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WASTE ISOLATION SAFETY ASSESSMENT PROGRAM
TASK 4
CONTRACTOR INFORMATION MEETING PROCEEDINGS

September 20-23, 1977

R. Jeff Serne
Chairman

BATTELLE MEMORIAL INSTITUTE • HUMAN AFFAIRS RESEARCH CENTERS
4000 N.E. 41st Street
SEATTLE, WASHINGTON 98105

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Prepared for the Office of Waste Isolation under its Contract
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PROCEEDINGS OF THE
TASK 4
CONTRACTOR INFORMATION MEETING
WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

Held at

Battelle Memorial Institute, Human Affairs Research Centers
4000 N. E. 41st Street Seattle, Washington 98105

September 20-23, 1977

R. Jeff Serne
Chairman

Prepared for the Office of Waste Isolation
under contract #W-7405-eng-26 with the U. S. Department of Energy

EDITOR'S NOTE: *Some of the papers and discussions included in this volume were edited by the Information/Publications Services staff of Battelle Memorial Institute, Human Affairs Research Centers. The views expressed remain the responsibility of the authors or participants where identified. Portions of the report have been reproduced directly from the best available copy.*

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We are grateful to Carol Watts and Vivian Hedrich of the Information/Publications Services staff, Battelle Memorial Institute, Human Affairs Research Centers, for the careful recording of notes on the discussions and workshops, for preparing summarizations of the transcripts, and for editing assistance.

We also wish to thank Pidge Eastland and Julie Swor 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.

We are grateful to the Office of Waste Isolation, a division of Union Carbide, for their monetary support and technical assistance. Three individuals in particular strongly supported and aided PNL's efforts:

Dr. Lester R. Dole, Dr. H. Clyde Claiborne and Dr. William C. McLain. Without their contribution and efforts this program may not have existed.

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

FOREWORD

This Contractor Information Meeting was part of the FY 77 efforts of Task 4 (originally Task 5) of the Waste Isolation Safety Assessment Program (WISAP). In Fy 78, tasks 1 and 2 have been combined and tasks 3 through 6 have been renumbered, so that the current FY 78 task equals FY 77, Task 1. Thus, in certain of the presentations to follow, the subject of these proceedings is referred to as Task 5. Materials prepared before October 1, 1977, and presented in this report, will use the old designation, Task 5.

The objectives of Task 4 Nuclide Transport Data are to:

1. Evaluate sorption-desorption measurement methods and recommend standard procedures.
2. Produce a generic data bank of nuclide-geologic interactions.
3. Perform statistical analysis and synthesis of these data.
4. Perform validation studies to compare short-term laboratory studies to long-term in situ behavior.
5. Develop a fundamental understanding of sorption-desorption processes.
6. Disseminate resulting information to the international technical community.

In order to accomplish these objectives a multiyear, laboratory-dominated, experimental program was initiated. The talents of approximately ten scientific groups at national labs and private institutions were mobilized in FY 77.

The purpose of the Contractor Information Meeting was to:

- Present an overview of OWI needs and schedules.
- Present an overview of WISAP goals and methodology.
- Reiterate Task 4 objectives.

- Present technical accomplishments of subcontractors during FY 77.
- 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 Waste Isolation, representatives from other waste disposal programs, and experts in the area of waste-geologic media interaction. An attendee list is appended to this document.

R. J. Serne, Manager
Waste-Geological Media Interactions Section,
Water and Land Resources Department,
Battelle Pacific Northwest Laboratories

Conference Chairman

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WASTE ISOLATION SAFETY ASSURANCE PROGRAM . TASK 4

CONTRACTOR INFORMATION MEETING

September 20 - 23, 1977 Battelle Seattle Research Center

MONDAY, SEPTEMBER 19

5:00- 9:00 pm	Registration
9:00-11:00 pm	Cocktail Reception/Preconference Mixer

TUESDAY, SEPTEMBER 20

INTRODUCTIONS

8:45-10:00 am	"An Overview of OWI's NWTS Program" L. R. Dole, OWI "An Overview of PNL's Waste Isolation Safety Assessment Program" H. C. Burkholder, PNL "An Overview of WISAP Task 4 - Nuclide Transport Data" R. J. Serne, PNL
10:00-10:15 am	Coffee Break
10:15-10:30 am	Questions and Answers

SUBCONTRACTOR TECHNICAL PROGRESS REPORTS

10:45- Noon	PNL, "Adsorption of Pu under Controlled pH and Eh by Soil Minerals" and "Identification of Pu Compounds and Their Solubility in Soils" D. Rai "Batch K_d Experiments with Common Minerals and Representative Groundwaters" J. F. Releya
Noon - 1:00 pm	Lunch

Subcontractor Technical Progress Reports (Continued)

1:00- 2:00 pm	Adaptronics, Inc., "Statistical Investigation of the Mechanics Controlling Radionuclide Sorption" A. N. Mucciardi
2:00- 3:00 pm	LBL, "Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks" J. Apps
3:00- 3:15 pm	Coffee Break
3:15- 4:30 pm	ANL, "Transport Properties of Nuclear Waste in Geologic Media" M. G. Seitz P. Rickert
4:30- 5:00 pm	Questions and Answers

WEDNESDAY, SEPTEMBER 21

8:00- 8:45 am	ORNL, "Systematic Study of Nuclide Absorption on Selected Geologic Media" R. E. Meyer
8:45- 9:45 am	LLL, "Studies of Radionuclide Availability and Migration at the Nevada Test Site" L. R. Ramspott
9:45-10:15 am	Questions and Answers
10:15-10:30 am	Coffee Break
10:30-11:30 am	ORNL, "Soil Chromatograph K_d Values" C. W. Francis M. Reeves
11:30- Noon	Rockwell-Hanford (RHO) - "The Kinetics and Reversibility of Radionuclide Sorption Reactions with Rocks" G. S. Barney
Noon - 1:00 pm	Lunch

1:00- 1:30 pm	Sandia, "Microstructural Interactions of Geologic Media with Waste Radionuclides" T. E. Hinkebein
1:30- 2:00 pm	LASL, "Laboratory Measurements of Radionuclide Distributions Between Selected Groundwaters and Geologic Media" B. Erdal
	ADJOURNMENT

THURSDAY, SEPTEMBER 22

INVITED PAPERS

8:30- 9:30 am	K. A. Apt., LASL, "Implications of Oklo to Waste Storage"
9:30-10:30 am	E. A. Jenne, USGS, "Trace Constituent Element Sorption by Sediments and Soils--Sites and Processes"
10:30-10:45 am	Coffee Break
10:45-11:00 am	Questions and Answers
11:00- Noon	L. Benninger, Yale University, "^{210}Pb Geochemical Studies"
Noon - 1:00 pm	Lunch

INFORMAL PARTICIPANT PRESENTATIONS

1:00- 3:00 pm	WIPP Program R. Dosch
	NRC Program D. Isherwood
	Savannah River Program I. W. Marine S. J. Fritz
	Louisiana State Program R. E. Ferrell, Jr.

	USGS Programs D. B. Stewart W. Wood
	Penn State Program D. Roy
	"ORNL Ecology Studies" E. Bondietti
3:00- 3:15 pm	Coffee Break

OPEN FLOOR DISCUSSION

3:15- 5:00 pm	R. J. Serne, Moderator

ADJOURNMENT

FRIDAY, SEPTEMBER 23

8:30-10:00 am	"Standardization and Site Specific Parameters and Methodology"
10:00-10:20 am	Coffee Break
10:20- Noon	"Standardization and Site Specific Parameters and Methodology"
Noon - 1:00 pm	Final Adjournment and Lunch
1:00- 4:00 pm	Optional Floor Discussion and Question and Answer Sessions

AN OVERVIEW

THE NATIONAL WASTE TERMINAL STORAGE (NWTS) PROGRAM

AN OVERVIEW OF THE OFFICE OF WASTE ISOLATION'S TECHNICAL SUPPORT PROJECTS TO SUPPORT THE DESIGN, CONSTRUCTION, AND LICENSING OF A DEEP GEOLOGICAL REPOSITORY FOR NUCLEAR WASTE

L. R. Dole
Office of Waste Isolation

INTRODUCTION

Because I am documenting the overview of the Office of Waste Isolation (OWI) Technical Support Program in May 1978, I will review the program as it now stands rather than reconstruct the situation of September 1977. I will present a brief outline of the program and discuss some of the background material on site selection. Also, I will cover some of the quality assurance program material that was originally scheduled for the September meeting. The following figures and attendant discussions constitute the narrative for the presentation.

Figure 1: Goals of Deep Geological Disposal (OWI-77-523R2)

The OWI approach to salt repositories emphasizes that the principal goal of geological disposal is the complete containment of radioactive waste from the biosphere using the inherent stable properties of the disposal horizon or formation. Therefore, most of the programs in the technical support area of OWI are aimed at designing and engineering a waste repository that does not insult the formation over geologic time.

Jeff Serne's nuclide migration program is relevant to quantifying goals 2 and 3, in regard to nuclide migration resulting from a repository breach. This project relates to the long-term safety assessment of a repository. By "long-term" in time and space, we mean that period of time after the decommissioning of a repository to a time from one to ten million years and over geologic distances of kilometers from the disposal horizon.

Figure 2: Schedule for Repository No. 1 (OWI-78-17)

This figure presents the repository schedule as it stood in January 1978. Although not now an accurate schedule, it illustrates that this engineering project has milestones and a critical path. The output from these studies will be used in preparing environmental impact statements and safety analysis reports for specific sites. The work done in this task, "Nuclide Migration Studies," encompasses generic studies of materials in and around salt as well as other formations of interest for geological disposal. This program will also supply analyses of nuclide retardation properties of materials from specific sites in partial support of the site selection process.

While this program has a strong mission/engineering orientation, we realize that the technology to characterize the retardation of nuclides in geologic media must be systematically and scientifically developed. Therefore, Serne has tried to balance the mission milestones with long-range scientific studies, investigating the thermodynamics, kinetics, and mechanisms of nuclide migration.

FIGURE 1

GOALS OF DEEP GEOLOGICAL DISPOSAL

GOAL 1

CONTAIN WASTE FOR LONG TERM ISOLATION FROM THE BIOSPHERE IN A SMALL ZONE OF A GEOLOGICAL FORMATION, REGARDLESS OF WHAT LOCAL AND TIME-DEPENDENT CHANGES OCCUR.

GOAL 2

PROVIDE ISOLATION FROM THE BIOSPHERE BY RETARDING THE MIGRATION OF NUCLIDES, REGARDLESS OF EXTERNAL FORCES, SUCH AS EARTHQUAKES, EROSION, ICE SHEETS, WAR, METEORITES, ETC.

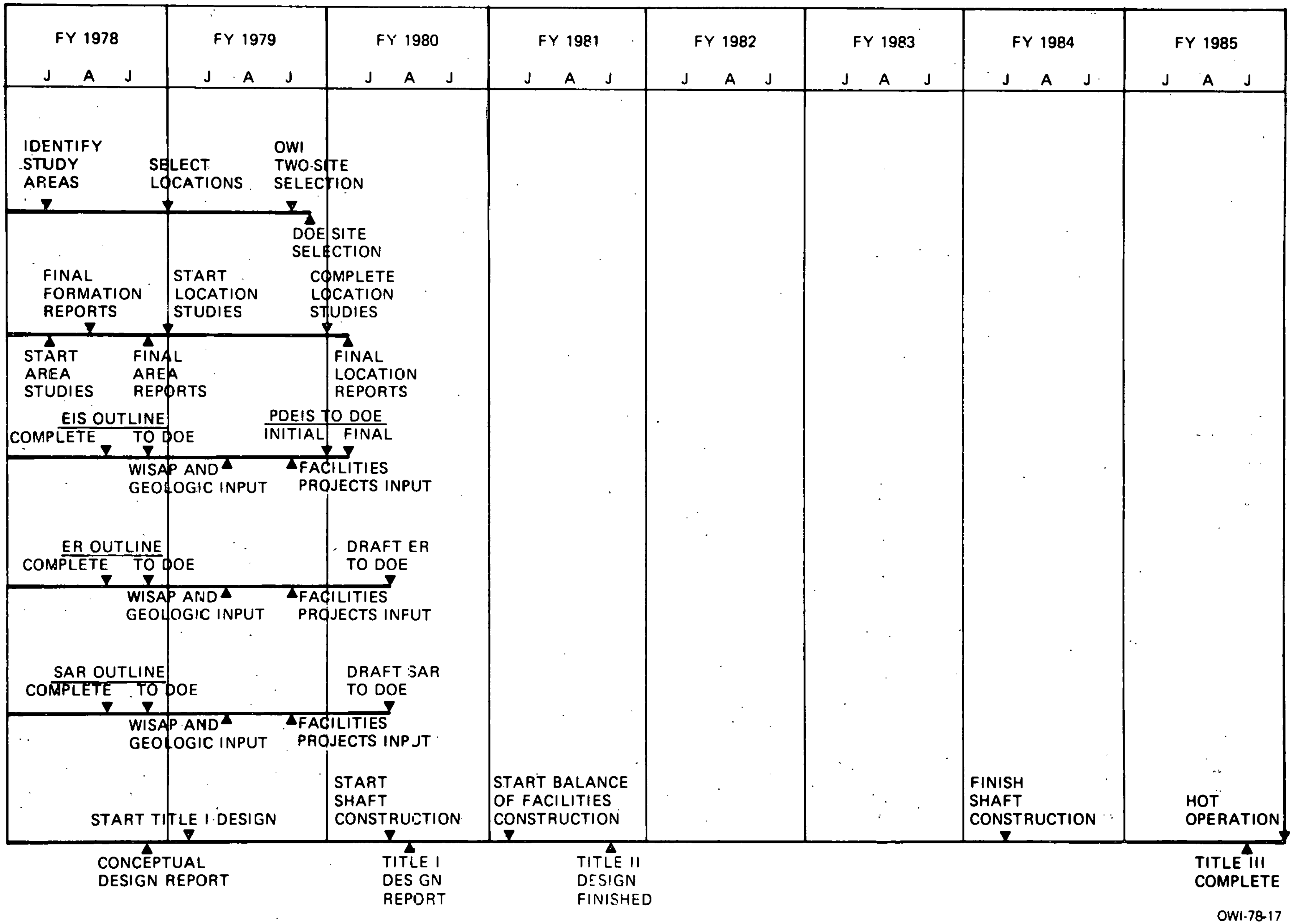
GOAL 3

MITIGATE ANY HEALTH EFFECTS AS CONSEQUENCE OF NUCLIDES REACHING THE BIOSPHERE.

[redacted]

FIGURE 2

SCHEDULE FOR REPOSITORY NO. 1



OWI-78-17
1/9/78
ASQ

Figure 3: I Give Up, Dear (OWI-77-478)

In constructing an event tree for the geologic disposal program, H. C. Clairborne of OWI establishes public acceptance as a top priority. Personally, I have difficulty seeing direct relationships between public relations and conducting a technically sound program.

To support the design and construction of a nuclear repository with scientific studies that achieve a good "scientific" basis as perceived by a consensus of knowledgeable experts in each particular field is necessary, but not sufficient, to assure public acceptance. There may be a direct tie between a good scientific study and nuclear licensing-public relationships contexts but it is, unfortunately, very weak.

Figure 4: Long-Term Storage Implies Unique Restraints (OWI-77-506R1)

This combination of engineering restraints drives many of the programs in the OWI technical support studies. If the natural stability of a salt formation is to be used, nuclear waste must be emplaced in such a manner as to minimize the insult to the formation. Therefore, we must be able to predict the thermal/mechanical responses of the far-field thermal gradients over time spans of 200 to 2000 years with reasonable accuracy. Retrieval periods of up to 25 years also demand accurate predictions of hole and room closures in near-field effects. In addition to the thermal/mechanical changes, geochemical changes are induced in the waste form and the surrounding host rock by heat and radiation which persist up to 2000 years.

Item 3 may appear redundant, but it emphasizes the geological sense of time that pervades the very long-range considerations of a repository whose functional life is to be upwards of one to ten million years. Predictions of stability and breaching events over periods of geologic time, encompassing multiple glaciations and the accompanying climatical cycles, represent a challenge.

Figure 5: Technical Support Projects (OWI-77-507R1)

The majority of studies represented by the first three items are aimed at characterizing the thermally-driven properties within the repository horizon. The heat transfer/thermal analysis studies input

[redacted]

"I give up, dear, what has Spike found buried in our back yard?"

FIGURE 3

SALT LAKE CITY, UTAH
DESERET NEWS
JUN 23, 1977

OWI-77-478
CDZ 7/14/77

FIGURE 4

LONG TERM STORAGE OF HIGH-LEVEL WASTE IMPLIES UNIQUE RESTRAINTS

1. HIGH HEAT AND RADIATION
2. PREDICTION IN LONG TIME AND SHORT TIME OF MECHANICAL RESPONSE
3. TIME SPAN OF THE PREDICTION

OWI-77-506R1
8/10/77
LRD

information is necessary to perform the rock mechanics modeling calculations and scope the test conditions of the close in waste/rock interaction. Serne's program to measure the nuclide interactions with various geologic materials pertains to the transport of nuclides beyond the boundary of the disposal horizon through the intervening rock strata to the biosphere. In the case of a salt repository, such hydrologic transport would be the result of an improbable breaching event.

Safety and reliability studies are performed under Harry Burkholder at Battelle Pacific Northwest Laboratories, and represent the effort to predict and characterize the probability of breaching scenarios for both specific and generic repositories. Burkholder describes the Waste Isolation Safety Assessment Program (WISAP) in more detail later in this report.

Borehole plugging studies include the development of special cement technologies and a demonstration program to be begun in FY 1978.

The data management task is aimed at developing a computerized geological data base and a flexible, graphic retrieval system.

Figure 6: Technical Support Projects (OWI-77-509R2)

This figure contains a list of waste/rock interaction studies presently underway through OWI. Figures 7-13 summarize those studies not directly relat to nuclide transport.

Figure 7: The Effects of Water in Salt Repositories (OWI-77-811)

Figure 8: USGS P-1 Physical Chemistry of Salt and Brine (OWI-77-809)

Figure 9: Chemical Reactions with Repository Rocks/Waste (OWI-77-815)

Figure 10: Consolidation and Brine Migration in Rock Salt (OWI-77-814)

Figure 11: USGS M-1 Mineralogical Characterization (OWI-77-810)

Figure 12: Geothermometry (OEI-77-813)

Figure 13: Strain-Related Radiation Damage Measurements on Rock Salt (OWI-77-808)

Figure 14: Nuclide Migration Program Organization (OWI-77-418R2)

The OWI technical program guidance matrix is composed of Clyde Claiborne, Glenn Jenks, and Les Dole. Claiborne has administrative responsibilities for

FIGURE 5

TECHNICAL SUPPORT PROJECTS

1. HEAT TRANSFER/THERMAL ANALYSIS
2. WASTE/ROCK INTERACTION
3. ROCK MECHANICS
4. SAFETY AND RELIABILITY
5. BOREHOLE PLUGGING
6. DATA MANAGEMENT

OWI-77-507R1
LRD 10/19/77

FIGURE 6

TECHNICAL SUPPORT PROJECTS

II. WASTE/ROCK INTERACTION

1. Nuclide Transport Data (WISAP Task 5)
   . . . Battelle Pacific Northwest Laboratories
   (Subcontractors - List)
2. Natural Fission Reactor Program (NFRP)
   . . . Los Alamos Scientific Laboratory
3. The Effects of Water in Salt Repositories
   . . . Oak Ridge National Laboratories
4. Consolidation and Brine Migration in Rock Salt
   . . . Pennsylvania State University
5. USGS P-1 Physical Chemistry of Salt and Brine
   . . . U. S. Geological Survey
6. Chemical Reaction with Rock/Waste
   . . . Pennsylvania State University
7. USGS M-1 Mineralogical Characterization
   . . . U. S. Geological Survey
8. Geothermometry of Shale
   . . . Georgia Institute of Technology
9. Strain-Related Radiation Damage
   . . . Brookhaven National Laboratory
10. Criticality Study of Nuclear Waste
    . . . Oak Ridge National Laboratory Engineering Technology

OWI-77-509R2
LRD 11/4/77

FIGURE 7

THE EFFECTS OF WATER IN SALT REPOSITORIES

OAK RIDGE NATIONAL LABORATORY

THE EFFECTS OF WATER ON:

1) THE MECHANICAL PROPERTIES OF SALT AND MINE INTEGRITY

2) ROLE OF CONSOLIDATION OF BACKFILLED SALT

3) RATE OF CANISTER CORROSION AND HYDROGEN GAS PRODUCTION

4) INTERACTION OF WASTE AND TRANSPORT MECHANISM
    A) BRINE MIGRATION
    B) EPISODIC FLOODING
    C) FLOWING AQUIFERS

OWI-77-811
LRD 11/4/77

FIGURE 8

USGS P-1 PHYSICAL CHEMISTRY OF SALT AND BRINE

PHASE RELATIONSHIPS OF $NaCl-CaSO_4-H_2O$ AND $NaCl-CaSO_4-MgCl_4-CaCl_2-H_2O$ SYSTEM AS FUNCTION OF TEMPERATURE AND COMPOSITION.

OWI-77-809
LRD 11/4/77

FIGURE 9

CHEMICAL REACTIONS WITH REPOSITORY ROCKS/WASTE

PENNSYLVANIA STATE UNIVERSITY

CONTACT METAMORPHISM OF WASTE WITH HOST ROCK DURING THERMAL PERIOD OF WASTE STORAGE

OWI-77-815
11-4-77
LRD

FIGURE 10

CONSOLIDATION AND BRINE MIGRATION IN ROCK SALT

PENNSYLVANIA STATE UNIVERSITY

1) DEVELOP MODELS TO PREDICT CONSOLIDATION BEHAVIOR FOR A WIDE RANGE OF CONDITIONS
2) EXPERIMENTAL COMPACTION BEHAVIOR
3) BRINE MIGRATION IN POLY-CRYSTALLINE SALTS IN A THERMAL GRADIENT

OWI-77-814
11-4-77
LRD

FIGURE 11

USGS M-1 MINERALOGICAL CHARACTERIZATION

1. ANALYSIS OF SALT CORES
2. FEASIBILITY STUDY OF K/AR DATING OF SALT RECRYSTALLIZATION AND WATER MOVEMENT.
3. INTERACTION OF HIGH LEVEL WASTE - SALT - SHALE MINERALS

OWI-77-810
LRD 11/4/77

FIGURE 12

GEOTHERMOMETRY

GEORGIA INSTITUTE OF TECHNOLOGY

DETERMINE THE THERMAL HISTORY OF ARGILLACEOUS ROCKS BY COMPARING

1) MINERALOGY
2) K/AR RATIOS
3) $0^{18}/0^{16}$ RATIOS
4) VITRINITE REFLECTANCE

FIGURE 13

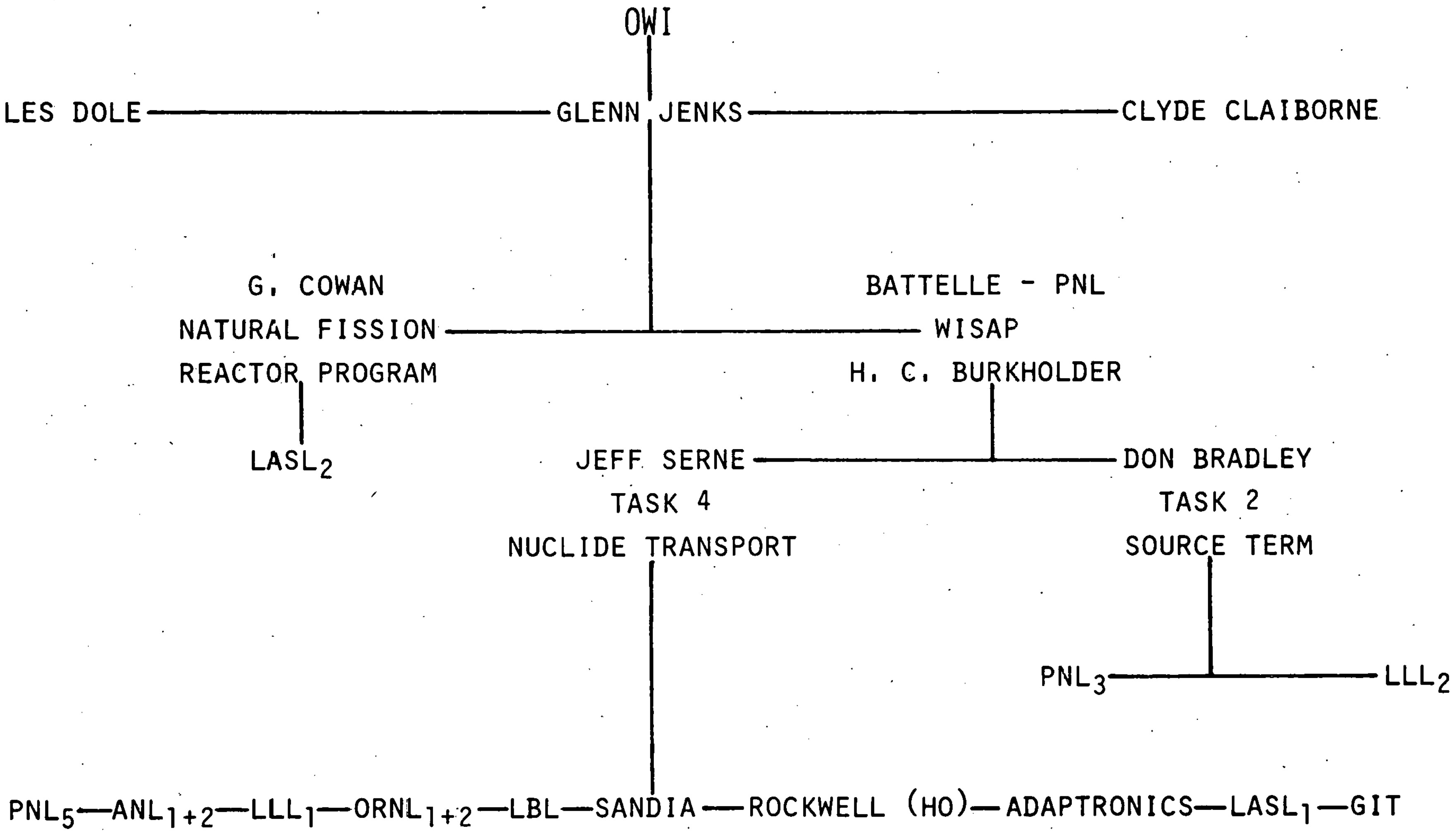
STRAIN RELATED RADIATION DAMAGE MEASUREMENTS ON ROCK SALT

ACCUMULATION AND ANNEALING OF GAMMA RADIATION DAMAGE (STORED ENERGY) IN ROCK SALT AS A FUNCTION OF TEMPERATURE AND STRAIN (50-200°C, 3×10^{10} RAD, RATE $\leq 3 \times 10^{5}$ RAD/HR)

OWI-77-808
LRD 11/4/77

FIGURE 14

NUCLIDE MIGRATION PROGRAM ORGANIZATION



OWI-77-418R2
LRD 11/4/77

tasks 1 through 3 of Burkholder's WISAP program, and Dole has administrative responsibilities for Task 4 under Serne. A fifth WISAP task, "Societal Affairs," is under the technical guidance and administrative control of A. S. Quist, OWI, Regulatory Affairs Department. The mission of the nuclide migration program is to supply data for use in the consequence analysis of various breaching scenarios generated by the probablistic modeling portion of the WISAP program.

The main point of this meeting is to discuss the details of the subcontractors' work under Serne's program. Burkholder will summarize the other WISAP tasks.

Figure 15: Deep Geological Hydrologic Transport Conditions (OWI-77-666)

In reality, the literature does not deal adequately with expected hydrologic transport conditions in the case of a deep geological repository. The general perception is that the retardation coefficients found in the literature are inconsistent and not fully characterized; that is, the experimental methods, geological materials, and solution chemistry are not usually specified in adequate detail. Therefore, OWI sponsored this systematic study to develop a data base.

Figure 16: Internal Subtask of Task #4 of the Waste Isolation Safety Assessment Program (WISAP) (OWI-77-665R1)

These subtasks, identified by Serne, are among those addressed in Task #4 of the WISAP program. Serne will discuss these specific items in a following presentation.

Figure 17: Oklo, Natural Fission Reactor Program (OWI-77-807)

This study under George Cowan, Los Alamos Scientific Laboratory, is divided into two parts. The first task, the Natural Fission Reactor Program is being phased out in FY 1978, and a second task, Characterization of Nuclide Diffusion through Uraninite Minerals, is being started.

Figure 18: Criticality Study of Nuclear Waste (OWI-77-812)

This study was completed by Ed Allen of the Oak Ridge National Laboratory. His data inputs into a study recently begun, under Doug Brookins of the University of New Mexico, to construct and model geochemical scenarios that could possibly

FIGURE 15

DEEP GEOLOGICAL HYDROLOGIC TRANSPORT CONDITIONS

1. ANOXIC REDUCING
2. STEADY-STATE SATURATED FLOW
3. NaCl CONCENTRATION GRADIENT

OWI-77-666
LRD 10/19/77

FIGURE 16

INTERNAL SUBTASK OF TASK #4
WASTE ISOLATION SAFETY ASSESSMENT PROGRAM
(WISAP)

1. STANDARDIZATION OF PROCEDURES
2. DATA BANK GENERATION
3. SYNTHESIS AND STATISTICAL ANALYSIS OF DATA
4. VALIDATION STUDIES
5. ANALYTICAL RATE AND MECHANISTIC STUDIES
6. TECHNICAL MANAGEMENT OF PROJECT INTERFACES

OWI-77-665R1
LRD 11/4/77

FIGURE 17

OKLO, NATURAL FISSION REACTOR PROGRAM

LOS ALAMOS SCIENTIFIC LABORATORY

STUDIES OF RADIONUCLIDE - GEOLOGIC MEDIA INTERACTIONS THAT CONTROL THE TRANSPORT OF RADIONUCLIDES.

OWI-77-807
11-4-77
LRD

FIGURE 18

CRITICALITY STUDY OF NUCLEAR WASTE

OAK RIDGE NATIONAL LABORATORY

CALCULATE CRITICAL MASS FOR ANY

1) ACTINIDE COMPOSITION
2) MODERATOR COMPOSITION
3) REFLECTOR COMPOSITION

OWI-77-812
LRD 11/4/77

result in a critical assembly from nuclear waste. If such scenarios can be determined, a third study of the probabilities and consequences of the scenarios will follow.

Figure 19: OWI Site Selection Study (OWI-78-390)

The OWI geological criteria for radioactive waste repositories are presented in Y/OWI/TM-47, November 28, 1977. Regional screening specifications for bedded salt in the Salina Basin and Gulf Coast Salt Domes are presented in Y/OWI/TM-48 and Y/OWI/TM-54, respectively.

To place nuclide retardation in perspective with other site selection criteria, it is necessary to understand the relative weight of the nuclide migration studies in relation to other geological properties and other sets of site criteria.

Figure 20: Site Selection for a Geological Repository Must be Based on Several Sets of Criteria)OWI-78-389)

Here is a list of criteria required for consideration in the selection of a particular site for a nuclear waste repository.

Figure 21: Hierarchy of Terms Used in Site Selection (OWI-77-398)

This represents a graphical illustration of the relative hierarchy of considerations in siting a nuclear waste repository. Each of the siting criteria, factors, measures, and specifications has a restricted definition that is spelled out in Y/OWI/TM-47.

Nuclide migration would be one factor among many others in deciding the suitability of a particular site. In the case of a salt repository, the probability of a breach of containment and subsequent hydrologic transport is considered extremely low, and the need for nuclide retention by surrounding strata is less than that of a repository in a fractured crystalline rock. In the latter case, the nuclide retention becomes more significant, because a hydrologic pathway is a reasonable certainty within the first 20 to 200 years. Parenthetically, we do not know but would expect to be able to site a nuclear repository in fractured crystalline rock that would have a very low hydrologic gradient. Nevertheless, it would be necessary to describe the nuclide transport from such a crystalline rock nuclear repository with greater accuracy, than from a salt repository. Hence, OWI has a great interest in developing an accurate nuclide data base, even though hydrologic transport is a small probability in the case of a salt repository.

FIGURE 19

OWI SITE SELECTION STUDY

THE CURRENT STUDY WAS DEVOTED ONLY TO GEOLOGIC CRITERIA.

- THEY ARE NECESSARY TO THE REPOSITORY GOAL
- THEY ARE LEAST SUBJECT TO CONTROL OR ALTERATION BY MAN
- THEY ARE NECESSARY PREDECESSORS TO SOME OF THE OTHER CRITERIA

OWI-78-390
6/8/77
LRD

FIGURE 20

SITE SELECTION FOR A GEOLOGIC REPOSITORY MUST BE BASED ON SEVERAL SETS OF CRITERIA

- GEOLOGIC
- ENGINEERING
- ECONOMIC
- SOCIAL
- POLITICAL

OWI-78-389
6/8/77
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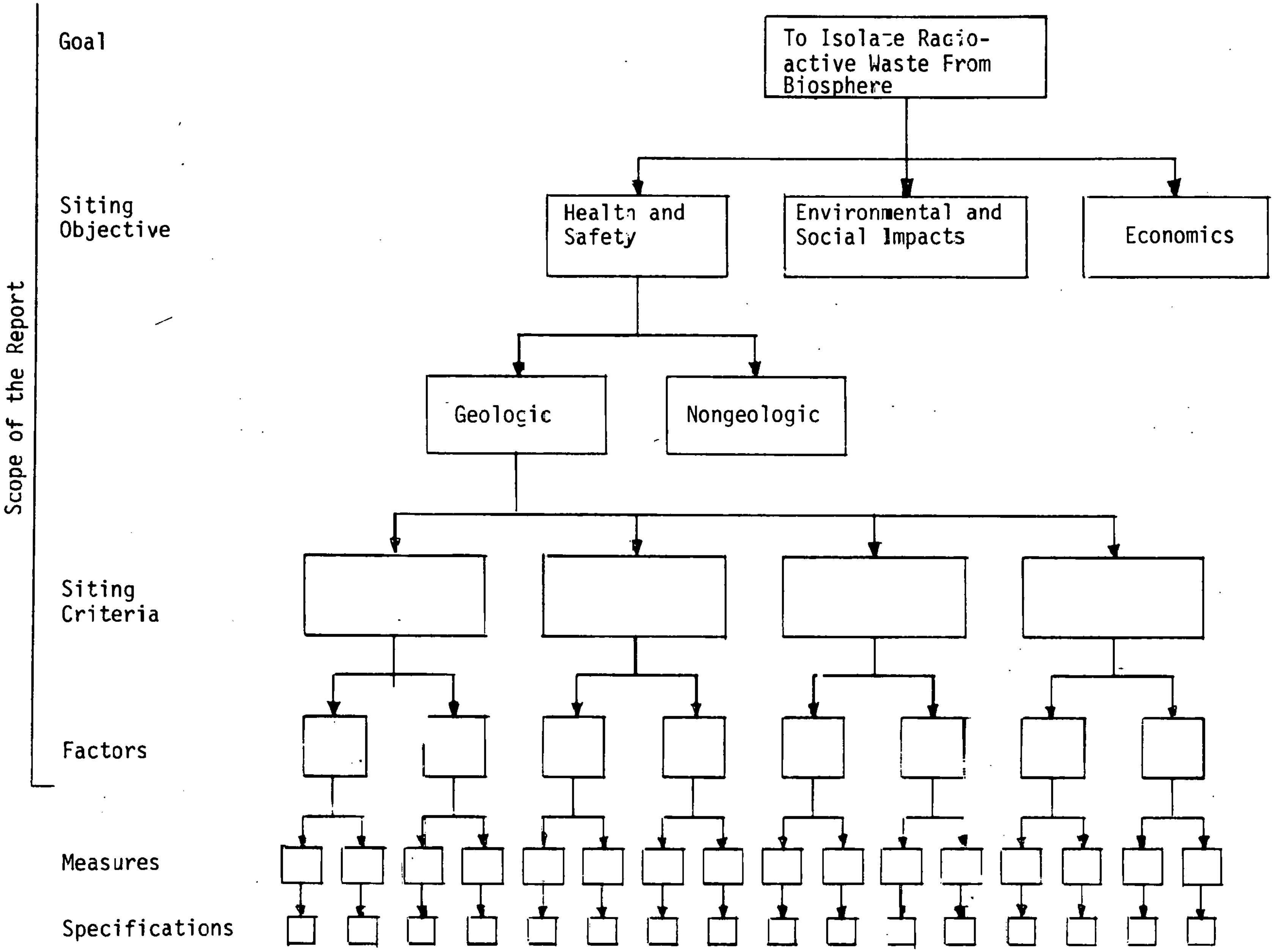

FIGURE 21

Hierarchy of Terms Used in Site Selection

QUALITY ASSURANCE REQUIREMENTS

Following is a brief discussion of the quality assurance program for WISAP and its subcontractors. This topic was originally scheduled for the September 1977 Information Meeting but was omitted because of insufficient time. The definition, goals, and relationship of quality assurance to the program are not well understood. Therefore, I will outline the background of Appendix B, Quality Assurance Requirements, and pertinent sections of the OWI quality assurance manual which are to be applied to these programs.

Figure 22: Quality Assurance (QA) Program (OWI-77-406)

Here is a list of project elements that must comply with 10 CFR 50 Appendix B. This task is that of testing for site evaluation and will be covered under Appendix B.

Figure 23 and 24: 10 CFR 50, Appendix B (OWI-77-408)

This presents an 18-point "laundry list" of program functions to which Appendix B requirements must be applied. The work under WISAP Task #4 is identified in the OWI quality assurance program as a special process, No. 9 on Figure 23.

Figure 25: Geology (Activities Covered by Appendix B-Type QA) (OWI-77-410)

A summary of activities associated with the nuclide migration program which must be conducted in compliance with Appendix B is presented. The status of the quality assurance program under OWI is that the OWI quality assurance manual was submitted to DOE-Headquarters and has not yet been approved. Some excerpts from the OWI manual that apply to the WISAP program and the nuclide migration measurements follows.

Figure 26: 9.0 Control of Special Processes (OWI-77-613)

This is taken from the section of the OWI quality assurance manual which identifies the sample taking and testing associated with the WISAP program.

Figure 27: 9.2.1 Quality Assurance is Responsible For: (OWI-77-614)

Here is an outline of the elements in the cooperative effort that must be achieved by OWI, Battelle Northwest, and the subcontractors.

Figure 28: 6.0 Document Control (OWI-77-616)

A coordinated and traceable documentation system must be achieved by all parties involved with site data. This involves the entire sample-handling and

FIGURE 22

QUALITY ASSURANCE (QA) PROGRAM

QA PROGRAM RESPONSIVE TO THE 18 SECTIONS OF 10 CFR 50 APPENDIX B MUST BE ESTABLISHED

REQUIREMENTS OF APPENDIX B APPLY TO ALL ACTIVITIES AFFECTING SAFETY-RELATED FUNCTIONS, INCLUDING:

- DESIGN

CONSTRUCTION

- PROCUREMENT
- TESTING
- FABRICATION
- OPERATION

SITE EVALUATION

OWI-77-406
6/16/77

FIGURE 23

10 CFR 50 APPENDIX B

I. ORGANIZATION
II. QUALITY ASSURANCE PROGRAM
III. DESIGN CONTROL
IV. PROCUREMENT DOCUMENT CONTROL
V. INSTRUCTIONS, PROCEDURES, AND DRAWINGS
VI. DOCUMENT CONTROL
VII. CONTROL OF PURCHASED MATERIAL, EQUIPMENT, AND SERVICES
VIII. IDENTIFICATION AND CONTROL OF MATERIAL, PARTS AND COMPONENTS
IX. CONTROL OF SPECIAL PROCESSES

OWI-77-408
6/16/77

(CONTINUED ON OWI-77-409

FIGURE 24

10 CFR 50 APPENDIX B
(CONTINUED)

X. INSPECTION

XI. TEST CONTROL

XII. CONTROL OF MEASURING AND TEST EQUIPMENT

XIII. HANDLING, STORAGE AND SHIPPING

XIV. INSPECTION, TEST, AND OPERATING STATUS

XV. NONCONFORMING MATERIALS, PARTS, OR COMPONENTS

XVI. CORRECTIVE ACTIONS

XVII. QUALITY ASSURANCE RECORDS

XVIII. AUDITS

OWI-77-409
6/16/77

FIGURE 25

GEOLOGY
(ACTIVITIES COVERED BY APPENDIX B-TYPE QA)

- ACTIVITIES RELATING TO COLLECTION OF INFORMATION ON WHICH SEISMIC AND GEOLOGIC DESIGN BASES ARE DETERMINED
- COLLECTION OF SAMPLES, DATA, AND RELATED RECORDS
- ANALYSES OF SAMPLES AND TESTS
- EVALUATION OF COLLECTED DATA

OWI-77-410
6/16/77

FIGURE 26

9.0 CONTROL OF SPECIAL PROCESSES

9.1.0 FOR THE PURPOSE OF THE REPOSITORY, SPECIAL PROCESSES ARE CORE BORING, GEOPHYSICAL TESTING, AND DOWN HOLE HYDROLOGICAL TESTING.

