Q: You didn't see indications of that though on your unweathered cross sections, from what I remember of the slides (you showed the weathered versus the unweathered); and I don't think the unweathered had those.

Q: By zoning, do you mean changes in compositions as you go from exterior to interior?

A: Yes. I didn't see any of that, although I wasn't looking specifically for it.

A: I think that most of what you were looking at probably wasn't zoned, but you ought to consider the fact that minerals cannot very often be zoned, and what you might be looking at is the zoning phenomenon, rather than a weathering phenomenon. Perhaps the two coupled.

A: That might be true.

Q: Now that you have weathered with nitrogen and air, maybe you would think about expanding this into weathering with water, pure water, and weathering with some type of ground-water compositions.

A: I haven't thought about that. I should.

Q: With all of the differences in your Kd, did you take into consideration the effects of the solution parameters?

A: I didn't do the sorption experiments myself. Scott, would you like to address that question?

A: All the experiments were conducted under the same conditions and experimental procedures.

Q: But the implication here is that the differences in Kd are due to weathering, but this may not be associated with the solution values problem.

A: Well, I think the difference is due to weathering whether there is a change in pH or not. We are doing the experiment identically. The only difference is that in weathered rock versus fresh crushed rock. I don't think that it is due to differences in pH. I think it is due to the difference in surface area.

Q: You mentioned one of the things that the future held was to investigate naturally weathered rocks, would you comment on the connection between naturally weathered rocks and rocks at depth in a candidate repository site?

A: Well, for basalt we have found areas in which there are large quantities of secondary minerals from the actual weathering. I'm hoping there aren't too many differences from what we've seen.

Q: I would like to add to Glenda's reply that we are doing some characterization work with secondary minerals at depth in conjunction with what we're doing in the laboratory and there are significant amounts of secondary mineralization at depth to 4,000 ft. As a matter of fact, in Pomona we have found, if I remember the dimensions correctly, about 2 ft x 18 in. deep into the wall. We don't know what the lateral extent out into the mine section was.

Q: Is it the same type of mineral basically that you might expect to get at the surface?

A: I don't know, we haven't done it yet.

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GENERAL DISCUSSION

Four 20-30 minute discussion periods were held during the meeting, and a four-hour discussion period was held on the morning of October 17. Following is a distillation of the primary concerns and suggestions offered by the group.

FACTORS AFFECTING SORPTION

Solubility was identified as a problem area in studies of actinides in particular. It was suggested that solubilities be calculated from available data and the problem of tracer precipitation would be eliminated. In theory this approach would work but the data available does not cover the pH or concentration range of interest in environmental studies. Much of the data is from work in acidic media with gram quantities of the radionuclides. Solubilities of actinides at very low concentrations and neutral pH are not easily determined because the solubilities depend on the solution concentration (ionic strength, complexes formed by the actinides and multiple oxidation states). Furthermore, the solid compounds are present in such small quantites that they are difficult to identify. Evidence was presented that some americium sorption Kd values in the literature were simply the result of the solubility of some unknown Am compound.

Colloids in solution may be formed by actinides because of hydrolysis (true radiocolloids) or by sorption of the actinides on some particle in solution (pseudo-colloid). Both types of colloid may behave the same in regard to migration. Much work has been done to separate solutions from solids by filtration and centrifugation. The major problem is that migration of colloids in porous media has not been quantified sufficiently. As yet there is no practical definition for determining what size colloid behaves as if it is in solution and is not filtered by a given porous medium.

Speciation of radionuclides in low-level solution is a problem for elements which have more than one possible oxidation state. Chemical behavior and migration potentials of an element's multiple oxidation states can be different enough to behave like separate elements. The concentration ranges (less than 10^{-6} $\underline{M}$) were beyond conventional chemistry of 20 to 40 years ago. Techniques are presently available for many oxidation state determinations and should be used before, during, and after an experiment when possible. Techniques should be developed for identification of oxidation states that cannot now be determined.

Diffusion has been identified as a mechanism responsible for Kd values that increase with time (usually observed in batch experiments) and for tailing (non-ideal behavior in column effluent). Diffusion may occur in batch experiments as the radionuclide diffuses from bulk solution into small pores in the rock particles. In fracture flow or column flow, diffusion would occur as radionuclides in the main flow channels diffuse into dead end channels or small pores. The time to reach equilibrium would be delayed by the restricted movement of radionuclides into these stagnant areas.

PROBLEMS IN MEASURING Kd VALUES

The batch method is often selected for making sorption and desorption Kd measurements. The claim was made that optimum measurements are obtained when about 50% adsorption occurs, that is when the initial tracer concentration is reduced by a factor of 2. This can be done by varying the solution to solid ratio in short term preliminary experiments. Previous work has shown that reliability of the batch method decreases rapidly when sorption of radionuclides is so large that final nuclide concentrations approach the lower limit of detectability. The other extreme (low Kd values) occurs when adsorption is low enough that no significant difference between influent and effluent is observed.

Adsorption isotherms for several nuclides (Cs in particular) has shown a strong dependence between nuclide concentration and Kd (increasing Kd with decreasing nuclide concentration). Batch measurements of sorption Kd values were pointed out to be lower than subsequent desorption Kd measurements. When the original solution is removed from a sample and replaced with unspiked solution for a desorption measurement, the final solution concentration is likely to be lower. The resulting Kd value is at a different point on the isotherm. Even in the case of a reversible sorption/desorption such methods may yield seemingly higher Kd values for desorption.

In the blank corrected batch Kd method, tube wall sorption of strongly adsorbed nuclides such as plutonium lowers the measured Kd. The method gives a conservatively low Kd (which is fine for safety assessment) but interferes with interpretation of data. Two reasons were presented for varying amounts of adsorption on walls. The first reason was that the nuclide was scraped off the wall by rock samples and depends on the rocks hardness and the amount of agitation. The second was that Pu is sorbed on almost any surface, thus in blank tubes with no sample it sorbs on the wall and in tubes with rock samples it sorbs mostly on the rock. Most participants felt that the latter reason (sorbed according to surface area) applied. The suggestion was made that accurate sorption data for these systems could be obtained by direct counting of the activity on the rock, thereby eliminating the need to make secondary corrections. However, caution must be taken to insure that precipitation is not the reason for nuclide disappearance from solution.

The manner of reporting Kd values was discussed. Some researchers are unsatisfied with the mean and standard deviation. These parameters <u>would</u> be valid if the Kd had a gaussian distribution. One participant introduced the group to the Cauchy distribution which comes close to describing the distribution of Kd values for a replicated experiment. He also pointed out that nuclide concentration distribution were truncated gaussian functions, thus the Cauchy distribution doesn't fit exactly. After this discussion the subject was dropped.

STANDARDIZATION: NAMES, UNITS, AND DATA

The name (or symbol) for the quantity which describes sorption was discussed at some length. Various names (distribution coefficient, distribution ratio, partition coefficient, sorption concentration ratio) are presently used in an interchangable and possibly incorrect manner. Symbols used presently include Kd, R_d, D, S_{cr} and D_{cr}. These differences arise because researchers from different scientific backgrounds use the symbol or name common in their field of interest. The distribution coefficient, Kd in chromatography or D to chemists, is an equilibrium thermodynamic quantity in the strict sense in which it is used for ion exchange. Many times the Kd is used to express a non-equilibrium ratio of the amount of radionuclide adsorbed per unit mass of solid to the solution concentration of that radionuclide. The distribution ratio, R_d, or sorption concentration ratio, S_{cr}, are used to denote non-equilibrium conditions. Several investigators feel that the most widely used term, Kd, should be reserved for equilibrium sytems which have been shown to be reversible and all other measured sorption coefficients should be symbolized by something else such as R_d or S_{cr}. One participant even suggested an empirical (non-equilibrium) bound fraction distribution ratio, B_{fd}.

Since chromatographic behavior is assumed for most safety assessment models, the bulk of both equilibrium and non-equilibrium sorption/desorption measurements is reported as Kd values. An observation was made to the effect that the Kd should be left alone. If Kd is reserved for equilibrium and Rd for non-equilibrium measurements, anyone using Kd had better be ready to prove equilibrium exists for that system. Simply define the symbol in each paper and show what experimental conditions were used. Too many symbols are used at this time and someone new to the field can easily be confused by the half dozen seemingly interchangeable terms.

The somewhat divided opinion of participants seemed to be that consistency is needed. Perhaps one symbol such as Kd should be used for equilibrium distribution coefficients and a different one for non-equilibrium measurements. Agreement was reached on the need to report as complete a system characterization as possible (pH, Eh or O_2 level, macro and trace elements in solution, solid phase mineralogy and/or chemical composition, radionuclide concentrations, etc.).

The possibility of having to report data in S.I. units was presented. Commonly, sorption data (Kd or Rd) has been reported in milliliters per gram (ml/g). S.I. units for the data would require units of cubic meters per kilogram according to one observer. Another observer claimed it makes little difference what units are used as long as everyone uses the same set of units. It was also pointed out that liters per kilogram (which were said to be S.I. units also) are numerically equivalent to milliliters per gram. From common usage in the past and ease of comparison ml/g or l/kg seem to be the favorite choice of units for sorption measurements.