OWI-77-613
LRD 9/19/77

FIGURE 27

9.2.1 QUALITY ASSURANCE IS RESPONSIBLE FOR:

1. ESTABLISHING PROCEDURES
2. MONITORING THE ACCOMPLISHMENT
3. PREPARATION AND IMPLEMENTATION
4. QUALIFICATION OF PERSONNEL
5. MAINTENANCE OF RECORDS

OWI-77-614
LRD 9/19/77

FIGURE 28

6.0 DOCUMENT CONTROL

6.3.1 A STANDARD DOCUMENT CONTROL PROCEDURE SHALL BE PREPARED TO PROVIDE A UNIFORM SYSTEM OF DOCUMENT IDENTIFICATION AND CONTROL. SEPARATE PROCEDURES SHALL BE PREPARED FOR THE CONTROL OF DOCUMENTS WITHIN QUALITY ASSURANCE, TECHNICAL PROJECTS, FACILITY PROJECTS, PLANNING AND ANALYSIS, REGULATORY AFFAIRS, AND PROCUREMENT IN ACCORDANCE WITH THE STANDARD SYSTEM.

OWI-77-616
LRD 9/19/77

date-taking process, from the driller in the field to the laboratory experimenter.

Figure 29: Quality Assurance Requirements for Generic and Regional Studies (OWI-77-612)

OWI considers the full and elaborate quality assurance requirements of Appendix B to apply to those efforts that involve the selection of a specific site. However, the generic studies and the regional studies now under way should not require such intense documentation. Therefore, at this stage of the program, OWI has determined that quality assurance requirements shall be met by conduct consistent with good industry and scientific practice. This is a list of quality assurance elements to be in force through Battelle-Northwest and OWI projects. Meetings such as the one held in Seattle accomplish the documented, periodic independent-project-review by peers. Normal contract procedures and project notebook practices accomplished in the first two goals.

In the case of Battelle-Northwest, we have not established a written quality assurance policy nor identified a program plan to implement quality assurance requirements. Such negotiations are included in FY 1978 Form 189C negotiations, presently underway.

This concludes the summary of the background and status of the quality assurance program associated with nuclide migration transport data task. As this program evolves into the characterization of specific sites, the intensity and rigor of the quality assurance program will increase, making it necessary for all of us to work out mutually-functional testing and documentation procedures.

DISCUSSION - L. R. Dole

DOE/NRC Overlap

Q. Isn't there a substantial amount of overlap between what OWI is doing for DOE and what NRC is doing in the same area?

A. The National Environmental Policy Act (NEPA) gives both DOE and NRC a mandate to assess the safety of various plans that have been proposed for isolating radioactive wastes. Although this dual mandate does create a certain degree of overlap, there is a difference in the focus of the agencies' efforts: OWI will use its data to prepare a generic environmental impact statement, while NRC will be

FIGURE 29

QUALITY ASSURANCE REQUIREMENTS FOR GENERIC AND REGIONAL STUDIES

1. DOCUMENT CONTRACTOR SELECTION IN ORDER TO DOCUMENT CONTRACTOR COMPETENCE.
2. PUBLIC ACCESS TO ALL PROJECT RECORDS AND NOTEBOOKS.
3. DOCUMENTED PERIODIC INDEPENDENT PROJECT REVIEW.
4. ESTABLISH WRITTEN QUALITY ASSURANCE POLICY AND PROGRAM TO IMPLEMENT THE ABOVE REQUIREMENTS.

OWI-77-612
LRD 9/19/77

involved in the selection of specific sites and in licensing activities. The methods and data developed by OWI during the preparation of the impact statement can then be used by NRC, either during the site selection process or as a safety-analysis tool after a particular site has been selected. It was further pointed out that, since the final legal responsibility rests with NRC, that agency needs to be able to assess the accuracy and completeness of the information provided to it by OWI; therefore, to a certain extent, it must develop similar capabilities.

Information Dissemination

Q. Will all those attending this conference receive, on a regular basis, copies of reports and other information on the progress of the OWI effort?

A. This has not been done to date, but it could be done.

Quality Assurance and Peer Review

Q. Does "quality assurance" refer to the development of a standard method for measuring Kd?

A. OWI's use of the term "quality assurance" does not refer to the accuracy or reliability of the product. Although one purpose of the program is to come up with a method of measuring Kd that is consistent, useful, and reliable, "quality assurance" refers not to the experimental methods used but to the documentation of the program's evolution, in terms of both generic and site-specific criteria. The role of peer review as a quality assurance tool is to help shape the program so that no oversights occur.

Q. How does peer review tie in with quality assurance?

A. Peer review allows participating contractors to identify their areas of concern, so that these may be incorporated into the program. Although all the suggestions may not be followed, at least there will be a documentation of the fact they were made.

AN OVERVIEW OF PNL'S WASTE ISOLATION SAFETY ASSESSMENT PROGRAM (WISAP)

H. C. Burkholder
Battelle Pacific Northwest Laboratories

ABSTRACT

The major objectives of the PNL Waste Isolation Safety Assessment Program (WISAP) were described (Figure 1). In FY 77, WISAP was divided into six specific but interrelated tasks. Conceptually the interrelations and final products from each task are shown in Figure 2. Figures 3-8 describe major activities within each task.

FIGURE 1 WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

- DEVELOP GENERIC METHODS TO ASSESS SAFETY OF GEOLOGIC ISOLATION REPOSITORIES
- OBTAIN GENERIC AND SITE-SPECIFIC DATA NECESSARY TO APPLY METHODS
- DEMONSTRATE ASSESSMENT METHODS FOR SPECIFIC SITE
- APPLY METHODS AND DATA TO MAKE SITE-SPECIFIC SAFETY ASSESSMENTS FOR NATIONAL WASTE TERMINAL STORAGE NWB PROGRAM
- IDENTIFY SOCIETAL ACCEPTANCE ISSUES AND DEVELOP METHODS OF COMMUNICATING ASSESSMENT RESULTS WHICH ENHANCE RATIONAL RESOLUTION OF THOSE ISSUES

FIGURE 2 WASTE ISOLATION SAFETY ASSESSMENT PROGRAM TASK INTERRELATIONSHIPS

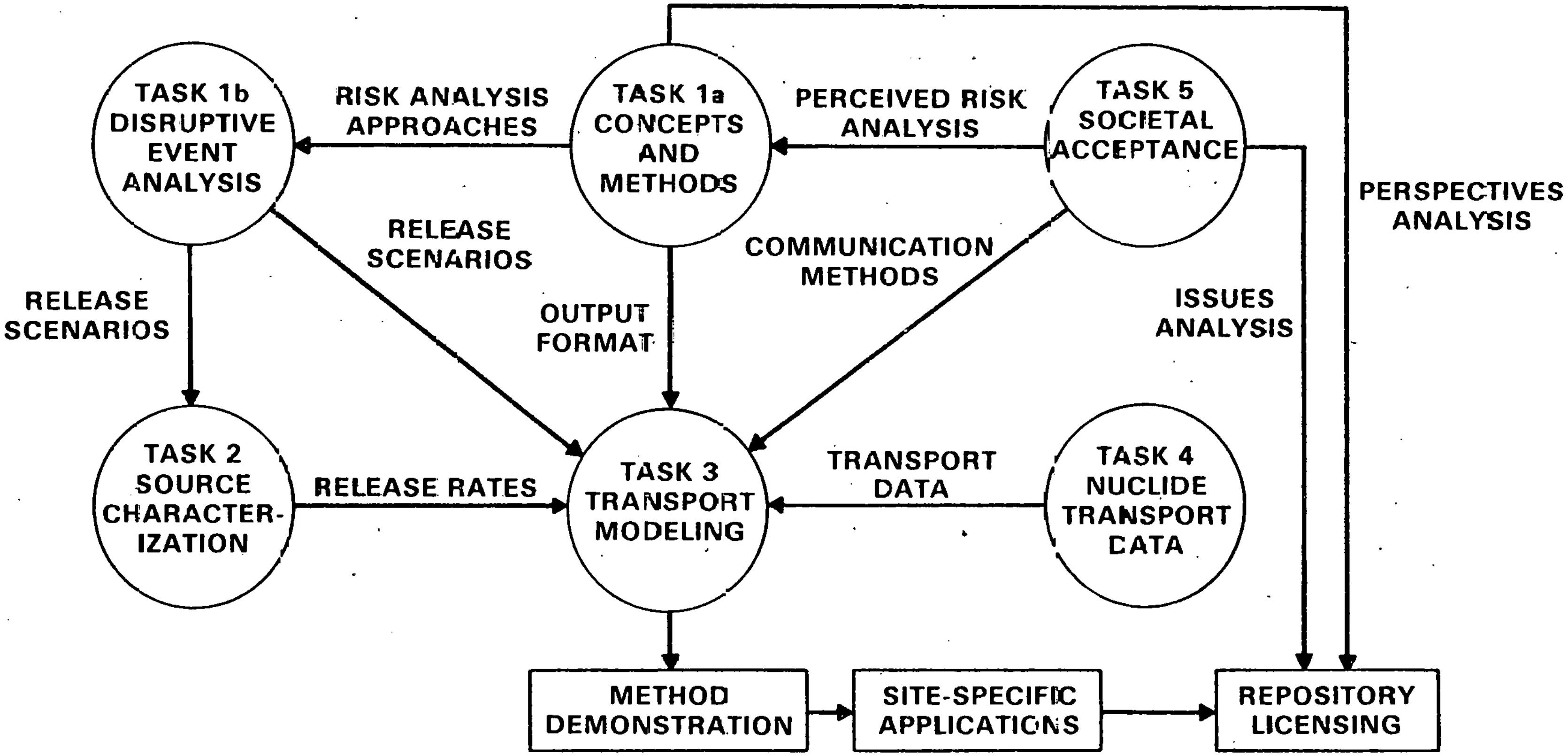

FIGURE 3 TASK 1a ACTIVITIES:

- EVALUATE GEOLOGIC ISOLATION SAFETY ASSESSMENT METHODS
- DETERMINE OUTPUT FORMAT FOR ASSESSMENT RESULTS

FIGURE 4 TASK 1b ACTIVITIES:

- IDENTIFY AND EVALUATE INTERDEPENDENCY OF EVENTS AND PROCESSES WHICH CAN INDIVIDUALLY OR IN CONCERT CAUSE CONTAINMENT FAILURE
- DEVELOP DETERMINISTIC AND/OR STOCHASTIC ANALYSIS METHODS
- DETERMINE PROBABILITIES FOR EVENTS AND RATES FOR PROCESSES
- DEMONSTRATE METHOD FOR SPECIFIC SITE
- APPLY METHOD TO SITES OF NWTS PROGRAM

FIGURE 5 TASK 2 ACTIVITIES:

- CHARACTERIZE WASTE FORMS DESTINED FOR GEOLOGIC ISOLATION
- MEASURE RADIONUCLIDE LEACH RATES
- PERFORM WASTE FORM DEGRADATION STUDIES
- EVALUATE THE EFFECTS OF PHYSICAL PARAMETERS ON LEACHING

FIGURE 6 TASK 3 ACTIVITIES:

- EVALUATE EXISTING RADIONUCLIDE TRANSPORT MODELS
- DEVELOP INTEGRATED TRANSPORT MODELING SYSTEM FOR:
  - — GEOSPHERE TRANSPORT
  - — BIOSPHERE TRANSPORT
- DEMONSTRATE SYSTEM FOR SPECIFIC SITE
- APPLY SYSTEM TO SITIES OF NWTS PROGRAM

FIGURE 7 TASK 4 ACTIVITIES:

- EVALUATE SORPTION MEASUREMENT METHODS AND ESTABLISH STANDARDIZED MEASUREMENT PROCEDURES
- MEASURE IN LABORATORY THE SORPTION BEHAVIOR OF BIOLOGICALLY SIGNIFICANT LONG-LIVED NUCLIDES BOTH FOR VARIOUS GEOLOGIC MATERIALS AND FOR ISOLATION CONDITIONS
- EVALUATE ACCURACY TO WHICH NEAR-TERM LABORATORY STUDIES PREDICT LONG-TERM IN-SITU BEHAVIOR

FIGURE 8 TASK 5 ACTIVITIES:

- ASSESS MAJOR LEGAL, INSTITUTIONAL, SOCIOLOGICAL, AND POLITICAL ISSUES WHICH IMPACT NWTS PROGRAM
- IDENTIFY PERCEPTUAL SAFETY ISSUES
- DEVELOP METHODS OF COMMUNICATING TECHNICAL SAFETY INFORMATION TO NONTECHNICAL AUDIENCES

DISCUSSION--HARRY C. BURKHOLDER

Implementation of WISAP Objectives

Q. Will the WISAP objectives be carried out in the order listed (see Figure 1), or concurrently?

A. Of the five WISAP objectives, most will be taken up in the order listed. Clearly, methods must be developed before they can be demonstrated; they must be demonstrated before they can be applied; and data are needed before the methods are either demonstrated or applied.

The social acceptance issue, however, is being worked on right now. Currently, the studies are dealing with the generic aspects of the problem. As the licensing of a particular site becomes more imminent, the investigations will focus on the particular issues surrounding the licensing of that site.

Nature of Safety Assessment Method

Q. Does "safety assessment method" refer specifically to a workable hydrological analysis?

A. In part, but it is much broader than that. It consists, first of all, of an analysis of the potential disrupting events that could result in the release of materials from the repository cavity. This portion of the effort involves two tasks: (1) a listing of all the events and processes that, individually or in concert, could lead to failure of containment; and (2) integration of this information with the necessary geological information and the assignment of ranges of values to the parameters, so that the likelihood of each of the release scenarios can be predicted. The second part of the development of a safety assessment method involves modeling efforts, for both the geosphere and the biosphere, to determine the consequences of the various release scenarios.

Q. You say there will also be a test of the method; what will this involve? Will it be a physical test or a modeling effort?

A. The test will consist of preliminary application of the method to a specific site, through the use of modeling techniques.

Involvement of Outside Participants

Q. Who are some of the primary actors in the various WISAP activities?

A. In the evaluation of methods, there has been extensive involvement of people from a variety of disciplines within Battelle; a consultant in safety assessment from the University of Tennessee has also been used. For the output format, the WISAP staff has consulted with health physicists and radiation biologists.

Output Format

Q. In what form should the data be given to the public?

A. From a technical standpoint, the only accurate way to express the risk is in terms of radiation dose rate per individual. There are too many uncertainties to determine future population dose rates, or health effects on future generations. However, since the nontechnical public is interested in these other questions, many feel that this type of information should be given too.

Q. But isn't it wrong to give the public meaningless information?

A. If OWI does not give out this type of information, some other person or group is sure to do so--and they may do it wrong. In giving out this information, OWI can identify it as nonmeaningful and explain why it is so. In this way, those who insist on having this type of information will have it in its least misleading form.

Q. But as your knowledge increases and you modify your numbers, the public will be aware of the fact that you are changing your calculations; won't this hurt your credibility?

A. Hopefully, at the time the information is given out, error boundaries will be identified.

Q. Doesn't that tie in with the social acceptance question? That is, if you give the number of cancer deaths for a future population, can you not also give an estimate of the date that cancer will be curable?

A. Yes. You can vary the parameters, specifying, for example, that after a certain point there will be no effect on health.

Leaching Studies

Q. In your evaluation of the effects of physical parameters on leaching (see Figure 5), will you be characterizing the chemical and physical form of the leachate?

A. Yes, we will. At some point in the program, we'll be doing leaching studies with actual materials destined for geologic isolation.

WISAP Emphasis

Q. Does WISAP give priority to salt studies?

A. WISAP is not a salt-specific program; rather, it calls for generic studies. However, there is a slight emphasis on salt because it is expected that the first repository will be in salt; therefore, salt answers will be needed earlier.

Q. Is the emphasis on reprocessed waste or spent fuel?

A. Both types of studies are under way at present.

Societal Acceptance Issues

Q. How do you assess societal issues impacting the waste isolation program?

A. A variety of techniques are used. In FY 1977, for example, the following studies are under way (or have been completed):

- Establishment of a library of nontechnical issues that have been raised concerning waste management.
- Study of socioeconomic issues.
- Projection of population impact.
- Study of state laws as they affect property rights (since OWI will have to acquire property for a waste repository).
- Analysis of federal and state agency responsibilities for policies relating to waste management; how these decisions are made, both on paper and in real life.
- Development of impact management guidelines (since the siting of a waste repository will have local impacts).
- Study of peoples' perceptions of and attitudes toward waste management and waste management safety.
- Case studies of attempts at waste repository siting and the siting of related facilities.

AN OVERVIEW OF TASK 4 NUCLIDE TRANSPORT DATA

R. J. Serne
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ABSTRACT

A multi-year program plan is presented to collect the necessary data on nuclide sorption-desorption interactions with geologic media.

Detailed activities which need to be performed in each of the six subtasks are described.

The general areas in which each subcontractor performed work in FY 77 were presented in the overview. Detailed technical discussions of each subcontractor's work will be presented in ensuing presentations.

INTRODUCTION

One of the most likely final storage plans for high level wastes is solidification and containerization followed by disposal in geologic media. The radiation and toxicity of high level wastes necessitate isolation for nearly a million years before radioactive decay will reduce the waste to safe levels. Meeting the extremely long isolation requirement will be dependent on geologic stability, failure rate of the container, weathering rate of the solid waste, hydrologic properties, radionuclide-geologic media interactions, and site engineering. The overall objective of the WISAP program is to develop and implement methods to use the above information for a comprehensive evaluation of the long-term safety of waste disposal.

Specific activities of Task 4 are: (1) evaluation of sorption-desorption measurement methods and development of standardized measurement procedures, (2) the laboratory measurement of the sorption-desorption behavior of significant long-lived radionuclides using a wide range of geologic media and groundwaters, (3) statistical analysis and synthesis of these data to provide information on which variables correlate best with the observed sorption-desorption and to allow empirical interpolations to be performed between environments studied, (4) performance of validation studies to assess the degree to which these short-term laboratory studies predict long-term in situ behavior, (5) development of a more fundamental understanding of sorption-desorption processes to permit prediction of nuclides' fate at a specific site from data available on other similar sites or from commonly measured parameters, and (6) formal information dissemination and coordination with other governmental and scientific organizations working in the area of nuclear waste disposal.

In FY 79 the Office of Waste Isolation will have to demonstrate a workable safety assessment model for final storage of high-level waste in deep geologic environments. In order to obtain data to meet this FY 79 time constraint and the needs of assessment modelers, the initial thrust of the program will be empirical, experimental, and engineering oriented to collect the necessary data. As time progresses, more attention will be given to theoretical, phenomenological, and mechanistic studies in order to generate a more comprehensive understanding of nuclide transport processes and general predictive tools.

The following is our concept of Task 4 including brief descriptions of its interaction with other tasks. This program plan should be viewed as a guide for the preparation of specific technical proposals (including time and cost estimates oriented toward meeting the task goals). Proposals which address aspects of nuclide migration not described in this plan will be reviewed and may be accepted, provided convincing technical argument is presented.

SUBTASK 1: EVALUATION OF EXPERIMENTAL SORPTION-DESORPTION METHODOLOGY

There are several unresolved issues in the area of sorption-migration data collection. Presently investigators from various laboratories determine sorption K_ds and/or migration rates for nuclides utilizing numerous experimental designs. 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. No systematic effort has been expended 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. Thus, it is imperative to study the various experimental methods for determining sorption-migration data and if possible form a consensus as to which method or methods should be proposed as a standard measurement technique.

The various laboratory methodologies will be evaluated using a wide range of geologic materials and nuclide-spiked groundwaters. K_d values for each method will be determined and evaluations performed on precision, ease of utilization, time and cost expenditures, and limitations. Disagreements and range of applicability for observed results will be investigated through further experimentation on the independent variables (geologic media, groundwater composition, pH, Eh, etc.).

The effects of variations in solution characteristics such as ph, EH, ionic strength, nuclide concentration, and speciation on the observed K_d will be assessed using a wide range of geologic materials. The degree of reversibility and sensitivity of different experimental designs to kinetic and temperature effects will also be investigated. The additional studies on these independent variables will provide additional information leading to standard procedure recommendations and will allow the formulation of more detailed work plans for the necessary mechanistic and validation studies.

Validation studies utilizing larger column lysimeters or field experiments may be used to aid in formulation of a standard or preferred method. If no technique proves to be more successful than others, cross correlations must be derived so that data generated using different experimental methodologies may be compared.

After the various experimental techniques have been evaluated, information on sample size requirements, time and cost estimates, and types of supplemental data required to accurately assess the transport of nuclides will be better identified. This information, which is partially missing at present, will be of great value to program managers and specific site coordinators. The information will be used to estimate allocations and to create sampling directives which are necessary to successfully obtain the critical data to assess nuclide movement within the proposed time schedule. Coordination with site managers performing geologic work is desirable so that sample gathering can occur at the same time as site exploration rather than necessitating separate field collection studies.

Specific details of programs which will be initiated to perform Subtask 1 will depend somewhat on contractor proposal responses. An outline of areas which have been delineated to data follows. Contractors who performed work on the subtasks in FY 77 and detailed work packages are designated in the following outline:

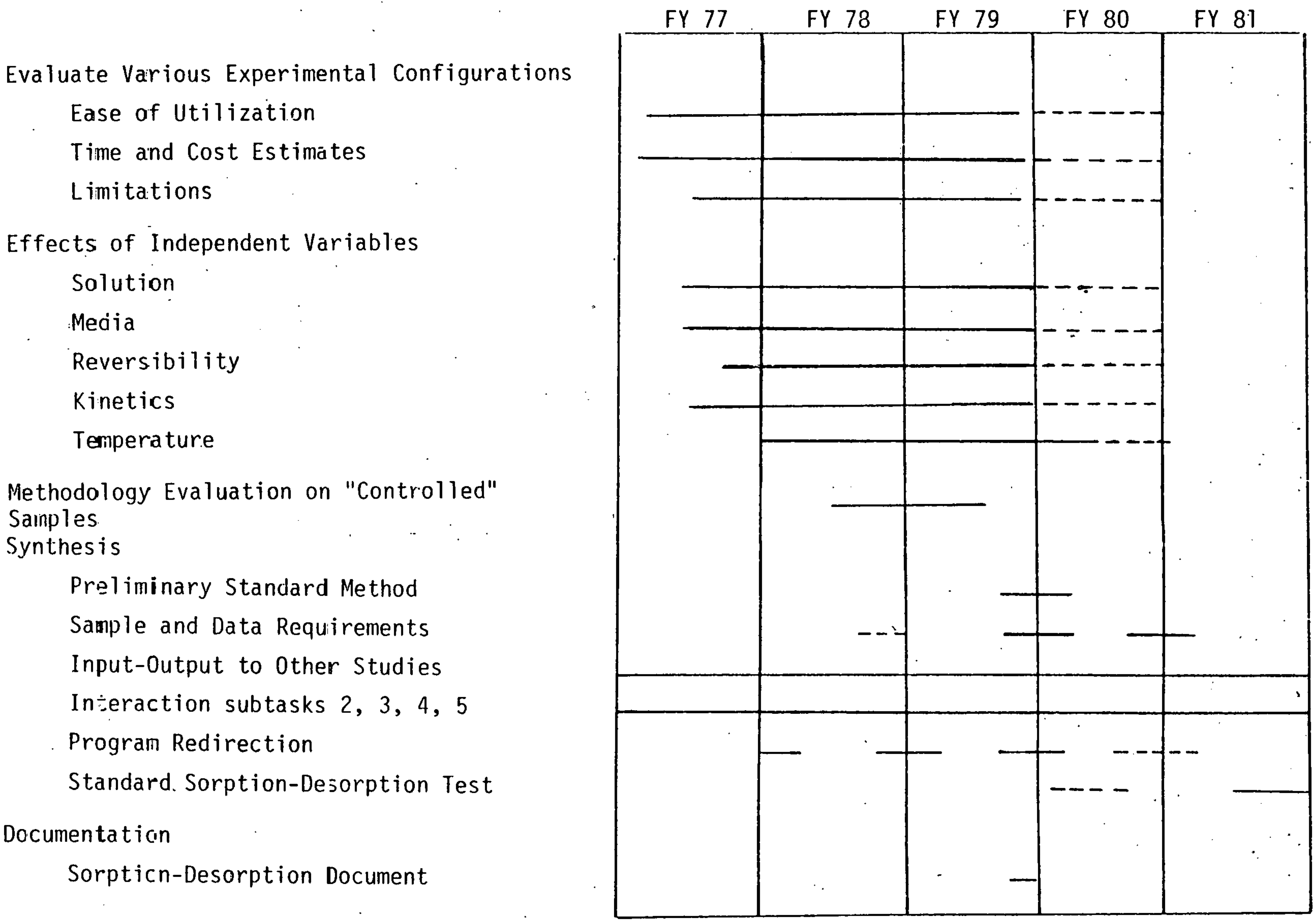

FIGURE 1. Subtask 1 - Evaluation of Experimental Sorption-Desorption Methodology

Figure 1 contains a time schedule and shows the interactions of Subtask 1 with other aspects of the PNL and OWI program. The subtask will be performed in FY 77 - FY 79 at which time (August, 1979) a critical assessment and synthesis of the derived knowledge would be used to redirect or culminate Subtask 1. If Subtask 1 remains viable, yearly assessments will be performed. The final product of this task will be recommendations on a uniform or standard procedure for determination of geochemical data necessary for the overall safety assessment.

A. Compare reliability, time and costs, and applicability of the following experimental designs for predicting migration of nuclides:

1. Batch K_d measurements (ORNL, PNL, LLL, ANL, RHO)
2. Flow-through small column K_ds (ANL, ORNL)
3. Thin-layer K_ds (ORNL)
4. Diffusion cell measurements
    a. Liquid-solid
    b. Solid-solid
5. High-pressure intact-core K_d's (ANL, LLL)
6. Axial filtration (ORNL)
7. Preloaded column (ORNL)
8. Larger scale columns or lysimeters

Batch K_d, axial filtration, thin-layer K_d, and flow-through small column K_ds are most commonly performed on unconsolidated media. The use of crushed materials eases difficulties which arise when trying to force water through intact cores and allows K_d determinations to be performed with less expenditure of time and money. It is hoped that K_d determinations on crushed materials can be related to in situ values in competent rock by normalization of results on a surface area basis. Some of the observed values on the crushed materials will be further investigated through studies on intact materials using methods 2, 5, and 8. Method 4--diffusion cells--represents a special hydrologic case where advection is not present or minimal, i.e., the hydrologic regime is stagnant. When geologic materials with very low permeabilities are studied by flow-through K_d techniques (methods 2, 3, 5, 7, and 8), long completion times may be required. High pressure fluid flow through intact cores will be evaluated for practicality and accuracy of predicting nuclide migration. The comparison of K_ds from intact cores versus crushed materials, calculated on an equivalent surface area basis, will be very important in assessing whether rapid and inexpensive laboratory techniques are acceptable to predict the aspects of geologic-water interactions needed for long-term safety assessment.

B. Investigate the effects of independent variables on above experimental designs for:
   1. Solution composition (PNL, ORNL, ANL, RHO) pH, Eh, salt concentrations ionic strength, complexants, nuclide concentration, nuclide speciation
   2. Geologic material (PNL, ORNL, ANL, LLL, RHO) salts, argillaceous, crystalline
   3. Unsaturated-saturated flow (ORNL)
   4. Temperature

C. Reversibility (ANL, PNL, RHO, ORNL)
   1. Sorption (Load)
   2. Desorption (Leach)

D. Scaling (ANL, ORNL, PNL, RHO)
   1. Time
      Kinetic data
      Time to reach equilibrium
      Residence time/flow rates
   2. Size
      Amount of geologic material
      Mass, cross-section, length
      Surface Area

E. Methodology evaluation on controlled samples

A few selected rocks or minerals will be obtained in large quantity, then carefully characterized and homogenized. These "standard" samples will be distributed to investigators at each lab. The samples will be tested with the various K_d methodologies to determine whether the results of several methods yield similar results. The contacting solution will also be specified so that variability in results should reflect methodology rather than geologic material-groundwater system differences.

This activity will also yield information on the time and costs which must be allocated to measure K_ds by the different methods. These improved time and cost figures will allow more knowledgeable predictions to be made for the geochemical studies which will be necessary at the specific sites chosen for detailed study.

F. Synthesis (PNL)

1. Contractor-consultant workshops
2. Cross correlation of results to obtain comparability
3. Preliminary universal sorption-desorption test
4. List of data and sample requirements necessary to evaluate nuclide geologic interactions-- i.e., what, how, and why to collect--should be available to geologic site managers so data and samples can be collected simultaneously
5. Use knowledge for redirection of Task 4 program
6. Coordination with other programs such as:
   Near repository (radiation, thermal backfill effects)
   Source term (Task 2)
   Transport modeling (Task 3)
   NRC
   EPA
   ERDA-Shallow land burial

SUBTASK 2: DATA BANK GENERATION

Currently there are many studies involved in computer model formulation in areas such as groundwater movement, geochemical interactions, terrestrial and aquatic food chains, radiation dose to man, geologic stability, and disruptive event analysis. Simplistic models already are functioning which can estimate the fate of nuclides in geologic, aquatic, or biotic systems given the necessary input data. In the area of nuclide migration there is a severe gap in our knowledge of quantitative estimates of the various geologic materials' ability to retard nuclide movement. These quantitative estimates become input data to all of the numerical assessment models. Thus, the lack of defensible sorption data for nuclides in geologic environments is limiting the credibility of the aforementioned simplistic models. The acquisition of sorption-desorption data on a wide range of representative geologic material with numerous groundwater types should proceed posthaste. Once this data bank is acquired, safety assessment modelers will have defensible data (from a geochemical standpoint) to attempt preliminary fate calculations. In order to obtain data to meet the needs of assessment modelers by FY 79, the initial thrust of the program will be empirical and engineering oriented. Since the first two repositories will likely occur in salt deposits, the migration rates of nuclides in salt solution will be stressed initially. Site specific data will be generated as samples become available.

These empirical data will be supplemented by portions of subtasks 1, 3, and 4. If several experimental designs are used and variances in results occur, the data may be used by the modelers as uncertainty bounds in sensitivity analysis. The data will also be used to make preliminary rankings in regard to geochemical acceptability of various media and to aid in general criteria development for final disposal sites. Finally, a critical review on the sorption data of the various geologic materials may shed valuable light on the controlling mechanisms and aid in the formulation of Subtask 5.

An outline of the suggested work undertaken in Subtask 2 follows, with contractor-supplied information in FY 77 delineated. A time schedule showing interaction with other subtasks appears in Figure 2. Table 1 portrays the type of supporting information (characteristics of the geologic media-groundwater suspension) necessary to establish the data bank. Without the ancillary information, predictive, extrapolative, and interpolative activities cannot be performed objectively. In the ideal case all the parameters listed would be determined, in real instances as many of the parameters as economically or logistically possible should be measured. A crude priority ranking (two categories) is furnished as guidance for the more important characteristics. Conceptually the generic data bank will contain the information shown in Figure 3.

A. Data Bank Generation (ANL, LBL, PNL)

1. Gather all existing data on sorption-desorption rock-nuclide interactions that are available in the literature. (A bibliography on transuranics which is available, BNWL-1983, will be updated and expanded to include fission and activation products by PNL on an existing EPA contract to be completed in early FY 78)
2. Quantify sorption-desorption phenomena for various geologic materials with expected indigeneous groundwaters utilizing several experimental approaches. Include adequate sample characterization such that the data bank (Figure 3) needs are satisfied
3. Obtain site specific data as samples become available
4. Continue site specific sorption-desorption data as sites are explored throughout OWI program
5. Possibility of large scale, field and/or in situ migration studies at proposed pilot plant sites

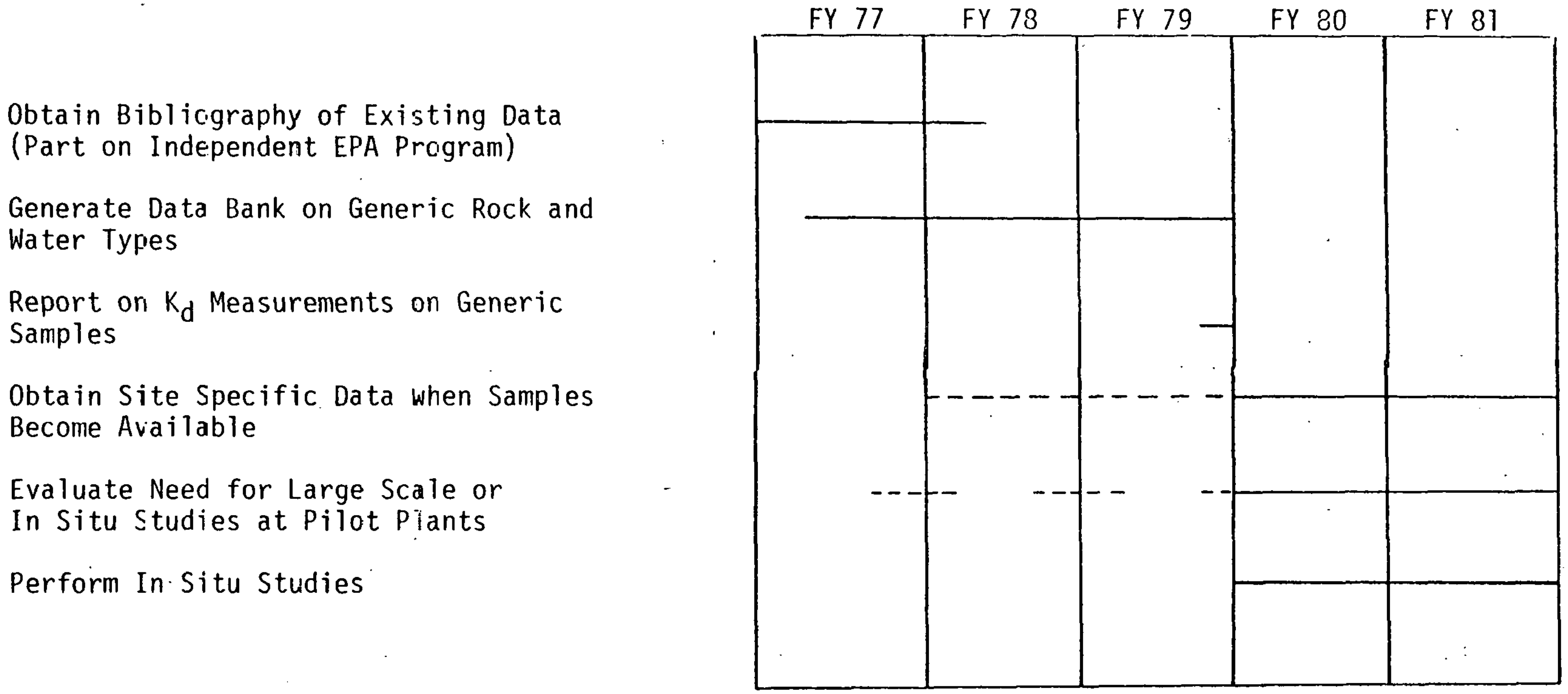

FIGURE 2. Subtask 2. Data Bank Generation

TABLE 1. Supporting Information Necessary to Complete K_d

There are numerous characterizations that should be performed on geologic media and their pore waters to allow calculations of migration rates or Kd's. The characterizations can be broken into two broad categories; physical or hydrologic and geochemical. A laundry list of characterizations and their relative importance follows. The relative importance is based on the assumption that insufficient time and funds will be available to perform the complete characterization. If only partial geochemical characterization is possible in general concentrate on the first seven. For the physical and hydrologic characteristics items 4, 5 and 6 or 7 are most important.

Important Geochemical Characterizations

1. Qualitative and quantitative mineralogy including primary and secondary crystalline materials, amorphous coatings, etc. determined primarily by x-ray diffraction, chemical treatment techniques, and petrographic examination. Calcium carbonate content and hydrous oxide content (amorphous and crystalline) as well of alumino-silicate contents are most important. Scanning electron microscopy and microprobes can be used to determine microstructural mineralogy. These techniques can be very important in assessing the differences between mineralogy and weathering environments of cracks and fractures from the bulk rock material.
2. Cation-exchange capacity
3. Pore Water pH, Eh
4. Pore Water major cation content (Na, Ca, Mg, K)
5. Pore Water major anion content (Cl. HCO_3-CO_3, SO_4, NO_3)
6. Pore Water SiO_2 content
7. Organic content of geologic material

Less Important Geochemical Characterizations

1. Anion exchange capacity
2. Distribution of major cations on exchange sites
3. Pore water organic content especially potential ligands (humic, fulvic acids)
4. Pore water minor constituents especially natural occurring isotopes of important waste nuclides (Sr, Cs, I, U, Ra) and chemically similar elements (Ba, Rb, Br)

For geologic environments which are presently devoid of water a saturated water extract should be prepared and the above mentioned pore water analyses performed.

Important Physical or Hydrologic Characterizations

1. Hydraulic conductivity
2. Percentage saturation
3. Permeability
4. Water velocities
5. Surface area and particle size distribution (unconsolidated materials)
6. Porosity
7. Percentage fractures or fissures (consolidated material)
8. In situ temperature

Independent Variables				Dependent Variable	Methodology
Geologic Material Properties		Groundwater Properties	Nuclide Properties	K_d Isotopes	
Mineralogy	Amount	pH	Tracer Concentration	a. Pu	(a) Method Details
Primary Minerals	%	Eh		b. Np	
Secondary Minerals	%	Major Cations	Tracer Valence State Distribution	c. Am	(b) Soil to Solution Ratio
$CaCO_3$	%	Major Anions		d. Tc	
Hydrous Oxides	%	Soluble Organic Composition		e. I	
Organic Content	%		Contact Time	f. etc.	(c) Misc.
Cation-Exchange-Capacity		Soluble SiO_2	Direction (adsorption or desorption)		
Anion-Exchange-Capacity		Soluble Minor Species			
Surface Area		Temperature			
Hydrologic Properties					
Hydraulic Conductivity					
Permeability					
Porosity					
Water Velocity					
Percentage Saturation					
Fissure Surface Area to Volume Ratio					

FIGURE 3. Parameters Important for a Generic Data Bank

SUBTASK 3: SYNTHESIS OF DATA BANK

A quantitative prediction tool which is capable of estimating the migration rate or K_d of a nuclide for any given geologic material and water type is the ultimate objective of Task 4. The data generated in subtasks 1, 2, and supplemented by literature values, will be quite large. With proper experimental design and media-water characterization, statistical methods can be used to relate the dependent variable (migration rate or K_d) to independent variables (rock type, solution type, etc.). Although the derived relationships do not prove "cause and effect," they do allow prediction of trends. Thus, from K_d data on a finite number of rock, mineral and water types, estimates can be made of K_ds for other rocks and water environments not directly studied, if certain precautions are observed.

Through the use of statistical methods, trends and correlations can be elucidated such that some basic understanding can be extracted from the multitudinous data points. The use of statistical techniques allows more information to be extracted from experimental data than can be obtained from unstructured perusal.

There are at least two statistical approaches which may be optimal for structuring the experimental data--nonlinear regression and adaptive learning networks. The strength and weaknesses of these and other approaches will be assessed in FY 77. Restrictions in experimental designs forced by statistical approaches will be noted.

The migration rates or K_d values generated in Task 4 must be relayed to the Task 3 modelers in a format understandable and compatible with their needs. Since the safety assessment model will be in a state of flux for the first two years of the program, repeated dialogue will be necessary to prevent misinterpretations or incompatible data requirements. Interplay with other personnel reponsible for preparing PSAR, SAR and EIS tasks at each site will be performed to assure technical support and review in the area of geochemical interactions.

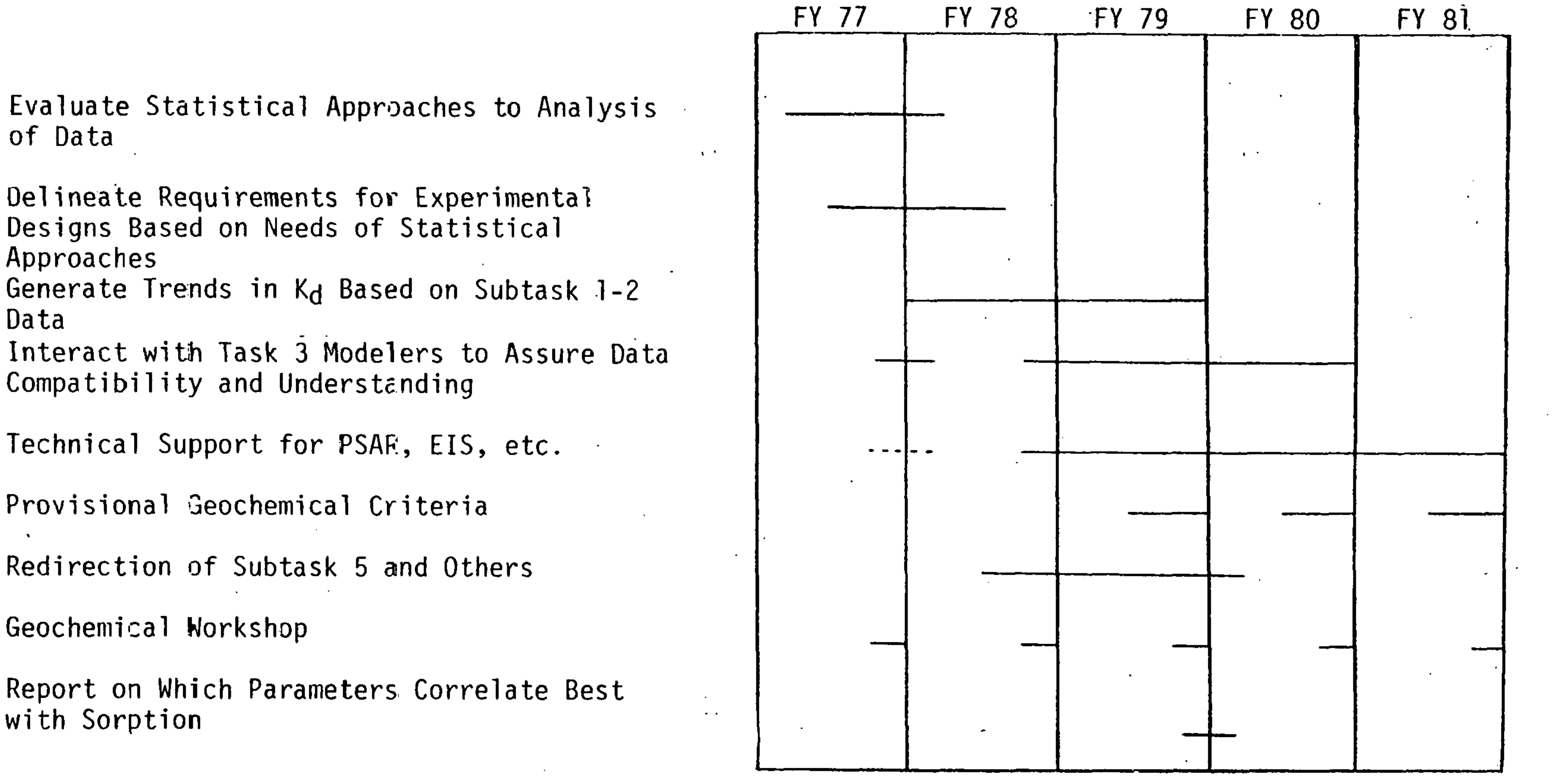

FIGURE 4. Subtask 3 - Synthesis of Data Bank

Other products of this subtask on data synthesis will be: (1) the formulation of geochemical criteria capable of ranking sites for isolation of nuclear wastes, and (2) delineation of more important variables which should be studied in greater detail in the Subtask 5 mechanism studies.

Presently the geochemical criteria are difficult to fully define, let alone quantify, thus an iterative process is envisioned. A list of provisional criteria will be prepared as data become available. The first few formulations will be based on the limited available data. As better data and a more thorough understanding become available, the criteria will be progressively updated. Such an iterative process may also isolate areas in which additional study is necessary.

A time schedule showing when these work units should be in progress and interactions with other tasks is found in Figure 4.

In FY 77 Adaptronics, Inc. has investigated the usage of regression and adaptive learning networks to analyze laboratory generated K_d values.

SUBTASK 4: VALIDATION STUDIES

The need for empirical data to estimate the long-term fate of nuclides in geologic environments is urgent. Present data collection methods rely on laboratory analyses characterized by short times and small sample sizes. The applicability of scaling these results to the million-year time frame and path lengths of miles has not been conclusively shown. In many instances the scale up is tacitly assumed to be valid without forethought.

A major effort of the validation subtask will be an evaluation of the scale up from short-term laboratory results. The short-term results will be extrapolated and compared against known theoretical concepts such as weathering, ore deposition geochemistry, mineral stability and thermodynamic Eh-pH diagrams. The short-term laboratory studies will also be compared with longer term observations made at existing pertinent sites such as the Oklo natural reactor, Nevada Test Site, Grants Mineral

Belt uranium deposit, and shallow land burial sites. Parts of this effort are being performed on independent contracts (LASL Natural Reactor Study) or can be compiled from the literature (thermodynamic data, migration at shallow land burial sites).

If gaps in the necessary thermodynamic data or additional pertinent geologic sites are identified which are not externally funded, PNL Waste Isolation Safety Assessment monies will be allocated; Lawrence Livermore Lab's existing field study at Nevada Test Site will receive supplemental funds from PNL.

Additional field studies and larger lysimeter, or intact, core laboratory studies may be performed in future years if justification becomes apparent.

An outline of Subtask 4 and the contractors involved in FY 77 are presented below. Figure 5 shows the work units, time schedule, and interactions with other tasks.

A. Theoretical studies (PNL, LBL, LASL)
   1. Eh-pH
   2. Mineral stability
   3. Weathering

B. Pertinent geological sites (LASL, LLL, PNL)
   1. Natural reactors, OKLO
   2. Uranium deposits
   3. Nevada Test Site
   4. Shallow land burial sites, Chalk River, U.S. ERDA sites, European sites

C. Additional field or lab studies (future years)

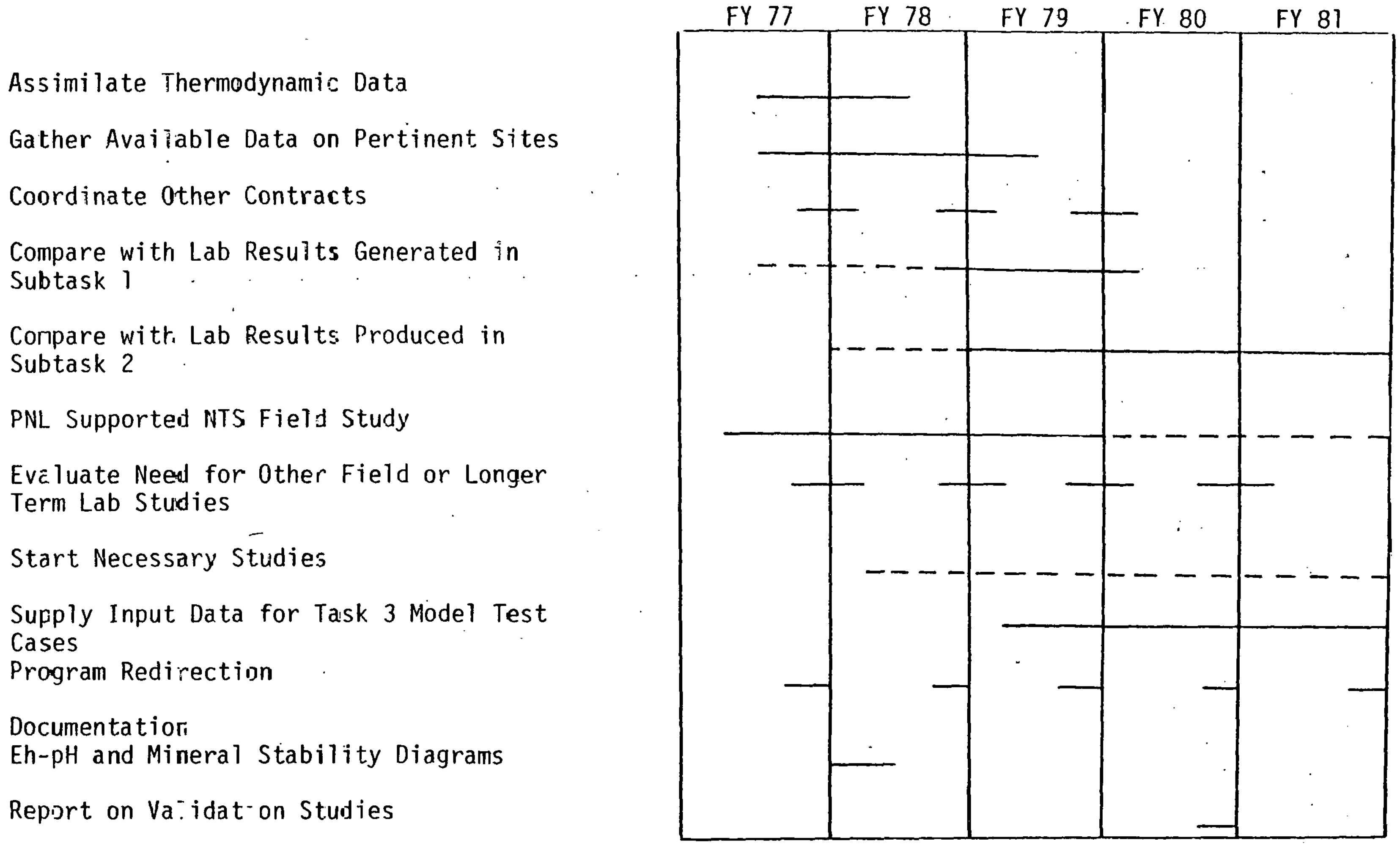

FIGURE 5. Subtask 4 - Validation Studies

SUBTASK 5: SORPTION-DESORPTION MECHANISM STUDIES

As discussed in Subtask 1, the determination of migration rates of nuclides by various methods often shows significant variation. In the future when this experimental design dependency is understood, there still will not be a general understanding of the mechanisms controlling the migration rates of nuclides. Subtasks 1, 2, and 3 are empirical and geologic material and solution specific. Results of this nature do not rigorously lend themselves to extrapolation to other situations or to an understanding of controlling mechanisms.

The emphasis of Subtask 5 will be to investigate the basic factors and their interactions that control the sorption-desorption of actinides, long-lived fission products, and activation products by geologic media. With knowledge of mechanisms, migration rate predictions can be performed from more theoretical and fundamental data (see Table 1) for any proposed storage environment. The use of theoretical and fundamental data may cut the costs expended to quantify the migration rates of nuclides at specific sites. Subtask 5 will have a lesser priority for the first three years but increase significantly in importance later in the program. The proposed outline will be modified with the mass of information obtained during subtasks 1 through 4 endeavors.

The following outline and Figure 6 describe the current formulation of Subtask 5. Nominal scouting studies on elucidation of sorption mechanism predominant for different rock types and the potential importance of physical sorption of colloids will be performed in FY 77 - FY 79 but the major thrust will be postponed until FY 80.

In FY 77 ORNL, Sandia, and PNL performed preliminary mechanism studies on the effects of solution ionic strength on nuclide sorption, microstructural identification of specific sorption sites, and controlled ph-Eh sorption experiments on Pu, respectively.

A. Solid matrix effects - The solid matrix constituents are mainly negatively charged but under low pH conditions also exhibit varying degrees of positive charge. The origin, extent, and intensity of the charge varies with different minerals. Depending upon the charge characteristics, the solid matrix will adsorb oppositely charged ions with varying strengths by an exchange process. Therefore, the adsorption-desorption isotherms for the following common constituents will be determined:

1. Standard rock and clay minerals
2. Amorphous oxides (Fe, Mn, Al)
3. Effect of CaCO3 which is ubiquitous in sedimentary rocks and in soils with high pH
4. Consolidated and unconsolidated rocks and sediments (limestones, granites, shales, salt, tuff)

B. Adsorption-desorption mechanisms - Solid compounds, adsorbed ions, and pore solution exist in a dynamic equilibrium with each other. Nuclides added to the pore solution may be adsorbed to varying degrees by the minerals and may precipitate as discrete solid phases or coprecipite with other solid phases as investigations with trace metals have shown. Many factors will influence the above reactions. Following is a list of the factors that would be investigated in order to evaluate these reactions:

1. pH
2. Oxidation-reduction potential
3. Nuclide ion valence states and concentrations
4. Concentration of complexing inorganic ligands such as carbonates, bicarbonates, phosphates, sulfates, fluorides, and natural organic ligands such as fulvic and humic acids
5. Concentrations of competing cations such as Ca, Mg, Na, and K

C. Movement and adsorption of fine particulate and colloidal species of actinides - Various actinide elements such as Pu and Am form colloidal particles to significant extent over a wide pH range. These colloidal particles, because of their larger size than the solution species and their change in ionic charge due to change in important variables such as pH may show a different movement and adsorption behavior than the solution species.

The movement of Pu with depth in sediment as fine particulate matter has been either observed or inferred. [1,2,3] However, no conclusive evidence is available whether this is due to the movement of fine discrete particles of PuO2 or due to association of Pu with the mobile fine inorganic fraction of sediments. This difference in form may be important to migration because of the expected variation in dispersion of the discrete and inorganic associated particulate Pu. In either case, the downward movement of particulate Pu will be different than the soluble species and would mainly depend upon the physical factors such as porosity, rate and amount of water movement, and the size of the particulates.

Column studies will be done to elucidate the movement and adsorption behavior of colloidal and particulate nuclides. Specifically, the following factors will be investigated:

1. pH
2. Ionic strength
3. Influence of solid matrix
4. Porosity and pore size distribution
5. Rate and amount of water movement
6. The sodium adsorption ratio

D. Forms of the actinides in the terrestrial environments - The actinide forms such as soluble, exchangeable, coprecipitated with other minerals, or discrete solid phases, to a large degree will give indications regarding the actinide avilability to plants, water pollution potentials, and the rate and amount of movement through consolidated and unconsolidated geologic materials. For example, soluble and exchangeable elements are readily mobile while geologic matrix-complexed actinides may be relatively tightly bound. From the knowledge of the discrete phases, their solubility products, and other solution parameters, it may also be possible to predict the amount of the actinide present in solution from theoretical thermodynamics.[4] Where data does not exist extrapolations using chemically similar minerals and elements may be used.

In order to determine the forms of the actinides, actual and laboratory contaminated sediments will be successively leached with chemicals which would predominantly remove a selected form of the actinide. Some of the extractions will be preceded and followed by the observation of the sediments with a high resolution petrographic microscope, microprobe elemental mapping, and radiography to determine the actinide solid phases present and attacked by the chemicals. For the results of these extractions to be meaningful, it is imperative that a given chemical remove mainly a given form. Some of the reagents used to remove water soluble, exchangeable, organically bound, amorphous iron bound, amorphous silica and aluminum oxide bound trace metals will be studied for their efficiency and accuracy to determine actinide forms. A few of the reagents that will be studied are: distilled water, a salt solution such as 1N $MgCl_2$, H_2O_2, sodium hypochlorite, acid ammonium oxalate, sodium dithionite-citrate-bicarbonate, and KOH. Water leachates, if sufficiently concentrated in Pu, will be used to determine the valence state and speciation of Pu. Solvent extraction techniques including procedures described by Bondietti, et al., [5,6] and laser spectroscopy [7] would be used. The speciation of other nuclides will be classified as: (1) suspended fine particulates, (2) soluble cationic forms, (3) soluble anionic forms, and (4) soluble uncharged forms using filtration and exchange resin techniques.

E. Rates and amounts of actinide movement - The program outlined in the first four work units will elucidate the effect of solid matrix, factors that influence the movement and adsorption of actinides, the mechanisms of adsorption, the exchange constants, and the possible solid phases and forms of the actinide present in geologic environments. From the results of these studies a geochemical model will be formulated to predict the behavior of a given actinide element under any given geologic environment.

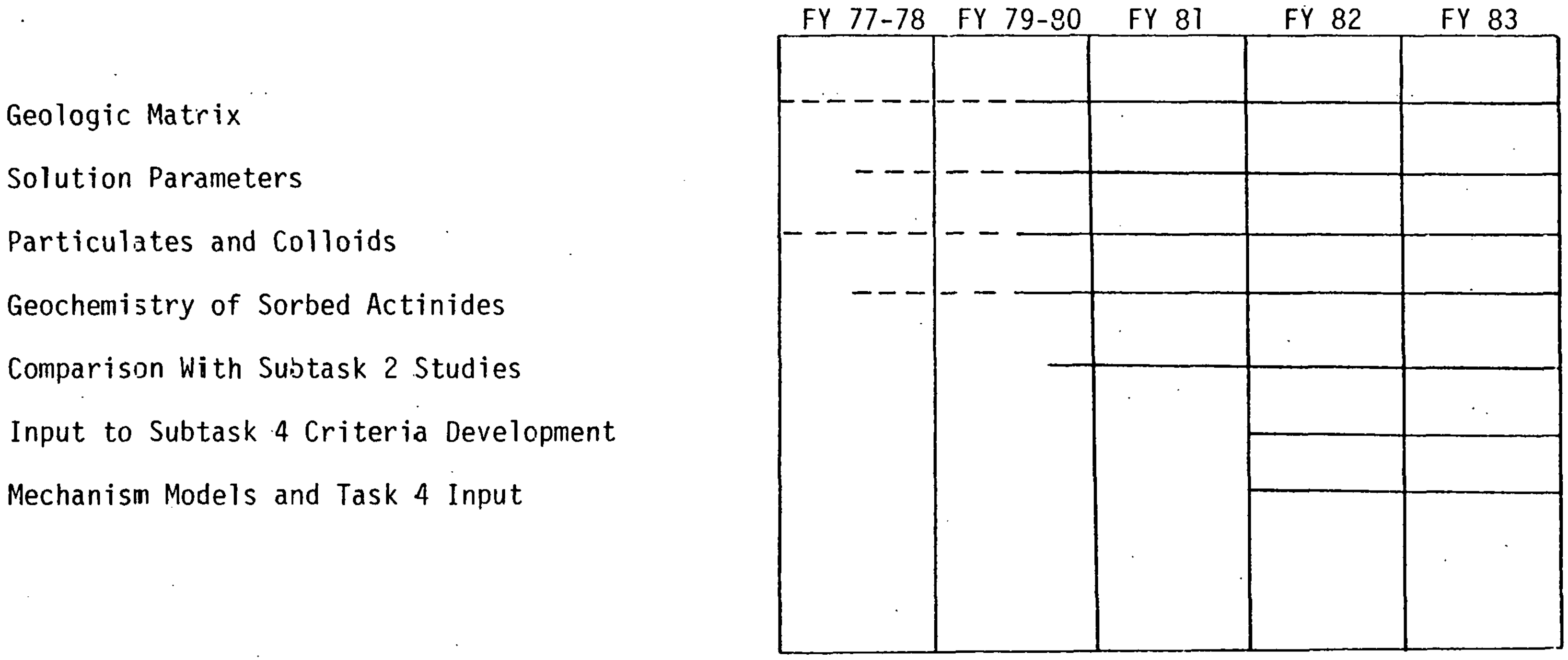

FIGURE 6. Subtask 5 - Sorption-Desorption Mechanism Studies

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SUBTASK 6: GEOCHEMICAL INTERACTIONS TECHNICAL MANAGEMENT AND INTERPLAY WITH OVERALL OWI PROGRAM

As previously mentioned, the overall objective of Task 4 is to provide geochemical interaction data to aid in the safety assessment of long term storage of solidified nuclear wastes. The overall assessment task will necessitate a broad, truly multidisciplinary, approach. Some of the major tasks of PNL, as managers of the nuclide migration portion of the OWI program, will be to: (a) coordinate the numerous subcontracts, (b) assure that the scope of work does not deviate from OWI needs, (c) see that the programs produce necessary data in a timely fashion, and (d) assure that the quality of the work is high.

In this era of information explosion it is also important to provide timely and widespread dissemination. As part of PNL's management objectives, formal interaction with other OWI work units, other ERDA divisions such as DBER and DPR, and other organizations will be stressed. This will aid in keeping the national and OWI needs in perspective and will point out areas of potential conflict and duplication.

Well publicized yearly technical workshops and peer review groups, covering geologic media-waste interactions and nuclide migration, will be initiated in FY 78. Output from these meetings and PNL-managed studies will be documented in open literature articles and yearly technical progress reports authored by each subcontractor.

Yearly summary reports of the technical work performed in Task 5 will be published by PNL. At the completion of each work unit a technical report will be published by the appropriate contractor. PNL will provide guidelines so that report formats from all contractors are similar.

The work units outlined below will be a continual effort over the length of the OWI program as shown in Figure 7.

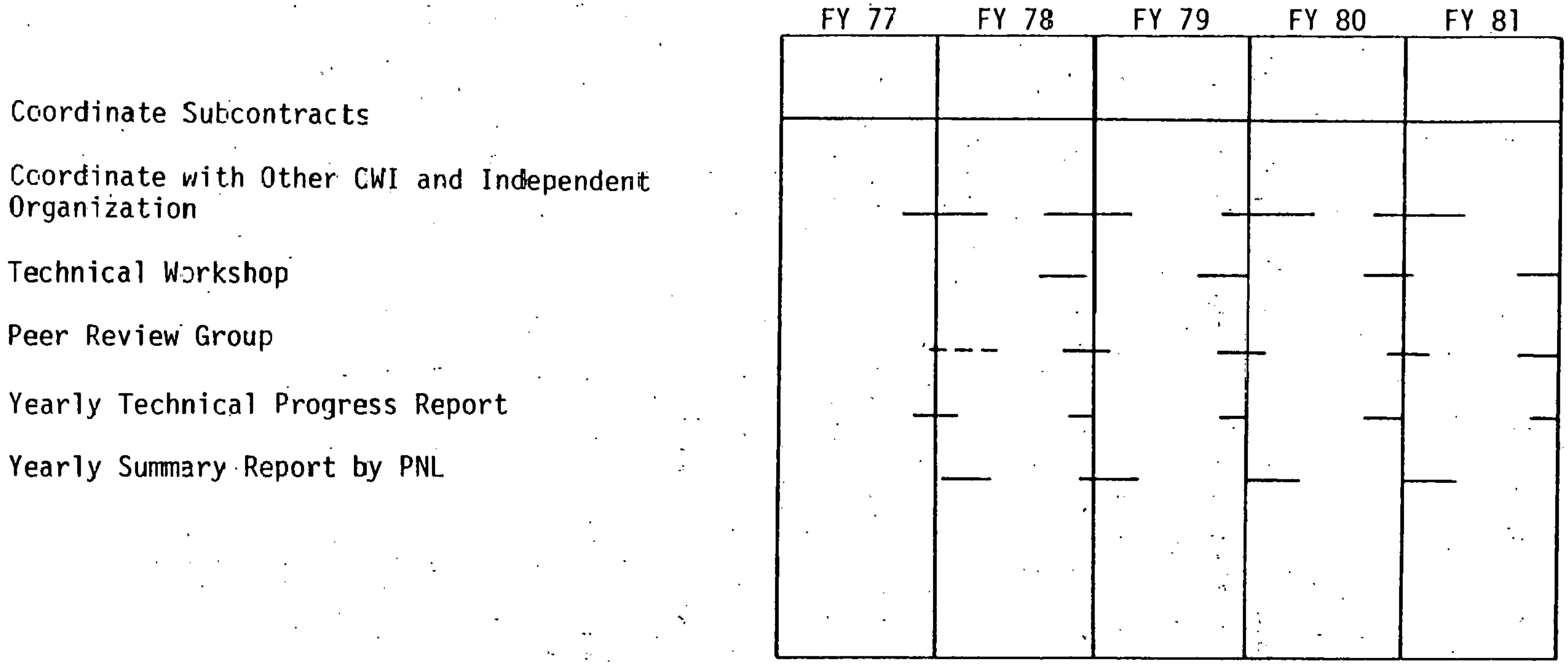

FIGURE 7. Subtask 6 - Geochemical Interactions Technical Management and Interplay with Overall OWI Program

A. Coordination of subcontracts (PNL)
B. Continual interaction with other OWI work units (PNL)
C. Coordination with other organizations (PNL)
D. Peer review group
E. Information dissemination
Yearly technical workshops (PNL)
Technical progress report (all contractors)
Yearly summary report (PNL)

Figure 8 is a conceptualization of how the six subtasks of Task 4 interrelate.

Figure 9 is a conceptualization of how the nuclide migration work package fits into the overall Waste Isolation Safety Assessment Program.

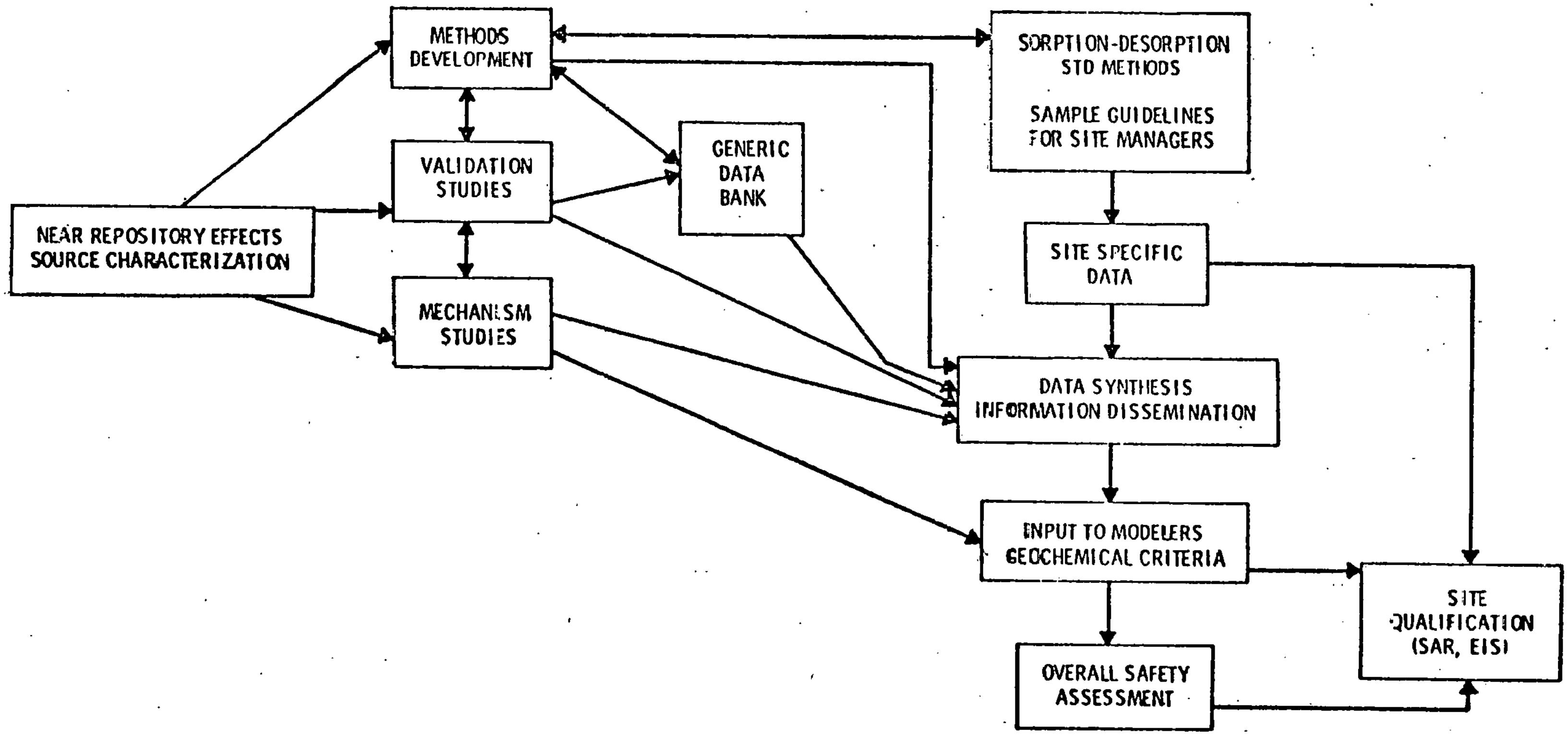

FIGURE 8. Interrelationship of the Task 4 Subtasks

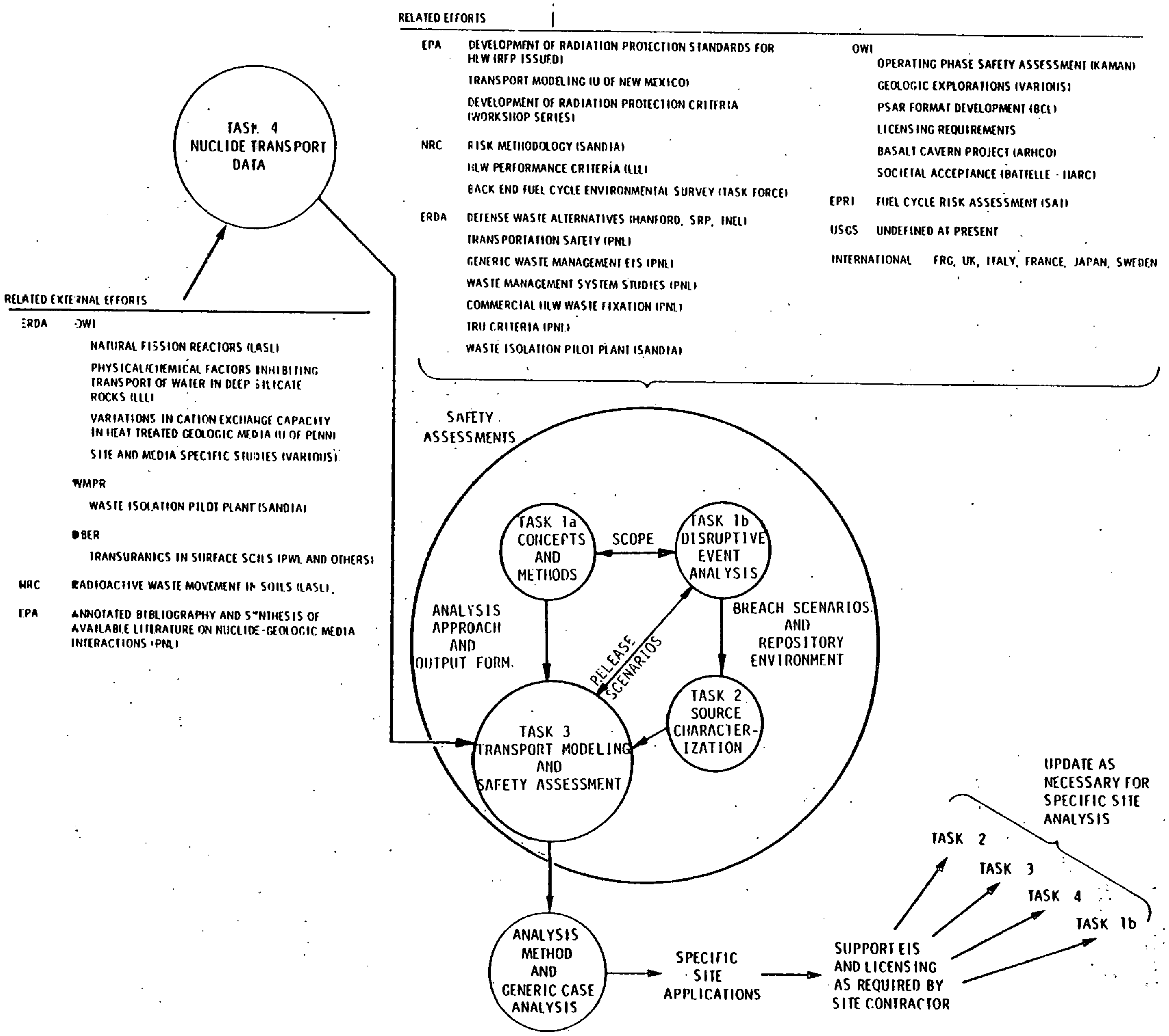

FIGURE 9. Overall WISAP Program and Other Related Efforts

DISCUSSION--R. J. SERNE

Focus of WISAP

Q. Have WISAP's generic responsibilities been taken away by the new focus on salt?

A. No, WISAP will continue to do generic studies. However, the hydrothermal programs and some of the other specific programs will be directed at salt for the time being.

Final Report

Q. With all of the contractors using different methods and obtaining different K_ds, who will write the final report, and what will the time frame be? Will you subcontract it out to an independent party to evaluate the date?

A. The report will be written by the Battelle staff, but there will be ample opportunity for all contractors to have input. Workshops will be a primary means of obtaining this input. Battelle will synthesize the feedback received from individual contractors at each workshop and present it in summarized form at the next; it will then incorporate new material and reactions from that workshop. The final output is expected to occur near the end of FY 1979; this should give contractors enough time to do adequate experiments. To meet OWI deadlines, however, Battelle will have to make preliminary assessments earlier.

Use of Term "K_d"

Q. Given all the confusion that has resulted from loose use of the term "K_d," can we agree to restrict the use of the term to its original meaning, and invent a new term for distribution as a function of time?

A. People in nuclear waste management have misused the term "K_d" from the start, resulting in a certain amount of confusion as to exactly what is meant whenever the term is used. On the other hand, introduction of a new term at this point could cause even more confusion. Perhaps this question could be dealt with at more length in the Open Floor Discussion at the end of the conference; the group could then be surveyed for its recommendations.

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This is a progress report based upon only a part of the results which will be collected for this study. Therefore, the conclusions drawn from this report or the results discussed herein are tentative and should not be quoted without the knowledge of the authors.

"ADSORPTION OF Pu(IV) AND Pu(VI) UNDER CONTROLLED pH AND Eh BY SOIL MINERALS"

by

Dhanpat Rai

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September 1977

ADSORPTION OF Pu(IV) AND Pu(VI) UNDER CONTROLLED pH AND Eh BY SOIL MINERALS[1]

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

Battelle-Northwest

INTRODUCTION

Elements such as Pu, Np, and Am may exist in several oxidation states in soil solutions. The adsorption, complex formation and movement of these elements in the geologic environment among other factors is dependent on the oxidation state. There are little data available on the effect of oxidation state on the adsorption of Pu by soil minerals under known pH conditions (Prout, 1959; Bondietti and Reynolds, 1976). There are no data available where Pu adsorption experiments were run under measured or controlled pH and Eh conditions such that the oxidation state distribution would not change during the experiment. Stock solutions containing Pu(III), Pu(IV), and Pu(VI) can be prepared for adsorption studies and with proper control of pH and Eh the dilute suspensions may be maintained in a specific oxidation state. One of the major difficulties with the data available in the literature is that little effort was made to control the pH and Eh of the suspensions during the adsorption experiment. Eh can be controlled by the addition of oxidizing or reducing agents. However, the effect of these oxidizing or reducing agents on the Pu adsorption by soil minerals is not known. Therefore, preliminary experiments on the use of the potentiostat to control Eh of the suspensions was investigated and found feasible. Since the potentiostat maintains Eh by an electron transfer process instead of adding some buffering chemical, the interference by this method on adsorption of elements should be minimal. The objective of this study was to investigate the adsorption of various oxidation states of Pu by soil minerals under different pH values and controlled Eh conditions.

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[1] This is not a final report but a progress report based upon only a part of the results which will be collected for this study. Therefore, the conclusions drawn from this report or the results discussed herein are tentative and should not be quoted without the knowledge of the authors.

MATERIALS AND METHODS

Various cells that can be used with a potentiostat to control the Eh of the solutions are described by Harrar (1975). All of the cells described by Harrar (1975) are made from glass and are used for coulometric determinations. For the present study it was necessary to centrifuge the cells and have cells that would withstand high centrifugal forces (∿6000 RPM). Therefore, a cell made of teflon was designed specially for this study (Figure 1). The cell is of 1 1/2" inside diameter and is about 3" long with a screw cap that holds a working electrode, counter electrode, salt bridge, pH electrode, gas inlet, gas outlet and solution spiking and sampling port. The working electrode consists of a 45 mesh bright platinum cylinder of 1 1/4" diameter and 1 1/4" height. The counter electrode was made by folding 52 mesh (2" x 1") platinum gauze lengthwise and soldering it to a platinum wire. The counter electrode is placed in the center of the working electrode and is isolated from the sample with glass tubing fitted at the end with a conducting porous (unfired) vycor glass frit. The glass tube containing the counter electrode was filled with 0.1N KCl solution. A saturated calomel electrode is used as a reference electrode. The reference electrode makes an electrical contact with the solution through a salt-bridge tube containing 0.1N KCl. The conducting tip of the salt-bridge was positioned a few mm away from the working electrode. A combination reference/glass electrode is used to continuously monitor the pH. The solution in the cell is stirred by a Teflon coated Spinfin (5/8" diameter) which sits in the center of the cell in a recessed cavity.

Since little information is available for the use of potentiostat in controlling the Eh of the soil slurries, a preliminary experiment was conducted to determine the feasibility of use of the potentiostat in controlling the Eh of the soil slurries. Kaolinite-water slurries were adjusted to different potentials with the potentiostat. The potential of the solution at various distances from the working electrode was determined with an independent electrode over a several hour time period. These independently determined potentials were not significantly different from the applied potential which had been set on the potentiostat, suggesting Eh control is possible.