Much more column work was done in FY-79 than in previous years. Results were presented by using pore volumes, column volumes and simply volume with no reference to column parameters. The major information gained from a column experiment is the relative velocity of a radionuclide to the velocity of moving groundwater (the retardation factor) and some standard is required for comparison of the two velocities. Information needed for characterization of a column experiment includes: porosity and bulk density of the porous media, column length, volumetric flow rate (darcy velocity or pore velocity can be determined using porosity, column length and flow rate). Ideally the static porosity should be measured for a column before (and perhaps after) and experiment. The effective porosity under flow conditions should also be determined for comparison with the static measurement. A question was raised about the definition of porosity since adsorbed water on some solid surfaces is strongly bound, thus not all void space is available for groundwater transport. Tracer methods for determining pore volumes under flow conditions are not thought to be exact because of anion exclusion from near negatively charged surfaces and the slight differences in behavior of tritiated versus natural water. Some investigators have used breakthrough times to quantify their retardation factors, but time is applicable only when flow rates and permeability are constant. As stated before, column experiments when reported, should include column volume, length, porosity, flow rate, and a break through for some mobile anion or ^3H.

DEFINITION AND SIMULATION OF REALISTIC CONDITIONS

A need was expressed to be able to convert laboratory data to something useful in the field by means of a scaling factor. Porous lab systems using granulated material are not necessarily related to in situ systems and a connection must be made between the chemistry observed in the lab and in situ.

A large amount of data on many radionuclides has been collected under wide ranges of pH, Eh, groundwater type and geologic media. However, probably not all of the combinations of nuclides and conditions imaginable can be covered. Arguments were given that the parameters under study can be limited by using knowledge available now. The groundwater and rocks have existed for hundreds of thousands of years and need to be characterized to place limits on the problem of nuclear waste management.

The following discussion concerned the definitions of Eh and anoxic conditions, how these parameters could be measured and how they relate to realistic conditions.

Anoxic is a descriptive term which denotes a lack of oxygen. The degree to which oxygen is actually removed from an experimental system depends on the equipment used, but the reported oxygen levels are limited by the ability to measure O_2 in the gas phase. The lower limit discussed here is about 0.2 ppm O_2 and corresponds to about 2×10^{-10} $\underline{M}$ dissolved oxygen in water compared to x 2×10^{-4} $\underline{M}$ aqueous O_2 in equilibrium with air. Assuming Henry's law holds; 0.2 ppm atmospheric O_2 is equivalent to 6×10^{-6} ppm dissolved oxyen, which is two to three orders of magnitude lower than present equipment can detect.

Redox potentials (or Eh) are defined theoretically by the thermodynamics of specific oxidation-reduction couples. However, experimental measurements of Eh do not always correspond with theory. A lack of oxygen in anoxic experiments is not sufficient for obtaining reducing conditions. If no electron donor species are present for the reaction being studied, no reduction can occur. Even if electron donor species are present, the quantity must be large enough to allow an observable reaction between oxidized and reduced system.

The lack of electron donor or acceptor species in most environmental systems was cited as a problem area. These systems are unpoised, which means that Eh readings made with Pt electrodes are of little use for predicting radionuclide behavior. Chemical analysis of Fe(II)/Fe(III) or sulfide/sulfate concentrations was suggested as a method for theoretical Eh determinations in groundwaters. The chemical analysis for specieis such as these is limited and results become uncertain in roughly the same Eh region (or just below) that electrodes fail.

Controlling the redox potential with Eh buffers (used in the past) was again suggested for this area. Organic dyes that act as Eh buffers might be used if they can be shown not to affect the system in some manner other than controlling the Eh. They could, for instance, affect radionuclide activities by complexation or by altering the solid phase. Solids as Eh buffers were discussed but they present the problem of additional surfaces and sorption sites.

Comments were made that implied that redox sensitive elements may not be the only radionuclides affected by Eh or oxygen level. Mineral stability can change between oxidizing and reducing conditions, thus changing the surfaces present. Ferric hydroxide, $Fe(OH)_3$, would dissolve under reducing conditions to form $Fe(OH)_2$ and Fe^{+3} in solution. The valence state of Sr^{2+} or Cs^{+} may not be affected, but their sorption behavior might change as new minerals are formed. Chemical composition of solution will also be functions of redox potentials, which could affect nuclide behavior. Subtle effect may also occur which are unrelated to Eh, such as the removal of CO_2 along with O_2.

The consensus was that the redox potential is an important parameter for determining radionuclide behavior in geologic systems. The Water Resources Division of the USGS was suggested as a source of information for understanding what chemical parameters and conditions can be used to determine Eh. Solutions and solids should still be characterized in an attempt to measure or estimate the redox potential. Until a specific site is selected (and perhaps afterward) experimenters should continue to be carried out over a range of oxygen levels and Eh values to determine what chemical/mineralogical parameters significantly affect radionuclide behavior and which parameters can be ignored.

DATA INPUT FOR TRANSPORT MODELS

The possibility was again mentioned that Kd values measured in the lab may not apply to field environments unless they are translated or scaled to field conditions. The scaling factor for lab to field for porous flow will probably be different than a scaling factor for lab data to fracture flow in the field. Characterization of experiments should be done with the translation of lab to field in mind.

The group was reminded that hydrologic models describing groundwater movement deal with a gross distribution of porosities and permeabilities. The role of dispersion (in the field) was also claimed to be sometimes exaggerated. The dispersion coefficient can usually be defined to within an order of magnitude (which is claimed to be better than what is possible for other transport parameters). Solute transport is much more sensitive to porosity or Kd than to dispersion.

APPENDIX A

PARTICIPANT LIST

APPENDIX A

WISAP TASK 4

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APPENDIX B

OVERVIEW OF WRIT PROGRAM

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OVERVIEW OF WRIT PROGRAM

Radioactive waste products, which result from commercial nuclear power production, require isolation from the biosphere for thousands of years. Current plans of the Department of Energy (DOE) call for final management of these wastes by isolation in deep continental geologic formations. The wastes are expected to be kept in isolation as a result of chemical, thermal, and mechanical stability of the waste package systems and geologic repositories.

The Department of Energy, through the National Waste Terminal Storage (NWTS) program, is developing nuclear waste isolation systems in geologic formations that prevent unsafe radionuclide concentrations from entering the biosphere. In order to assess the safety of geologic repositories, the following factors must be addressed: 1) geologic and repository stability, 2) magnitude and direction of possible transport media flow, 3) concentration and nature of species of the radionuclides in the transport fluid, and 4) biological uptake of radionuclides by food chains.

The Waste Isolation Safety Assessment Program (WISAP) was begun in 1976 to respond to these needs. The purpose of this program is to develop a suitable methodology for evaluating the relationship of the above factors and the effectiveness of deep geologic disposal for waste isolation. The efforts of WISAP were divided into two areas: 1) Release Scenario and Release Consequence Analysis (modeling effort), and 2) Waste Form Release Rate and Sorption/Desorption Analysis (experimental effort). Modeling efforts have been consolidated for FY-1980 into the AEGIS Program (Assessment of the Effectiveness of Geologic Isolation Systems) and the experimental work has been consolidated into the WRIT Program (Waste/Rock Interaction Technology).

The WRIT program is specifically designed to address the concentration and nature of the radionuclides species the transport fluid. To accomplish this goal, the WRIT program will develop the necessary data and predictive capability on the release and subsequent geochemical interactions of radionuclides with engineered barriers and natural geologic media. The major products of the planned research in the WRIT program are: 1) the generation of defensible, reproducible data on leaching, sorption, and nuclide released processes through the use of scientifically acceptable methodologies, and 2) the development of credible models of leaching, sorption, and release processes based on underlying theory and experimental observation that can be used in consequence analysis.

To enable the prediction of the concentration and nature of the species of radionuclides in transport media, an understanding of the dynamic equilibrium that exists between the solution, solid phases, and any adsorbed ions must be developed at a variety of locations within the repository and the surrounding geologic media. Changes in one of these phases will result in changes of the other phases. For example, the concentration of radionuclides close to the repository will be affected by the solubility of the waste form and the interaction of the waste package materials with the ground-water solution under conditions of elevated temperature and radiation levels. These processes must be coupled with our knowledge of waste form leaching to determine a "source term" for potential migration from the repository. As the radioactive solution moves away from the repository, it acquires the properties of the solution phase of the surrounding geomedia. Several processes may take place which change the solution chemistry, including the precipitation of new solid phases, dissolution, changes in the concentration of ligands (and thus, solution species), and ion exchange and other surface sorption mechanisms. These processes are all affected by pH, Eh, and other solution parameters. The emphasis of the WRIT program is to develop predictive capability for above processes through the understanding of underlying mechanisms and experimental observation.

The work under WISAP has emphasized two major processes which affect the release and geochemical interaction of nuclides: leaching and adsorption/desorption. Past efforts have been directed toward experimentation in simple binary waste-solution and radionuclide-geomedia tests. These tests have provided a sound basis for the initiation of three research efforts in support of the WRIT goals. The first effort is a series of laboratory experiments on complex waste-package/geologic-media interactions. These tests will simulate anticipated repository conditions, as well as provide valuable data on the interactions of all of the waste-package and geomedia elements. The second effort will strive to improve our understanding of the solution chemistry of important radionuclides, through the development of a thermodynamic equilibrium model. The third effort entails the development of reliable leaching, sorption, and release models for use in consequence analysis. The use of these models, in concert with other models (transport model, release scenario stability model, dose model) that are being developed under the Assessment of the Effectiveness of Geologic Isolation Systems (AEGIS) and WIPAP programs, will result in a suite of models capable of assessing the safety of geologic repositories.