For the adsorption experiments, one gram of the mineral sample was added to the cell containing 30 mls of 0.03N $CaCl_2$ solution. The Eh of this soil suspension was adjusted to the value where either Pu(IV) or Pu(VI) oxidation states are expected to be relatively stable (Table 1). Prepurified N_2 gas was

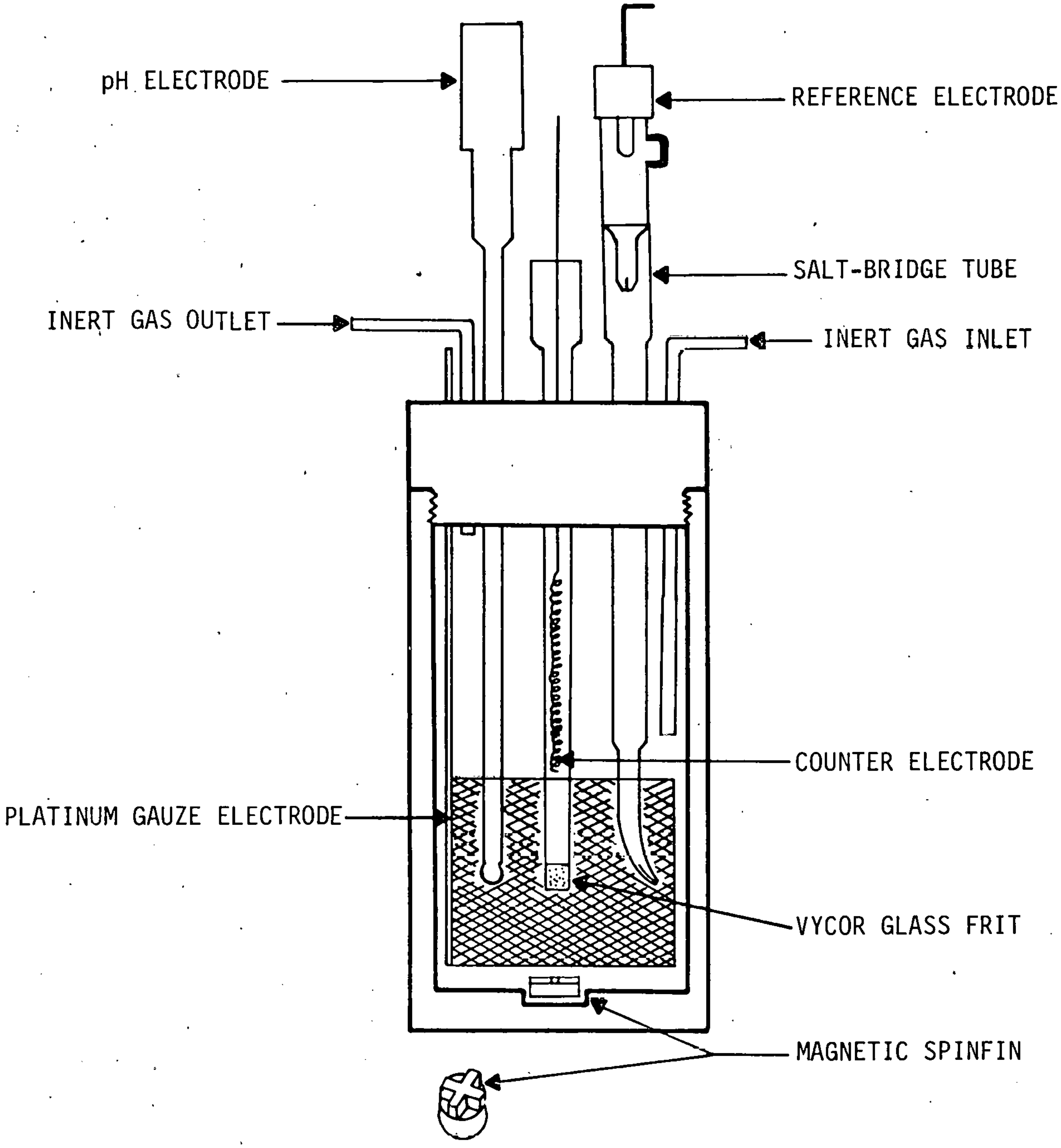

FIGURE 1. Teflon Cell Used to Control the Potential of Solutions

TABLE 1

SELECTED POTENTIALS FOR Pu(IV) AND Pu(VI) ADSORPTION

Oxidation State	pH of Solution	Selected Potential vs the Standard Calomel (Volts)
Pu(IV)	4	-0.9
	7	-0.7
Pu(VI)	4	-1.1
	7	-0.9

passed continuously over the solution surface in order to create an inert atmosphere. The sample was pre-equilibrated for approximately half an hour at the applied potential to assure proper Eh. Then a small aliquot (0.02 to 0.05 ml) of the Pu^{239} stock solution in strong acid containing 3.951 x 10^6 dpm Pu(IV) or 2.137 x 10^6 dpm Pu(VI) was added. The pH of the suspension was adjusted to a desired value as soon as it was possible after Pu addition with HCl or NaOH.

At the end of several time intervals, the suspensions were centrifuged at ∿6000 RPM for approximately 10 minutes. A small aliquot (0.1 ml) of the supernatant solution was withdrawn for Pu determinations. The centrifuged solids were resuspended and the equilibration was started again.

In order to determine Pu, the samples were spiked with Pu^{242}, digested in concentrated HNO_3, and evaporated to dryness. The Pu was taken up in H_2SO_4 titrated with NH_4OH and electroplated at pH 1.8 to 2.0. The concentrations of Pu^{242}, Pu^{239}, and Pu^{238} were determined with alpha energy analyzers.

RESULTS AND DISCUSSION

The results obtained so far on adsorption of Pu(IV) and Pu(VI) are presented in Figures 1 through 3. These figures, in general, indicate that the major amount of adsorption or change in solution concentration occurs in the first 15 minutes. Pu(IV) concentrations in solutions at any given pH are much lower than the Pu(VI) concentrations (Figures 2 and 3). Plutonium concentrations in solution in contact with montmorillonite at pH 4.0 were much lower than the blanks or the solutions in contact with kaolinite (Figure 2). At pH 7, the Pu(VI) concentrations in contact with kaolinite were much lower than the blanks (Figure 3).

From the foregoing, it appears that the oxidation state, pH, and surface area and/or cation exchange capacity has a significant influence on the adsorption of plutonium. In general the Pu(VI) adsorbs less than the Pu(IV). An increase in pH increases the percentage adsorption. An increase in surface area and/or cation exchange capacity appears to increase the adsorption.

Figures 2 and 3 indicate that the concentration of plutonium, in solutions without clays, decreases in blank solutions also. This decrease in concentration may be due to precipitation and/or adsorption by the cell wall and electrodes. In order to avoid possible precipitation the solution

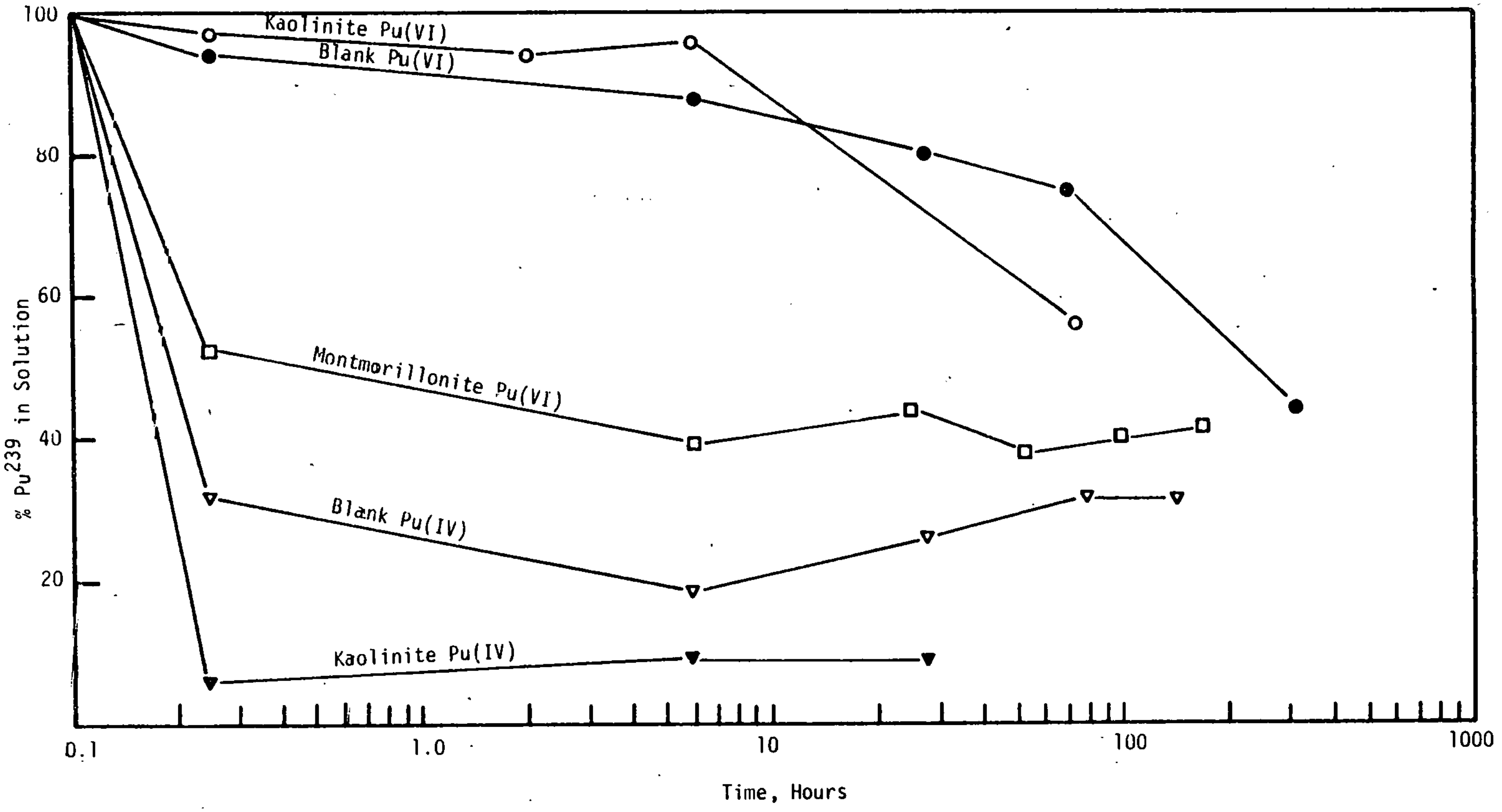

FIGURE 2. Changes in Pu^{239} Concentration in Solution with Time in a pH 4.0 and 1:30 Clay to Solution (0.03N Ca) Ratios.

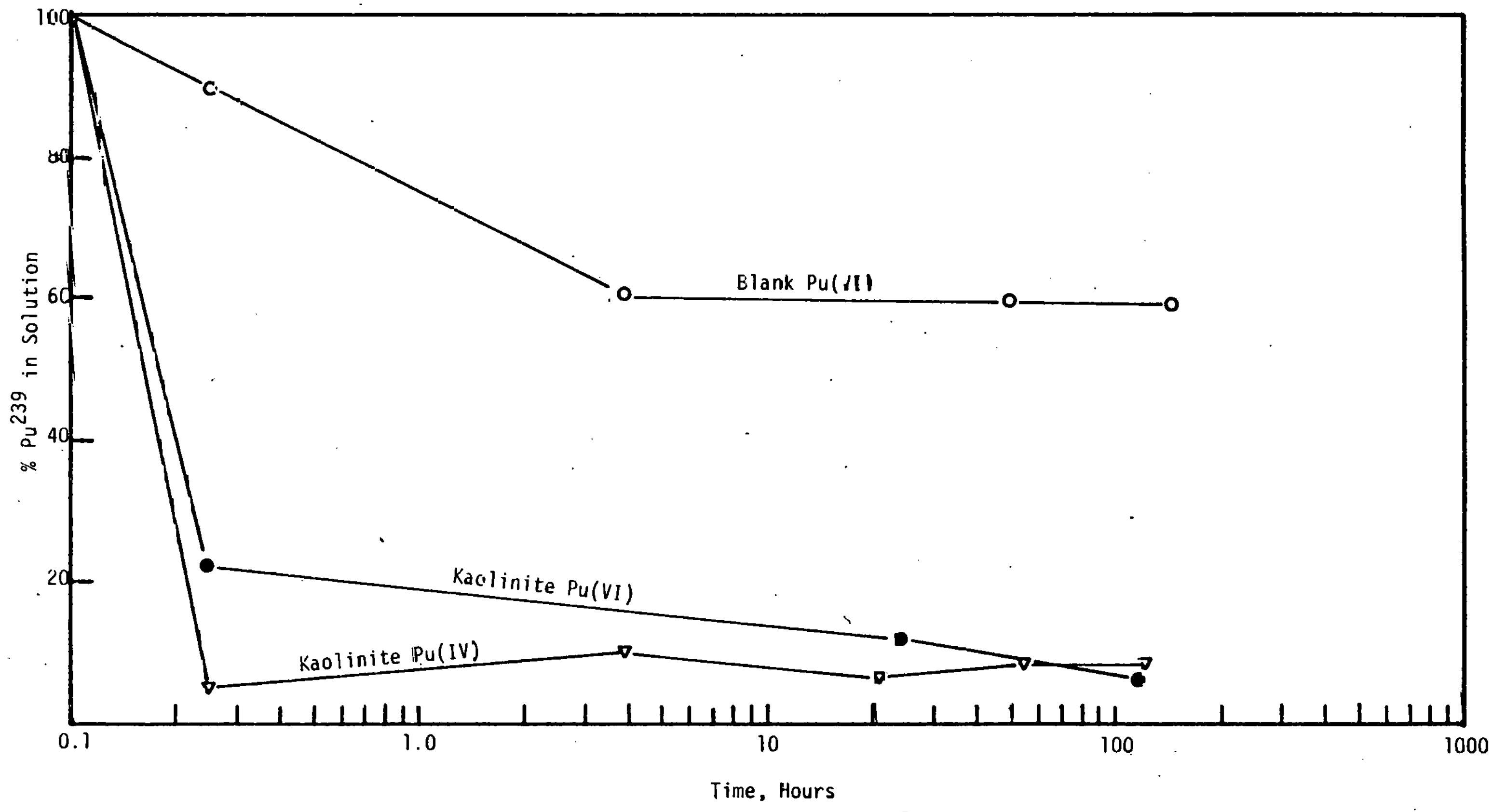

FIGURE 3. Changes in Pu^{239} Concentration in Solution with Time in Suspensions of pH 7.0 and 1:30 Clay to Solution (0.03N Ca) Ratios.

concentrations in future experiments will be selected such that the plutonium concentration in the equilibrium solutions does not exceed that which can be maintained by $Pu(OH)_4$ and/or PuO_2. The results reported by Rai and Serne (1977) would help in selecting these concentrations. In order to check whether a certain amount of plutonium is electroplated or adsorbed by the electrodes, the concentration of Pu in solutions with and without the potentiostatic Eh control were determined (Figure 4). The concentration of Pu in solutions with and without the electrodes did not differ significantly. Therefore, it can be stated that the electrodes used to control the solution potentials would have negligible effect on the change in Pu concentration in solution over pH and Eh ranges studied in this experiment.

FUTURE PLANS

Future plans include the study of adsorption of Pu(III), Pu(IV), and Pu(VI) by several minerals for a specific time period under differing total concentrations of Pu. These data will be collected for pH 4 and 7. This study would help rate the minerals according to their relative importance in adsorption of Pu under a given pH, oxidation state, and differing total Pu concentrations.

ACKNOWLEDGEMENTS

We would like to thank Dr. Robert W. Stromatt, an electroanalytical chemist with HEDL, for his many helpful suggestions and discussions during the planning stages of the experiment.

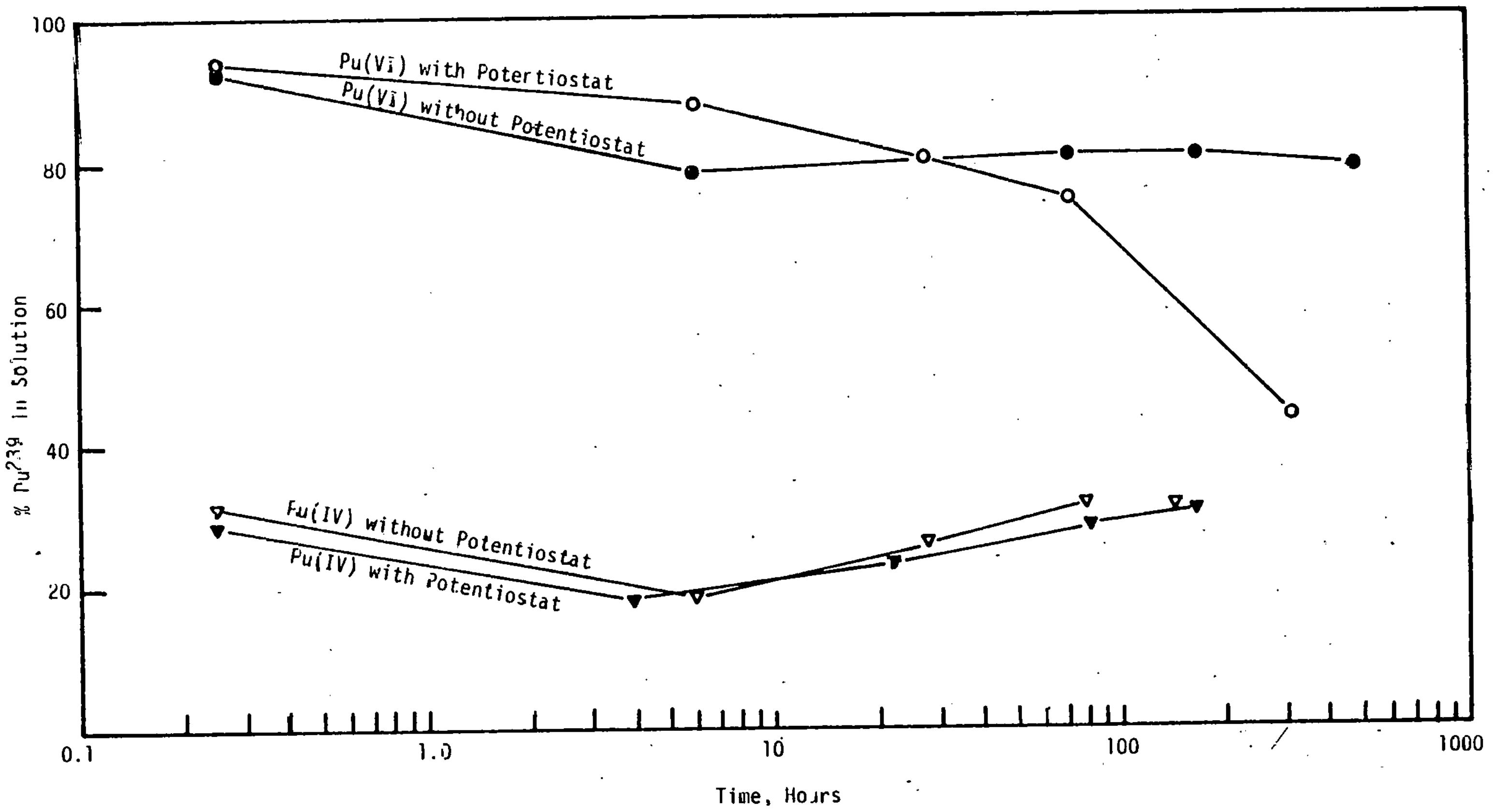

FIGURE 4. Changes in Pu^{239} Concentration in Solution with Time in a pH 4.0 and 0.03N Ca Solutions Containing Pu(IV) (131706 dpm/ml) and Pu(VI) (71230 dpm/ml).

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DISCUSSION--DHANPAT RAI

Changes in Pu^{239} Concentration Over Time at pH 4.0 (Figure 2)

Q. What was your initial Pu concentration?

A. About 10^{-6} M.

Q. What is the solution in contact with besides clay?

A. It's in contact with all the electrodes in the cell, as well as the salt bridge (see Figure 1).

Q. What is the gas that is passed through the solution and how pure is it?

A. Nitrogen, and it's about 99.99% pure.

Q. How is the solid phase separated from the liquid phase?

A. The whole cell is centrifuged at 6,000-7,000 rpm; after the solids have settled, a sample of the supernatant is taken.

Q. How did you determine that Pu(VI) would be stable at that particular Eh?

A. First, because of the way in which the solution was prepared, we were reasonably sure that the amount of Pu in a given valence state was 99% or better. Then, based on the work of Dr. Cohen, we assumed that, if we could create the highest oxidizing condition possible without introducing free oxygen ions, Pu(VI) added to the system would remain stable.

Q. Why did the concentration of the Pu(VI) blank drop after about 80 hrs?

A. I'm not sure; it could be an artifact or it could be an actual drop. If the drop is real, it could mean that the oxidation state is not being maintained.

Q. Isn't it an artifact of plotting Pu concentration as a logarithmic function of time?

A. That could also be true.

Q. Is the drop in Pu concentration due to precipitation?

A. We haven't had time to check this out thoroughly, but we assume that at least part of it is going into the cell walls.

Q. What criteria were used to determine that 10^{-6} M is too great to be considered a trace concentration?

A. We looked at reports, which indicate that 70% of the Pu disappears from the solution. This makes us think that some mechanism other than adsorption is going on--perhaps precipitation. We plan to look at much lower concentrations, however; this should help us determine what in fact is happening.

Q. Can you be sure that bacteriological growth is not affecting the results?

A. Yes; the minerals we used were pure minerals, from which the organic matter had been removed. Therefore, there should be very little biological activity occurring.

Q. Do you use sterile water?

A. We use repurified distilled water, but it's not sterile.

Q. Was the montmorillonite definitively characterized as a single mineralogical phase?

A. Yes, it was.

Q. Did you subject the solution to any pretreatment or preloading?

A. Yes--with Ca.

Q. What is the total surface area of the minerals?

A. About 30 m^2 for kaolinite, and 800 m^2 for montmorillonite.

Q. What method did you use to determine surface area?

A. The ethylene glycol method; most soil scientists use this method, and we feel that it gives a fairly reliable measurement.

Q. How does that relate to the BET method?

A. BET gives external surface area only; glycol gives you the total area--internal plus external.

Q. How many replications does each point represent?

A. Right now, only one; but we have samples of the solution in storage, and we plan to analyze these again later.

Q. After the experiment was complete and you had measured the amount of Pu(VI) in the supernatant, did you then determine its oxidation state?

A. Not yet, but we're planning to do that.

Q. Do you have any data on Pu(VI) concentrations in the presence of montmorillonite?

A. We're in the process of obtaining it.

Changes in Pu Concentration Over Time at pH 7.0 (Figure 3)

Q. Why does shifting the pH to 7.0 cause the Pu(VI) concentration in the presence of kaolinite to change so dramatically?

A. I'm not sure; it's probably a precipitation phenomenon.

Q. Did you try the experiment with both Pu(IV) and Pu(VI) in the starting solution?

A. No, these are separate experiments.

Q. Have you done experiments where both oxidation states are present initially?

A. No, I haven't.

Q. Are Pu(IV) and Pu(VI) the oxidation states that could be expected to be present in natural groundwater systems?

A. Pu(IV) is; Pu(VI), however, is not very stable.

Q. What about Pu(III)?

A. In a system like this, where there is no reducing condition in the soil system, Pu(III) would oxidize to Pu(IV).

This is a progress report based upon only a part of the results which will be collected for this study. Therefore, the conclusions drawn from this report and the results discussed herein are tentative and should not be quoted without the knowledge of the authors.

"IDENTIFICATION OF PLUTONIUM COMPOUNDS AND THEIR SOLUBILITY IN SOILS"

by

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September 1977

IDENTIFICATION OF PLUTONIUM COMPOUNDS AND THEIR SOLUBILITY IN SOILS[1]

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Battelle-Northwest

INTRODUCTION

The solid compounds of Pu that may be present in soils would 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 would, in turn, largely control the distribution of Pu in the environment. Therefore, the knowledge of Pu compounds present in the soil and their solubility is necessary in order to predict the behavior or fate of Pu in the soil.

The reliable data on solubility of PuO_2, $Pu(OH)_4$, and $PuO_2(OH)_2$, the compounds most likely to form in soils, at environmental pH and Eh values are lacking (Rai and Serne, 1977). An extensive review (Ames, Rai, and Serne, 1976) on actinides indicated that numerous workers have studied the Pu concentrations and distribution with depth in soils. 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 the contaminated soils and analyzed them with electron microprobe and X-ray diffraction. They were able to identify a large portion of the material as PuO_2 but were not able to identify the nature of the compounds associated with soil silicates. Price and Ames (1975) results are consistent with the theoretical calculations of Rai and Serne (1977) who predicted that the PuO_2 would be the most stable mineral at equilibrium in the pH and Eh ranges found in terrestrial environments.

It is clear from the above discussion that information regarding the solubility of various Pu compounds and the nature of the solid compounds that may be present in the soils is needed. The objectives of this study were to:

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[1] This is a progress report based upon only a part of the results which will be collected for this study. Therefore, the conclusions drawn from this report or the results discussed herein are tentative and should not be quoted without the knowledge of the authors.

1. determine Pu concentrations in equilibrium with $PuO_2(OH)_2$, $Pu(OH)_4$, and PuO_2 at environmental pH and Eh conditions;
2. identify Pu compounds in soils; and
3. provide guidelines for the trace Pu concentrations needed for adsorption experiments to assure that Pu precipitation would be negligible or absent.

METHODS AND MATERIALS

Three pure compounds used in this study were PuO_2, $Pu(OH)_4$, and $PuO_2(OH)_2$. PuO_2 was obtained from Oak Ridge National Laboratory. $Pu(OH)_4$ and $PuO_2(OH)_2$ were prepared by neutralizing ∿8M HNO_3 solutions containing Pu(IV) and Pu(VI) with NaOH (Cleveland, 1970). The precipitates were washed free of Na with distilled water.

In order to determine the solubility of various plutonium compounds, approximately 8 mg of each solid compound was transferred to a different polycarbonate centrifuge tube. Twenty mls of 0.003N $CaCl_2$ solution was added to each of these tubes and the pH values were adjusted to 4.0, 5.5, 7.0, and 8.5 using NaOH or HCl as needed. The whole experiment was duplicated. The suspensions were aged. At various time intervals (7 days, 21 days, 90 days, ...) the suspensions were centrifuged at 6,000 RPM for approximately 40 minutes and a small aliquot (0.1 ml) of the supernate was withdrawn for Pu analysis. The pH of the suspensions was periodically readjusted (approximately every fifth day). The pH 4.0, 5.5, and 7.0 suspensions needed little adjustment after the second or third adjustment, whereas pH 8.5 suspensions tended to decrease to approximately 8. This experiment has been going on for a little over 100 days. No pH adjustment was made after 21 days of aging.

In order to determine the nature of the plutonium compounds present in the contaminated soils, three contaminated soils from Hanford waste disposal cribs (Z9-4-5A; Z9-4-11A; Z12-1D) were used. The soils were washed once with distilled water to remove soluble salts and then equilibrated with 0.003N Ca solution in duplicate. Equilibrations were carried out with soil only, soil plus 5 mg PuO_2, and soil plus 3 mg $Pu(OH)_4$. Samples of Z9-4-11A were also adjusted to various pH levels as discussed under dissolution studies. At various time intervals (7 days, 21 days, 90 days, ...) the suspensions were centrifuged at 6,000 RPM for approximately 40 minutes and a small aliquot (0.1 ml) of the supernate was withdrawn for Pu analysis.

The aliquots of supernate containing Pu were spiked with Pu^{242}, digested in concentrated HNO_3, and evaporated to dryness. The Pu was taken up in H_2SO_4, titrated with NH_4OH and electroplated at pH 1.8 to 2.0. The concentrations of Pu^{242}, Pu^{239}, and Pu^{238} were determined with alpha energy analyzers. The above method is most useful when a very small amount of various radioisotopes is present in a large volume of solution. Most of the samples used for this study contained 1) only Pu, 2) relatively high concentrations of Pu in the solutions, and 3) solutions with low ionic strength ($\mu \sim 0.0045$). Therefore, an aliquot of the solution was dried on a stainless steel plate and directly counted for gross alpha which was used to calculate the concentration of Pu in the solution. The results presented in Figures 1 and 2 were obtained by using an electroplating method. The other results were obtained by the gross alpha method.

RESULTS AND DISCUSSIONS

PURITY OF THE COMPOUNDS USED FOR THIS STUDY

Pure PuO_2 crystalline microspheres enriched (>99.1 percent) with Pu^{239} were obtained from Oak Ridge National Laboratory. In order to further check the purity of the PuO_2 and predissolution properties, powder X-ray diffraction patterns were obtained. The d spacings obtained for this sample are reported in Table 1 along with the d spacings reported in ASTM for PuO_2. Almost perfect match of the sample d spacing with the values reported in ASTM (1966) indicates that the PuO_2 sample used for this study is indeed crystalline.

$Pu(OH)_4$ used in this study was very pure since the Pu solutions used to precipitate $Pu(OH)_4$ were free of radionuclides other than Pu and the solutions contained 99^+ percent of Pu(IV). As expected, the X-ray diffraction pattern of $Pu(OH)_4$ samples indicated it to be an amorphous compound. The purity of $PuO_2(OH)_2$ was ascertained by analyzing Pu(VI) solutions (used for precipitation) for radionuclides other than Pu. The Pu(VI) solutions contained only Pu thus indicating that $PuO_2(OH)_2$ used for this study was also pure.

DISSOLUTION OF PLUTONIUM COMPOUNDS

The concentrations of Pu in solution in contact with PuO_2 and $Pu(OH)_4$ were first determined after 21 days. The results on PuO_2 (Figure 1) indicated a wide variation (as high as 30 fold in some cases) in Pu concentration of duplicate aliquots withdrawn from a sample, and that the variation was greatest in high pH samples. The results on $Pu(OH)_4$ dissolution showed similar large variations (Figure 2). It was hypothesized that this large variation may be due to 1) the presence of plutonium particles in solution which do not flocculate on centrifuging at 6,000 RPM for 40 minutes and/or 2) the Pu analyses (electroplating and then alpha energy) method. Viewing showed that the PuO_2 microspheres had broken down into small particles. A large number of PuO_2 and $Pu(OH)_4$ samples had a film of Pu particles on the solution surface even after centrifuging at 6,000 RPM for 40 minutes. In order to make sure whether the Pu particles were causing the scatter in results, the centrifuged samples were filtered through 0.1μm and 0.015μm filters. Elimination of scatter in filtered samples would

TABLE 1

X-RAY POWDER DATA FOR PuO_2 SAMPLE

hkl	PuO_2 Sample d(A°)	PuO_2 Data from ASTM File d(A°)
110	3.118	3.08
200	2.696	2.67
220	1.909	1.894
311	1.627	1.617
222	1.559	1.548
331	1.239	1.234
420	1.208	1.203
422	1.103	1.100
511, 333	1.041	1.037

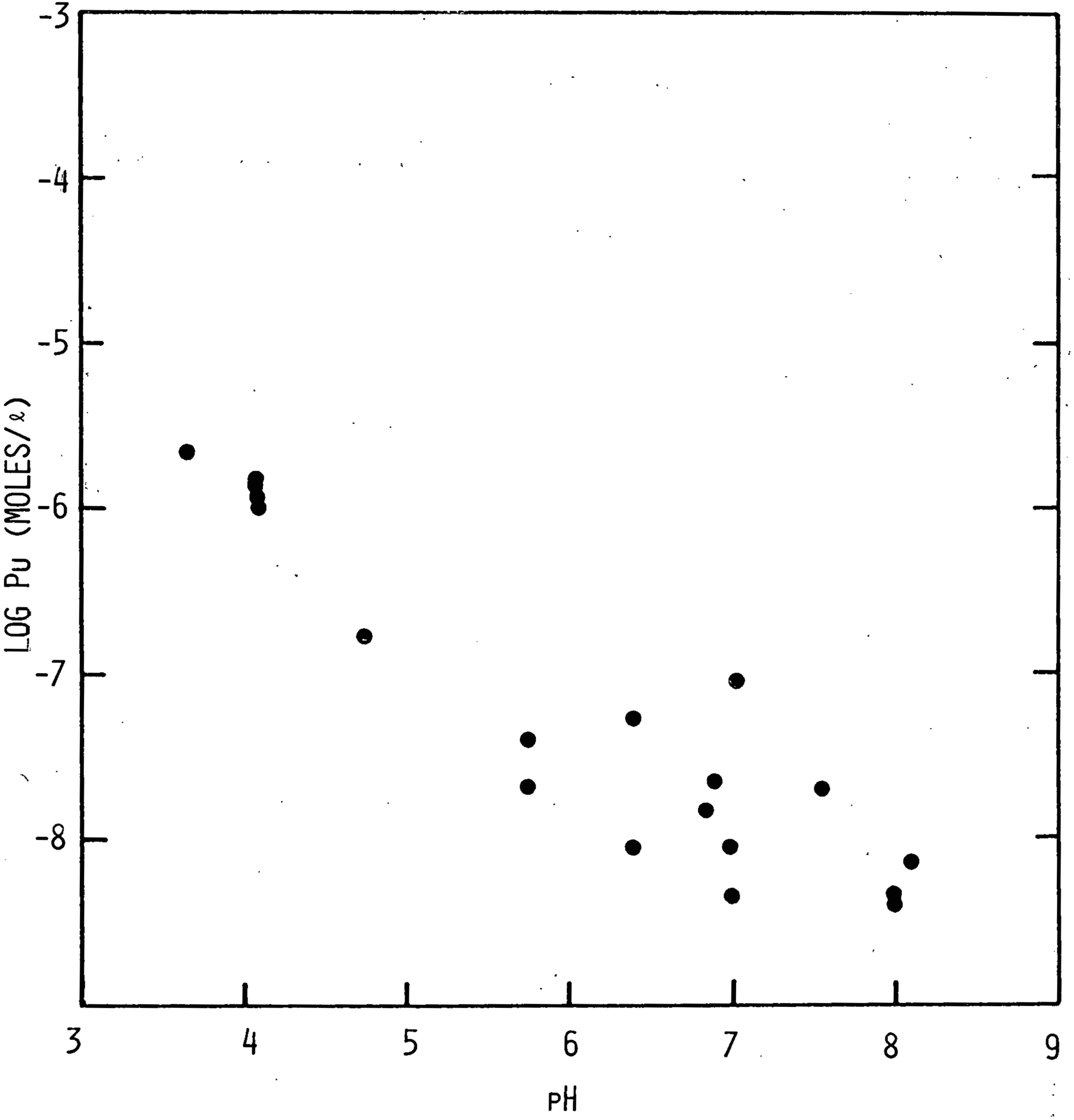

FIGURE 1. Pu Concentration in Unfiltered Solution when PuO_2 was Contacted with 0.003N $CaCl_2$ for 21 Days.

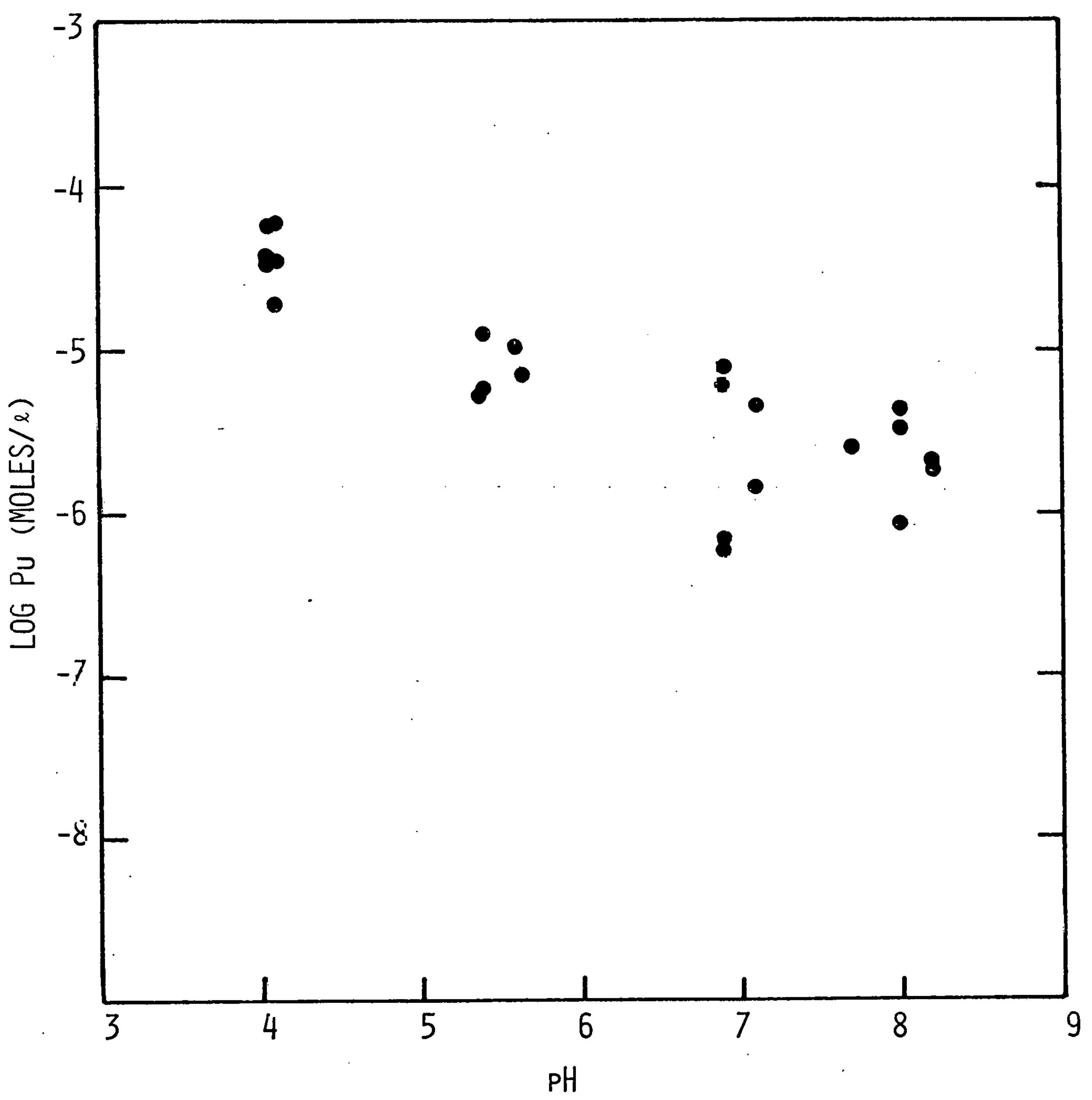

FIGURE 2. Pu Concentration in Unfiltered Solution When $Pu(OH)_4$ was Contacted with 0.003N $CaCl_2$ for 21 Days

indicate the presence of Pu particles that do not flocculate on centrifugation. The results on filtered and unfiltered solutions in contact with PuO_2 and $Pu(OH)_4$ for 90 days are presented in Tables 2 and 3. Low standard deviation in most cases indicates that reproducible results can be obtained by gross alpha counting instead of electroplating and then analyzing for radioisotopes. The samples filtered through 0.1 and 0.015μm do not differ significantly from each other, indicating the concentration of Pu particles >0.015μm and <0.1μm was small in these solutions. The Pu concentration in filtered solutions decreased with the increase in pH. The Pu concentrations in unfiltered low pH samples were generally closer to the filtered solutions; however, Pu concentrations in unfiltered relatively high pH solutions differed significantly from the filtered solutions suggesting colloidal Pu problems are more prevalent in basic solutions.

Scanning electron micrographs, electron microprobe, and X-ray diffraction patterns of the Pu retained on 0.1μm filters used for PuO_2-18 and PuO_2-20 samples were performed. The electron probe analyses of particles on PuO_2-18 filter indicated that these were definitely Pu particles and that they were similar in morphology to the untreated PuO_2 particles. However, these particles were so fine in size that X-ray diffraction patterns could not be obtained. The particles on a 0.1μm filter of a PuO_2-20 sample were similar to the PuO_2-18 sample; however, it was possible to obtain an X-ray diffraction pattern on these particles. X-ray diffraction patterns of PuO_2-20 indicated it to be a crystalline PuO_2. The foregoing discussion indicates that 1) the PuO_2 microspheres broke down in size due to contact with solution; 2) the scatter in Pu concentration with change in pH in unfiltered solutions is largely due to the PuO_2 crystalline particles in the case of PuO_2 samples; 3) the solutions do not contain significant amounts of colloidal or polymeric particles <0.1μm and >0.015μm; and 4) the concentration of Pu in filtered solutions can be used to represent the solubility of the compounds.

At the end of the 90 days of equilibration, two samples of PuO_2 and two of $Pu(OH)_4$ were analyzed for morphology and crystallinity of the particles. The results showed that the PuO_2 samples were crystalline and $Pu(OH)_4$ samples were amorphous, as was the case at the beginning of the experiment. Pu concentrations in 0.1μm filtered solutions in contact with PuO_2 and $Pu(OH)_4$ (Tables 2 and 3) for 90 days are plotted

TABLE 2. Concentration of Pu in 0.003N $CaCl_2$ Solution in Contact with Crystalline PuO_2 Particles of Pu^{239} for Approximately 90 Days

		Concentration** of Pu^{239} in $\log_{10}$ (moles/l)		
Sample No.*	pH	Unfiltered	Filtered 0.1µm	Filtered 0.015µm
PuO_2-13	3.80	-6.14±0.02	-6.17±0.01	-6.12±0.01
PuO_2-14	3.80	-6.09±0.04	-6.08±0.01	-6.05±0.01
PuO_2-15	4.3	-6.42±0.01	-6.60±0.01	-6.57±0.00
PuO_2-16	4.3	-6.43±0.02	-6.43±0.00	-6.44±0.00
PuO_2-18	5.40	-5.69±0.14	-7.28±0.00	-7.29±0.00
PuO_2-17	5.45	-6.15±0.06	-7.46±0.03	-7.47±0.06
PuO_2-19	7.30	-6.33±0.13	-8.70±0.07	-8.55±0.33
PuO_2-20	7.30	-5.62±0.18	-8.71±0.06	-8.78±0.03

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*All the samples contained approximately 8 mg PuO_2 and 20 mls of 0.003N $CaCl_2$ solution.

**All the samples were centrifuged at 6,000 RPM for approximately 40 minutes.

TABLE 3. Concentration of Pu in 0.003N $CaCl_2$ Solution in Contact with Amorphous $Pu(OH)_4$ Precipitate of Pu^{239} for Approximately 90 Days

Sample No.*	pH	Concentration** of Pu^{239} in $\log_{10}$ (moles/l) Unfiltered	Filtered 0.1μm	Filtered 0.015μm
$Pu(OH)_4$-21	3.95	-4.40±0.02	-4.44±0.02	-4.46±0.03
$Pu(OH)_4$-22	4.00	-4.54±0.03	-4.54±0.01	-4.52±0.02
$Pu(OH)_4$-5	4.00	-3.90±0.01	-4.31±0.01	ND
$Pu(OH)_4$-6	4.00	-3.93±0.01	-4.22±0.02	ND
$Pu(OH)_4$-24	5.00	-5.26±0.02	-5.25±0.00	-5.25±0.01
$Pu(OH)_4$-23	5.05	-5.43±0.02	-5.44±0.00	-5.47±0.04
$Pu(OH)_4$-8	5.25	-4.99±0.03	-5.17±0.01	ND
$Pu(OH)_4$-7	5.30	-5.19±0.15	-5.31±0.01	ND
$Pu(OH)_4$-26	6.60	-6.51±0.06	-6.77±0.01	-6.79±0.02
$Pu(OH)_4$-25	6.70	-6.56±0.03	-6.83±0.00	-6.98±0.00
$Pu(OH)_4$-10	6.80	-5.18±0.03	-6.63±0.00	ND
$Pu(OH)_4$-9	6.83	-5.71±0.13	-6.73±0.01	ND
$Pu(OH)_4$-27	7.50	-7.43±0.06	-7.54±0.00	-7.58±0.01
$Pu(OH)_4$-28	7.70	-7.19±0.06	-7.77±0.04	-7.79±0.01
$Pu(OH)_4$-12	7.85	-5.21±0.02	-7.11±0.01	ND

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*Samples $Pu(OH)_4$-5 through $Pu(OH)_4$-12 were started first in one batch and the rest of the samples in another batch after approximately one week. All the samples contained approximately 8 mg $Pu(OH)_4$ and 20 mls of 0.003N $CaCl_2$ solution.

**All the samples were centrifuged at 6,000 RPM for approximately 40 minutes. ND in the last column means not determined. The concentrations were determined by gross alpha activity.

against pH (Figure 3). As expected (Rai and Serne, 1977), $Pu(OH)_4$ maintains a higher Pu concentration in solution at environmental values of pH than PuO_2. The solubility of both PuO_2 and $Pu(OH)_4$ decreases with the increase in pH. High linear correlations (r^2>0.97) between the Pu concentration in solution and the pH indicate that pH would be a very important factor in controlling Pu concentrations in soils in equilibrium with the Pu compounds. Pu concentration in equilibrium with PuO_2 and $Pu(OH)_4$ decreases 537 and 708 percent respectively with an increase of one pH unit. The kinetics of $Pu(OH)_4$ precipitation is extremely rapid. Time and/or conditions required for PuO_2 precipitation or conversion of $Pu(OH)_4$ to PuO_2 under environmental pH conditions is not known. $Pu(OH)_4$ samples used in this study have been aging for 100 days but there has been no detectable change in $Pu(OH)_4$ crystallinity thus far. It appears from the above discussion that $Pu(OH)_4$ may initially dictate the upper limit for the amount of plutonium that can be present in solution in a given pH. The total concentration of plutonium present in solution in contact with PuO_2 and $Pu(OH)_4$ in the absence of strong complexing ligands may be obtained from Figure 3. 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 $Pu(OH)_4$ solubility line but preferably below the PuO_2 solubility line (Figure 3).

IDENTIFICATION OF PLUTONIUM COMPOUNDS IN CONTAMINATED SOILS

If solid Pu compounds are present in sediments, they could govern the concentration of plutonium in solution and the further movement and dissemination into the environment. Thus, it is important to find out the nature of the solid compounds that may be present in sediments. If no solid compounds are present, ion exchange or adsorption reactions would govern the concentration of plutonium in solutions.

Large quantities of Pu solid compounds would not be expected to be present in sediments. Therefore, it would be difficult to physically isolate, for identification, the trace amounts of 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 identification of plutonium solid compounds present in sediments.

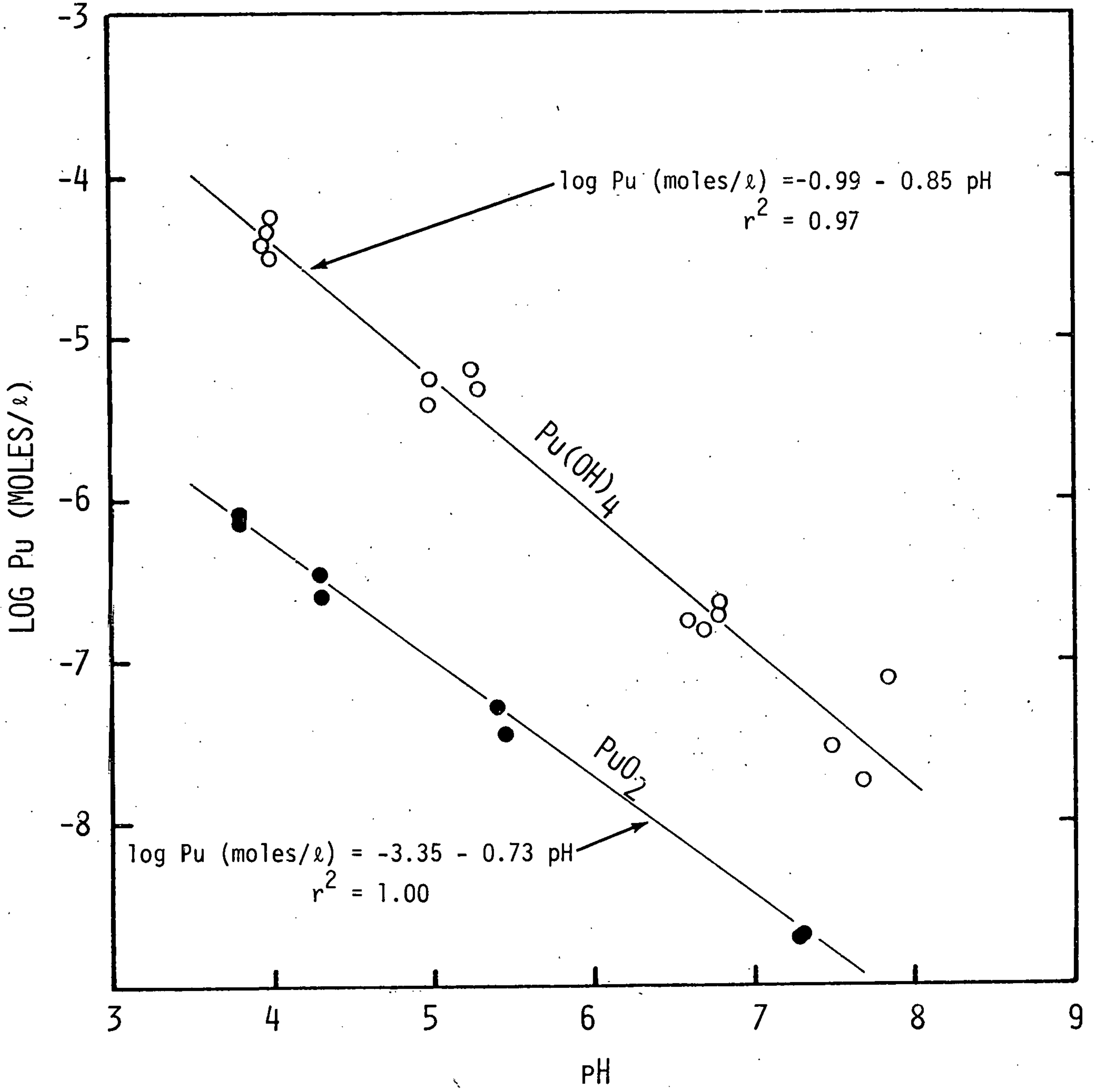

FIGURE 3. Pu Concentrations in Filtered (0.1μm) Solutions when PuO_2 and $Pu(OH)_4$ were Contacted with 0.003N $CaCl_2$ for 90 Days

The soil solution data are plotted in Figure 4 where experimental solubility lines for PuO_2 and $Pu(OH)_4$ for a 90 day equilibration period are traced for reference. The soil results reported in Figure 4 are also for a 90 day equilibration period. It can be seen that the soil solution points for soils Z9-4-11A and Z9-4-5A fall on the PuO_2 solubility line; however, the solution points for soil Z12-1D fall considerably below the PuO_2 solubility line. When PuO_2 was added to these soils the solution concentration for Z9-4-11A and Z9-4-5A did not change. The solution concentration of Z12-1D soil increased considerably and approached that of the PuO_2 solubility line. Thus, soils Z9-4-11A and Z9-4-5A appear to contain PuO_2 since the soil solution points fall close to the PuO_2 solubility line and the soil solution concentration did not change with the addition of PuO_2. Solution concentrations of soil Z12-1D indicate that this soil does not contain PuO_2. The Pu concentration in all the soil solutions studied were much lower than the $Pu(OH)_4$ solubility line, indicating that the soils do not contain $Pu(OH)_4$. The addition of $Pu(OH)_4$ to soil Z12-1D increased the Pu concentration in the soil solution to that of the $Pu(OH)_4$ solubility line. The results presented in this section also 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, the concentration of Pu in solution would be lower than the PuO_2 solubility line and would be governed by adsorption reactions. On the other hand, Pu concentrations in solutions percolating through PuO_2 contaminated sediments would be expected to be similar to the concentrations obtained from PuO_2 solubility line (Figure 3). Such an event might occur in the immediate vicinity of stored wastes.

Two of the soils 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 suspension devoid of organic ligands. It is possible that the organic ligands originally disposed into these soils have degraded over the period when the wastes were first disposed (approximately 20 years). This hypothesis is supported by

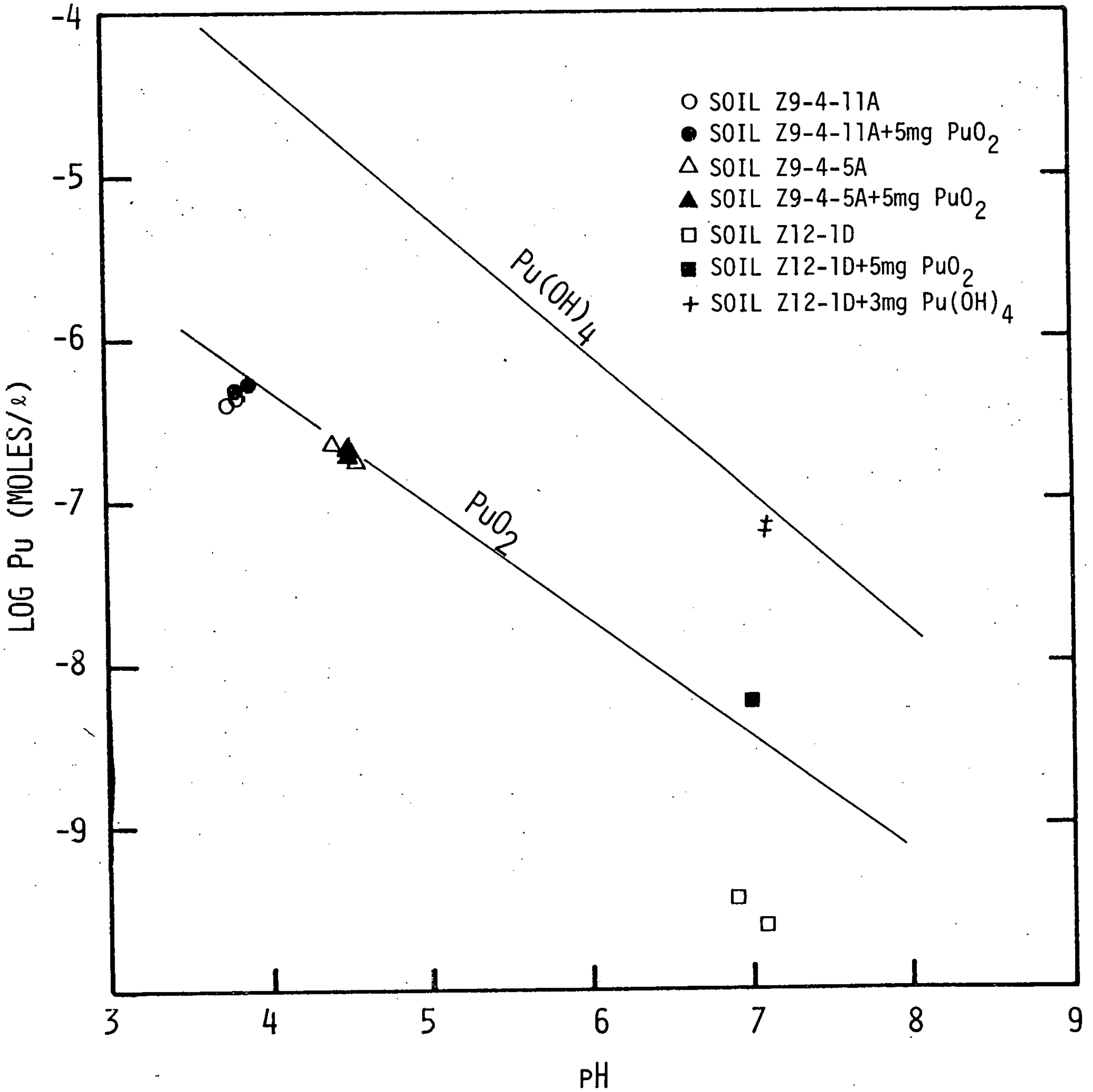

FIGURE 4. Pu Concentration in Filtered (0.1μm) Solutions from Hanford Soils when Contacted with 0.003N $CaCl_2$ for 90 Days

the results of Cleveland (1977)[2] who found no evidence of organics in Rocky Flats soil that had been contaminated by lathe cooling oil. It is also possible that the wash given to the soils used in this study removed a large portion of these organic wastes.

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[2] Dr. J. M. Cleveland, Chief, Transuranium Research Project, USGS, Denver, Colorado. Personal communication, September 1977.

FUTURE PLANS

The experiments outlined in this report will be continued until an equilibrium is established. At the end of the equilibrium period the solutions will be analyzed for Pu(IV), Pu(VI), Pu polymer, Eh, pH, and ionic strength. The crystallinity of the solid compounds of Pu used for dissolution will also be determined. Soils Z9-4-5A and Z9-4-11A will be adjusted to different pH values in order to find out whether the Pu concentrations follow the PuO_2 solubility line, which would be expected if these samples are in equilibrium with PuO_2. Using an alpha track, scanning electron microscope, and X-ray diffraction, the kind of Pu compounds present in these soils will also be determined to confirm the presence or absence of the PuO_2 mineral in these soils as predicted from solubility experiments.

These studies would help to determine precipitation-dissolution behavior of Pu in natural environments, probable Pu solid forms present in geochemical systems, total concentrations of Pu that can be expected at equilibrium when Pu solids are present, and the nature of the concentration of Pu which should be used in sorption experiments in order to minimize the precipitation effects.

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Changes in Pu Concentration with Changes in pH (Figure 3)

Q. How was the pH adjusted?

A. With hydrochloric acid or sodium hydroxide. Very little is needed since the water is distilled.

Q. Would you comment on the slopes of the lines?

A. Yes; there is about a five to sevenfold decrease for each pH unit increase.

Q. Can the solubility products themselves be used to determine the solubilities of Pu in equilibrium with hydroxides?

A. Yes and no. If you plot the solubility only of the Pu(IV) present in the solution, you will see this fourfold decrease for each unit of pH increase. However, you would not in fact obtain this result. Because of the other oxidation state present in the system, you would be measuring total solubility, rather than just that of Pu(IV).

This is a progress report based upon only a part of the results which will be collected for this study. Therefore, the conclusions drawn from this report or the results discussed herein are tentative and should not be quoted without the knowledge of the authors.

"BATCH K_d EXPERIMENTS WITH COMMON MINERALS AND REPRESENTATIVE GROUNDWATERS"

by

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September 1977

BATCH Kd EXPERIMENT WITH COMMON MINERALS AND REPRESENTATIVE GROUNDWATERS[1]

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INTRODUCTION

Many studies are in progress at various institutions that involve computer modeling to investigate groundwater movement, geochemical interactions, terrestrial and aquatic food chains, radiation dose to man, geologic stability and disruptive event analysis. Simplistic models reported in literature(1,2,3,4) can be used to estimate the fate of nuclides in geologic, aquatic, or biotic systems, provided the necessary input data is available. In the area of nuclide migration there is a gap in our knowledge of quantative estimates of the ability of various geologic materials to retard nuclide movement. Thus, the lack of adequate sorption data for nuclides in geologic environments limits the utilization of the aforementioned simplistic models. The acquisition of sorption-desorption data on a wide range of representative geologic material with numerous groundwater types should proceed post-haste. This study was designed to be generic in nature by covering a wide range of geologic materials and possible groundwaters.

As the first two repositories will likely occur in salt deposits the migration rates of nuclides in salt brine were included initially. Site specific data will be generated as samples become available.

Once this data bank is acquired, safety assessment modelers will have defensible data (from a geochemical standpoint) to attempt preliminary fate calculations. In order to obtain data to meet the needs of assessment modelers by FY 79, the initial thrust of the program will be empirical and utilize crushed rock materials in batch tests.

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[1] This is not a final report but a progress report based upon only a part of the results which will be collected for this study. Therefore, the conclusions drawn from this report or the results discussed herein are tentative and should not be quoted without the knowledge of the authors.

METHODS AND MATERIALS

Geologic Materials

Minerals and rock samples were obtained from Wards Natural Science Establishment, Inc., Rochester, New York 14603. The bulk samples were split into halves. One half was crushed and ground to <100 μm size with standard jaw crushers and ball mills. The other half is in storage for future experiments.

Subsamples of the crushed minerals were treated with pH 5 sodium acetate buffer to remove calcium carbonate and with hydrogen peroxide at 80°C to remove organic matter. Portions of each mineral were treated separately with 1N sodium chloride and 1N calcium chloride and washed with distilled water to obtain sodium and calcium saturated minerals.

For initial generic experiments twelve common primary and secondary minerals were chosen. Table 1 lists the minerals which constitute the building blocks of most alumino-silicate rock materials.

The treated minerals were further characterized to determine mineral purity (x-ray diffraction), surface area (ethylene glycol)[5] and cation-exchange-capacity (^{85}Sr tracer method)[6].

Solutions

Four synthetic solutions (Table 2) representing simplified groundwaters were used for preliminary batch sorption-desorption tests. The solutions represent a salt brine, a calcium dominated groundwater, a diluted brine or sodium dominated groundwater, and a bicarbonate-carbonate dominated groundwater. These solutions were traced with the nuclides Sr, Tc, I, Cs, U, Np, Pu, Am and Cm. The form of the nuclides in the stock solutions added to the synthetic groundwaters were Sr^{+2}, TcO_4^-, I^-, Cs^+, UO_2^{+2}, NpO_2^+, Pu^{+4}, Am^{+3}, and Cm^{+3}.

Counting Information

The tracers Sr, Cs and Tc were mixed together and counted on a high efficiency-high resolution Ge(Li) detector. The I and Am were mixed and counted on a high resolution intrinsic Ge detector. Np and Pu were not mixed with other isotopes and were counted on intrinsic Ge and Ge(Li) detectors, respectively. U and Cm will be mixed together and counted by Ge(Li) gamma spectroscopy or

TABLE 1
MINERALS USED FOR SORPTION EXPERIMENTS

- Illite
- Kaolinite
- Montmorillonite
- Vermiculite
- Quartz
- Albite
- Anorthite
- Microcline
- Biotite
- Hornblende
- Enstatite
- Augite

TABLE 2
COMPOSITION OF SYNTHETIC SOLUTIONS

Salt Brine	5130 meq/l NaCl pH 7
Calcium Groundwater	30 meq/l $CaCl_2$ pH 7
Sodium Groundwater or Dilute Brine	30 meq/l NaCl pH 7
Bicarbonate Dominated Groundwater	30 meq/l $NaHCO_3$ Natural pH

alpha spectroscopy. In order to efficiently analyze U by gamma spectroscopy, uranium concentration in the ppm range is needed. This concentration is probably unrealistically high compared to expected high level glass leachate. Counting details are shown in Table 3.

Batch Kd Experimental Design

For the sodium dominated groundwaters, minerals with sodium saturated exchange sites were used. Conversely the calcium groundwater was contacted with minerals whose exchange sites were calcium saturated.

One-half gram samples of the crushed and treated minerals were placed in 50 ml polycarbonate centrifuge tubes. The minerals were rinsed three times with the synthetic groundwater solutions without tracers. The suspensions

TABLE 3

COUNTING INFORMATION

Isotope	Energy Level	Counting Equipment
^{85}Sr	.511 Mev γ	Ge(Li)
^{95m}Tc	.204 Mev γ	Ge(Li)
^{129}I	.040 Mev X-ray	Intrinsic Ge
^{137}Cs	.662 Mev γ	Ge(Li)
^{235}U	.185 Mev γ	Ge(Li)
	4.40 Mev α	Silicon Surface Barrier
^{233}U	4.82 Mev α	Silicon Surface Barrier
^{237}Np	.0294 Mev X-ray	Intrinsic Ge
^{237}Pu	.097 and .101 Mev γ	Ge(Li)
^{241}Am	.0596 Mev γ	Intrinsic Ge
^{243}Cm	.0996 and .104 Mev γ	Ge(Li)

were shaken on a linear oscillating shaker at a moderate speed overnight for each wash. The wash steps were performed to allow the systems to approach equilibrium. The suspensions were centrifuged at 7000 RPM for 20 minutes and the first two washes were discarded. After the third wash the supernate was analyzed for major cations, anions, and pH. The quantity of residual solution not removed by centrifugation after the third wash was also determined. This residual solution was used as an input for the Kd calculations.

A final aliquot (15 mls) of solution with nuclides present was contacted with the minerals. At the end of approximately 3, 10 and 20 days the suspensions were centrifuged and ten ml of the solution phase was removed. The solutions were analyzed for pH, Eh, and nuclide activity. The Kd's for each nuclide were determined by the loss in solution activity.

Container sorption was monitored for each solution and nuclide by contacting centrifuge tubes without minerals present in the same fashion. All experiments were run in triplicates.

The Kd is calculated using the following equation:

$$Kd = \left(\frac{r \cdot A_{Blank} - A_{Effluent}}{A_{Effluent}}\right) \cdot \left(\frac{\text{Total Volume Solution}}{\text{Wt of Mineral}}\right)$$

where

r = ratio of tracer solution volume to total volume (tracer + excess)

A_{Blank} = activity of nuclide in blank systems (containers only)

$A_{Effluent}$ = activity of nuclide in centrifuged solutions

Total Volume (ml) = tracer solution (15 ml) + excess cold solution left after removal of third wash

Wt of Mineral = 0.5g used in this experiment

Desorption experiments are planned after the third Kd determination. The tracer solution will be removed after centrifugation and cold solution of the same recipe introduced to the system. Two cold washes will be used to determine the amount of nuclide which can be removed from the minerals to allow estimates of desorption and reversibility.

Results and Discussion

The cation-exchange-capacity and surface area measurements are shown in Table 4.

The x-ray diffraction patterns for standard minerals (montmorillonite, nontronite, vermiculite, kaolinite, illite, and biotite) were obtained after various treatments (Mg-54% RH, Mg-ethylene glycol, K-105 C° dry air, K-105 C° 54% RH, K-550 C° dry air) in order to find out the purity of these minerals. The tracings of these patterns are provided in the enclosed figures (Figures 1-3). All these samples were pretreated to remove $CaCO_3$. The results show that montmorillonite, nontronite, vermiculite, and biotite do not have significant amount of crystalline impurities. Kaolinite samples have a minor amount of mica. The illite sample is poorly crystallized and has a poorly crystallized 10-14Å broad peak which collapses to 10Å and has a minor amount of kaolinite.

In general the cation-exchange capacity data and surface area results correlate. A high C.E.C. usually reflects a high surface area. The secondary clays montmorillonite, vermiculite and illite show the highest exchange capacity. Quartz and common feldspars such as albite and anorthite have the

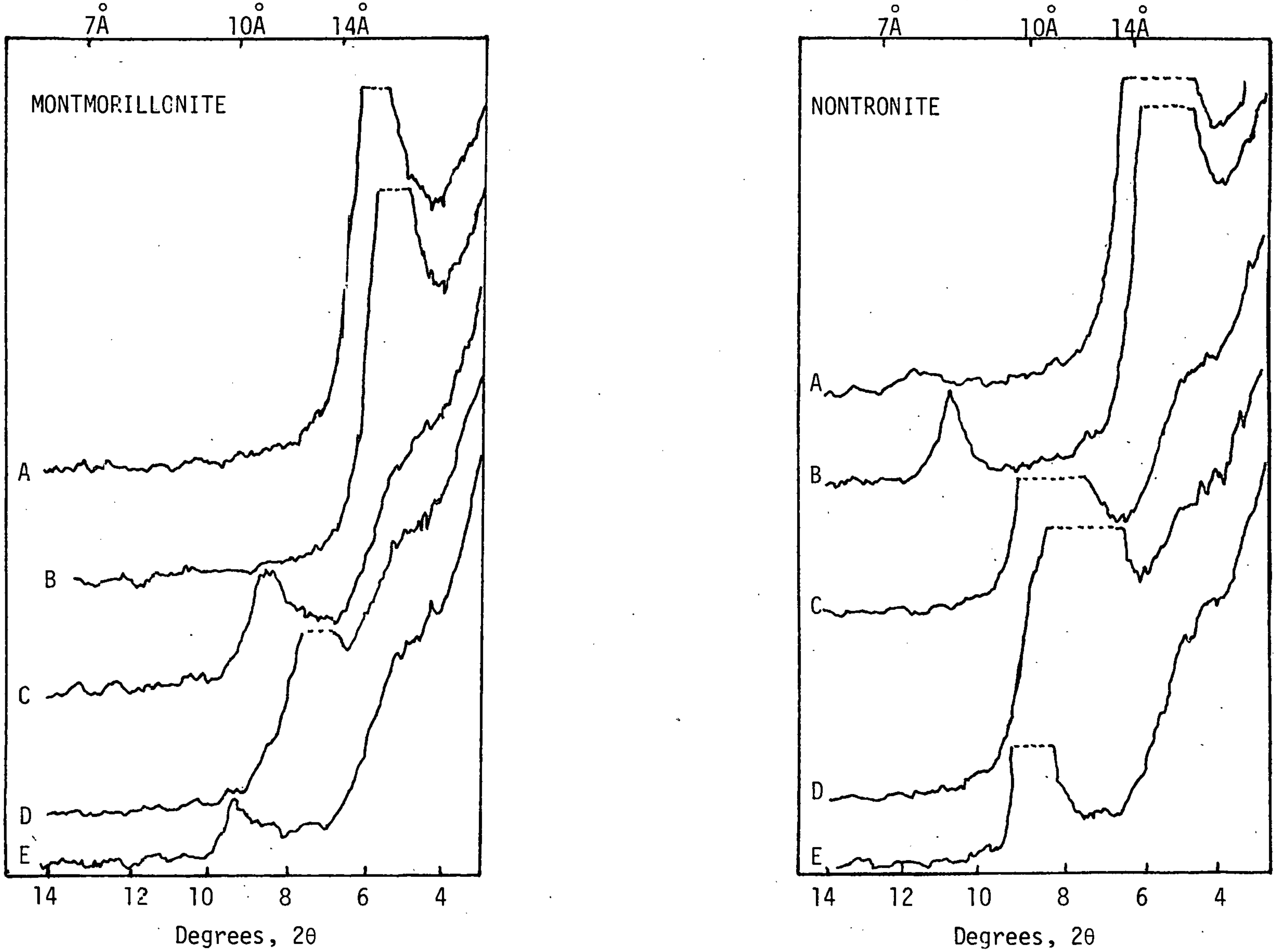

Figure 1. X-Ray Diffraction Patterns of Oriented Samples:
A. Mg 54% RH B. Mg-Ethylene Glycol C. D-105°C Dry Air
D. K-105°C 54% RH E. K-550°C Dry Air

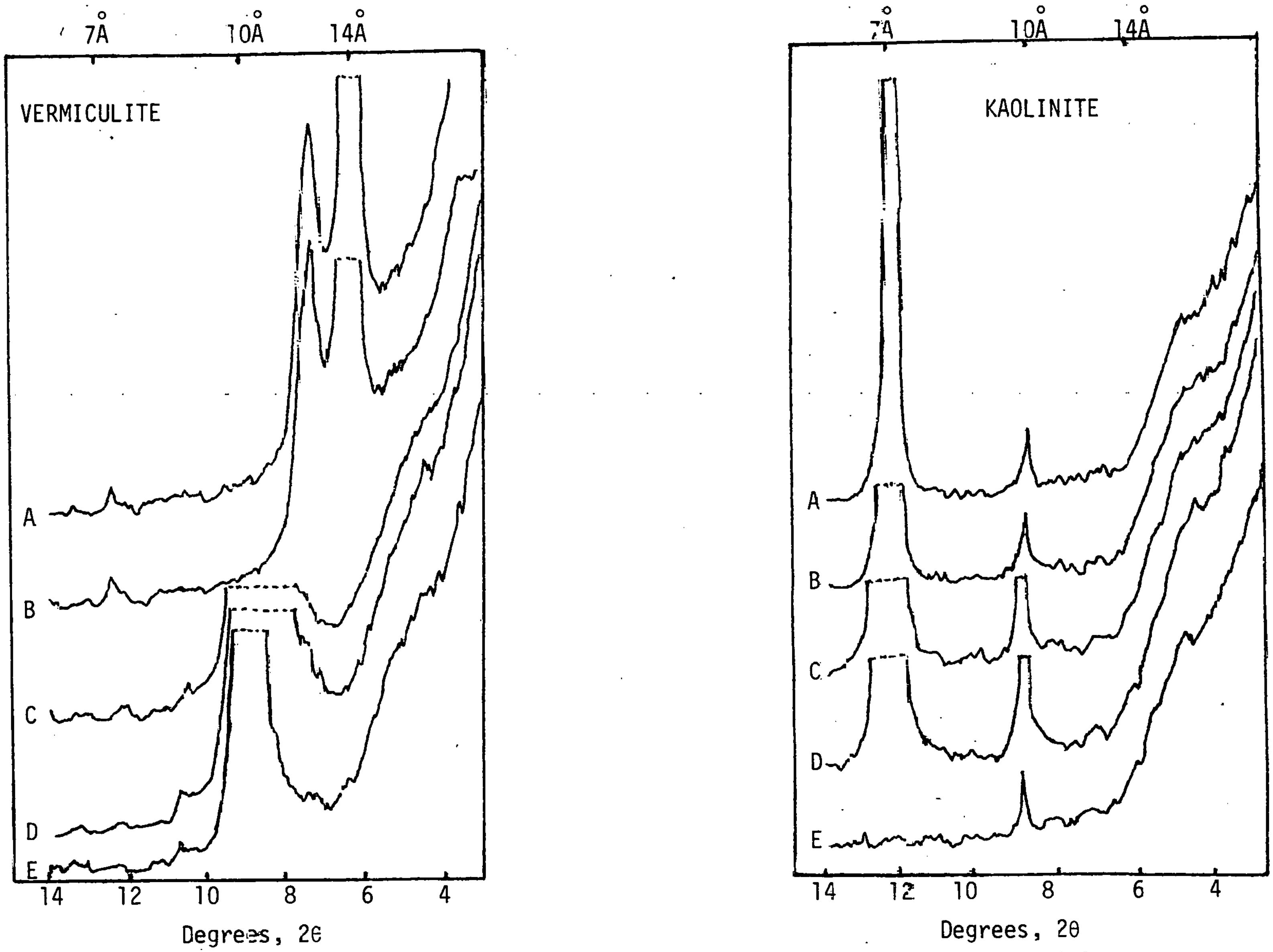

Figure 2. X-Ray Diffraction Patterns of Oriented Samples:
A. Mg 54% RH B. Mg-Ethylene Glycol C. D-105°C Dry Air
D K-105°C 54% RH E. K-550°C Dry Air

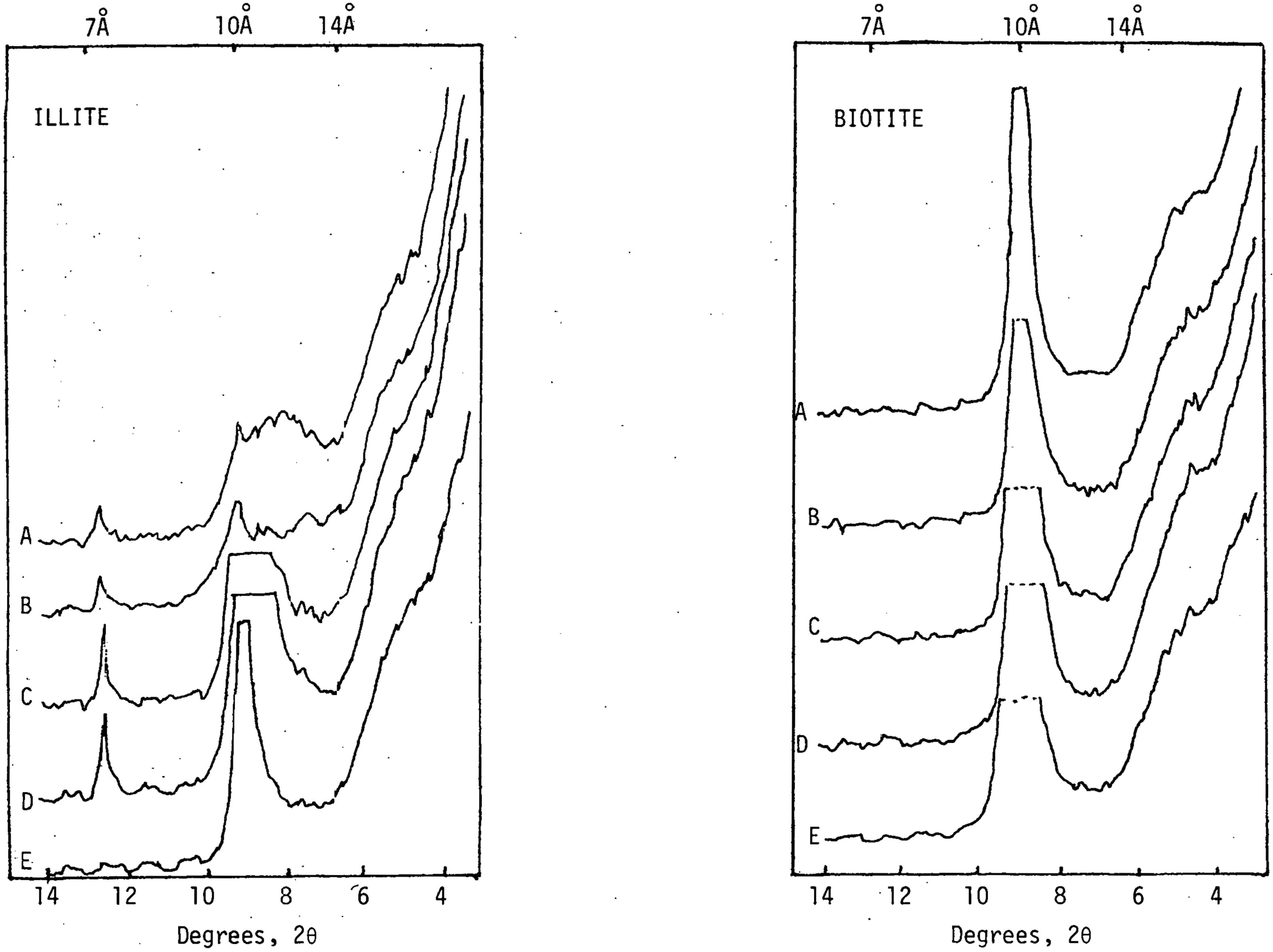

Figure 3. X-Ray Diffraction Patterns of Oriented Samples:
A. Mg 54% RH B. Mg-Ethylene Glycol C. D-105°C Dry Air
D. K-105°C 54% RH E. K-550°C Dry Air

TABLE 4

CHARACTERIZATION OF MINERAL SAMPLES

	Cation-Exchange Capacity meq/100g	Surface Area m^2/g
Illite	13.8 ± .8	165.4±3.3
Kaolinite	5.0 ± .9	30.7±0.5
Montmorillionite	87.4 ±2.7	722.2±6.9
Vermiculite	77.0 ±4.8	312.5±7.8
Quartz	0.15±0.07	2.8±0.2
Albite	1.5 ±0.3	8.4±3.7
Anorthite	1.8 ±0.4	9.2±1.3
Microcline	1.2 ±0.2	5.1±1.0
Biotite	15.3 ±1.1	68.8±0.8
Hornblende	2.9 ±0.5	4.3±0.8
Enstatite	1.9 ±0.3	15.7±1.0
Augite	4.5 ±0.6	7.1±0.4

± - one standard deviation of triplicate analyses.

lowest exchange capacities. The dependence of Kd for the nuclides studied on cation exchange capacity and surface area will be addressed after statistical studies are performed by Adaptronics, Inc.