In summary, systematic studies of the waste package and geologic media elements of waste repositories are needed to develop an understanding of geochemical interactions, especially nuclide release, and are necessary to enable credible assessments required for specific geologic isolation systems.

OBJECTIVES

The objectives of the Waste/Rock Interactions Technology (WRIT) Program are as follows:

1. identify and characterize the mechanisms of waste form radionuclide release and subsequent geochemical interactions with engineered barriers and natural geologic media, e.g., leaching, solubility, and sorption;
2. collect data, develop and evaluate the effectiveness (develop a perspective on applications/limitations of each model) of models that predict leaching, sorption, and release processes in the repository and surrounding media;
3. obtain, through verification studies and documentation, the most acceptable test methodologies for sorption, leaching, solubility limitations, and waste package/geomedia interaction studies;

4. support repository site characterization and licensing specifically through data generation, analysis, and predictive model formulation.

SCOPE

There are two basic elements to this program:

1. development of knowledge of waste form radionuclide release and subsequent interactions with engineered barriers and natural geologic media
2. dissemination of this developed knowledge in the form of sorption, leaching, and release models, verified test methodologies, and data banks.

The Waste/Rock Interactions Technology program consists of a management task and four technical tasks (Figure 1). These five tasks are integrated into the WRIT program to produce the needed data and models pertaining to waste package-geologic media interactions. These tasks involve work at PNL and numerous other laboratories, and are listed below.

1. Program Management
2. Waste Package Interactions - Nuclide Release Studies
3. Geologic Media - Nuclide Interactions Studies
4. Nuclide Solution Chemistry Studies
5. Predictive Model Development.

Figure 1 displays the program organization, a number of the key management and technical contributors, and the work breakdown structure (WBS) elements.

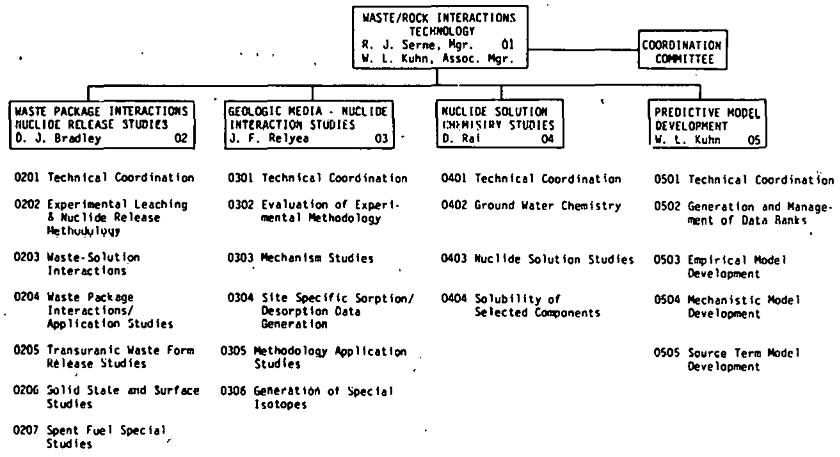

FIGURE 1. WRIT Organization

PROGRAM COORDINATION

As stated earlier, the WRIT and AEGIS programs are an outgrowth of the previous WISAP program. To assure programmatic coordination between WRIT and AEGIS, five interfaces have been identified as follows:

1. The associate program manager of WRIT will be the data and sample interface for all site-related work. This individual will work with the assigned individual within AEGIS to ensure the timely provision of available sorption, leaching, and solubility values for each site-related study.
2. A geochemist in the Methodology Development branch of AEGIS will be assigned a monitor role to follow the technical work of the WRIT program and identify areas of research needs for both programs.
3. There will be a complementary effort within each program to monitor the licensing process as it develops and thus provide guidance to both programs. The individual within AEGIS will follow this effort from a procedural and methodological framework, working closely with the WRIT program manager who will approach this process from a technical criteria standpoint.
4. A Coordination Committee will be established, consisting of the project manager and associate project manager of each program. This committee will meet quarterly to review long-range plans, coordination, and project status. The Coordination Committee will be chaired by the Water and Land Resources Department Manager, and will include the cognizant manager in the Nuclear Waste Technology Programs Office (NWTPO). This approach will assure the commitment of the PNL line management structure and the NWTPO office to the cooperative efforts of the WRIT and AEGIS programs.
5. A peer review group of a variety of scientists will monitor both programs, providing guidance for each in the context of the large safety assessment problem.

WRIT OBJECTIVES FOR FY-1980

The emphasis for WRIT during FY-1980 will be to establish a coordinated and efficient program which, over the next several years, can expeditiously accomplish the objectives set forth. In addition, efforts will be expended to interact with the AEGIS program to ensure that data needs continue to be met.

Specific technical objectives include completion of the analytical backlog on leaching tests; start of experimentation on mixed waste form, water, and rock-nuclide release studies; continuation of generic sorption and sorption mechanistic experiments; and initiation of leaching, sorption, and nuclide release predictor computer models.

WBS ELEMENT OBJECTIVES, DEFINITION, AND MAJOR CONTRIBUTORS

The WRIT program consists of the five tasks described below.

TASK 1 - PROGRAM MANAGEMENT

Activities within this task are directed toward the successful performance of planned work within schedule and budget. These activities include:

- direct and participate in the planning of the work, including the statement of objectives, work scope, work breakdown structure, task descriptions, resource commitments, schedules, and costs estimates
- provide close liaison with DOE and ONWI to ensure proper communication and responsiveness
- coordinate the work within the program tasks
- enhance interface with interrelated research and development efforts
- participate in the overall Coordination Committee for the WRIT and AEGIS programs
- implement an approved quality assurance program
- provide fiscal control and management.

WBS Element 0101 - Program Management

Major Contributors: R. J. Serne and W. L. Kuhn.

This work element will provide the overall administrative management for WRIT, including internal and external programmatic coordination, program planning and control, fiscal control and management and quality assurance. An annual Technology Program Plan for WRIT will be submitted in draft for ONWI review each September. The plan will include statement of objectives, work scope, work breakdown structures, task descriptions, resource commitments, milestones, schedules, and cost estimates.

This work element will also provide periodic progress reports. These reports are of two types. Monthly progress reports will be prepared in letter form by the tenth of each month, and transmitted to ONWI and DOE. These monthly reports will include technical progress against milestones, and information on costs and manpower. Quarterly technical progress reports will be prepared and submitted to the PNL Nuclear Waste Technology Program Office (NWTPO) and ONWI on the fifteenth day of the first month of each quarter. Publication of the quarterly reports is the reponsibility of ONWI.

WBS Element 0102 - Interface with Interrelated Programs

Major Contributors: PNL: R. J. Serne, W. L. Kuhn, and task leaders.

This task is designed to provide the necessary technical interchange and data exchange between interrelated waste management programs and the WRIT program. Efforts in this task will be expended toward closer communication with projects involving waste form and package development, engineered barriers development, overall repository design, waste-geologic media interactions studies, geochemical research, and hydrologic transport studies. These communications will be directed toward: 1) gathering design and operational criteria for waste package components to be used in the formulation of responsive geochemical tests performed under the WRIT program, 2) effectively transmitting the data generated and knowledge gained in the WRIT program to the interrelated research programs through an annual workshop, 3) identifying overlapping work among the various research projects, and 4) continue to input to subgroup 2 of the Earth Sciences Technical Planning (ESTP) committee.

Waste-media interactions and hydrology projects of particular interest in this data exchange task are taken from the second draft ESTP document (November 1979) and other sources listed below:

ONWI Sponsored:

Waste-Media Interactions

3.1.1 Near-Field Waste-Rock Interactions (PSU)
3.1.3 Salt Brine-Waste-Canister Interactions (USGS)
3.1.6 Effect of Water on Salt Repository (ORNL)

3.1.7 Radiolysis of Brine (ORNL)
3.1.8 Strain Related Radiation Damage (BNL)
3.1.10 Thermodynamic Properties of Actinides (LBL)
3.1.16 Release Rates of Reactor Products (LASL)
3.1.17 Engineered Barriers (Lehigh)

Rock Mechanics

3.2.12 Independent Measurement Laboratory (NBS)

Geology

4.1.20 Natural Fission Reactor Program, OKLO (LASL)
4.1.21 Study of the Morro do Ferro Thorium Deposits (NYU)

Geochemistry

4.2.4 Organic Compounds in Ground Water (BCL)

Hydrology

4.3.3 Development of Analytical Transport Models (LBL)

Performance Assessment

4.4.1 Performance Assessment Program (to be determined)

Basalt Waste Isolation Program (BWIP) Sponsored:

3.1.2 Characterization of Waste Form and Geologic Environment
3.1.18 Engineered Barriers Optimization
3.1.19 Waste/Barrier/Rock Interactions in Basalt
4.2.8 Chemical Environment Modeling

Waste Isolation Pilot Plant (WIPP) Sponsored:

3.1.4 High-Level-Waste-Container Interactions with Rock Salt and Brine

3.1.5 Brine Migration

3.1.13 Transuranic Waste Characterization Studies Under Conditions of Geologic Isolation

United States Geologic Survey (USGS) Sponsored:

3.1.9	Geochemistry of Transuranium Elements
3.1.11	Redox Potentials and Chemistry of Actinides in Water
4.1.22	Geochemical Study for Verification of Complex Solute Transport Models
4.3.2	Solution of Solute Transport Equations

Other PNL Programs:

High Level Waste Immobilization Program, Task 3 (R. E. Westerman)
Alternative High-Level Waste Forms (J. M. Rusin)
Alternative Transuranic Waste Forms (C. R. Palmer)
Materials Characterization Center (R. D. Nelson)
Systems Study of Engineered Barriers (M. O. Cloninger)

WBS Element 0103 - Coordination with AEGIS and MCC

Major Contributors: PNL: R. J. Serne, W. L. Kuhn, and D. J. Bradley.