Tables 5 to 16 report the average Kd values for Tc, Sr, Cs and Np at three equilibration times for part of the minerals (Table 1) and solutions (Table 2). Most negative Kd values represent cases in which the average activity in blank tubes is less than the activity in the mineral suspension effluents. Negative Kd values occur only in systems where mineral sorption is extremely low which allow the Kd calculation counting statistics or a slight difference in container adsorption between blanks and mineral systems to become very important. Therefore, for nuclide fate calculations, most negative Kd values are not significantly different from zero. In the case of the TcO_4^- anion adsorption by the secondary

TABLE 5

BATCH Kd_{Tc} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 3 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	0.3±0.7	0.0±0.5	-0.3±0.7	-1.1±0.1
Kaolinite	-0.5±0.2	-0.1±0.2	-0.2±0.7	0.2±0.4
Montmorillonite	0.4±0.5	-0.5±0.1	-0.7±0.3	-1.8±0.9
Vermiculite	0.0±0.2	-0.5±0.1	-0.8±0.4	-0.6±0.0
Quartz	0.4±0.6	0.4±0.9	0.0±0.4	-0.5±0.4
Albite	1.4±0.3	1.6±0.3	0.4±0.4	0.1±1.3
Anorthite	1.8±0.1	0.4±0.3	0.9±2.3	-0.7±0.5
Microcline	2.3±0.3	-0.5±0.5	0.9±0.7	-0.5±0.6

TABLE 6

BATCH Kd_{Sr} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 3 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	2.7±0.8	7.8±0.3	99 ± 0.6	544± 44
Kaolinite	0.3±0.5	3.6±3.0	78.4± 1.6	172± 8
Montmorillonite	2.7±1.0	28.7±1.8	1,500 ±310	1,800±200
Vermiculite	2.1±1.2	28.7±1.8	990 ±120	1,500±200
Quartz	1.6±0.5	0.7±1.1	9.4± 0.5	546± 19
Albite	6.0±0.3	4.6±0.4	142 ± 7	518± 37
Anorthite	6.7±0.8	4.2±0.8	81.6± 5.2	349± 20
Microcline	4.1±0.2	3.4±0.2	227 ± 5	571± 94

TABLE 7

BATCH Kd_{Cs} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 3 Days

Mineral	NaCl Brine	Cl G.W.	Na G.W.	HCO_3^- G.W.
Illite	544 ±36	$1.4x10^4 ± 0.3x10^4$	5,800 ±3,400	5,700± 570
Kaolinite	4.7± 0.5	5,000 ±1,100	477 ± 24	577± 19
Montmorillonite	34 ± 2	276 ± 4	1,100 ± 60	1,300± 200
Vermiculite	80 ± 2	276 ± 4	5,800 ± 700	3,600±1,800
Quartz	1.4± 0.8	52.5± 13.4	48.4± 3.5	40± 4
Albite	15.5± 0.5	1,100 ± 200	550 ± 31	521± 58
Anorthite	16.8± 0.9	688 ± 49	437 ± 34	521± 58
Microcline	5.4± 1.1	333 ± 47	419 ± 14	472± 73

TABLE 8

BATCH Kd_{Np} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 3 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	9.8± 3.0	15.5±5.0	12.8±0.6	145 ±2
Kaolinite	3.5± 2.4	0.5±1.2	4.9±5.7	116 ±8
Montmorillonite	163 ± 4	16.5±3.5	60.0±3.3	6.0±0.3
Vermiculite	34.5±12.6	17.6±3.1	41.2±1.0	11.8±0.3
Quartz	-0.5± 0.2	0.9±0.9	3.8±0.8	3.5±2.0
Albite	8.8± 2.6	0.5±0.8	3.3±1.5	3.0±2.0
Anorthite	130.3±19	0.3±0.1	7.5±0.8	9.0±3.6
Microcline	10.2± 1.2	2.3±0.8	16.8±2.3	4.8±2.1

TABLE 9

BATCH Kd_{Tc} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 10 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	0.7±0.3	0.7±0.2	4.1±1.0	-0.6±1.1
Kaolinite	-0.4±1.2	-0.3±0.9	0.0±1.0	0.1±0.4
Montmorillonite	-0.3±0.3	0.3±0.1	-0.7±0.5	-1.9±0.2
Vermiculite	-0.6±0.4	0.3±0.9	-0.7±0.4	-0.7±0.8
Quartz	0.3±0.8	1.3±0.3	0.3±0.3	-0.6±0.6
Albite	6.2±1.0	2.1±0.1	0.5±0.7	-0.1±0.8
Anorthite	0.9±0.3	1.1±0.6	0.6±0.3	-0.6±0.7
Microcline	5.6±0.3	0.2±0.8	2.4±2.1	-0.2±0.4

TABLE 10

BATCH Kd_{Sr} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 10 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	1.4±0.3	6.6±0.7	63.7± 6.0	487± 35
Kaolinite	0.6±1.0	0.7±0.3	79.9± 7.7	205± 20
Montmorillonite	0.9±0.3	28.2±2.0	1,155 ± 82	1,237±146
Vermiculite	1.7±1.3	25.7±2.2	988 ±178	1,190±242
Quartz	1.0±1.5	1.0±0.7	10 ± 1.5	507± 6
Albite	4.4±0.7	4.6±0.9	128 ± 7	486± 52
Anorthite	3.1±0.8	3.6±0.1	63.2± 4.2	422± 23
Microcline	3.5±0.3	3.2±0.5	194 ± 12	501± 37

TABLE 11

BATCH Kd_{Cs} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 10 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	502 ±30	>53,000	>43,000	4,190 ±2,350
Kaolinite	4.8± 1.3	2,486 ± 524	750 ± 94	745 ± 101
Montmorillonite	31.6± 2.3	341 ± 145	1,223 ± 23	1,036 ± 122
Vermiculite	80.6± 4.8	100,000 ±40,000	7,175 ±658	4,590 ±2,723
Quartz	0.9± 1.6	41.7± 13.6	56.8± 5.7	39.1± 3.7
Albite	16.9± 1.0	861 ± 76	397 ± 24	377 ± 30
Anorthite	14.5± 1.6	612 ± 1.54	4,500 ± 85	422 ± 55
Microcline	6.8± 0.7	223 ± 65	276 ±190	445 ± 46

TABLE 12

BATCH Kd_{Np} RESULTS (AVERAGE OF 3 RESULTS)

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	18.3± 0.6	12.5±5.5	15.3±9.9	235 ±6
Kaolinite	5.8± 2	2.5±2.3	3.4±4.4	130 ±8
Montmorillonite	112 ±11	21.4±2	60.1±2.2	11.7±2.8
Vermiculite	61.6±10.9	28.2±4.2	44.0±2.9	17.3±1.5
Quartz	1.7± 2.7	3.1±0.3	7.8±2.6	10.9±1.1
Albite	23.1± 3.4	4.2±2.0	8.1±1.1	8.6±1.0
Anorthite	138 ± 6	3.9±1.2	13.0±1.5	16.0±3.6
Microcline	22 ± 4	7.7±5.0	33.4±0.9	10.4±2.9

TABLE 13

BATCH Kd_{Tc} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 29 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	4.7±0.5	0.5±0.5	10.3±1.1	-0.9±0.4
Kaolinite	0.4+1.0	3.0±5.3	-0.4±0.6	-0.2±0.9
Montmorillonite	0.2±0.5	-0.6±0.1	-0.6±0.4	-1.5±0.3
Vermiculite	0.6±0.7	-0.8±0.3	0.4±1.0	0.0±0.2
Quartz	1.6±0.9	0.7±1.0	1.4±1.5	-0.4±0.3
Albite	18.0±3.3	2.8±1.3	0.7±0.5	-0.4±0.7
Anorthite	4.4±1.0	0.5±0.7	1.8±1.0	0.0±0.1
Microcline	15.5±4.0	0.1±0.4	5.8±1.2	0.6±0.1

TABLE 14

BATCH Kd$_{Sr}$ RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 29 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	1.2±0.5	6.2±1.5	36.5± 1.0	298± 84
Kaolinite	0.2±1.0	0.6±0.2	77.1± 2.6	284±107
Montmorillonite	1.4±0.6	27.7±0.6	1074 ±92	1353±330
Vermiculite	1.9±1.1	23.8±1.0	760 ±18	1041±103
Quartz	1.1±0.4	-0.1±1.1	8.8± 1.6	348± 70
Albite	5.2±1.0	4.1±0.4	105 ± 2	545± 48
Anorthite	5.0±1.3	3.0±0.3	51.3± 3.5	459± 58
Microcline	4.1±1.1	3.6±0.9	159 ± 7	461± 26

TABLE 15

BATCH Kd$_{Cs}$ RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 29 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	564 ±35	$4.4x10^4 \pm 6.9x10^4$	12,950 ±6,190	$5.5x10^4 \pm 8.2x10^4$
Kaolinite	7.3± 0.8	$4.6x10^4 \pm 6.7x10^4$	909 ± 215	863 ± 37
Montmorillonite	33.2± 1.6	218 ± 4.6	1,020 ± 81	1,560 ±370
Vermiculite	93.3± 8.6	$>8.2 \pm 10^4$	$5.9x10^4 \pm 7.1x10^4$	$2.0x10^4 \pm 1.5x10^4$
Quartz	2.2± 0.8	33.7± 14	57.5± 7.7	37.3± 5.0
Albite	20.4± 2.2	821 ±123	519 ± 11	528 ± 10
Anorthite	22.4± 1.2	774 ± 48	440 ± 35	608 ± 36
Microcline	7.5± 1.8	222 ± 76	391 ± 18	343 ± 21

TABLE 16

BATCH Kd_{Np} RESULTS (AVERAGE OF 3 RESULTS)

Equilibration Time - 19 Days

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	42.0± 3.9	13.6±5.7	26.8± 1.0	295 ±25
Kaolinite	4.2± 1.8	0.5±1.9	3.6± 2.0	122 ±19
Montmorillonite	80.4± 7.0	17.7±2.3	45.9± 4.9	9.1± 1.3
Vermiculite	61.4±13.9	27.7±0.6	33.2± 6.3	16.9± 4.3
Quartz	-0.1± 0.7	3.6±2.3	4.1± 1.0	6.6± 4.3
Albite	39.1± 3.8	7.0±2.5	9.8± 2.1	7.8± 2.5
Anorthite	142 ±18	6.4±2.4	13.4± 2.4	15.7± 4.5
Microcline	42.6±18.9	10.1±2.5	68.3±51.0	8.0± 1.6

TABLE 17

FINAL pH VALUES

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	6.5	7.0	5.7	8.8
Kaolinite	6.4	6.1	6.6	9.3
Montmorillonite	8.1	7.8	8.6	9.2
Vermiculite	8.2	7.9	8.3	9.3
Quartz	6.5	7.0	7.0	9.4
Albite	7.2	7.7	8.0	9.4
Anorthite	8.0	7.7	8.4	9.3
Microcline	6.9	7.6	7.8	9.3

TABLE 18

FINAL Eh VALUES

Mineral	NaCl Brine	Ca G.W.	Na G.W.	HCO_3^- G.W.
Illite	205/250*	280/315	310/275	320/260
Kaolinite	205/240	285/315	300/275	315/260
Montmorillonite	210/250	285/320	290/280	310/255
Vermiculite	205/250	286/310	300/280	320/280
Quartz	210/250	285/310	300/280	320/255
Albite	210/245	285/320	300/275	315/255
Anorthite	210/240	285/320	295/275	310/255
Microcline	210/245	285/320	295/275	310/250

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*First value measured at 20 days in Tc-Sr-Ca tagged systems, second value obtained at 19 days in the Np tagged systems.

minerals illite, montmorillonite and vermiculite, some Kd values are significantly less than zero due to anion exclusion from inner surfaces. Tables 17 and 18 display the final pH and Eh values respectively.

Final analyses of trends and a discussion of the geochemical meaning of such trends will be deferred until statistical studies performed by Adaptronics, Inc. are complete.

FUTURE PLANS:

The preliminary results reported herein appear to be yielding useful information. Therefore the rest of the permutations of the experimental design (12 minerals x 4 groundwaters x 9 nuclides x 3 equilibration times) of the Kd experiment will be completed after the statistical evaluation is completed. Desorption experiments with the resulting contaminated minerals will be performed.

Future experiments will incorporate natural rock materials which have been characterized for surface area, cation-exchange capacity, semi-quantitative mineralogy and other chemical and physical properties.

To further develop the generic data bank, other synthetic groundwaters, nuclides, and a few more minerals may be studied.

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DISCUSSION--J. F. RELYEA

Selection of Minerals

Q. Many of the minerals you list (see Table 1) don't seem to be relevant to those that would actually be found in a burial site, while some that would be likely to be found--e.g., a zeolite--have not been included. What basis did you use for your selection?

A. The list is generic in nature; we want to get as many minerals as we can. Many of the primary minerals listed are feldspars and are likely to be found in granite or basalt, while the secondary minerals are likely to be found in shales. Later, we'll add calcites and other minerals. However, since the experimental design restricts us to working with 12 minerals at a time, we've picked these 12 to start with.

Q. Actually, the current emphasis on basalt, granite, and salt may be the wrong approach. If there is a breach of confinement, the total pathway to man will go through a large spectrum of minerals, of which those that are actually in the repository may be a trivial part.

(No answer given)

Characterization of Minerals

Q. Was any attempt made to characterize the primary minerals chemically, for example, was a quantitative chemical analysis done so that a detailed structural formula could be developed?

A. Cation exchange capacity and surface area measurements were done for all minerals. X-ray diffraction patterns were run and the amount of purity determined for most of them. However, we haven't done a quantitative chemical analysis yet.

Q. Couldn't that be a problem? For example, most of those minerals that you are now using decompose to form complex arrays; these could have enormous effect on the properties you're measuring. This is why it's not sufficient to characterize a mineral as "pyroxene"; that term includes a whole family of mineral species. Furthermore, minerals like enstatite react with water, weathering immediately and produce a complex surface material that is not very representative of an enstatite. Thus, you may end up with a common reaction product that is independent of the original material you started with. For example, whether you start with enstatite or olivine, you may end up with the same hydrated silicon layer which will do the actual reacting.

A. This is part of the program--to compare methods. The only way to do a batch K_d is with ground material. These results will be compared with those from some of the high-pressure, flow-through intact cores. If there is extensive weathering caused by crushing and adding solution, it should show up when K_d's are compared with those of other labs.

Q. Since your particles vary greatly in size, shouldn't you define K_d in terms of surface area?

A. That will also go into Adaptronics analysis. We have measured the surface area of the minerals; we've also done CEC and X-ray diffraction analysis. All of these data have gone into the analysis. The K_d's have been reported on both a weight and surface area basis.

Q. Isn't it possible that the purity of the minerals isn't really very important? For example, if 20 different minerals are found to have the same sorption rate, then the purity of each one would not be so important. On the other hand, if one or two minerals are found to have sorption rates that are very different from the others, then purity would be important.

A. We consider what we're doing to be one step better than identifying a sample as "basalt," for example. What we're doing is distinguishing between types of basalt. The next step would be to characterize the actual lattice of minerals, but that would take forever.

Q. Many of the primary minerals dissolve incongruently in a water solution. Thus, the solid phase could be contaminated with a minute amount of a different solid phase, and the system will be changing during the experiment. Couldn't these factors be important in interpreting your results?

A. Yes, we'll have to make some sort of characterization of the final material when we're through with the experiment.

Equilibrium pH Values (Table 17)

Q. How large are your particles?

A. Less than 100μ; some are probably less than 2μ--for example the kaolinite.

Q. Isn't it difficult to centrifuge down the montmorillonite in the $NaHCO_3$ solution?

A. There is an excess of solution. We centrifuge the mixture at about 7,000 rpm for 20-30 minutes. We find that most of the minerals will flocculate at 30 meq/l; montmorillonite, however, tends to stay fairly fluffy. With respect to K_d's, we find that most of the $NaHCO_3$ K_d's are high. We don't know whether that's due to precipitation of the radionuclides or some other factor.

Q. In your pH values for quartz, I understand the 7.0 for $CaCl_2$ and NaCl, and the 9.4 for $NaHCO_3$, but why should it be 6.5 for NaCl brine? Is it possible that your electrode is sodium-sensitive, and is not really responding to the H ion? If this is so, then some of your pH measurements taken in brine concentrations may be considerably off.

A. We adjusted the pH of the brine before we started so that it read 7.0 (±0.1); then we measured the pH with the same electrode as the experiment progressed. At that low a concentration of the H ion in the brine, however, we are not sure whether the pH has as much effect as the ionic strength of the brine. So, you're right--we may not be getting an accurate reading of the pH of the brine.

Batch K_d Results (Tables 5-16)

Q. What do the two sets of numbers mean? For example the K_d's, for kaolinite, in NaCl brine, you have 4.7±0.5.

A. The first number is the mean K_d; the second represents one standard deviation.

Q. In what chemical form was the Tc?

A. I believe it was pertechnitate anion--TcO_4.

Q. Did you preload the minerals with solution?

A. Yes; we contacted the minerals first with three cold washes of the same solution, and then with the spiked solution. For each cold wash, the minerals were contacted with the solution overnight, and it was then centrifuged off.

Q. Was the equilibration time experimentally determined?

A. No; that's just how long we measured the reaction.

Q. Then shouldn't you call it reaction time instead of equilibration time?

A. All right.

Q. Did you take a series of measurements during that reaction time?

A. Yes, we took one measurement at 3 days, another at 10 days, and the last one at either 19 days, 29 days, or 35 days. However, we don't expect to find much difference between measurements taken at 19 or 29 days.

Q. Are these measurements blank-corrected?

A. Yes; we ran a blank with them. We used the blank to determine how much was added to the sample tube.

Q. What kind of results would you get if you calculated the K_d just using the blank adsorption, knowing your initial solution?

A. There was no blank adsorption to speak of on the Np, Tc, and Sr, because the K_d's were so low. Most of the concentrations for Tc were 10^{-10}M or 10^{-11}M; for Np they were from 2 to 5 x 10^{-7}M. We started running into problems, however, with Cs when it hit an illite-type clay, because it was almost totally absorbed.

Q. For Cs, why is the standard deviation so large for vermiculite in NaCl and $NaHCO_3$?

A. There was a very wide scatter of data points, so that one standard deviation of the scatter was larger than the mean.

Q. What's the explanation for high figures for Cs in illite?

A. The K_d's are just extremely high, and there's not much left in solution. We used 4,000 counts/min as the influent in all the experiments; this was enough for everything except Cs in illite-type clays. The difference between having one or two counts left in solution represents one order of magnitude; yet, in some cases, we had statistically negative results, with more being adsorbed than was left in solution. Some of the K_d's were approaching infinity.

Q. Did you take groundwater and then add the 30 meq to it?

A. No, we used distilled water--a synthetic. Our concept is to begin with crude basic building blocks, and then move to actual rock materials and actual groundwaters.

"STATISTICAL INVESTIGATION OF THE MECHANICS CONTROLLING RADIONUCLIDE SORPTION"

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1. INTRODUCTION, SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

1.1 INTRODUCTION

This report presents the results of the development and comparison of empirical models describing the transport of radionuclides in several geological environments. Battelle Pacific Northwest Laboratories (PNL) is concerned with the problem of isolating high level nuclear waste in a geological medium most likely to prevent contamination in the event of the failure of the storage containers. A study is being conducted to evaluate the ability of several geological media to absorb the radionuclides and retard their travel into the water and food cycle of animals and human beings.

Experiments have been performed to provide a data base for the purpose of modeling the distribution coefficient, K_d, of several radionuclides. This data base was employed to synthesize a model using the nonlinear Adaptive Learning Network (ALN) techniques and to synthesize a model using linear regression techniques. The two models have been subjected to statistical analysis to evaluate their success in modeling K_d.

1.2 SUMMARY

Experiments utilizing different approaches will be performed by PNL to obtain the K_d for various geological materials and solutions. Four radionuclides were studied, each in media comprised of combinations of eight minerals and four solutions as shown in Table 1.1. The K_d was measured three times at intervals of several days. Each nuclide-mineral-solution experiment was repeated three times. The experimental data base was then transmitted to Adaptronics.

TABLE 1.1

RADIONUCLIDES, MINERALS, AND SOLUTIONS USED IN K_d EXPERIMENTS

Radionuclide	Sorption Coefficient	Time Measurement Taken
Technetium	K_d(Tc)	3, 10, and 29-day intervals
Strontium	K_d(Sr)	3, 10, and 29-day intervals
Cesium	K_d(Cs)	3, 10, and 29-day intervals
Neptunium	K_d(Np)	3, 10, and 19-day intervals

Mineral (Soils)

Primary	Secondary
Quartzite	Illite
Albite	Kaolinite
Anorthite	Montmorillonite
Microcline	Vermiculite

Solutions (Groundwaters)	Concentration Level
Salt Brine	5130 meq/ℓ NaCl
Calcium Dominated	30 meq/ℓ $CaCl_2$
Dilute Brine	30 meq/ℓ NaCl
Bicarbonate Dominated	30 meq/ℓ $NaHCO_3$

Two approaches -- time dependent and time independent -- were adopted. The results were compared to evaluate the influence of time. The data base used for the time-dependent analysis was comprised of 288 observations, which were the 96 observations taken at three time intervals and catenated. The time independent data base was comprised of 96 observations of 32 different experiments, where those independent variables changing with time were averaged (pH and Eh) and the dependent variable to be modeled, K_d, was taken to be the K_d at the final time period.

A subset of each data base was then selected as the design set and used to synthesize the ALN and linear models. A second subset was used to evaluate the performance of the models. Performance criteria used to evaluate and compare the models included the average absolute error and the correlation coefficient between the true K_d and that estimated by the models, $\hat{K}_d$.

The analyses performed on each data base included:

- Univariate statistical analysis
- Model synthesis
- Model performance tests
- Comparison of the models
- Sensitivity analysis
- Multivariate statistical analysis

1.3 CONCLUSIONS

The results of the statistical analyses warrant the conclusion that it is feasible to model K_d empirically as a function of geologic media and groundwater characteristics. The parameters measured to describe the geologic media were shown to be significant in the modeling process, and the ability to establish their interactions has been demonstrated. It has also been shown that the perturbations in these interactions resulting in changes in K_d can be used to establish quantitative relationships.

The performance evaluation of the ALN models was superior to that of the regression models in all of the models of both data bases. The overall improvement of the ALN models over the regression was 22 percent. For the individual models, the range of improvement of average absolute error was from 7 to 46 percent; for the correlation coefficient, it ranged from 5 to 56 percent. Table 1.2 presents the performance improvement of ALN techniques over regression techniques for each model.

On an absolute basis, the ALN predicted K_d was within 90 percent of the true K_d for all four nuclides for the time-dependent data base.

The success of the ALN models over the regression models indicates that nonlinear media-solution interactions exist. These interactions may be different for different radionuclides.

1.4 RECOMMENDATIONS

The ALN modeling techniques were demonstrated to be superior to regression techniques, and it is recommended that all future work be concentrated on developing ALN models of the radionuclide sorption coefficients.

Thought should be given to the composition of the data base for future modeling efforts. There is an indication that some of the minerals may be redundant, especially in a given solution.

TABLE 1.2

AMOUNTS ALN MODELS IMPROVE OVER REGRESSION MODELS

	Radionuclides							
	Tc		Sr		Cs		Np	
Time	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient
Independent	46%	26%	17%	6%	13%	15%	39%	56%
Dependent	13%	5%	25%	6%	7%	23%	21%	39%

Overall Average Absolute Error Improvement: 22.6%

Overall Correlation Coefficient Improvement: 22.0%

For example, the independent variables of three primary minerals (albite, anorthite, microcline) in the calcium dominated solution appear to have similar effects. Also, in the bicarbonate solution, all the primary minerals as well as kaolimite tended to cluster together. Cation exchange capacity and surface area are the only mineral descriptors in the current data base; perhaps more could be included. Other parameters might also be included such as temperature and pressure. Once the experimental parameters have been established, all of the laboratories conducting experiments of a similar nature should be provided with the parameter list and asked to prepare a data base from their experiments using this format. These data could become part of the data base to be used by Adaptronics for further modeling and analyses.

2. RADIONUCLIDE K_d DATA BASE

2.1 INTRODUCTION

A data base was required to synthesize the empirical models of K_d. The results of a series of experiments to measure the K_d of several nuclides in various geological media was provided by PNL.

2.2 CHARACTERISTICS OF THE DATA BASE

Each of the eight minerals chosen for experimentation was combined with each of four solutions to produce 32 geological media in which to test four nuclides (Table 1.1). The K_d's of the nuclides were measured after three days, again after 10 days had elapsed, and finally Np was measured at 19 days while the rest were measured for the last time at 29 days. This produced three sets of data for each of the 32 experiments. In addition, each experiment was triplicated, so there were 96 experiments measured at three different times.

The three sets of 96 experiments were catenated to form a time-dependent data base of 288 observations. A time-independent data base of 96 observations was also created for a similar analysis by averaging those variables that changed with time -- pH and Eh -- and selecting the final K_d's for modeling. Each data base was subjected to a complete analysis.

Each experiment or observation measured a K_d as the dependent variable and the following as independent variables:

1. Cation Exchange Capacity (CEC)
2. Surface Area (SA)
3. Sodium content (Na)
4. Calcium content (Ca)
5. Chloride content (Cl)
6. Carbonate content (HCO_3)
7. Time (for the time-dependent data base) (t)
8. pH
9. Eh

A more detailed description of the data base may be found in Appendix A.

3. CONSTRUCTION OF K_d MODELS VIA ADAPTIVE LEARNING TECHNIQUES

3.1 ADAPTIVE LEARNING NETWORK (ALN) MODEL

In principle, models that predict K_d's can be derived either analytically or empirically.

An analytical model is one obtained by "reasoning from first principles." That is, the investigator attempts to interrelate all pertinent physical laws thought to influence K_d. The problem with the analytical approach to modeling is that many physical processes are so very complex as to defy reasoning from first principles. Constructing a mathematical model necessarily requires a number of approximations about the relationship of one variable to another. If the guesses are wrong, the model proves to be inaccurate. Furthermore, the model may become quite cumbersome due to a large number of coupled equations, and thus the computer processing time increases to unacceptable amounts.

Empirical predictive methods involve finding a predictive equation that best fits the observed experimental data. But, with conventional empirical modeling methods, one still has to know which interrelationships are important in order to write the general terms of the equation. And the resultant models, like analytical ones, are inflexible. If unanticipated changes occur in the process, the models become obsolete.

A different approach introduced by Adaptronics incorporates "self-learning" principles. To construct a self-learning model, the analyst first decides what variables may be important, but it is not necessary to consider the effects of the variables upon one another. What is needed instead is a collection of data that is reasonably representative of the variety of situations that can occur in the system being modeled.

The next step is to construct a mathematical network, known as an Adaptive Learning Network (ALN), which is a nonlinear hypersurface linking inputs to output. A generalized equation is constructed to link an output value to each possible pair of input variables. Special purpose computer programs are used to find the coefficients (the weights assigned to the variables) for each equation that makes it best fit the data. Those equations and variables that consistently produce the smallest prediction errors are determined. Additional equations are then constructed that examine interactions among four, eight, or more variables instead of only two. These additional equations result in added layers in the network and are retained if they can improve the prediction accuracy.

A model in the form of a network that has had its coefficients determined and has been reduced to the essential variables is called "adaptively trained." The synthesis of this model has proceeded directly from examination of an experimental data base without human intervention; hence the term "self-learning." To make certain that the model has indeed discovered for itself the pertinent physical laws, additional experimental data <u>not</u> used in the training, or synthesis, phase are introduced to test the ability of the model to generalize on its prior experience in dealing with new situations.

3.2 FORM OF ALN MODELS

The methodology associated with ALN synthesis is described more fully in References 1 through 6 by Barron and Mucciardi. In summary, two-input one-output "elements" are used to construct an adaptive learning network. The output of each element, y, is a quadratic function of its two inputs x_i and x_j:

$$y = w_o + w_1 x_i + w_2 x_j + w_3 x_i x_j + w_4 x_i^2 + w_5 x_j^2$$

All combinations of inputs are considered two-at-a-time as above. For given identities of x_i and x_j, an optimization algorithm is used to find the coefficients, w, that yield the smallest error in fitting y to the values of x_i and x_j in a "fitting" subset of the data. Those combinations of variables yielding a low-error rate (on an independent "selection" subset of the data) are then retained and the rest discarded. Thus, the candidate input list is pruned to the most informative subset. This produces the first layer in the ALN.

The outputs of Layer 1 become inputs to Layer 2, and the process is now repeated. Since each input to Layer 2 is a function of two x's, we are now considering functions of functions; thus the complexity of the model increases, but more slowly than its functional power. Only those combinations from Layer 1 are retained that produce the greatest improvement in accuracy. Now the outputs from Layer 2 become inputs to Layer 3, and so on.

The training procedure is terminated when it is established that the addition of further layers would produce an "overfitting" condition; that is, the model would become so adept at fitting the data used to train it that it would be unable to generalize to data not previously seen. Special algorithms are used to detect and avoid this condition.

An ALN model thereby assumes the form of a multinomial -- a polynomial in many variables -- of the (automatically) selected inputs. The extent and type of nonlinearities in model structure can be discovered and implemented during model synthesis. Thus, the ALN methodology is a powerful tool for use in data modeling instances where little or no knowledge exists regarding the functional relationship of dependent to independent variables.

4. STATISTICAL INVESTIGATION OF THE MECHANICS CONTROLLING RADIONUCLIDE SORPTION

4.1 UNIVARIATE STATISTICAL ANALYSIS

After preparation of the two data bases, time independent and time dependent, the covariance and correlation matrices were computed. The covariance matrix is needed only to compute the correlation matrix and will not be discussed further. The correlation matrices for the two data bases are shown in Figures 4.1 and 4.2. Each matrix shows the correlation of four separate dependent variables, the sorption coefficients $K_d(Tc)$, $K_d(Sr)$, $K_d(Cs)$, and $K_d(Np)$, with the eight independent variables CEC, surface area (SA), sodium content, calcium content, chloride content, bicarbonate content, pH, Eh, and, in the time-dependent data base, time.

A study of the matrices reveals a high correlation between the CEC and the surface area. This is not very surprising, as a greater surface area would imply a greater cation exchange capacity. Another not unexpected result is a strong correlation between bicarbonate and pH.

The perfect correlation of sodium and chloride is an artifact. The possible amounts of sodium (Na) and chloride (Cl) that can occur in any solution are 0, 30, and 5,130 meq/ℓ. The amounts (in meq) of Na and Cl in the four solutions are as follows:

Solution	Sodium	Chloride
Strong brine	5130	5130
Calcium	0	0
Weak brine	30	30
HCO_3	30	0

	K_d(Tc)	K_d(Sr)	K_d(Cs)	K_d(Np)	CEC	SA	Na	Ca	Cl	HCO_3	t	pH	pH
CEC	-.26	.50	.14	.14	1.00								
SA	-.24	.48	.07	.19	.93	1.00							
Na	.33	-.34	-.15	.17	.00	.00	1.00						
Ca	-.08	-.34	.25	-.26	.00	.00	-.34	1.00					
Cl	.33	-.35	-.15	.17	.00	.00	1.00	-.33	1.00				
HCO_3	-.27	.56	-.09	.20	.00	.00	-.33	-.33	-.34	1.00			
t	.29	-.06	.05	.07	.00	.00	.00	.00	.00	.00	1.00		
pH	-.31	.59	-.12		.26	.21	-.27	-.34	-.28	.78	.07	1.00	
pH				.28	.23	.20	-.41	-.23	-.41	.77	.09		1.00
Eh	-.27	-.12	.03		-.08	-.08	-.07	.17	-.07	-.21	-.87	-.28	
Eh				-.18	-.02	-.03	-.20	.28	-.20	-.20	-.89		-.18

FIGURE 4.1: CORRELATION MATRIX - TIME DEPENDENT DATA BASE

	K_d(Tc)	K_d(Sr)	K_d(Cs)	K_d(Np)	CEC	SA	Na	Ca	Cl	HCO_3	pH	pH
CEC	-.30	.49	.27	.04	1.00							
SA	-.28	.47	.10	.08	.93	1.00						
Na	.44	-.35	-.17	.14	.00	.00	1.00					
Ca	-.17	-.34	.22	-.26	.00	.00	-.34	1.00				
Cl	.44	-.35	-.17	.14	.00	.00	1.00	-.33	1.00			
HCO_3	-.31	.60	-.08	.23	.00	.00	-.33	-.33	-.34	1.00		
pH	-.40	.64	-.09		.27	.22	-.28	-.35	-.29	.80	1.00	
pH				.26	.24	.21	-.43	-.25	-.44	.82		1.00
Eh	.16	-.51	.18		-.26	-.25	-.22	.54	-.21	-.69	-.84	
Eh				-.32	-.05	-.07	-.54	.75	-.53	-.54		-.40

FIGURE 4.2: CORRELATION MATRIX - TIME INDEPENDENT DATA BASE

Note that Na and Cl both have the same values for two of the solutions; i.e., 5,130, 5,130, and 30, 30. The other two solutions also have the same values but in reverse order; i.e., 0, 30 and 30, 0. These sets of values for Na and Cl are repeated throughout the data base. Therefore, the data set of Na is statistically equivalent to the data set of Cl indicating perfect correlation.

There is some correlation indicated between two of the dependent variables and the independent variables, notably:

Dependent Variable	Independent Variable
K_d(Tc)	Na, Cl
K_d(Sr)	CEC, SA, HCO_3, pH

At this point, the hypothesis was made that, when the ALN algorithms designed the models for dependent variables K_d(Tc) and K_d(Sr), the correlated independent variables would be selected as inputs. Since Na and Cl were themselves highly correlated, as well as CEC and SA, and also HCO_3 and pH, only one of each could be selected. This hypothesis was proven to be correct, as the K_d(Tc) models selected Cl as one of its inputs and the K_d(Sr) models selected CEC and pH.

The correlation between the independent variables and time (in the time-dependent data base) was particularly noted, and when very little correlation was seen (only K_d(Tc) showed a slight correlation to time), it was conjectured that the time-dependent data base (three times as large as the time-independent data base) would not produce significantly better modeling results.

4.2 MODEL SYNTHESIS

Two empirical models were synthesized for each dependent variable from each data base using only the design subsets: (1) linear regression and (2) nonlinear ALN.

The linear regression model was synthesized using the stepwise linear regression program from the Biomedical Computer Program package available publicly. The model may be represented by

$$K_d = \sum_{i=1}^{n} A_i X_i$$

where X_i is the list of n independent variables. Both the A_i's and the X_i's appear in a linear form in the above equation.

The ALN model is synthesized using the ALN procedure discussed in Section 3. The independent variables and the coefficients are nonlinear

$$K_d = f(W, X')$$

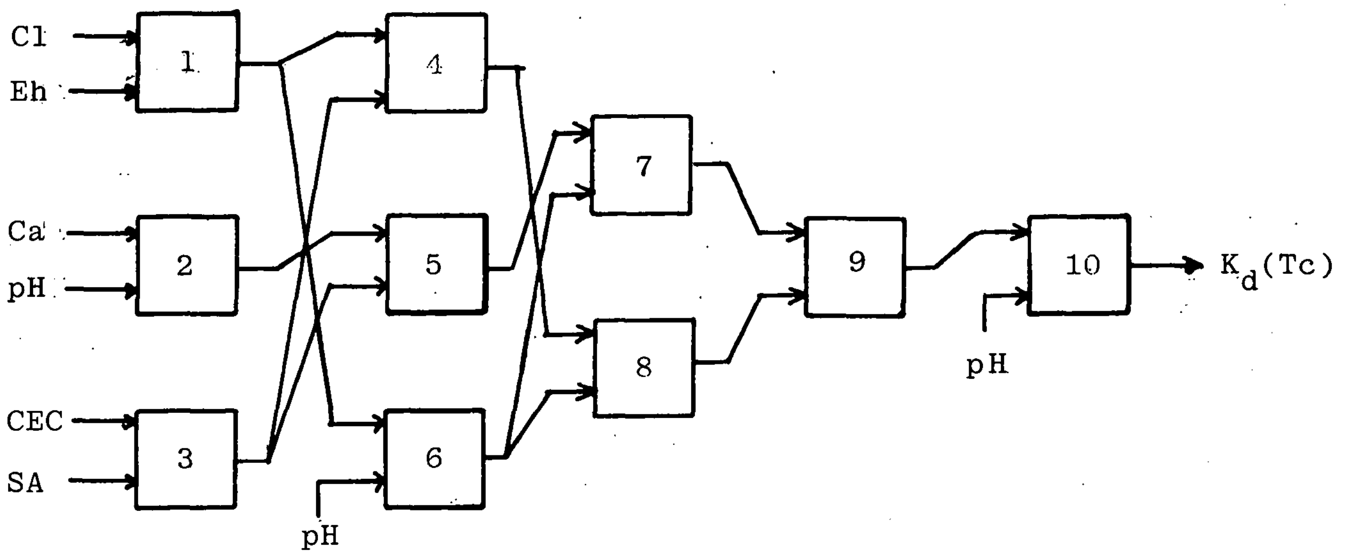
where X' is the subset of the independent variables selected as model inputs.

The eight linear models and the eight ALN models are shown in Figures 4.3 through 4.10, along with the performance of the design sets. The criteria used to judge performance are the average absolute error and the correlation coefficient of the model outputs compared to the desired outputs. In both sets of models, the K_d's for Sr, Cs, and Np had ranges of values of several orders of magnitude, so a "modified" log function of the K_d's was modeled instead of the actual K_d's. The modified log function was an approximation to a natural logarithm to allow for negative and small values of y:

$$f(y) = \begin{cases} 1. + \ln y, & \text{if } y > 1. \\ y, & \text{if } -1 \le y \le 1. \\ 1. - \ln|y|, & \text{if } y < -1. \end{cases}$$

This approximation of a log function is linear between y = ± 1.