A PNL Coordination Committee will be formed to assure an adequate interface between WRIT and AEGIS, both with respect to long-range program planning and to ongoing technical work. This committee will support and enhance the interaction and exchange between the WRIT and AEGIS programs to ensure prompt delivery of needed data for site qualification and licensing needs. The committe, which will meet quarterly, will consist of the following PNL staff members:

D. B. Cearlock	(Chairman) Manager, Water and Land Resources Department
A. Brandstetter	Project Manager, AEGIS
D. J. Silviera	Assistant Project Manager for Methodology Development, AEGIS
F. H. Dove	Assistant Project Manager for Site Applications, AEGIS
R. J. Serne	Program Manager, WRIT

W. L. Kuhn	Associate Program Manager, WRIT
D. J. Bradley	Technical Leader, WRIT
M. R. Kreiter	Project Manager, Nuclear Waste Technology Program Office
J. H. Jarrett	Manager, Nuclear Process Technology and Analysis Section.

This work element also includes coordination with the Materials Characterization Center (MCC). A coordination committee similar to the above will meet periodically to facilitate interaction. The committee will consist of the following PNL staff members:

WRIT:	R. J. Serne W. L. Kuhn D. J. Bradley J. F. Relyea
MCC:	R. D. Nelson W. A. Ross R. P. Turcotte O. F. Hill
Line Managers:	R. A. Walter J. H. Jarrett
Program Office:	M. R. Kreiter L. T. Lakey

WBS Element 0104 - WRIT Peer Review

Major Contributors: PNL: (see below)

During FY-1980, two review committees will be established to provide peer review and monitor the programmatic direction of WRIT.

An internal PNL peer review committee will meet annually. It will then meet prior to the ONWI mid-year review of WRIT to evaluate the program's progress and the need for program redirection. The following composition of the internal peer review committee is planned:

J. R. Burnham	Staff Scientist in the Energy Systems Department;
R. Burns	Consultant to DOE, formerly in Chemical Technology Department;
G. W. Dawson	Associate Manager of the Water and Land Resources Department;
H. Harty	Staff Scientist in the Engineering Physics Department;
I. L. Levy	Senior Staff Scientist, Materials Department;
H. B. Parker	Senior Staff Scientist in the Director's Office;
A. M. Platt	Manager of the Nuclear Waste Technology Programs Office.

The external peer review committee will meet annually to review overall WRIT progress and direction. The committee will also be invited to attend WRIT workshops covering special technical topics to review technical progress in more detail. It is presently planned that ONWI would directly fund this external committee and have final say on members and timing of the annual review.

TASK 2 WASTE PACKAGE INTERACTIONS - NUCLIDE RELEASE STUDIES

The objective of this task is to measure and understand radionuclide release rates for waste forms and waste package systems anticipated for geologic isolation. Waste package interactions are created by solutions migrating to and then from nuclear wastes placed in a geologic repository.

Two major sets of possible waste package/solution conditions may exist that require an understanding of how the waste package will behave. The first case assumes that a breach has occurred which short-circuits the multiple barriers protecting the waste form. Thus, a bare waste form is in contact with a solution system that allows minimal interaction with the barriers placed in the repository for sorption or water exclusion properties.

The second condition is concerned with a slow permeation of solution through the waste package barriers, which may eventually reach the waste form. In this condition, interactions between the waste form, solution, and waste package barriers are most important. More complex studies addressing these interactions must be addresssed in the second condition.

The input needed to study the first breach condition is a description of the properties of the solution that contacts the waste form. This solution definition will be determined via input from AEGIS and ONWI activities, and by studying solution/rock interactions as described in Task 4 (Solution Chemistry). The resulting solution will then be used in waste form/solution leaching tests to determine the rates, types, and characteristics of radionuclide release, along with surface/structural or bulk changes in the waste form. The output of tests addressing this first breach condition are as follows:

1. Radionuclide release rates and types are placed into a data bank and are made available for those performing safety assessments (AEGIS).
2. Radionuclide characteristics, mainly valence state and chemical species, are used to interpret both the leaching tests and sorption tests -- as the solutions generated by the waste form/solution tests are then used in the natural media/sorption studies described in Task 3. This completes the path from the waste form to the rock media outside the temperature and radiation zones of the repository. This information is also input into Task 5 (Predictive Model Development) to assist in model interpretation and formulation.
3. Surface and structural analyses of the waste form, coupled with the above information, will assist in mechanistic interpretation (and prediction) of the release process to be made. Thus, the information feeds directly to Task 5, the work element pertaining to leach model development, which will predict radionuclide source terms.

At this point, work has progressed on items (1) and (3) above, using spent fuel, waste glass, and TRU waste forms where the release dependencies on generic solution composition, time, temperature, and solution flow rate are being investigated. In the future, other waste forms being developed (such as synrock, supercalcine, etc.) will be incorporated if they continue to be viable alternatives after current DOE studies reach conclusions.

These tests must continue through points (1), (2) and (3) (more extensively) to allow their full potential to be attained. Future tests on site-specific solutions will be more limited in scope due to the knowledge gained from the generic studies.

As stated above, the second major condition is concerned with a slow permeation of solution through the various barrier systems, which may reach the waste form itself. Here, barrier/solution/waste form interactions are maximized. The solution reaching the waste form is likely to be different from the previously discussed case. The solution chemistry will be influenced by the components of the waste package system (waste form, canister, engineered barrier, backfill) with respect to ionic strengh, pH, and Eh. The effects on radionuclide solubilities, as well as corrosion properties on the canister and waste form, may be different from those in the first condition.

The experimental program in this area is just beginning. Initial experiments will study the effects of a metal canister, rock media, and ground water on radionuclide release under a range of possible repository environments. More advanced tests will add engineered barriers, as they are developed and selected by other programs, and intact rock cores. The effects of scaleup will also be addressed by using large autoclave equipment placed within hot-cells to simulate near field environments.

These tests will be run on a more limited basis than those described for the first condition (which will provide a foundation for the more complex tests in the second condition) as the reactions are expected to be more complex and require much greater care and analytical expense to do a thorough job. In addition to the points discussed for the first condition, surface and bulk examination will have to be performed on the rock, barriers, and canister materials as well.

Solutions generated by these tests will again be used by Task 3 to study their sorption properties. A nuclide release model will be constructed and refined, in collaboration with Task 5, based upon the solution chemistry, surface and bulk properties resulting from the waste package interactions tests.

It is expected that in FY-1980 efforts will be expended in consulting with the Office of Nuclear Waste Isolation (ONWI) and in detailed review of the Earth Sciences Technical Plan (ESTP) on these matters. There will be a cooperative waste package systems test with Sandia Laboratories. Task 2 will also maintain an interface with other groups interested in large-scale and/or insitu testing of waste package systems.

WBS Element 0201 - Technical Coordination

Major Contributors: D. J. Bradley and G. L. McVay.

This work element will provide the overview and technical guidance to the other subtasks, including experimental design assistance and coordination of Task 2 efforts, to preclude overlap with other similar studies. Also, this effort will coordinate topical reports on Task 2 technical work.

WBS Element 0202 - Evaluation of Experimental Leaching and Nuclide Release Methodology

Major Contributors: PNL: D. J. Bradley, G. L. McVay, and Y. B. Katayama.

An assessment will be made to determine any inherent biases or dependencies among the various WRIT leach tests in use. A critical assessment will be performed to document the strengths, weaknesses and applicability of the various WRIT leaching methods to probable repository environments, including the waste form/waste package interface. A major effort of this subtask will be to evaluate the scaleup made from short-term laboratory leaching and release experiments on small-scale waste forms to real-world conditions.

In addition, this documentation of WRIT leaching and release methodology will be submitted via ONWI to independent certification bodies, such as the Materials Characterization Center and the National Bureau of Standards, for formal comment.

WBS Element 0203 - Waste - Solution Interactions

Major Contributors: PNL: G. L. McVay, Y. B. Katayama, C. O. Harvey, and
D. J. Bradley.
ANL: H. Diamond and A. Friedman.

The waste form itself constitutes the innermost barrier of the waste isolation system. Consequently, the behavior of the ground-water/waste form system in the event of failure of the other barriers must be understood. Being able to understand this relatively simple system will provide a baseline for interpreting the complex system tests that will be carried out in WBS 0204. This subtask is concerned with performing tests on spent fuel and high-level waste glass to provide the required nuclide release fluxes and understanding of the leaching process through solution speciation studies and surface analysis under WBS 0206. In the future, other waste forms may be studied.

This effort is a continuation of IAEA and static leach testing previously begun on spent fuel, and cold and actinide doped glass. The spent fuel tests are coming to completion. A test will be continued to determine the effect of anoxic leach solutions on the release rate of actinides from glass, since anoxic conditions are likely in a repository. The latter test will be performed at Argonne National Laboratory (ANL).