ALN Model



```
                                       NETWORK WEIGHTING COEFFICIENTS
    ELEM          W0               W1              W2             W3                W4               W5

       1   -.10022E+03     -.11906E+03      .13341E+01    -.63508E+00       .10527E+03     -.20199E+01
       2    .26604F+01     -.16975E+01     -.17292E+01     .10539E+01       .45255E+00     -.45653E+00
       3   -.38048E+02     -.15866E+02     -.77004E+02    -.10309E+04       .36896E+03      .62574E+03
       4   -.58590E+00     -.21697E+00      .80190E+00     .25064E+00       .91930E-01     -.10774E+00
       5   -.30710E+00      .72819E-01      .56675E+00     .36210E+00       .43103E-02     -.11284E+00
       6    .17951E+01     -.14650E+01     -.21123E+01     .10469E+01       .42711E+00      .11924E+00
       7   -.11631E+00      .30535E+00      .15151E+00     .13486E+00
       8    .52504F+00      .31049E-01      .10324E-01     .13478E+00
       9    .45588E+00      .94416E+00     -.53526E+00     .45208E-01
      10   -.57590E-01      .14673E+01     -.76912E-01     .53012E+00
```

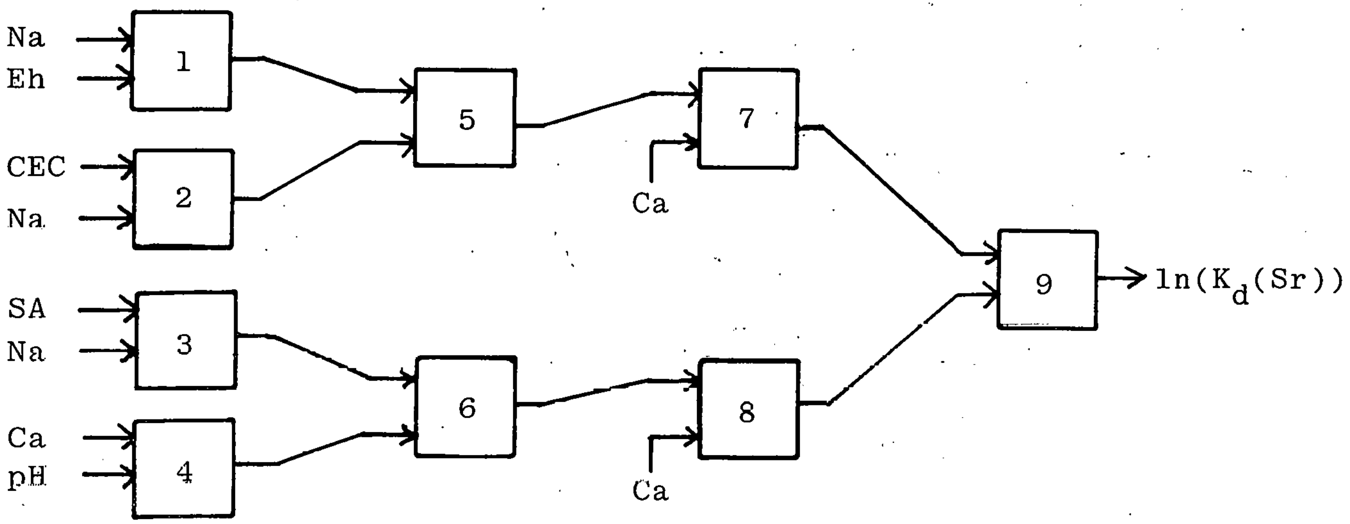
Linear Model

$$K_d(\mathrm{Tc}) = 2.051 - .802(\mathrm{CEC}) - .311(\mathrm{SA}) - .860(\mathrm{Ca}) + 1.209(\mathrm{Cl}) - .608(\mathrm{HCO_3}) - 1.257(\mathrm{pH}) - .569(\mathrm{Eh})$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	1.338	.961
Regression	2.442	.579

FIGURE 4.3: TECHNETIUM MODELS - TIME INDEPENDENT

ALN Model



NETWORK WEIGHTING COEFFICIENTS

ELEM	W0	W1	W2	W3	W4	W5
1	.93769E+02	.10141E+03	−.12418E+01	−.56926E−01	−.89940E+02	−.52219E+00
2	.13441F+03	.17995E+00	.15007E+03	−.40058E+00	.47434E+00	−.13194E+03
3	.13499E+03	.79942E+00	.15007E+03	−.40087E+00	−.11685E+00	−.13194E+03
4	.25419E+01	−.21142E+01	.19706E+01	.25510E+00	.17517E+01	.28034E+00
5	−.21536E+01	.10418E+01	.83940E+00	.62350E−01	−.63142E−01	−.68433E−01
6	.45834E+00	.50593E+00	.52776E−01	−.45525E+00	.24698E+00	.26832E+00
7	−.22158E+00	.10650E+01	.10811E+00	.48075E−01		
8	−.54831E+00	.12363E+01	−.91624E+00	.42129E+00		
9	.10653E+00	.63805E+00	.28587E+00	.89800E−02		

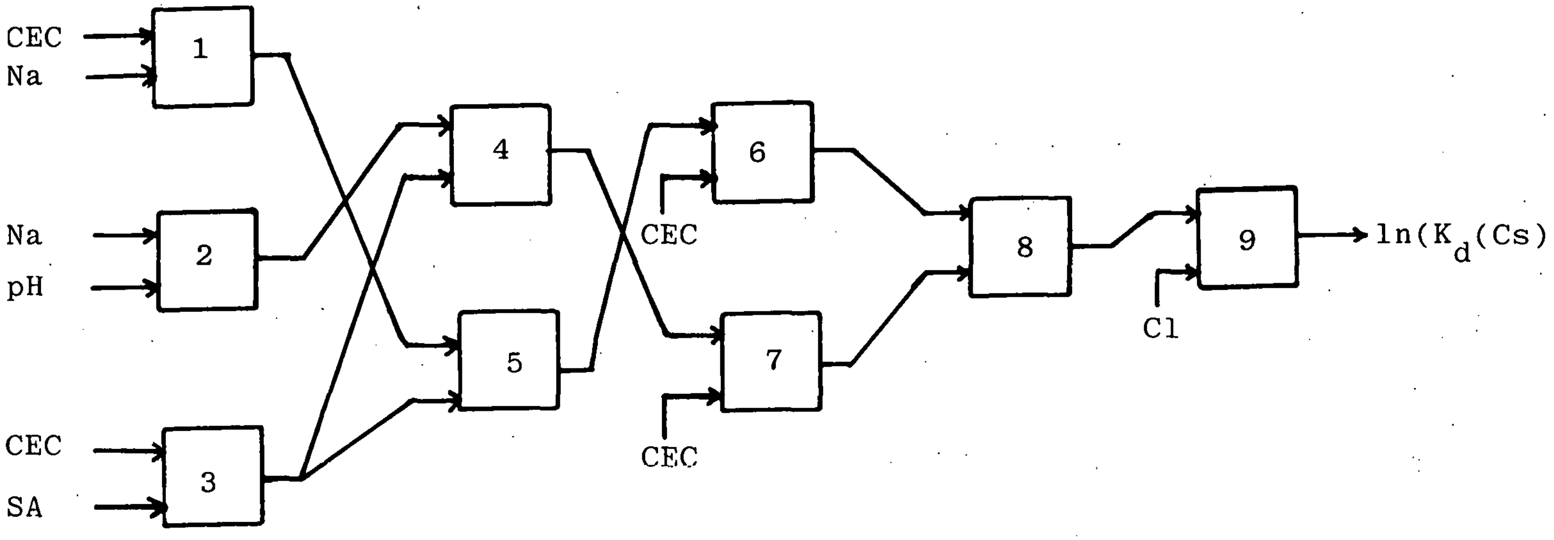
Linear Model

$$\ln(K_d(Sr)) = 4.236 + .489(CEC) + .067(SA) - 1.383(Ca) -1.387(Cl) + .396(HCO_3) + 1.077(pH) + .599(Eh)$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	59.716	.951
Regression	72.814	.922

FIGURE 4.4: STRONTIUM MODELS - TIME INDEPENDENT

ALN MODEL



```
                                    NETWORK WEIGHTING COEFFICIENTS
            ELEM      W0              W1           W2            W3             W4             W5

              1   .70693E+01    .80253E+00  -.16789E+01
              2   .70671E+01   -.17597E+01  -.26639E+00
              3   .70693E+01    .20548E+01  -.13531E+01
              4  -.15014E+01    .13261E+00   .13497E+00   .12532E+00
              5   .83568E+01   -.36122E+00  -.11394E+01   .18416E+00
              6   .14588E+01    .19417E+01   .47382E+01   .31637E-01  -.69489E-01  -.44715E+01
              7   .43717E+01    .93814E+00   .53936E+01  -.11579E+00   .10047E-02  -.39383E+01
              8   .16651E+00    .59167E+01  -.49060E+01  -.70291E+00   .31953E-01   .66627E+00
              9   .62002E+01    .36649E+01   .24175E+02  -.66600E+00  -.16596E+00  -.17127E+02
```

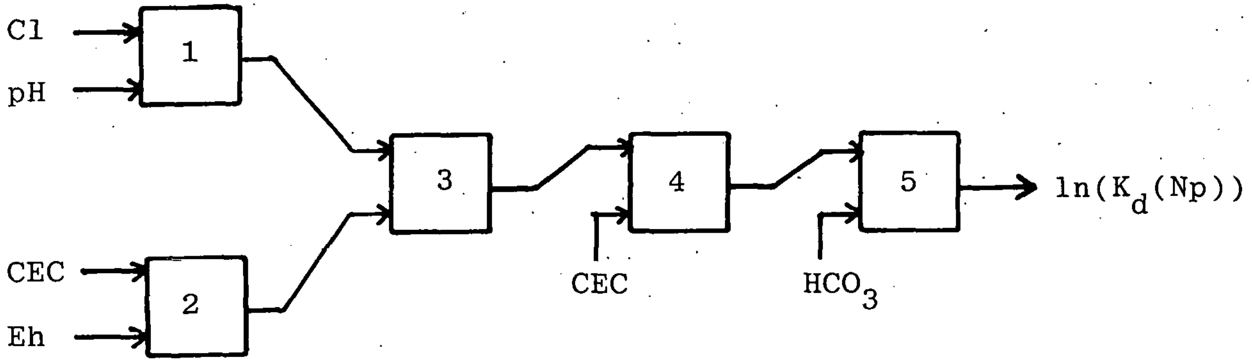
Linear Model

$$\ln(K_d(Cs)) = 7.003 + 3.555(CEC) - 2.666(SA) - 3.842(Na) - 4.401(pH) - 3.973(Eh)$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	6,124.1	.668
Regression	6,338.0	.610

FIGURE 4.5: CESIUM MODELS - TIME INDEPENDENT

ALN MODEL



```
                                    NETWORK WEIGHTING COEFFICIENTS
 ELEM          W0              W1              W2              W3              W4              W5

   1    -.88544E+02    -.10848E+03    -.12519E+00     .33531E+00     .94641E+02    -.13480E+01
   2     .52989E+01     .16656E+01    -.22252E+00    -.72217E-01    -.11839E+01    -.36964E+00
   3    -.19593E+02     .34319E+01     .70493E+01    -.75688E+00     .63967E-01    -.42900E+00
   4    -.13975E-01     .10218E+01     .42280E+00    -.13801E+00
   5    -.11524E+01     .12823E+01    -.24910E+01     .59719E+00
```

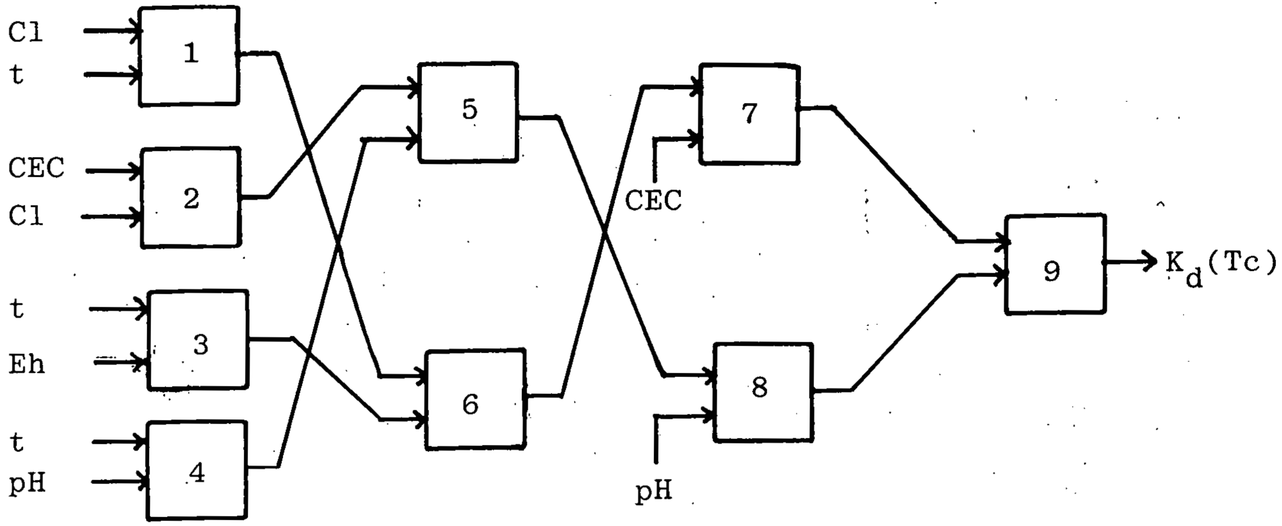
Linear Model

$$\ln(K_d(Np)) = 3.664 - .399(CEC) + .502(SA) + .878(Na) - .426(Ca)$$
$$0\ .802(HCO_3) + 1.761(pH) + .640(Eh)$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	17.497	.802
Regression	27.336	.259

FIGURE 4.6: NEPTUNIUM MODELS - TIME INDEPENDENT

ALN Model



NETWORK WEIGHTING COEFFICIENTS

ELEM	W0	W1	W2	W3	W4	W5
1	.35174E+02	.40729E+02	.10267E+01	.78276E+00	-.34377E+02	-.78537E-01
2	.35514E+02	-.25372E+00	.40729E+02	-.44393E+00	-.41965E+00	-.34377E+02
3	.23395E+00	-.31254E+00	-.10197E+01	-.89232E+00	-.14672E+01	.13262E+01
4	.13013E+01	.11506E+01	-.81750E+00	-.41409E+00	-.85999E-01	-.35835E+00
5	-.25031E+00	.41594E+00	.52312E+00	.51092E+00	-.48781E-01	-.12247E+00
6	.25121E+00	.78882E+00	.27023E+00	.14650E+01	-.93750E-01	-.14755E+01
7	.21764E-02	.95572E+00	-.32962E+00	-.41994E+00		
8	.13610E+00	.14367E+01	.36611E+00	.47557E+00		
9	.13015E-01	.13013E+00	.52251E+00	.58077E-01		

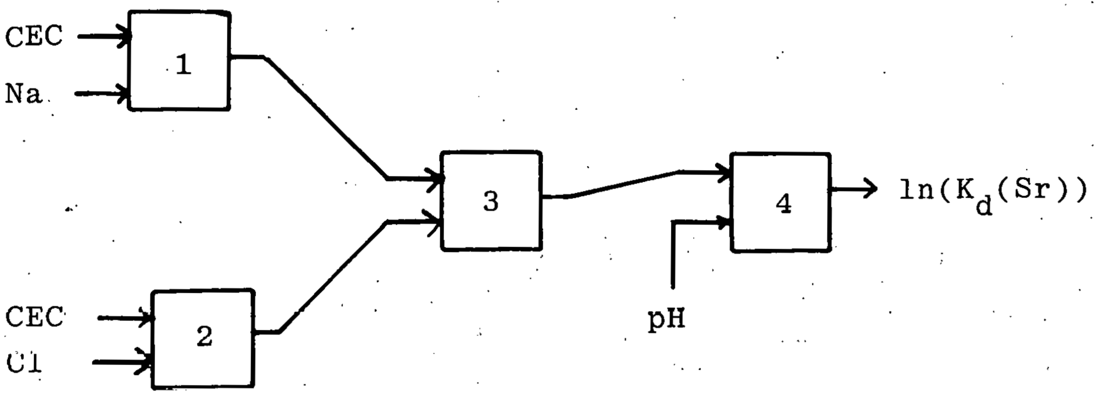
Linear Model

$$K_d(\text{Tc}) = .897 - .516(\text{CEC}) - .217(\text{SA}) - .199(\text{Ca}) + .666(\text{Cl}) - .500(\text{HCO}_c) + .085(t) - .411(\text{pH}) - .934(\text{Eh})$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	1.262	.683
Regression	1.514	.548

FIGURE 4.7: TECHNETIUM MODELS - TIME DEPENDENT

ALN Model



NETWORK WEIGHTING COEFFICIENTS

ELEM	W0	W1	W2	W3	W4	W5
1	.13279E+03	.36512E+00	.14728E+03	-.48517E+00	.21190E+00	-.12912E+03
2	-.95195E+02	.36512E+00	-.11643E+03	-.48428E+00	.21190E+00	.99667E+02
3	-.14978E+01	.87207E+00	.11722E+01	.83364E+00	-.38902E+00	-.53565E+00
4	.46297E+00	.93316E+00	.79227E+00	-.10052E+00		

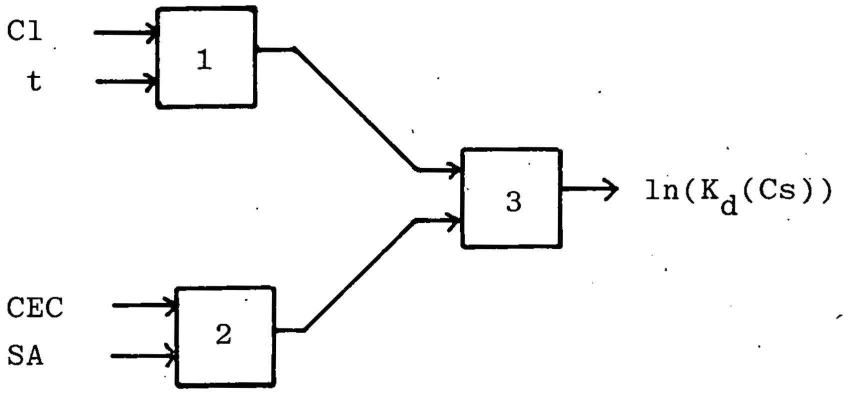
Linear Model

$$\ln(K_d(Sr)) = 4.341 + .601(CEC) - .044(SA) - 1.403(Ca) - 1.790(Cl) + .284(HCO_c) - .235(t) + .432(pH) - .121(Eh)$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	59.72	.960
Regression	83.47	.902

FIGURE 4.8: STRONTIUM MODELS - TIME DEPENDENT

ALN Model



NETWORK WEIGHTING COEFFICIENTS

ELEM	W0	W1	W2	W3	W4	W5
1	.21806E+02	.15428E+02	.18119E+00	.32902E-03	-.14840E+02	-.10524E+00
2	.20369E+01	.15859E+02	-.38909E+02	-.37529E+03	.11950E+03	.23273E+03
3	-.55295E+01	.70522E+00	.88560E+00	.34347E-01	.47954E-02	-.87093E-02

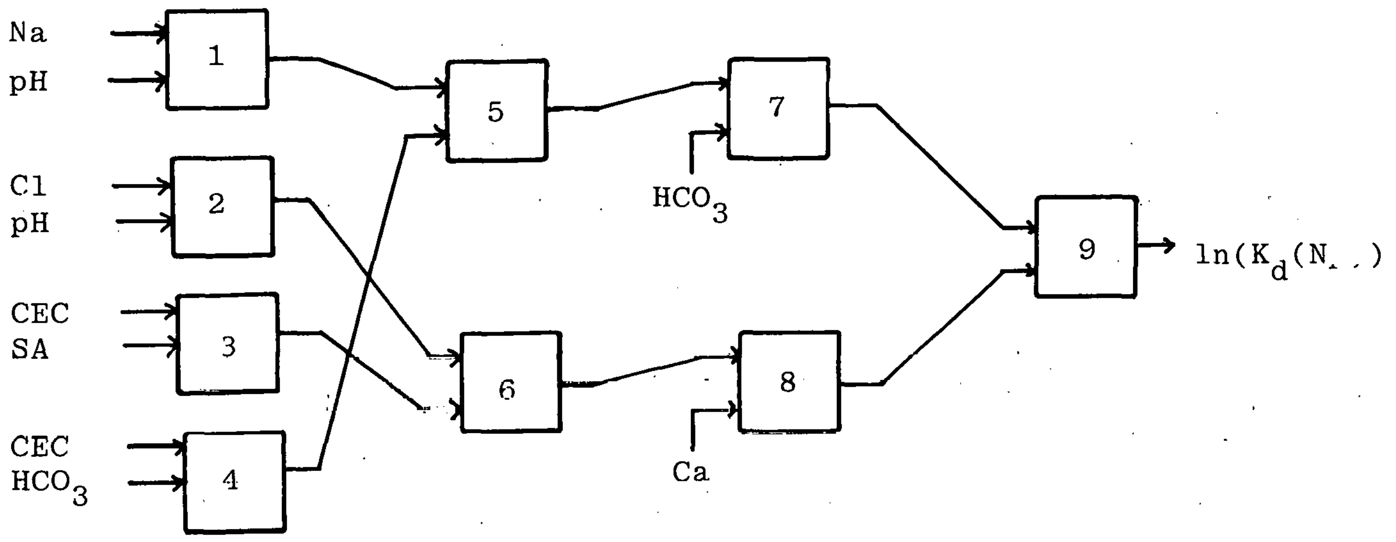
Linear Model

$$\ln(K_d(Cs)) = 6.872 + 1.749(CEC) - .860(SA) - 1.703(Na) + .630(HCO_3) + .318(t) - .901(pH) + .128(Eh)$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	5,882.2	.457
Regression	6,378.9	.439

FIGURE 4.9 CESIUM MODELS - TIME DEPENDENT

ALN MODEL



NETWORK WEIGHTING COEFFICIENTS

ELEM	W0	W1	W2	W3	W4	W5
1	.38399E+02	.40495E+02	.71035E+00	.42180E+00	-.34561E+02	-.34836E+00
2	.14240E+02	.13025E+02	.10383E+01	.40469E+00	-.10631E+02	-.16648E+00
3	-.91518E+01	.42774E+01	-.38150E+02	-.42881E+03	.14656E+03	.26309E+03
4	.81250E+01	.18212E+01	.41250E+01	-.42172E+00	-.11615E+01	-.33750E+01
5	-.18320E+01	.18861E+01	-.37261E+00	-.42428E+00	.59864E-01	.34772E+00
6	-.14464E+01	.12168E+01	-.69775E-01	-.33336E+00	.10205E+00	.28529E+00
7	-.22783E+01	.15688E+01	-.42629E+01	.10405E+01		
8	.11995E+00	.97500E+00	-.91177E+00	.16558E+00		
9	-.48766E+00	.72936E+00	.47829E+00	-.17829E-01		

Linear Model

$$\ln(K_d(Np)) = 3.468 + .376(SA) - .402(Ca) + .343(Cl) - .629(HCO_3) + .219(t) + 1.111(pH) + .121(Eh)$$

	PERFORMANCE	
	Average Absolute Error	Correlation Coefficient
ALN	18.377	.739
Regression	23.818	.344

FIGURE 4.10: NEPTUNIUM MODELS - TIME DEPENDENT

The inspection of the correlation matrix had implied that Na or Cl might be selected by the ALN model for technetium and, in both the time-dependent and time-independent models, Cl was selected. Similarly, the strontium models used CEC and pH, as predicted.

4.3 MODEL SYNTHESIS EVALUATION

The true test of a model is its performance on data that were not used in its design. The independent evaluation subset was therefore used to evaluate and compare the two empirical models. The performance criteria were again the average absolute error and the correlation coefficient. The comparison of the eight linear models with the eight ALN models is found in Table 4.1. In all cases, the ALN model did a significantly better job of modeling the sorption coefficients. The interactions between the K_d's and the independent variables are therefore demonstrated to be nonlinear in nature.

The outputs of the ALN and regression models (estimated $\hat{K}_d$'s) for each nuclide along with the desired or true outputs (K_d's) are shown in Tables B.1 through B.4 of Appendix B. Only the tables for the models synthesized from the time-independent data base are included.

4.4 SENSITIVITY ANALYSIS

Empirical models often can give researchers insight into physical relationships that might previously have been either unknown or only suspected. The design of the ALN model itself is often revealing, as it is observed which independent variables are selected, which ones are cross-coupled, how often each one appears, and so on. Another means of using the model for gaining information is to study the reaction of the independent variable to perturbations of each independent variable that is an input to the model.

TABLE 4.1

PERFORMANCE OF TWO MODELING TECHNIQUES ON DATA NOT USED IN MODEL SYNTHESIS

	Tc (0-22)[1]		Sr (0-1,680)		Cs (1.3-140,000)		Np (0-7,324)	
	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient
Time Independent								
ALN	1.3	.88	75.4	.91	5,481	.67	15.4	.87
Reg.	2.4	.62	91.0	.85	6,330	.52	25.4	.31
Time Dependent								
ALN	1.3	.65	59.4	.96	4,151	.41	18.4	.74
Reg.	1.5	.60	79.4	.90	4,452	.18	23.3	.35

---

[1] Numbers in parentheses denote the range of values of K_d for the particular nuclide.

A sensitivity analysis determines the changes in the sorption coefficient due to unit changes in each independent variable in turn. The results of the analysis can be used to determine both the absolute influence and the relative importance of each of the independent variables on K_d. They can also be used to eliminate those variables which have very little influence on the model.

For a linear model, the sensitivities, $\Delta K_d/\Delta x_i$, are the coefficients themselves. For the ALN model it was necessary to compute the derivatives numerically. This was done in the following way. For each observation in the data base, a unit change was made in each input variable, and the partial derivative of the model to that variable was determined by observing the change in K_d. The entire data base was used to determine the overall, average sensitivity of K_d to each input.

Table 4.2 shows, in tabular form, the percentage of the influence each variable has in each K_d model. The time-dependent and time-independent models showed very little sensitivity to time with the exception of the time-dependent ALN model for technetium. The conclusion may be made either that time is not a very important variable or that perhaps its influence is felt indirectly via another variable which, while considered to be an independent quantity, may be itself dependent on time.

In general, each model is uniquely sensitive to its selected parameters, but in most cases of both the linear and nonlinear models the pH is found to be very influential. Examination of the parameters selected as model inputs reinforces this conclusion, because pH is selected by all but one of the models. Cation exchange capacity is another parameter that has a strong influence on most of the models.

TABLE 4.2

PERCENTAGE OF SENSITIVITY OF K_d TO PARAMETERS FOUND SIGNIFICANT BY TWO MODELING TECHNIQUES

	Time-Independent Radionuclide								Time-Dependent Radionuclide							
Id.	Tc		Sr		Cs		Np		Tc		Sr		Cs		Np	
Var.	ALN	Reg.	ALN	Reg.	ALN	Reg.	ALN	Reg.	ALN	Reg.	ALN	Reg.	ALN	Reg.	ALN	Reg.
CEC	-31.0	-14.2	1.3	9.1	28.1	19.3	2.1	7.4	-2.5	-14.6	7.8	12.2	69.3	27.8	31.3	11.7
SA	-22.6	-5.5	0.1	1.3	-1.3	-14.5		9.2		-6.1		-0.9	29.5	-13.7	59.5	11.7
Na			34.1		-0.2	-20.8		16.3			69.3			-27.1	0.3	
Ca	-5.0	-15.3	1.1	-25.5				-7.9		-5.6		-28.6			-0.1	-12.5
Cl	10.0	21.5		-25.7	10.6		26.7		0.9	18.9	-2.7	-36.5	0.7		0.005	10.7
HCO_3		-0.9		7.4			2.0	-14.8		-14.2		5.8		10.0	-1.8	-19.6
t									56.2	2.4		-4.8	0.6	5.0		6.8
pH	30.1	22.4	63.3	20.0	-58.4	-23.9	-68.5	32.5	35.9	-11.7	20.2	8.8		-14.3	7.0	34.7
Eh	1.2	-0.1	-0.03	11.1		-21.5	-0.06	11.8	4.5	-26.5		-2.5		2.0		3.8

4.5 MULTIVARIATE ANALYSIS AND PROFILES OF CLUSTER STRUCTURE

Prior to the modeling process, the independent variables only in each data base were subjected to a clustering algorithm to confirm that the design subset and the evaluation subset of the data were equally representative of the process. Since one set of the triplicated experiments was held out as independent data for evaluation, it was gratifying to see that almost every observation of the evaluation set fell in the same multidimensional cluster as that of the other two observations of the same experiment.

The most interesting use of the clustering algorithm was to cluster only the independent variables selected by an ALN model. (In the cases where the ALN chose two highly correlated variables, such as cation exchange capacity and surface area, only one was retained for clustering.) The average K_d's of all the observations falling in each major cluster was generally unique; i.e., one major cluster gave a mean K_d of a low value while another gave a high value. The clusters tended to group the observations with comparable values of K_d.

Examination of the major clusters with respect to the independent variables indicated that the most significant parameter defining the clusters was the pH. The only exception was the time-dependent model for Cesium. The K_d's for Cesium were the most difficult to model, and it is believed that additional experimental parameters are necessary for this model. Three of the models -- time-dependent K_d(Np), time-independent K_d(Tc), and K_d(Sr) -- showed a tendency to separate the clusters with Ca content as well as pH. To a lesser degree, the Eh helped to discriminate clusters in all the time-independent models except Cesium.

In general, the results of the multivariate analysis supported conclusions arrived at by model synthesis analysis and sensitivity studies. More conclusive results should be obtained when additional parameters and observations are added to the data base.

5. REFERENCES

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2. Mucciardi, A. N. and E. E. Gose, "An Automatic Clustering Algorithm and Its Properties in High-Dimensional Spaces," IEEE Trans. Computers, Vol. SMC-2, No. 2, April 1972, pp. 247-254.

3. Mucciardi, A. N., "Elements of Learning Control Systems with Applications to Industrial Processes, "Proc. 1972 IEEE Conference on Decision and Control, New Orleans, La. December 13-15, 1972, pp. 320-325.

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DISCUSSION--A. N. MUCCIARDI

Basic Modular Elements of Learning Network (Section 3.2)

Q. Why did you select that function?

A. First, for computational efficiency; it is the smallest thing one can do and still develop a network. Second, biologically, it seems to be the smallest elemental building block. Finally, the function we're building up involves putting together small pieces of this overall multivariate function, and it turns out that the amount of data needed for these small pieces is reduced by keeping the number of inputs down. Nevertheless, using more inputs or a different kind of function produces more or less the same mathematical results. The output is a function of the input, and the results will have the same mathematical properties although they may look different.

Evolution of Adaptive Network (Section 3.2)

Q. How is the error determined--do you use an f test or residuals, or something else?

A. You could use any method you choose--you could have a minimum squared error, a correlation between the two, or a weighted penalty type of test; you could bias the results in the direction of the observations in which you have more confidence; you could choose to be more accurate on certain types of minerals than others, etc.

Q. What do you mean by "true value"?

A. Experimentally measured value.

Q. If your function y is known to be logarithmic in the x value, then how does the power series expansion work?

A. Any function can be represented by power series expansion. The fact that it is a logarithmic function just means that a few more layers are needed.

Detection of Overfit (Section 3.2)

Q. To what extent can you make those two subsets independent?

A. We perform a clustering analysis on the data. This may break it up into many modes, but then we will randomly select from each one. In this way, we know that, however scattered the data may be, the model will be designed and tested on a subset of the data that covers the whole range.

Sensivity of K_d to Parameters
According to Two Modeling Techniques (Table 4.2)

Q. Is the sign of these figures an artifact of the calculation?

A. No. dYdX, if it's negative, would mean that as X increases, Y decreases.

Q. What do the blank squares mean?

A. They mean that that variable was not picked up by this model.

Q. Does regression analysis pick up the same variables as the ALN method?

A. Not necessarily. With Np and Na, for example, regression analysis showed the reaction to be very strong, and ALN did not, while for Sr and Na the reverse was the case. So the two analytical methods show very different pictures. But when you look at how well the two models perform--which one provides more meaningful data for a particular variable--you see that the ALN method considerably outperforms the other.

Accuracy of Model

Q. Is there a way to determine the amount of experimental error of the model, so that you can come up with an estimated uncertainty in your coefficients?

A. Yes, there are a number of ways. First, you could repeat the experiment three times, as Battelle did. When John Relyea did this, he got quite a spread in the average K_d--particularly for Cs--where the difference was six orders of magnitude. Thus, with this method, enough replicates are incorporated so that statistical error is built into the model. Second, if you have a strong feeling that certain data are much more precise than others, you can build this bias into the model, forcing it to be more accurate for some minerals than for others. Thus, either implicitly or explicitly, you can influence the amount of experimental error. You can also measure the amount of error by testing the model on new data.

Q. How can you tell if you're missing an important parameter?

A. There are a couple of ways. As a baseline, you can do a type of coin-flipping experiment. You calculate the percentage of error that you would have if you simply predicted the average K_d of a nuclide. Then, if your experimental results cannot beat that error margin, you know something important is missing.

A more effective way, however, is based on the fact that, if there is a functional relationship between a dependent variable and a combination of independent variables, the data will show a trend. If you find that, in clustering the x data, the associated y's are all over the map, then you know that you've measured something irrelevant, and that something is missing. When the models converge, on the other hand, you know you've found all the important parameters.

Q. Have you tried the model with data from other sources? With conditions that are theoretically similar?

A. We'll be doing that this coming year. This was just a start to see if there was any value in going further.

Cross-Checking Capability

Q. Is cross-checking capability built into the method? With different laboratories using different methods and obtaining different results, there needs to be a way to determine whether a particular result is an artifact of the method or of the laboratory.

A. Once we begin to analyze data from different laboratories, we will have a number of options available. We can, for example, remodel to fit the conditions of a particular experiment or site; or we can attempt to design one model that will incorporate all factors. We can also cluster the data to see if one particular group or one particular condition always produces results that are different from the others. We have many different ways of checking and cross-checking the data.

Comparison with Other Methods

Q. In view of the large discrepancy between the results of regression analyses and your model, what criteria do you have to show that yours is superior?

A. The ultimate superior model comes from physics--that of true relationships. What we're trying to do here is to close the loop with experimental mathematics. Instead of saying that there's a bewildering variety of interactions that must be taken into account, we're saying that maybe there are only a few key ones, and we are developing models based on those.

Q. In other words, this is the simplest first level?

A. Yes. The model should be viewed in two ways. First, it is an engineering solution to a problem, providing a meaningful answer right away. Second, if it is correct, it will feed information back to theorists, to help them develop even better models in the future.

Q. How does your treatment compare with standard factor analysis?

A. Factor analysis won't provide a model. It can be useful as a data reduction technique--a preprocessing step--indicating the degree of correlation among individual parameters; it can provide an idea of the number of true variables. Cluster analysis would be a more relevant technique for actually developing a model, however.

Uniqueness of Solution

Q. How sure are you: (1) that there is a unique solution in existence for these data, and (2) that this is that solution?

A. We're fairly sure that it is not a unique solution. With these types of problems, just as we have to replace "correlations" with "functional relationships," we have to replace "unique" with "good." This is basically an engineering solution. If we perturbed the data, some things would change. However, the overall surface doesn't change much, and the primary findings--such as that pH is a dominant variable in predicting the K_dNP--don't change much, either.

Characterization of Minerals

Q. What bothers me is that eight minerals were taken to be equally reactive, as though they all had the same cation sites, surface characteristics, etc.

A. The minerals were implicitly encoded via variables such as the cation exchange capacity and surface area. These variables changed as the minerals changed. Thus, if one finds that, in a particular case, cation exchange capacity is very influential in controlling K_d, and that small perturbations in this capacity result in a much larger perturbation in K_d than anything else does, that means that that particular mineral is very strong.

Q. But you've only used extensive variables. You need intensive variables, such as energy potential, too.

A. We agree that we need more detailed characterization; that our characterization has been too implicit and needs to be made more explicit. This is particularly true in the case of Cs. Our recommendation for the next time is that as much characterization as possible be used; if a factor is measurable, it should be included.

Chemical Analysis

Q. Is any effort being made to understand these effects on a chemical basis?

A. We ourselves are not in a position to do more than raise questions. However, as we feed our data back to people such as yourselves, you can then tell us whether or not it is meaningful, analyze it in chemical terms, etc. These data were obtained only recently so there has not yet been time to solicit this feedback, but that is an important part of the program.

Time Dependency

Q. How many data points do you have?

A. There are 96 nine-dimensional points--96 experiments for each isotope. It should also be noted that the data were recorded three times--once at 3 days, once at 10, and once at either 19 or 29, depending on the isotope. Now, we found that, of the nine inputs, six did not change with time, and three did. These three were time, pH, and Eh. To obtain the time-independent solution, which is what we've shown you here, we took the final value of K_d (at the 19th or 29th day), and averaged the three values of pH and Eh. However, we've also created models for time-dependent variables. These models involved three times as much data--3 x 96--for the three variables that changed over time, and show changes in K_d as a function of time, pH, and Eh.

Other Dependencies

Q. You've treated all of the variables as being independent from one another, but aren't there in fact other interdependencies?

A. The interdependencies enter the picture in that certain variables were paired together--for example, on Figure 4.3, Cl and Eh were paired, Ca and pH were paired, etc. Thus, even though the variables were treated as independent, these kinds of interdependencies were elicited after the fact.

Q. If you wrote out the model that you developed for Figure 4.3, wouldn't you have 6^7 unknowns?

A. No, that's what is nice about the network approach: it keeps the arithmetic linear. That is, the number of parameters only grows linearly as a function of layer. In this case, for example, you have 10 x 6 or 60 parameters. If you wrote it out as a fourth-order equation in three variables, you might end up with 90-100 individual coefficients on each of the terms. With this kind of structure, however, not only are the inputs--the x's--not linearly independent, but the coefficients are not linearly independent, either. Thus, coefficients in one block are multiplied by those in another, and so on. Thus, within that family of polynomials represented by this order of function, you can realize a smaller subset--yet one that is still almost infinitely rich.

"THEORETICAL AND EXPERIMENTAL EVALUATION OF WASTE TRANSPORT IN SELECTED ROCKS"

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INTRODUCTION

This report summarizes the progress and results obtained during fiscal year 1977 for LBL Contract No. 4590lAK, "Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks." This project is part of the Waste Isolation Safety Assessment Program (WISAP), which is managed for the DOE Office of Waste Isolation by Battelle Pacific Northwest Laboratories. In particular, this project supports task 4 of WISAP, the collection and generation of transport data. Within task 4 are subtasks, which address the problem of understanding the mechanisms of radionuclide transport and the impact of such mechanisms on radionuclide distribution coefficients. The goal of this project is to establish a basis on which radionuclide distribution coefficients can be reliably predicted for geological environments of the type anticipated for terminal radioactive waste storage facilities.

It is well known that the distribution coefficient (K_d), defined thus:

$$K_d = \frac{\text{mole of radionuclide sorbed/g}}{\text{moles of radionuclide in solution/ml}}$$

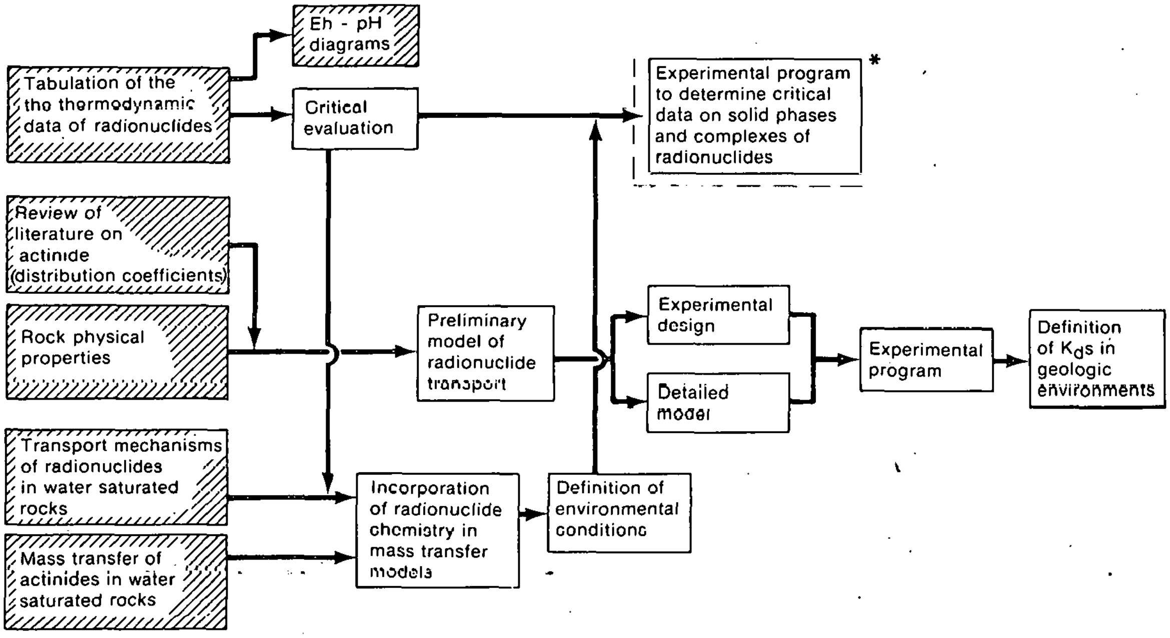
is a semiempirical parameter, subject to variation as a result of the chemical and physical conditions under which it is measured. These conditions vary greatly, depending on whether the environment is adjacent to a terminal storage facility or is similar to the environment normally encountered in a laboratory experiment. Laboratory measurements of K_d vary significantly from experiment to experiment. Therefore, the applicability of currently available measurements to the prediction of radionuclide behavior in rocks is questionable. Table 1-1 gives a tentative list of factors that might influence a typical K_d determination and the errors that might result from omitting these factors when extrapolating data from laboratory to subsurface conditions expected in a host rock adjacent to a terminal storage repository. It is obviously important to identify the critical factors influencing the magnitude of empirical distribution coefficients for given radionuclides, and to establish the variation in those factors under differing host rock conditions.

TABLE 1-1. Factors influencing K_d for a given radionuclide, based on a comparison between conditions in a typical soil column adsorption study and conditions expected in a terminal storage repository.

Parameters	Principal effect	Soil column test	Subsurface terminal storage facility	Potential effect on K_d
1. Solution chemistry				
a. Major components	Ionic strength Activity coefficients Complexing	Very variable. Composition determined by condition the test is designed to simulate.	Determined by host rock chemistry and by other factors including the leaching chemistry of the waste product.	Unpredictable — probably 10^{-3} to 10^{+3}.
b. Minor components	Complexing	Same as above.	Same as above.	Same as above.
c. pH	Complexing Chemical potential	2-11, depending on the nature of the test	5 - 8. Buffering of heterogenous and homogeneous equilibria keep the pH range within narrow limits.	10^{-5} to 10^{+5}
d. Eh	Chemical potential	Variable, usually oxidizing, and dependent upon pH.	Variable, over a narrower range, usually reducing.	Up to 10^{10} or even more
2. Radionuclide concentration and speciation	Supersaturation Polymerization Metastable equilibrium	10^{-6} to 10^{-9} mole/kg. As ionic, polymeric, and particulate forms.	Uncertain, but probably very low, depending on leaching characteristics of waste product form (glass) possibly 10^{-9} to 10^{-12} mole/kg. Principally as ionic species.	Difficult to estimate, but could be very large for amphoteric species near the isoelectric point ($\sim 10^6$).
3. Flow rate	Metastable equilibrium Transport Mechanisms Changes in apparent surface area contacted	$\sim 10^{-3}$ to 10^{-1} cm/sec	10^{-3} to 10^{-7} cm/sec	Sufficient flow rates could lead to different rate controlling transport mechanisms (e.g. ionic or molecular diffusion) also lead to different thermodynamic controls (0 to 10^6)
4. Permeability	Flow rate (see above)	10^{-2} to 10 Darcys	10^{-3} to 10^{-8} Darcys	Same as above.
5. Duration	Radionuclide decay Daughter formation Front reinforcement	$\sim 10^5$ sec	Up to 10^{13} sec	None considered at this time.
6. Surface area	Adsorption	Up to 10^5 cm^2/g; Dispersed clays, humus, fine particulates, loess, etc.	$\sim 10^2$ cm^2/g Fractures, microfractures, intergranular pores	$\sim 10^3$
7. Path length	Dispersion	10^2 cm	2×10^7 cm	No anticipated effect on K_d.
8. Temperature	Complexing Solubility Adsorption	25°C	10 to 100°C	Up to 10^3

The radionuclides chosen for this study include thorium, uranium, plutonium, neptunium, americium, curium, iodine, and technetium. During fiscal year 1977, emphasis has been placed on the actinides plutonium, neptunium, americium, and curium. The host rock types being considered include acid igneous rocks (granite, rhyolite), basic igneous rocks (gabbro, dolerite and basalt), sedimentary rocks (argillites, sandstone, and limestone), and metamorphic rocks (if deemed appropriate). Although the study is generic and does not pertain to a specific site, greater emphasis is being placed on rocks from the Nevada Test Site and the Hanford Reservation near Richland, Washington.

The project includes both theoretical and experimental investigations organized into several interrelated subtasks, as illustrated in Fig. 1-1. These subtasks all support an attempt to define the environmental conditions expected in the water-saturated host rocks of a terminal storage



*Not included in current project.