The IAEA tests, which have been used internationally, were the first started to gain information on the effects of solution chemistry on the release rate. The static leach testing is being used to study release rates for the condition of low flow of solution past the waste form. This test will yield information on the effect of dissolved species and possible precipitation/structure alteration reactions on release rates when evaluated with data from continuous flow tests. The continuous flow test has concluded at Lawrence Livermore Laboratory, and the effort in this type of test method has been expanded to include rock media (see WBS 0204).

In addition to static and IAEA tests, autoclave tests on spent fuel and glass will be run to determine the effect of waste solution interactions on nuclide release, simulating conditions when the repository is at elevated temperatures. In addition, for many matrix-related processes on solids, higher temperatures simulate prolonged time periods. The kinetic data obtained under autoclave conditions may enable the extrapolation to long-term, low-temperature effects. Solubility of the leached radionuclides will be, in part, determined by tests using autoclaves.

The waste-fluid interaction studies tests will be made with three different levels of radioisotope activity:

1. nonradioactive
2. doped with special isotopes, such as the actinides
3. fully radioactive.

The purpose of this is to maximize the data and hold costs within reason.

In summary, these studies will provide the functional relationships between element release and laboratory time, temperature, solution composition, and solution flow rate.

WBS Element 0204 - Waste Package Interactions/Applications Studies

Major Contributors: PNL: J. W. Shade, J. H. Westsik, Jr., Y. B. Katayama,
G. L. McVay, and D. J. Bradley.
LLL: D. Coles and H. Weed.

In addition to understanding waste solution interactions, it is of great importance to test the behavior of the waste form (spent fuel, HLW glass, etc.), ground water, canister, backfill, engineered barrier, and host rock components. This integrated test more accurately describes the real repository, and we must gain some understanding of the effect of this complex system on the degradation of the waste form, release of radioisotopes and their interactions with the immediate surroundings, the very near-field zone. This understanding is necessary to develop confidence in our safety assessment and nuclide migration predictions. Nuclide release in this case is a combination of leaching and sorption/desorption interactions complicated by recrystallization and precipitation reactions and mass transport considerations.

It must be emphasized that detailed solid state and solution analyses must be incorporated into these studies to gain knowledge of the mechanisms of release. In addition to isotope release concentrations, valence state and nuclide solution species experiments need to be performed. Solid state analyses should include detailed mineralogic studies to identify alteration products, such as recrystallized minerals. This level of analysis applies to all tests under WBS 0204.

Studies in this area will first combine the waste form + canister + host rock + equilibrated ground water using as much site-specific detail and realistic repository conditions as possible. Studies involving spent fuel must be conducted in a hot cell and will be very expensive; moreover, a reference scheme for packaging spent fuel has not been selected. Consequently, initial studies will involve nonradioative, simulated high-level waste glass; spent fuel studies will begin once an appropriate system is defined. The effects of engineered barriers and backfill will be assessed by adding them to this system as they are developed.

These tests will proceed from laboratory scale (inches) to intermediate scale (feet) to take advantage of gaining as much information as possible from tests that are easier to fabricate and relatively inexpensive (laboratory scale). The test will also provide enough sample solution, waste form, and rock media for the solid state solution and sorption/desorption studies. The effects of scaleup (intermediate scale) will also be addressed. Tests will be replicated to ascertain the reproducibility of the intermediate results.

The intermediate-scale tests will contribute to activities to assess whether it is meaningful and valid to use laboratory-scale data to model real-world potential near-field interactions. This assessment of application of laboratory methods to prediction of real-scale in situ near-field geochemical interactions and subsequent nuclide release will be a primary goal of WBS 0204.

It must be pointed out that sorption/desorption analyses are an intimate part of these systematic studies. The combination of waste-form leaching, the mineralogic alteration of the waste package system, and sorption reactions control the nuclide source term from the very near field. As outlined in WRIT Tasks 3 and 5, the leachate and this source term are used as input for the far-field studies, thus making the connection from the waste form to far-field migration.

WBS Element 0205 - Transuranic Waste Form Release Studies

Major Contributors: PNL: D. J. Bradley.
BNL: P. Colombo and R. Neilson.

Transuranic (TRU) waste constitutes the largest quantity of waste to be isolated from the biosphere. Current repository planning includes possible co-storage of high-level wastes and TRU waste. Therefore, the release behavior of transuranic waste forms under storage conditions must be known. Leach tests will continue paralleling those at PNL on concrete, ureaformaldehyde, bitumen, and plastic polymers using the IAEA and static leach tests. Work will be started on a glass TRU waste form and continuous flow leach tests will be initiated.

WBS Element 0206 - Surface and Solid State Studies

Major Contributors: PNL: L. R. Pederson, G. L. McVay, J. W. Shade, D. Rai,
and M. T. Thomas.
ANL: D. Karim and D. Lam.

The primary objective in this work element is to correlate solid-state changes in engineered waste form, barriers, and rocks with leachate and groundwater analyses in the various experiments undertaken in Tasks 2, 3, and 4. The work at PNL will focus mainly on physical structure evaluation of leached surfaces and on kinetic theory evaluation of the leaching processes. The ANL effort will focus on generating and understanding the complex spectral information needed on actinide and rare-earth elements in waste forms. Between PNL and ANL, an effort will also be started to determine the nuclide species in solution to include valence state and chemical form. These studies will primarily involve application of auger electron spectroscopy, elemental profiling techniques, electron spectroscopy for chemical analysis (ESCA), and secondary ion mass spectroscopy (SIMS) to evaluate the physical and chemical changes occurring at the surface of the waste form as leaching occurs.

Efforts will also begin in FY-1980 to study surface and solid-state effects on the canister, rock, and barrier material involved with the waste-package interaction tests.

The importance of chemical bonding/thermodynamic theory in the leaching processes will be evaluated in conjunction with the findings from the other subtasks. A strong interface exists between this subtask, Task 4, Solution Chemistry, and Task 5, Modeling Studies. Information gleaned from these mechanistic studies will form a base for supporting and formulating the release models developed in Task 5, initially with empirical data and later with transport theory considerations.

Mechanistic studies in this subtask are clearly necessary to achieve a general understanding of leaching processes. The experimental objective here is to perform laboratory studies needed to correlate solid state changes with leachate and ground-water analysis to known thermodynamic principles. It is expected that two major questions will be resolved:

- Can predictive use of relatively short duration leaching experiments be justified for a specific set of conditions and long time frames?
- Can a general understanding of leaching processes based on physicochemical principles be developed?

WBS Element 0207 - Spent Fuel Special Studies

Major Contributors: Y. B. Katayama, J. L. Ryan, and R. Wang.

The objective of the spent fuel special studies subtask is to gain understanding of the effects of degree of oxidation and chemical distribution on nuclide release from spent fuel. An oxidation study will precede anoxic tests in order to establish necessary analytical methods for the study of oxidation phenomena, using experiments where the phenomena are expected to be easily observable. Once established, the methods will be applied to anoxic tests. Initial efforts will also work with crystalline UO_2 to maximize information on the behavior of the uranium matrix without the very high radiation levels associated with spent fuel.

The oxidation study includes two tasks: 1) measure the radionuclide release rates after oxidation of the spent fuels in various ground-water solutions, and 2) identify the release mechanism at single crystal UO_2 surfaces. The first task will determine the congruent dissolution period and release rate for spent fuels oxidized in solutions. The increase of radionuclide release rate, which may be due to oxidation of the UO_2 matrix to $UO_3 \ XH_2O$, will be related to the amount of dissolved oxygen content in water. The second task will compare the oxidation and leaching kinetics at elevated temperatures for single crystal UO_2 surfaces and other UO_{2+x} surfaces. The composition and microstructure of the uranium oxide and uranium oxide-hydrate films will be characterized and correlated to the leaching kinetics. A high activation energy oxidation path will be sought for stabilization of the UO_2 surfaces for the case of oxygen present in ground-water solutions.

Predicting release from spent LWR fuels requires an assumption of the distribution of radionuclides at the leachate-spent fuel interface. This radionuclide distribution is heterogeneous and is dependent on burnup and irradiation temperatures. There is a need to know the leach rate variation with degree of inhomogeneity of the radionuclides. The first phase will involve the measurement of fission product chemistry distribution in spent fuel with known in-reactor parameters. This distribution, based on temperature and burnup, will be compared to calculations based on thermodynamic and mass transport predictions. The second phase will involve measurement of leach rates for spent fuel samples with known chemical distribution and repeat of the chemical distribution analysis to detect the changes in surface chemistry.

TASK 3 - GEOLOGIC MEDIA - NUCLIDE INTERACTIONS STUDIES

This task is designed to develop knowledge on radionuclide interactions with natural geologic media. Work under way in this task is described in the following WBS elements, and includes: 1) the evaluation of different test methods used to study adsorption and desorption, 2) performance of laboratory experiments to facilitate development of waste/rock interactions models, 3) the study of radionuclide adsorption and desorption mechanisms, and 4) sitespecific sorption/desorption data generation (licensing support). The fourth effort is in support of the AEGIS program, and is related to WRIT WBS Element 0103.

WBS Element 0301 - Technical Coordination

Major Contributors: PNL: J. F. Relyea.

This work element is to provide the overview and technical guidance to Task 3. This effort will coordinate topical reports on Task 3 and any ONWI/DOE requests for technical assistance on related topics.

WBS Element 0302 - Evaluation of Experimental Methodology

Major Contributors: PNL: J. F. Relyea, R. J. Serne, D. Rai,
R. G. Strickert, and W. L. Kuhn.
Subcontractors: LASL, LLL, RHO, ANL, and ORNL.

Several unresolved issues exist in the area of sorption/desorption data collection. Presently, investigators from various laboratories determine sorption Kds and/or migration rates for nuclides utilizing numerous experimental techniques. Unfortunately, it appears that the resultant data are dependent not only on the type of solution and geological material utilized, but also on the experimental methods used. A systematic effort will be expended in this subtask to resolve the apparent method dependencies, to assess which method or methods yield the most accurate results, or to determine what conversions can be made to compare the results of different methods. It is imperative that the various experimental methods be studied and, if possible, consensus be formed as to which method or methods should be proposed as a standard measurement technique. Such standardization of measurement techniques may be critical to providing credibility to the data that will be used in site qualification and licensing procedures. The process of producing defensible data and test methods involves three steps: verification tests by involved research organizations; documentation of recommended test methodologies; and certification of test methodologies by an independent certification body, presently planned to include the Materials Characterization Center (MCC) and possibly the National Bureau of Standards.

In this subtask, various laboratory methodologies will be evaluated using a wide range of geologic materials and nuclide-spiked ground waters. Each method will be evaluated for its ease of utilization, time and cost expenditures, precision, and limitations. Disagreements and range of applicability for observed results will be investigated through further experimentation on the independent variables (geologic media, waste form, ground-water composition, pH, Eh, and temperature).

030201 Comparison of batch method with columns packed with crushed material and intact core column flow through methods. Parameters to be varied are residence time (batch), flow rate (columns), and surface area. ANL (limestone and basalt), PNL (sandstones), LASL (argillite and granite), and ORNL (clays).

030202 Effects of solid to liquid ratio on sorption. LASL (argillite and granite).

030203 Effects of temperature on Kd values and solution composition. PNL, LASL.

030204 Assessment of solid solution separation techniques, centrifugation, and filtration (LASL, LLL, PNL), and colloid filtration by porous media (GIT).

030205 Generation and certification of proposed "standard" method(s). PNL.

Documentaton of verified test methodolgies completed in WBS 0301 will be submitted to an independent certification body, such as the Materials Characterization Center (MCC) or National Bureau of Standards (NBS), for certification. A purpose of this task is to effectively coordinate WRIT's verification studies with the MCC, the Materials Review Board (MRB), and the Independent Certification Laboratory (ICL). Work within this task includes not only the submission of documentation (such as test results, data bases, and recommended methodologies) to the body, but also participation in the resolution of data and/or analytical discrepancies.

WBS Element 0303 - Mechanism Studies

Major Contributors: PNL: D. Rai, R. G. Strickert, D. A. Moore, and
R. W. Fulton.
Subcontractors; ORNL, RHO, GIT, LBL, LASL, LLL, and ANL.

As noted from previous work on methodology evaluation, WBS 0302, the determination of migration of radionuclides often shows significant variation across methods. Resolution of the discrepancies will not give a general understanding of the mechanisms controlling the migration rates of radionuclides. Further, WBS 0302 and 0304 are empirical and geologic media/solution specific. Interpolations within ranges of parameters actually measured are possible; however, to increase the defensibility of interpolations, understanding of the operative sorption/desorption mechanisms is needed.

Mechanistic studies will be directed toward a predictive capability on radionuclide concentrations in solution. Near the repository, the concentration of the radioactive elements in solution will be governed by the nature of the precipitated solid phases. In other locations and circumstances, where solid phases are absent, the elemental concentrations will mainly be governed by exchange and surface phenomena occurring in the geomedia. The solid phases of the radionuclide, the solution, and the adsorbed ions are in a dynamic equilibrium with each other. Therefore, the studies conducted will be directed toward a description of the system. The effects of the following variables on the interaction with rock minerals will be investigated: pH, Eh, complexing ions, competing ions, oxidation states of radionuclides, concentration of the elements, and structural, mineralogical, and chemical composition of the geologic materials. These investigations will result in adsorption isotherms of various radionuclides in different geologic environments. When this information is combined with the minerals and their solubilities, an understanding of the concentrations of radionuclides expected in different geologic media can hopefully be developed.

030301 Ion exchange is the most predominant surface sorption mechanisms. Effects of pH on the exchange capacity and competition from other ions in solution are needed for modeling this process at concentrations below the solubility limit. Sorption isotherms (loading) for many nuclide-solid-solution systems will be studied. The surfaces will be characterized for surface area, cation exchange capacities, and mineralogy.

ORNL 1) Single mineral-nuclide systems using oxides-hydrous oxides of Al(III), Fe(III), and Si(IV). Nuclides: Cs, Sr, Eu, I, Tc, and U.
2) Mixtures of clay plus oxide (with Sr initially) for comparison with predicted Kd values from (1) above.

RHO Effects of tracer concentrations of Cs, Sr, Np, and Se (loading) on Hanford basalts, NTS granites, and their secondary mineral weathering products.

LBL Loading, pH, and salt concentration effects on sorption of Cs and U on a smectite, and SiO_2 and Cs on albite and clinoptilolite.

LASL Loading effects on sorption of Sr, Cs, Ba, Ce, Eu, Tc, U, Pu, and Am on NTS argillite and granite.

PNL Literature data indicate that Cm sorption by minerals may be controlled by precipitation reactions on surfaces. Studies of Cm behavior (as a function of Cm concentration), pH, mineral type, and ionic strength will be conducted to determine ranges in which ion exchange and surface precipitation mechanisms dominate.

030302 Redox reactions between solids and nuclides.

RHO Anoxic sorption of Np, Se, Tc, and I on NTS granite and basalt.

LASL Sorption of Sr, Cs, Ba, and U in mixtures of calcite-dolomitesiderite in an anoxic environment. Sorption of Sr, Cs, Ba, Ce, Eu, Tc, U, Pu, and Am on argillite and granite in anoxic environment with CO_2 and with CO_2 removed. Sorption of Pu in fractured granite core and crushed granite and argillite in anoxic atmosphere (Pu, Am, Tc, and with crushed material in column).

PNL Sorption of the different oxidation states of Pu by rock-forming minerals will be investigated by batch and column methods. Parameters studied will be: Eh, pH, mineral type and composition, Pu concentration, and oxidation state.

030303 Nuclide sorption and rock dissolution kinetics. RHO. Cs, Sr, Np, Se, and I on secondary minerals from basalt and granite, and Np, Se, Tc, and I in anoxic environment on basalt and granite.

030304 Particulate transport (GIT). Determination of particle mobility as a function of particle size and physical properties of the media (permeability, porosity, pore size distribution, effective flow porosity, etc.). Determination of particle mobility as affected by solution and solid chemistry (pH, CEC, SAR, and ionic strength).

WBS Element 0304 - Site-Specific Sorption/Desorption Data Generation

Major Contributors: PNL: J. F. Relyea.

The objective of this subtask is to perform site-specific Kd experiments on geologic materials and ground waters supplied to WRIT by AEGIS and ONWI. These analyses will be performed using ONWI or AEGIS determined conditions that simulate the in-situ environment. The manpower and funding estimated for this work element are based on the analyses of six samples, since it is unknown at this time the number of site-specific samples that will be available. In addition, control of funds and responsibility for obtaining funds resides with AEGIS.

This work element is related to WBS Element 0103. Resource allocations to this task will be obtained via AEGIS and will be used to analyze only those that involve the analysis of site-specific samples requested. Data that involve existing information will be provided to AEGIS on a work order basis only.

WBS Element 0305 - Methodology Application Studies

Major Contributors: PNL: J. F. Relyea, D. Rai, and R. G. Strickert.
Subcontractors: LLL, ANL, and LASL.

Defensible, empirical data to estimate the long-term fate of nuclides in geologic environments are urgently needed. Present data collection methods rely on laboratory experiments, which are characterized by short times and small sample sizes. The uncertainty involved in scaling these results to the million-year time frame and to path lengths of many kilometers has not been determined. In many instances, the scaleup is tacitly assumed to be valid without proof. However, it will be necessary to demonstrate the validity of short-term data measurements used for long-term analyses, if the safety assessments which utilize these data are to be defensible in the licensing process.

A major effort of the verification subtask will be to evaluate the scaleup made from short-term laboratory results. Using models developed in Task 5, the short-term results will be compared with theoretical concepts, such as weathering, ore deposition geochemistry, mineral stability, and thermodynamic

Eh-pH diagrams. Results from the LASL Natural Reactor Study, uranium ore bodies or literature data on migration at shallow-land burial sites will be studied to see if WRIT data are verified.

Another effort, laboratory verification, utilizing intact and fracture core and/or rock blocks under flow-through conditions similar to repository far-field conditions, will be performed. Results will be compared with shorter term batch, column work on disaggregated rock and small intact core migration experiments. Experimentation with actual waste-form leachate will also be compared with synthetic tracer solutions. ONWI will also be consulted on in-situ testing or field migration tests. Past WISAP subcontractor feasibility studies and technical proposals have been forwarded to ONWI.

30501 Development of large core techniques for application to: 1) porous media flow, 2) flow in fractured media, and 3) in situ testing. ANL.

30502 Application of column methodology to fracture flow.

ANL Effects of diffusion controlled sorption kinetics on flow through artificial planar fractures (packed and unpacked) compared with chromatographic (Kd) theory.

LASL Sorption behavior in high pressure flow through intact cores with natural fissures. Microautoradiography of sectioned cores for identification of nuclide sorbing minerals.

30503 Comparison of nuclide migration in waste form leachate versus synthetic leachate solutions. ANL, PNL.

30504 Experimental verification of MINEQL versus pH, ionic strength, and loading. LBL.

30505 Comparison of WRIT data to OKLO, U ore, shallow land burial, and available field literature. PNL.

WBS Element 0306 - Generation of Special Isotopes

Major Contributors: PNL: R. G. Strickert.
Subcontractors: ANL.

To examine the migration of actinide elements in rock and soil strata, complicated and expensive wet chemical extraction procedures are usually needed to detect the alpha-emitting isotopes. It is possible to generate x-ray and gamma-emitting isotopes of several of these actinides by cyclotron activation. Analyzing gamma-emitters is much easier than analyzing alpha-emitters, so the use of special isotopes has greatly facilitated the Task 4 experimental program. In addition, the use of these isotopes allows the behavior of more than one element to be observed in a single experiment, thus saving time and eliminating the uncertainties of duplicating exact conditions across experiments. Because of these considerations, the emphasis of this subtask is to both identify the X-ray and gamma-emitting isotopes needed by the other subtasks and ensure their timely production.

TASK 4 - NUCLIDE SOLUTION CHEMISTRY STUDIES

Among factors that influence radionuclide behavior in the geologic environment, the solution chemistry, as it affects solid phases and solution species of the radionuclides, is one of the most important. Through their precipitation and dissolution, solid phases cause changes in solution concentration which, in turn, affect the distribution of adsorbed ions. Discrete solid phases of radionuclides may be present within the repository because of the high inventory of radionuclides. In the absence of discrete solid phases, the nuclide may be distributed throughout the rock matrix and sorption reactions may control solution concentrations. However, if the concentration of the element in solution is such that a solid phase can precipitate, knowledge of this solid phase and solution ions would help in predicting the solution concentrations available for transport. Granted the importance of the total solution concentration of the element, the nature of the predominant solution species are important since they affect: 1) charge dependent ion exchange, 2) surface sorption, 3) movement through the rock and sediment matrices because of their physical size, and 4) biological uptake.

Information on possible solid phases and solution species of elements that may be present in different environments is sparse, especially for the elements with unstable isotopes and those not naturally occurring (e.g., Np, Pu, Cm, Am). In order to bridge this gap, available thermodynamic data have been reviewed under the WISAP program to construct Eh-pH diagrams that predict stable phases and solution species of Am, Sb, Ce, Cs, Co, Cm, Eu, I, Np, Pu, Pm, Ra, Ru, Sr, Tc, U, and Zr. Unfortunately for some of the elements, the reliability of thermodynamic predictions is limited by: a) the inaccuracy of the data, b) nonavailability of the data for all the solid phases and solution species that may form in a geomedia, and c) the disregard of kinetic effects. More reliable predictions can be made with this approach only as the necessary laboratory data become available.

Needed studies for understanding solution chemistry of important radionuclides are outlined below. These studies will concentrate on elements (Am, Cm, Cs, I, Np, Ni, Nb, Pd, Pu, Ra, Se, Sn, Tc, Th, U, and Zr) that are shown to have radioisotopes with long half-lives and that are liable to be present in relatively large concentrations in solidifed nuclear wastes to be isolated in deep geologic repositories.

WBS Element 0401 - Technical Coordination

Major Contributors: D. Rai.

This work element is to provide the overview and technical guidance to Task 4. This effort will coordinate topical reports on Task 4 and any ONWI/DOE requests for technical assistance on related topics.

WBS Element 0402 - Ground-water Chemistry

Major Contributors: PNL: D. Rai and J. W. Shade.
Subcontractor: LBL.

Literature and selected laboratory experiments will be reviewed and performed, respectively, to delineate long-term mineral/ground-water reactions to ensure that leaching and sorption experiments use realistic solutions and mineral assemblages. This work element will provide a rationale for extrapolating short-term mobility data to longer time periods. The mineral systems, which will be selected to perform laboratory experiments, will be chosen on the following bases:

1. They should be the dominant mineral-water reaction system leading to wall rock alteration in a given repository rock type (i.e., Hanford basalt, Nevada Test Site quartz monzonite (granite), welded tuff, argillite, etc.).
2. Experimental data or reliable extrapolations of a specific mineral's solubility, alteration, and formation germane to proposed repository temperatures are lacking.
3. Thermodynamic data on important end member mineral reactants and products are lacking.

Fortunately, for the repository rock types currently receiving the most attention, these data and criteria, for the most part, are available in the economic geology and geothermal literature; thus, laboratory efforts should be manageable. For example, using the system potash feldspar-kaolinite-quartz-H_2O (representing granite alteration) and albite-chlorite-quartz-H_2O, or plagioclase-montmorillonite-quartz-H_2O (representing basalt alteration), it would be possible to design experiments with buffered, known solute activities at P and T. In an actual repository, the ground-water composition will be controlled by rock/ground-water interactions; specifically, mineral/ground-water interactions. Because the volume of the rock/ground-water system is much larger than the waste-canister system in the event of an accident, any nuclides leached from the waste-canister system would almost immediately be under control of the rock-ground water system. Consequently, resultant mobility, adsorption, new mineral precipitation, fracture filling, replacement reactions, and related processes will be dominated by mineral/ground-water equilibria.

The behavior of the waste package in appropriate mineral/ground-water systems could be more readily quantified than it could in the more chemically complex systems using the whole rock. Moreover, because properly characterized mineral reactions are the dominant alteration reactions in the rock, the resulting data can be compared with the whole rock data to provide a more quantitative interpretation of whole rock waste package/geologic media tests. Both the mineral/waste package and whole-rock/waste package results can then be compared with observed alteration in appropriate rock types from the geothermal data base to address transport, corrosion, and precipitation questions. These studies will also provide a foundation from which to investigate the efficiency of radionuclide mobility retardants and overpack materials, such as hydrous oxides, zeolites, serpentine, and clays.

In summary, increased emphasis on mineral/ground-water reactions will provide a more efficient and defensible study than total reliance on whole-rock/waste interaction data, and will also provide data which will be useful in assessing and modifying existing thermodynamic models.

WBS Element 0403 - Nuclide Solution Species

Major Contributors: PNL: D. Rai, J. Swanson, and R. J. Serne.
Subcontractor: ORNL.

It is important to understand the distribution of solution species because they contribute to total concentration of the element in solution, affect sorption by geologic materials, and affect the solubility of solid phases. However, their amount is dependent upon the nature and amount of the ligands, relative formation constants of various complex ions and the other solution parameters such as Eh and pH.

Partial data are available on the formation constants of most metal ions expected in the radioactive wastes, with the common ligands (HCO_3, OH, Cl, SO_4) expected in geomedia. To check the accuracy of these formation constants, and to fill in all the gaps, would require long times and large funds. Instead the following approach will be taken. The formation constants of radioelement species will be determined for those that are most likely to be dominant and for which thermodynamic data are suspect. Additionally, methods will be selected or developed to determine the oxidation states of multivalent elements in solutions, because the oxidation-reduction potential (Eh) of the solution affects the oxidation state which, in turn, affects the solution species. The first effort will be to evaluate what data are missing and coordinate with independently funded programs at LBL (Edelstein and Bucher) and USGS (Cleveland).

WBS Element 0404 - Solubility of Selected Compounds

Major Contributors: D. Rai and Y. B. Katayama.

Many of the actinides and lanthanide fission products that are important in safety assessment calculations, appear to form solid phases under geologic conditions (natural or basic pH) having very low solubilities. These solid phases, if present, would control the upper concentration of the element in the ground water and might control the leach rate from proposed waste forms.

Knowledge of the thermodynamic solubility constants (K_{sp}) for important mineral compounds of these nuclides would facilitate long-term predictions of nuclide migration potential. Part of this work element include a critical assessment of literature data on K_{sp} values and the effects of geochemical parameters, such as pH, Eh, and ligand concentrations on nuclide solubilities. Experimental studies will be performed to collect missing data and/or verify critical data at probable repository conditions.

TASK 5 - PREDICTIVE MODEL DEVELOPMENT

The objective of this task is to develop models predicting leaching, solubility, sorption, and waste-package release processes in the repository and surrounding media. The scope will ultimately include accumulation and management of data developed in other tasks, reduction of data to empirical models, developing predictive mechanistic models and testing them against the data, and constructing models of radionuclide release from a repository to the "far field": the "source term" for geotransport calculations. These activities can be separated from the associated experimental tasks and are collected in this task in order to provide a strong, central contact with the AEGIS program and other related programs, such as WIPAP (Waste Isolation Performance Assessment Program) and engineered barrier programs, which will exchange data and models with WRIT. This task will coordinate closely with the experimental tasks both to assure timely accumulation and correct interpretation of data, and to propose mechanisms for explanation of data and for construction of predictive models.

Activities in FY-1980 will include primarily establishing a WRIT sorption data bank, continuing sorption data reduction using adaptive learning methods, evaluating existing computer codes, and proposing simple source term models for use by AEGIS.

WBS Element 0501 - Technical Coordination

Major Contributor: W. L. Kuhn.

The objective of this work element is to coordinate and guide technical activities and communications in Task 5. The scope includes coordinating topical reports, responding to ONWI or DOE requests for technical assistance or consultation for related work (e.g., WIPAP), and studying the literature sufficiently to assure that available technology is utilized and appropriate contacts are maintained with related programs.

The current scope of WRIT excludes testing models by conducting release tests at large scale and for long times, either in situ or in a large hot-cell engineering facility. Should DOE or ONWI intiate such tests, this work element will include coordination of WRIT personnel with test personnel in order to advise and recommend experiments testing the validity of WRIT models of leaching, sorption, and waste-package release. Recommendations will be available regarding choice and extent of experiments, facilities, and cost and schedule estimates based on experience in WBS 0204.

WBS Element 0502 - Generation and Management of Data Banks

Major Contributors: D. D. Hostetler, R. J. Serne, D. J. Bradley,
J. F. Relyea, and O. F. Hill (MCC).

The objective of this work element is to make the extensive data generated in experimental tasks available through a computer storage and retrieval system. Ultimately, leaching, sorption, solubility, and waste-package release data will be included; these will comprise tens of thousands of data, requiring computer storage to make either data reduction or data transfer feasible. Work is already under way on a sorption data bank; during FY-1980 it will be expanded and work will begin on a leaching data bank.

Initial emphasis will be on establishing data banks facilitating data transfer to AEGIS and for WRIT data reduction work (see WBS 0503), and data retrieval in response to DOE or ONWI requests or requests from related programs. Ultimately, data banks can be constructed to match national or international formats, as sponsor interest and resources dictate. Effort on this subtask will be interfaced with the MCC.

WBS Element 0503 - Empirical Model Development

Major Contributors: J. F. Relyea, R. J. Serne, R. D. Peters, and
D. J. Bradley.
Subcontractor: Adaptronics, Inc.

The objectives of this work element are to: a) construct empirical models serving to reduce data to a relatively few coefficients in equations "fitting" the data according to appropriate statistical criteria; b) make empirical models available to AEGIS, WIPAP, or related programs; and c) initiate geochemical criteria for ranking potential repository sites. The equations will be developed primarily by using the "adaptative learning networks" methods, for which Adaptronics, Inc., is expected to be a subcontractor. Empirical models will ultimately be developed for leach rates, sorption coefficients, and solubility constants; in FY-1980 emphasis will be on continued reduction of sorption data.

Empirical models will be cast into the form of relationships between functions (leach rates, sorption coefficients, solubilities) and parameters (geochemical, hydrologic) on which they depend, such that leaching, sorption, or solubility "subroutines" can be made available to AEGIS, WIPAP, etc., for geotransport safety assessment computations. The relationships are expected to identify by their form the most important parameters, thereby helping to guide WRIT sorption, leaching and release studies.

These models will also facilitate development of geochemical criteria for the ranking of potential repository sites by quantitatively relating geochemistry and geotransport.

As geochemical data are accumulated and reduced as part of this work element, preliminary criteria for ranking potential repository sites according to geochemistry will be proposed to ONWI. Criteria will be revised as new data and technical reviews warrant. It is anticipated that review of the criteria will help guide WRIT experimental studies.

WBS Element 0504 - Mechanistic Model Development

Major Contributors: W. L. Kuhn, G. L. McVay, D. Rai, R. G. Strickert,
J. F. Relyea, and R. D. Peters.
Subcontractor: LLL.

The objective of this work element is to develop credible models for leaching, sorption, and solubility, based on mechanisms acting over the duration of waste package release or geotransport, and to make the models available to AEGIS, WIPAP, or related programs. The scope will ultimately include: a) addressing mechanisms identified by Tasks 2, 3, and 4; b) formulating mathematic models describing the mechanisms; c) constructing computer codes which "solve" or "evaluate" the mathematical models to describe leach rates, sorption coefficient, or solubility in terms of geochemical/hydrologic parameters; d) testing computer codes against experimental data; and e) casting computer codes into the form of "subroutines" which can be used by AEGIS, WIPAP, etc. FY-1980 activites will be limited to assessing our understanding of mechanisms controlling leaching, sorption, and solubility, discussions with AEGIS and WISAP personnel to determine any constraints which current geotransport codes would place on the mathematical form of WRIT mechanistic models, and recommending priorities for investigation of mechanisms.

It is necessary that WRIT models ultimately be based on physicochemical phenomena in order to establish predictive capability. Waste/rock interactions are expected to involve many kinds of phenomena, such as:

- leaching of the waste form (chemistry, diffusion, kinetics, etc.)
- chemical effects of radiation
- corrosion
- ion exchange

- adsorption
- precipitation, coprecipitation, crystallization
- redox reactions
- formation of complexes in solution
- mineral replacement
- thermochemical phenomena
- steric phenomena
- diffusion
- colloid/particulate behavior.

As funding and technical priorities dictate, these or other phenomena will be studied and characterized as part of the experimental tasks. From these studies will come an understanding of controlling mechanisms, from which mathematical models will be developed in collaboration with experimental tasks as part of this work element. Together, the resulting models will quantitatively describe the role and efficacy of engineered barriers, as well as the behavior of released isotopes during geohydrologic transport away from waste packages and into a repository, and away from a repository and into the biosphere.

As part of the experimental tasks, experiments will be designed to discover or elucidate mechanisms controlling radionuclide release and transport. As mechanistic models are subsequently developed and tested against experimental data, possible changes in emphasis, method, or level of effort deemed to aid this work element will be recommended to the experimental tasks.

The development of predictive, mechanistic models is organized into three subtasks to reflect the requisite collaboration with the three experimental tasks.

050401 Waste Form Release Model

This work element comprises the construction of a computer subroutine predicting the release of radionuclides from the waste form (spent fuel, borosilicate glass) as a function of geochemical and hydrologic parameters (e.g., temperature, pH, Eh, identity of rock with which ground water equilibrates, water velocity, or others). The subroutine is to be used both for release calculations, where the ground water is presumed to breach other engineered barriers and contact the waste form directly, and as part of overall waste package release calculations (see WBS 0505).

Experiments conducted as part of Task 2 will be interpreted in that task to propose or verify mechanisms affecting the release from the waste form. Through this task, the mechanisms will be interpreted mathematically to develop quantitative, predictive models suitable for construction of a computer subroutine. The model will be tested against corresponding experimental data; based on the comparison, recommendations regarding waste form or waste package studies will be made to Task 2.

050402 Geomedia Sorption Model

This work element comprises the construction of a computer subroutine predicting the sorption of radionuclides on natural geomedia as a function of geochemical parameters. The subroutine is to be used both for "far field" geotransport calculations (e.g., by AEGIS or WIPAP), and for "source term" calculations (see WBS 0505).

Experiments conducted as part of Task 3 will be interpreted in that task to propose or verify mechanisms affecting the sorption of radionuclides on natural geomedia. Through this task, the mechanisms will be interpreted mathematically to develop quantitative, predictive models suitable for construction of a computer subroutine. The model will be tested against corresponding experimental data; based on the comparison, recommendations regarding sorption studies will be made to Task 3.

050403 Solution Equilibria Model

This work element comprises the construction of (or adoption of an existing) computer subroutine predicting or bounding the concentration of radionuclides and geochemical species that coexist in ground water during geotransport. The subroutine is to be used in either "near field" or "far field" calculations to determine the geochemical environment affecting waste form release (i.e., to provide some of the information needed for other subroutines) or to establish bounds on radionuclide concentrations that may occur during release or sorption/desorption processes (potentially nonequilibrium processes), and for "source term" calculations (see WBS 0505).

Computer subroutines already exist (e.g., at LLL) predicting species concentrations prevailing as various geochemical substances equilibrate in the presence of water. In collaboration with Task 4, existing computer codes will be assessed in terms of possible early application to radionuclide/geomedia equilibrium calculations. This includes assessing the adequacy of existing thermodynamic data and the probable additional data on radionuclides forthcoming from Task 4. Either existing codes will be adopted, or specialized codes of limited scope will be developed to meet the uses described above. As it evolves, the desired computer subroutine will be tested against data developed in Tasks 2, 3, and 4; based on the comparison, recommendations regarding equilibrium experiments will be made to these tasks.

WBS Element 0505 - Source Term Model

Major Contributors: W. L. Kuhn, R. D. Peters, and J. W. Shade.

The objective of this work element is to construct a "source-term" computer subroutine providng one of the boundary conditions (radionuclide mass flux or radionuclide concentration at the repository) required for "far field" geotransport calculations. The scope will utlimately include: a) combining models of waste form release, sorption, and solution equilibria with waste package descriptions (from other ONWI or DOE programs) and a description of the "near field" conditions in the repository (e.g., based on scenarios investigated by AEGIS) to predict the overall release to the "far field;" b) casting the combined models into the form of a computer subroutine conveniently attached to and used by "far field" geotransport codes; c) conducting parametric studies based on hypothesized mechanistic models to determine their potential importance to overall source-term calculations, and d) recommending experimental work deemed to optimize confidence in source-term calculations. FY-1980 activities will be limited to developing simple source term models utilizing available solubility limits, assessment of suitability of current experimental studies for incorporation into source-term models, and some initial parametric studies.

An important part of this work element is testing source-term models against data obtained in WBS 0204 (Waste Package Interactions), and as appropriate to aid design of waste package experiments using parametric studies based on the phenomena to be studied. As appropriate, models of engineered barrier behavior developed as part of other ONWI or DOE programs will be utilized in this work element.

In general, the "source term" will involve simultaneous fluid flow and heat and mass transfer, coupled with thermodynamic equilibria and chemical reaction and sorption/desorption kinetics. In light of the extreme complexity of the problem, the philosophy adopted here is to attack the problem step by step as new information warrants, striving to keep the model from being, at any given time, the weak link in overall repository safety assessment calculations.

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