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Figure 1-1. Logic chart for LBL Waste Isolation Safety Assessment Program-5: Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks. Hatching indicates that task is complete.

facility and to determine the transport mechanisms of radionuclides in these rocks. This information can then be used to relate the thermodynamic and transport properties of radionuclides to the corresponding distribution coefficients, which then can be used with confidence in a computer simulation of radionuclide transport. Without such an effort, there is a danger that experimentally obtained distribution coefficients will be misinterpreted when calculations are made to determine transport through rock to the biosphere.

During fiscal year 1977, the following subtasks were performed.

1. Thermodynamic data were tabulated for those aqueous complexes and solid phases of plutonium, neptunium, americium, and curium likely to form in the natural environment.
2. Eh-pH diagrams were computed and drafted for plutonium, neptunium, americium and curium at 25°C and one atmosphere.
3. The literature on distribution coefficients of plutonium, neptunium, americium, and curium was reviewed.
4. Preliminary considerations were determined for an experimental method of measuring radionuclide transport in water-saturated rocks.
5. The transport mechanisms of radionuclides in water-saturated rocks were reviewed.
6. A computer simulation was attempted of mass transfer involving actinides in water-saturated rocks.

Progress in these tasks is reported in the following sections. Subtasks 1, 2, 3 and 4 are complete. The progress made in subtask 5 is represented by an initial theoretical survey to define the conditions needed to characterize the transport of radionuclides in rocks. This task will be refined and will continue in fiscal year 1978. Subtask 6 has begun but is not complete. Progress in this task will be reported more fully in 1978.

SECTION 2: TABULATION OF THERMODYNAMIC DATA OF AQUEOUS COMPLEXES AND SOLID PHASES OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM LIKELY TO FORM IN THE NATURAL ENVIRONMENT

INTRODUCTION

In subtask 1 of this study, information from the published literature was gathered on free energies of formation, solubility products, dissociation constants, and related topics as they pertain to plutonium, neptunium, americium, and curium. The information is summarized in Tables 2-1 through 2-4, below. No attempt was made to reinterpret or modify the published information. All sources are referenced and cross referenced where information has been published in review articles.

The table for each element is divided into two sections:

1. free energy data, including
    a. aqueous species, and
    b. solid species; and
2. reaction constant data.

The second section of each table gives additional information identifying the reaction studied, the technique used, the nature of the aqueous media, the temperature(s) at which the measurements were made, the value of the constant, the free energy of the reaction, and the source reference(s).

The compilation was made for three reasons.

1. To use "original source" information as the basis for computing refined free energy or reaction constant data that are internally consistent with and conform to standard state conditions. The processed data will be needed for use in computer simulations of ground water chemistry in the presence of the radionuclides under consideration.
2. To identify gaps or uncertainties in our knowledge regarding phase relations or speciation of the actinides, so that new experimental programs might be proposed in order to rectify these deficiencies.
3. To maintain a library of hard-to-find literature for use by other workers in the WISAP program.

See References Cited for a complete list of references used in the tables.

TABLE 2-1. Thermodynamic data for plutonium.

FREE ENERGY DATA	$\Delta G^{o}_{f,298^{\circ}}$ (kcal $mole^{-1}$)	Reference
Aqueous Species		
Pu^{3+}	-138.3 ± 0.8	Fuger and Oetting, 1976
Pu^{4+}	-115.1 ± 0.8	Fuger and Oetting, 1976
PuO_2^{+}	-203.1 ± 1.8	Fuger and Oetting, 1976
PuO_2^{2+}	-180.9 ± 1.7	Fuger and Oetting, 1976
Solid Species		
Pu_2O_3	413.0	Polzer. 1971
PuO_2	-240.4	Polzer, 1971
$Pu(OH)_3$	-280.2	Polzer, 1971
$Pu(OH)_4$	-340.0	Polzer, 1971
$PuO_2(OH)_2$	-281.9	Polzer, 1971

REACTION CONSTANT DATA

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal $mole^{-1}$)	References
Pu III	$Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^{+}$	titra.	0.069<u>M</u> $HClO_4$	298	7.5×10^{-8}	+9.7	Cleveland, 1970; Kraus and Dam, 1949 a,b,c
	$Pu(OH)_3(s) \rightleftharpoons Pu(OH)_3(aq)$	—			2×10^{-20}		Cleveland, 1970; Katz and Seaborg, 1957
	$Pu^{3+} + Cl^{-} \rightleftharpoons PuCl^{2+}$	ion ex.	1.0 <u>M</u> HCl	--	14.7^{a}		Cleveland, 1970; Ward and Welch, 1956
		reduc.	1.0 <u>M</u> HCl	298	0.78	+0.15	Degischer and Choppin, 1975; Connick and McVey, 1953
		cal.	0.1 <u>M</u> HCl		3.72		Degischer and Choppin, 1975; Martin and White, 1958
		spec.	(conc. LiCl)	298	3.71×10^{-3}	+3.3	Degischer and Choppin, 1975; Shiloh and Marcus, 1966
	$Pu^{3+} + SO_4^{2-} \rightleftharpoons PuSO_4^{+}$	cat. ex.	$[H^{+}] = 1.0$ <u>M</u>	301	18.13 ± 0.44	-1.73	Cleveland, 1970; Nair et al., 1967
		kin		298	10.0 est.		Degischer and Choppin, 1975; Newton and Baker, 1956
	$Pu^{3+} + HSO_4^{-} \rightleftharpoons PuHSO_4^{2+}$	ion ex.	~1 <u>M</u> $NaClO_4$	301	9.94 ± 0.24	-1.37	Cleveland, 1970; Nair, 1968
Pu IV	$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^{+}$	poten.	I = 2<u>M</u> $HClO_4 - LiClO_4$	298	0.054 ± 0.001	+1.73	Cleveland, 1970; Rabideau, 1956; Perez-Bustamente, 1965
	$Pu(OH)_4(s) \rightleftharpoons Pu(OH)_4(aq)$				7×10^{-56}		Cleveland, 1970; Katz and Seaborg, 1957; Kraus, 1945; Latimer, 1952; Evans, 1949; Kasha, 1949; Kraus, 1949; Peppard et al., 1962

Table 2-1 (continued)

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal $mole^{-1}$)	References
Pu IV	$Pu^{4+} + F^- \rightleftharpoons PuF^{3+}$	spec.	1<u>M</u> HNO_3	298	8.7×10^{7} (a)		Cleveland, 1970; Patil and Ramakrishna, 1976
		spec.	1<u>M</u> HNO_3	298	5.9×10^{6}	-1.1	Degischer and Choppin, 1975; McLane, 1949
	$Pu^{4+} + Cl^- \rightleftharpoons PuCl^{3+}$	cat. ex.	4<u>M</u> $HClO_4$	293	1.4 ±0.2	-0.2	Cleveland, 1970; Grenthe and Noren, 1960
		spec.	2<u>M</u> $HClO_4$	298	0.38	+0.57	Degischer and Choppin, 1975; Hindman, 1949
		reduc.	1<u>M</u> $HClO_4$	298	0.57	+0.33	Degischer and Choppin, 1975; Rabideau and Cowan, 1955
		reduc.	μ = 1.0	298	1.38	-0.19	Degischer and Choppin, 1975; Rabideau, 1958
		reduc.	1<u>M</u> HCl	298	0.8	+0.14	Degischer and Choppin, 1975; Kabanova and Palei, 1960
	$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{2+} + H^+$	cat. ex.	0.5<u>M</u> acid	298	9.45	-1.3	Cleveland, 1970; Marov and Chmutova, 1961
	$Pu^{4+} + SO_4^{2-} \rightleftharpoons PuSO_4^{2+}$	reduc.	1.0<u>M</u> $HClO_4$	298	4.58×10^{3}	-5.0	Degischer and Choppin, 1975; Rabideau, 1955; Lemons, 1951
	$Pu^{4+} + 2HSO_4^- \rightleftharpoons Pu(SO_4)_2 + 2H^+$	cat. ex.	0.5 acid	298	20.0	-1.8	Cleveland, 1970; Marov and Chmutova, 1961
	$Pu^{4+} + 3HSO_4^- \rightleftharpoons Pu(SO_4)_3^{2-} + 3H^+$	cat. ex.	0.5 acid	298	125	-2.9	Cleveland, 1970; Marov and Chmutova, 1961
	$Pu^{4+} + HPO_4^{2-} \rightleftharpoons PuHPO_4^{2+}$	solub.	2.0<u>M</u> HNO_3 0.012 - 2.0<u>M</u>	298	8.3×10^{12}	-17.6	Cleveland, 1970; Denotkina, et al., 1960
	$PuHPO_4^{2+} + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_2$	solub.	H_3PO_4	298	6.7×10^{10}	-14.8	Cleveland, 1970; Denotkina, et al., 1960
	$Pu(HPO_4)_2 + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_3^{2-}$	solub.	H_3PO_4	298	4.8×10^{9}	-13.2	Cleveland, 1970; Denotkina, et al., 1960
	$Pu(HPO_4)_3^{2-} + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_4^{4-}$	solub.	H_3PO_4	298	6.3×10^{9}	-13.4	Cleveland, 1970; Denotkina, et al., 1960
	$Pu(HPO_4)_4^{4-} + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_5^{6=}$	solub.	H_3PO_4	298	6.3×10^{8}	-12.0	Cleveland, 1970; Denotkina, et al., 1960

Table 2-1 (continued)

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal $mole^{-1}$)	References
Pu V	$PuO_2^+ + Cl^- \rightleftharpoons PuO_2Cl$	poten.	--	--	0.67	--	Cleveland, 1970; Rabideau, 1958
Pu VI	$PuO_2^{2+} + H_2O \rightleftharpoons PuO_2OH^+ + H^+$	titra.	0.000186$\underline{M}$ HNO_3	--	4.7×10^{-4}	--	Cleveland, 1970; Krevinskaya, et al., 1960
	$PuO_2OH^+ + H_2O \rightleftharpoons PuO_2(OH)_2 + H^+$	titra.	0.000186$\underline{M}$ HNO_3	--	$9\pm1\times10^{-5}$	--	Cleveland, 1970; Krevinskaya, et al., 1960
	$PuO_2(OH)_2 + H_2O \rightleftharpoons PuO_2(OH)_3^- + H^+$	--	--	--	$2\ 10^{-10}$	--	Cleveland, 1970; Kraus and Dam, 1949 [a,b,c]
	$PuO_2^{2+} + Cl^- \rightleftharpoons PuO_2Cl^+$	spec.	I = 1$\underline{M}$	296	0.73±.07	+0.19	Cleveland. 1970: Rabideau, 1956
		spec.	2$\underline{M}$ $HClO_4$	293	0.56	+0.34	Degischer and Choppin, 1975; Rabideau and Lemons, 1951
	$PuO_2^{2+} + HF \rightleftharpoons PuO_2F^+ + H^+$	cat. ex.	I = 2.0$\underline{M}$ $[H^+]$=2.0$\underline{M}$	298	12.	-1.5	Patil and Ramakrishna, 1976
	$PuO_2^{2+} + H_2PO_4^- \rightleftharpoons PuO_2H_2PO_4^+$	electroph.	0.206-5.88$\underline{M}$ H_3PO_4	298	8.5×10^3	-5.36	Cleveland, 1970
	$PuO_2^{2+} + 2OH^- + CO_3^{2-} \rightleftharpoons PuO_2CO_3(OH)_2^{2-}$	solub.	0.17-0.44$\underline{M}$ NH_4CO_3	293	2.3×10^{22}	-30.0	Cleveland, 1970; Gel'man, et al., 1962
	$PuO_2OH^+ + CO_3^{2-} \rightleftharpoons PuO_2CO_3OH^-$	solub.	0.17-0.44$\underline{M}$ NH_4CO_3	293	4.5×10^{22}	-30.4	Cleveland. 1970: Gel'man, et al., 1962
	$Pu_2^{2+} + 2CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{2-}$	solub.	0.17-0.44$\underline{M}$ NH_4CO_3	293	6.7×10^{13}	-18.5	Cleveland, 1970; Gel'man, et al., 1962

[a] corrected to the standard state, I = 0.

TABLE 2-2. Thermodynamic data for neptunium.

FREE ENERGY DATA	$\Delta G^o_{f\ 298^o}$ (kcal $mole^{-1}$)	Reference
Aqueous Species		
Np^{3+}	- 123.6 ± 0.8	Fuger and Oetting, 1976
Np^{4+}	- 120.2 ± 1.8	Fuger and Oetting, 1976
NpO_2^+	- 218.7 ± 1.3	Fuger and Oetting, 1976
NpO_2^{2+}	- 190.2 ± 1.3	Fuger and Oetting, 1976
Solid Species		
NpO_2	- 232.8	Huber and Holley, 1968

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal $mole^{-1}$)	References
Np III	$Np^{3+} + H_2O \rightleftharpoons NpOH^{2+} + H^+$	titra.	$0.1\ \underline{M}\ NaClO_4$	298	3.7×10^{-8} $\pm.09$	+10.1	Mefodeva, et al., 1974
	$Np^{3+} + Cl^- \rightleftharpoons NpCl^{2+}$	spec.	conc. LiCl	298	3.8×10^{-3}	+3.3	Burney and Harbour, 1974; Shiloh and Marcus, 1966
Np IV	$Np^{4+} + H_2O \rightleftharpoons NpOH^{3+} + H^+$	--	--	--	9×10^{-3}	--	Burney and Harbour, 1974; Mikailov, 1973
	$Np(OH)_4(s) \rightleftharpoons Np(OH)_4(aq)$	--	--	--	6×10^{-56}	--	Burney and Harbour, 1974; Moskvin, 1971b
	$Np^{4+} + HF \rightleftharpoons NpF^{3+} + H^+$	ion ex.	$4.0\underline{M}\ HClO_4$	293	1.6×10^4	-5.6	Burney and Harbour, 1974; Ahrland and Brandt, 1966
		extrac.	$1.0\underline{M}\ HClO_4$	298	4.6×10^4	-6.4	Choppin and Unrein, 1976
		ion ex.	$1.0\underline{M}\ HClO_4$	298	3.6×10^4	-6.2	Degischer and Choppin, 1975; Krylov, et al., 1968a
		ion ex.	$1\underline{M}\ HNO_3$	293	1.7×10^4	-5.7	Degischer and Choppin, 1975; Krylov, et al., 1968a
	$Np^{4+} + Cl^- \rightleftharpoons NpCl^{3+}$	distri.	$1.0\underline{M}\ HClO_4$	293	0.91	+0.05	Burney and Harbour, 1974; Shilin and Nazarov, 1965
		emf	$1.0\underline{M}\ HClO_4$	298	0.49	+0.42	Burney and Harbour, 1974; Stromatt and Peekema, 1958
		distri.	$2.0\underline{M}\ HClO_4$	293	1.02	-0.12	Burney and Harbour, 1974; Shilin and Nazarov, 1966
		distri.	$4.0\underline{M}\ HClO_4$	298	0.77±0.06	+0.15	Burney and Harbour, 1974; Danesi, et al., 1971
	$Np^{4+}\ SO_4^{2-} \rightleftharpoons NpSO_4^{2+}$	distri.	$2.0\underline{M}\ HClO_4$	298	2.7×10^2	-3.3	Burney and Harbour, 1974; Sullivan and Hindman, 1954
		ion ex.	$4.0\underline{M}\ HClO_4$	293	5.0×10^2	-3.6	Degischer and Choppin, 1975; Ahrland and Brandt, 1966

TABLE 2-2 (continued)

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔG$_R$ (kcal mole^{-1})	References
Np V	$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH(aq) + H^+$	poten.	$HClO_4$	--	1.25×10^{-9}	--	Burney and Harbour, 1974; Katz and Seaborg, 1957
	$NpO_2OH_{(s)} \rightleftharpoons NpO_2OH(aq)$	poten.	HNO_3	--	1.85×10^{-10}	--	Sevostyanova and Khalturin, 1973
	$NpO_2^+ + Cl^- \rightleftharpoons NpO_2Cl$	ion ex.	2.0M $HClO_4$	298	0.51	+0.41	Burney and Harbour, 1974; Gainar and Sykes, 1964
	$NpO_2^+ + HPO_4^{2-} \rightleftharpoons NpO_2HPO_4^-$	ion ex.	0.2M NH_4ClO_4 $HClO_4$	293	7.1×10^2	-3.8	Degischer and Choppin, 1975; Zvagintsev and Sudarikov, 1958
	$NpO_2^+ + H_2PO_4^- \rightleftharpoons NpO_2H_2PO_4$	ion ex.	0.2M NH_4ClO_4 $HClO_4$	293	6.5	-1.1	Degischer and Choppin, 1975; Zvagintsev and Sudarikov, 1958
	$NpO_2^+ + HCO_3^- \rightleftharpoons NpO_2HCO_3$	ion ex.	$\mu=0$	--	2.7×10^2	--	Burney and Harbour, 1974; Moskvin and Mefodeva, 1965
Np VI	$NpO_2^{2+} + Cl^- \rightleftharpoons NpO_2Cl^+$	distri.	4.0M $HClO_4$	298	0.69± 0.05	+0.22	Burney and Harbour, 1974; Danesi, et al., 1971
		kin.	3.0M $HClO_4$	273	1.26	-0.13	Degischer and Choppin, 1975; Cohen, et al., 1955
	$NpO_2^{2+} + HF \rightleftharpoons NpO_2F^+ + H^+$	extrac.	1.0M $HClO_4$	294	8.6±2.1	-1.3	Burney and Harbour, 1974; Ahrland and Brandt, 1968a
		ion ex.	1.04M $HClO_4$	298	157±9	-3.0	Degischer and Choppin, 1975; Krylov, et al., 1968b
	$NpO_2^{2+} + SO_4^{2-} \rightleftharpoons NpO_2SO_4$	extrac.	1.0M $HClO_4$	293	79	-2.6	Burney and Harbour, 1975; Ahrland and Brandt, 1968b
		reduc.	1.0M ClO_4^-	298	13	-1.5	Degischer and Choppin, 1975; Stromatt and Peekema, 1958
		distr.	2.0M $NaClO_4$	298	43.7	-2.2	Degischer and Choppin, 1975; Sykes and Taylor, 1962
	$NpO_2^{2+} + H_2O \rightleftharpoons NpO_2OH^+ + H^+$	solub.	NH_4ClO_4	293	4.3×10^{-4}		Moskvin, 1971b
	$NpO_2OH^+ + H_2O \rightleftharpoons NpO_2(OH)_2 + H^+$	solub.	NH_4ClO_4	293	3.6×10^{-6}		Moskvin, 1971b
	$NpO_2(OH)_2 + H_2O \rightleftharpoons NpO_2(OH)_3^- + H^+$	solub.	NH_4ClO_4	293	2.0×10^{-10}		Moskvin, 1971b

TABLE 2-3. Thermodynamic data for americium.

FREE ENERGY DATA	$\Delta G^{o}_{f,298^{\circ}}$ (kcal mole^{-1})	Reference
Aqueous Species		
Am^{3+}	-143.2 ± 0.3	Fuger and Oetting, 1976
Am^{4+}	-89.2 ± 2.4	Fuger and Oetting, 1976
AmO_2^{+}	-177.1 ± 1.3	Fuger and Oetting, 1976
AmO_2^{2+}	-140.4 ± 0.8	Fuger and Oetting, 1976

REACTION CONSTANT DATA

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole^{-1})	References
Am III	$Am^{3+} + H_2O \rightleftharpoons AmOH^{2+} + H^{+}$		$I = 0.1$ ClO_4^{-}	296	1.2×10^{-6}	+8.0	
	$Am(OH)_3(s) \rightleftharpoons Am(OH)_3(aq)$	--	--	--	3.9×10^{6}	--	Schulz, 1976; Weaver and Shoun, 1971
	$Am^{3+} + F^{-} \rightleftharpoons AmF^{2+}$	solv.ext.	$I = 1.0\underline{M}$ $NaClO_4$	298	3.09×10^{3}	-4.76	Schulz, 1976; Choppin and Unrein, 1976
	$Am^{3+} + Cl^{-} \rightleftharpoons AmCl^{2+}$	spec.	$13.7\underline{M}$ LiCl	298	6.2×10^{-3}	+3.0	Schulz, 1976; Marcus and Shiloh, 1969
		solv.ext.	$I = 1\underline{M}$ $NaClO_4 - NaCl$	303	1.04	-0.024	Schulz, 1976; Khopkar and Narayanankutty, 1971
		solv.ext.	$I = 1\underline{M}$ $NH_4ClO_4 - NH_4SCN$	303	1.33	-0.17	Schulz, 1976; Khopkar and Narayanankutty, 1971
		ion ex.	$I = 1\underline{M}$ $NaClO_4 - NaCl$	297	0.90	+0.06	Schulz, 1976; Bansal, et al., 1964
		solv.ext.	$1\underline{M}$ $HClO_4 - HCl$	295	0.90	+0.062	Schulz, 1976; Peppard et al., 1961
		solv.ext.	$4\underline{M}$ $NaClO_4$	298	1.41	-0.20	Schulz, 1976; Sekine, 1964; Sekine, 1965
		ion ex.	$0.5\underline{M}$ $HClO_4$		0.58		Schulz, 1976; Ward and Welch, 1956
		ion ex.	$I = 4.0\underline{M}$ $HClO_4 - HCl$	293	0.69	+0.21	Schulz, 1976; Grenthe, 1962
	$Am^{3+} + SO_4^{2-} \rightleftharpoons AmSO_4^{+}$	ion ex.	$I = 0.5-0.6\underline{M}$	298	72	-2.5	Schulz, 1976; Aziz, et al., 1968
		ion ex.	$0.75\underline{M}$ NH_4Cl	293-298	60.0	--	Schulz, 1976; Lebedev, et al., 1960
		ion ex.	$1 - 1.3\underline{M} = I$ $NaClO_4$ pH=3	299	30.9	-2.0	Schulz, 1976; Bansal, et al., 1964

TABLE 2-3 (continued)

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole^{-1})	References
Am III	$Am^{3+} + SO_4^{2-} \rightleftharpoons AmSO_4^{+}$ (continued)	ion ex.	1.5$\underline{M}$ NH_4ClO_4	293-298	57.6	--	Schulz, 1976; Lebedev, et al., 1960
		solv.ext.	1.0$\underline{M}$ $NaClO_4$	298	37.2	-2.1	Schulz, 1976; Sekine, 1964; Sekine, 1965
		solv.ext.	2.0$\underline{M}$ $NaClO_4$	298	26.9	-1.9	Schulz, 1976; DeCarvalho and Choppin, 1967
		ion ex.	0.5$\underline{M}$ $NaClO_4$	298	72.5	-2.5	Schulz, 1976; Aziz et al., 1968
		ion ex.	I = 1$\underline{M}$ $HClO_4$ NH_4ClO_4	300	16.6	-1.7	Schulz, 1976; Nair, 1960
	$Am^{3+} + H_2PO_4^{-} \rightleftharpoons AmH_2PO_4^{2+}$	ion ex.	I = 1$\underline{M}$ NH_4Cl	293	30.2	-2.0	Schulz, 1976; Moskvin, 1969

TABLE 2-4. Thermodynamic data for curium.

FREE ENERGY DATA	$\Delta G^{o}_{f,298°}$ (kcal mole^{-1})	Reference
Aqueous Species		
Cm^{3+}	-142.4 ± 1.5	Fuger and Oetting, 1976
Cm^{4+}	~ -214	Calculated from Nugent et al., 1971; Myasoedov, et al., 1974

REACTION CONSTANT DATA

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole^{-1})	References
Cm III	$Cm^{3+} + H_2O \rightleftharpoons CmOH^{2+} + H^{+}$	extrac.	I = 0.1$\underline{M}$ $HClO_4 - LiClO_4$	300	1.20×10^{-6}	-8.0	Desire, et al., 1969
	$Cm^{3+} + F^{-} \rightleftharpoons CmF^{2+}$	extrac.	1.0$\underline{M}$ $NaClO_4$	298	4.10×10^{2}	-3.6	Choppin and Unrein, 1976
	$Cm^{3+} + Cl^{-} \rightleftharpoons CmCl^{2+}$	ion ex.	0.5$\underline{M}$ HCl	--	1.51	--	Ward and Welch, 1956
	$Cm^{3+} + SO_4^{2-} \rightleftharpoons CmSO_4^{+}$	ion ex.	0.15$\underline{M}$ NH_4Cl NH_4ClO_4	293-298	56	--	Ward and Welch, 1956; Lebedev, et al., 1960
		distri.	2.0$\underline{M}$ $NaClO_4$ Na_2SO_4	298	22	-1.8	DeCarvalho and Choppin, 1967
		ion ex.	0.5-0.6$\underline{M}$ $NaClO_4$	298	71.9	-2.5	Aziz, et al., 1968
		distri.	0.5$\underline{M}$ $NaClO_4$	297-298	73.3	-2.5	Aziz, et al., 1968
		distri.	0.5$\underline{M}$ $NaClO_4$	298	68	-2.5	Aziz, et al., 1968

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SECTION 3: Eh-pH CALCULATIONS AND ILLUSTRATIONS FOR PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM AT 25°C AND ONE ATMOSPHERE

INTRODUCTION

Eh-pH diagrams are useful in identifying the stability fields of solid phases and aqueous species for a given element over a range of oxidation states, pH levels, and other predetermined conditions. The purpose of this chapter is to compute simple Eh-pH diagrams of the actinides plutonium, neptunium, americium, and curium and to predict their oxidation states and the stability of their hydroxyl species under conditions expected in the natural environment. Eh-pH diagrams are based on the assumption that Eh and pH are independent variables. The stability fields and phase or species boundaries delineated on the diagrams are defined by equations in which the coefficients are determined by the reaction specified and by the free energies of participating species. The figures illustrating this chapter are all drawn for 25°C and one atmosphere, and use free energy data compiled in Section 2 of this report.

The equations used to prepare the Eh-pH diagrams follow the procedure given in Krauskopf (1967). First a chemical equation for a reduction reaction is written. For example:

$$PuO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons Pu^{4+} + 2H_2O \quad .$$

From this reaction, the number of electrons, hydrogen ions, and water molecules which participate in the reaction are noted. Next, the standard free energy of the reaction, ΔG_R^o is determined. In this case:

$$\Delta G_R^o = \Sigma\Delta G^o_{products} - \Delta G^o_{reactants}$$

$$\Delta G_R^o = (-115.1) + 2\ (-56.7) - (-180.9) - (-0)$$

$$= -47.6 \text{ kcal mole}^{-1} \quad .$$

Using the relationship between free energy and standard potential,

$$\Delta G_R^o = -nFE_o$$

the standard potential of the reaction, E_o, is obtained. Here, n is the number of electrons participating in the reaction and F is Faraday's constant. In this example

$$E_o - 1.03 \text{ V}$$

The standard potentials can be related to oxidation-reduction potentials and activity of solution species through the Nernst Equation which for this reaction is:

$$Eh = E_o - \frac{2.303\ RT}{nF} \log \frac{[Pu^{4+}]}{[PuO_2^{2+}][H^+]^4}$$

where n = 2 and T = 298K. This equation is used to determine the boundary between the domains of two species where $[Pu^{4+}] = [PuO_2^{2+}]$. Hence the equation reduces to:

$$Eh = E_o - 0.0295 \log \frac{1}{[H^+]^4}$$

or

$$Eh = 1.03 - 0.118 \text{ pH}.$$

Certain reactions have no pH dependence, such as:

$$PuO_2^{2+} + e^- \rightleftharpoons PuO_2^+$$

so that only the standard potential need be found. Hydrolysis reactions, which are only pH and not Eh dependent, such as

$$Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^+$$

can be located using the hydrolysis constant alone.

Boundaries between aqueous species and solid phases can be determined in an analogous manner to those between aqueous species. For example,

$$PuO_2(s) + 4H^+ + e^- \rightleftharpoons Pu^{3+} + 2H_2O$$

In this equation, the correlation of the aqueous species is assigned an arbitrary value, such as 10^{-6}, mole ℓ^{-1}. The activity of the pure solid is unity, by definition, and water is also assumed to have unit activity. The corresponding equation relating Eh and pH is

$$Eh = 0.49 - 0.236 \text{ pH} - 0.059 \log [Pu^{3+}]$$

where $[Pu^{3+}]$ is arbitrarily set at some activity such as 10^{-6}, 10^{-12}, or 10^{-18}.

The actual equations used for each of the diagrams are listed under the respective headings for the actinides being considered.

PLUTONIUM

The Eh-pH diagram for plutonium given in Figure 3-1 shows the stability fields of the aqueous species Pu^{3+}(III), $Pu(OH)^{2+}$(III), PuO_2^+(V), PuO_2^{2+}(VI), $PuO_2(OH)^+$(VI), $PuO_2(OH)_3^-$(VI) and the solid phase PuO_2(IV). Equations defining species boundaries are derived as follows.

Aqueous Species Boundaries

$$PuO_2^+ + 4H^+ + 2e^- \rightleftharpoons Pu^{3+} + 2H_2O$$

$$\Delta G_R^o = -48.6 \text{ kcal mole}^{-1}$$

$$E_o = \frac{\Delta G_R^o}{nF} = 1.05$$

$$Eh = 1.05 - \frac{0.059}{2} \log \frac{1}{[H^+]^4} \quad \text{when } [Pu^{3+}] = [PuO_2^+]$$

$$Eh = 1.05 - 0.118 \text{ pH}$$

$$Pu^{4+} + e^- \rightleftharpoons Pu^{3+}$$

$$\Delta G_R^o = -23.2 \text{ kcal mole}^{-1}$$

$$E_o = 1.00$$

$$Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^+$$

$$\Delta G_R^o = 7.6 \text{ kcal mole}^{-1}$$

$$2.303 \frac{-\Delta G_R^o}{RT} = \log K_H = -5.6$$

$PuO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons Pu^{4+} + 2H_2O$

$\Delta G_R^o = -47.6$ kcal mole^{-1}

$E_o = 1.03$

$Eh = 1.03 - \frac{0.059}{2} \log \frac{1}{[H^{+\,4}]}$ when $[Pu^{4+}] = [PuO_2^{2+}]$

$Eh = 1.03 - 0.118$ pH

$PuO_2^{2+} + e^- \rightleftharpoons PuO_2^+$

$\Delta G_R^o = -22.2$ kcal mole^{-1}

$E_o = 0.96$

$PuO_2^+ + 3H^+ + 2e^- \rightleftharpoons PuOH^{2+} + H_2O$

$\Delta G_R^o = -41.0$ kcal mole^{-1}

$E_o = 0.89$

$Eh = 0.89 - \frac{0.059}{2} \log \frac{1}{[H^+]^3}$ when $[PuOH^{2+}] = [PuO_2^+]$

$Eh = 0.89 - 0.089$ pH

$PuO_2^{2+} + H_2O \rightleftharpoons PuO_2OH^+ + H^+$

$\Delta G_R^o = 4.6$ kcal mole^{-1}

$2.303 \frac{-\Delta G_R^o}{RT} = \log K_H = -3.4$

$PuO_2OH^+ + H^+ + e^- \rightleftharpoons PuO_2^+ + H_2O$

$\Delta G_R^o = 26.8$ kcal mole^{-1}

$E_o = -1.16$

$Eh = -1.16 - 0.059$ pH when $[PuO_2^+] = [PuO_2OH^+]$

$PuO_2OH^+ + 2H_2O \rightleftharpoons PuO_2(OH)_3^- + 2H^+$

$\Delta G_R^o = 21.0$ kcal mole^{-1}

$2.303 \frac{-\Delta G_R^o}{RT} = \log K_H = -7.70$

$e^- + PuO_2(OH)_3^- + 3H^+ \rightleftharpoons PuO_2^+ + 3H_2O$

$\Delta G_R^o = 47.8$ kcal mole^{-1}

$E_o = -2.07$

$Eh = -2.07 - 0.177$ pH

Solid-Aqueous Species Boundaries

$PuO_2(s) + 4H^+ + e^- \rightleftharpoons Pu^{3+} + 2H_2O$

$\Delta G_R^o = -11.3$ kcal

$E_o = 0.49$

$Eh = +0.49 - 0.236 \text{ pH} - 0.059 \log [Pu^{3+}]$

$[Pu^{3+}]$ is set at 10^{-6}, 10^{-12}, and 10^{-18} mol ℓ^{-1}, and the equation is then plotted on the Eh-pH plane.

$PuO_2(s) + 3H^+ + e^- \rightleftharpoons PuOH^{2+} + H_2O$

$\Delta G_R^o = -3.7$ kcal mole^{-1}

$E_o = 0.16$

$Eh = +0.16 - 0.177 \text{ pH} - 0.059 \log (PuOH^{2+})$

$$PuO_2^+ + e^- \rightleftharpoons PuO_2(s)$$

$$Eh = \frac{RT}{nF}\left(\frac{\Delta G_R^o}{RT} - \ln\left[\frac{1}{PuO_2^+}\right]\right)$$

$$PuO_2^{2+} + 2e^- \rightleftharpoons PuO_2(s)$$

$$Eh = \frac{RT}{nF}\left(\frac{\Delta G_R^o}{RT} - \ln\left[\frac{1}{PuO_2^+}\right]\right)$$

$$PuO_2OH^+ + H^+ + 2e^- \rightleftharpoons PuO_2(s) + H_2O$$

$$\Delta G_R^o = -64.1 \text{ kcal mole}^{-1}$$

$$E_o = 1.39$$

$$Eh = 1.39 - 0.059\ pH - 0.059 \log\left[(PuO_2OH^+)\right]$$

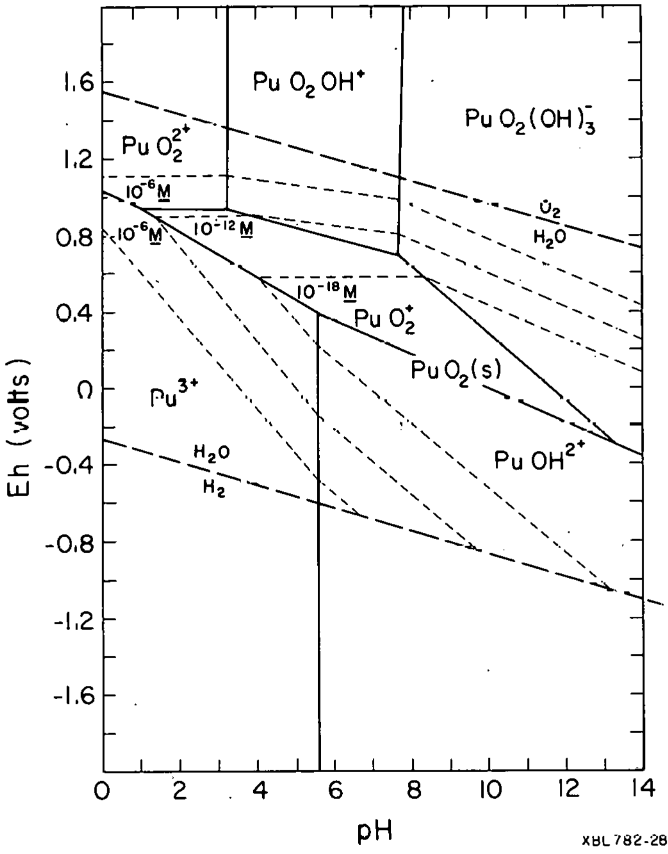

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Figure 3-1. Eh-pH diagram for plutonium at 25°C and one atmosphere.

$PuO_2(OH)_3^- + 3H^+ + 2e^- \rightleftharpoons PuO_2(s) + 3H_2O$

$\Delta G_R^o = -85.1$ kcal mole^{-1}

$E_o = 1.85$

$Eh = 1.85 - 0.177\ pH - 0.059 \log [PuO_2(OH)_3^-]$

The thermodynamic data for the plutonium Eh-pH diagram were taken from Fuger and Oetting, 1976 and Polzer, 1975. The diagram (Figure 3-1) is very similar to that produced by Polzer (1975). Discrepancies are negligible and are due to small differences in thermodynamic values used by Polzer for the reaction equations.

NEPTUNIUM

The Eh-pH diagram for neptunium given in Figure 3-2 is plotted to show the stability fields of the aqueous species Np^{3+}(III), $NpOH^{2+}$(III), Np^{4+}(IV), NpO_2^+(V), NpO_2OH(V), NpO_2^{2+}(VI), NpO_2OH^+(VI), $NpO_2(OH)_3^-$(VI), and the solid phase NpO_2(IV). Equations defining species boundaries are derived as follows.

Aqueous Species Boundaries

$Np^{4+} + e^- \rightleftharpoons Np^{3+}$

$\Delta G_R^o = -3.4$ kcal mole^{-1}

$E_o = 0.15$

$NpO_2^+ + 4H^+ + 2e^- \rightleftharpoons Np^{3+} + 2H_2O$

$\Delta G_R^o = -18.3$ kcal mole^{-1}

$E_o = 0.40$

$Eh = 0.40 - 0.118\ pH$ when $\left[Np^{3+}\right] = \left[NpO_2^+\right]$

$Np^{3+} + H_2O \rightleftharpoons NpOH^{2+} + H^+$

$\log H_H = -7.4$ (Mefodeva, et al., 1974)

$NpO_2^+ + 4H^+ + e^- \rightleftharpoons Np^{4+} + 2H_2O$

$\Delta G_R^o = -14.9$ kcal mole^{-1}

$E_o = 0.65$

$Eh = 0.65 - 0.236$ pH when $[Np^{4+}] = [NpO_2^+]$

$NpO_2^{2+} + e^- \rightleftharpoons NpO_2^+$

$\Delta G_R^o = -28.5$ kcal mole^{-1}

$E_o = 1.23$

$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH + H^+$

$\log K_H = -8.9$ (Sevostyanova and Khalturin, 1973)

$NpO_2OH^! + 2H_2O \rightleftharpoons NpO_2(OH)_3^- + 2H^+$

$$K_{2-1} = \frac{[NpO_2(OH)_2][H^+]}{[NpO_2OH^+]} = 3.6 \times 10^{-6}$$ (from Moskvin, 1971)

$$K_{3-2} = \frac{[NpO_2(OH)_3^-][H^+]}{[NpO_2(OH)_2]} = 2.0 \times 10^{-10}$$

$$K_{3-1} = \frac{[NpO_2(OH)_3^-][H^+]^2}{[NpO_2OH^+]} = 7.2 \times 10^{-16}$$

$[H^+] = 2.68 \times 10^{-8}$

$pH = 7.6$

Solid Aqueous Species Boundaries

$$Np^{4+} + 2H_2O \rightleftharpoons NpO_2(s) + 4H^+$$

$$\Delta G^o_R = 0.80 \text{ kcal mole}^{-1}$$

$$2.303 \frac{-\Delta G^o_R}{RT} = \log K_H = -0.15 \quad \text{when} \quad [Np^{4+}] = 1M$$

$$\Delta G^o_R = -4.2 \text{ kcal mole}^{-1}$$

$$E_o = 0.18$$

$$Eh = 0.18 - 0.059 \text{ pH}$$

$$NpO_2^+ + e^- \rightleftharpoons NpO_2(s)$$

$$\Delta G^o_R = -14.10 \text{ kcal mole}^{-1}$$

$$Eh = \frac{RT}{nF}\left(\frac{-\Delta G^o_R}{RT} - \ln\left[\frac{1}{NpO_2^+}\right]\right)$$

Solubility lines for $NpO_2(s)$ - NpO_2OH were drawn considering the hydrolysis reaction

$$NpO_2^+(s) + H_2O \rightleftharpoons NpO_2OH + H^+ + e$$

which means that the lines must have a slope of -0.059 and consistency requirements that they meet solubility lines for NpO_2^+.

The standard free energies of formation of NpO_2OH^+ and $NpO_2(OH)_3^-$ have not been calculated. However, their domain boundaries may be determined from their hydrolysis constants and the hydrogen ion dependence of their reduction reactions to NpO_2^+ and NpO_2OH. For example, the domain boundary between NpO_2OH^+ and NpO_2^+ has a slope of -0.059 and must intersect with the domain boundaries between NpO_2^{2+} and NpO_2^+

and between NpO_2^{2+} and NpO_2OH^+. Similar consideration of consistency requirements produced domain boundaries for

$NpO_2(OH)_3^- - NpO_2^+$

$NpO_2(OH)_3^- - NpO_2OH$

$NpO_2^+ - NpOH^{2+}$

$NpO_2OH - NpOH^{2+}$

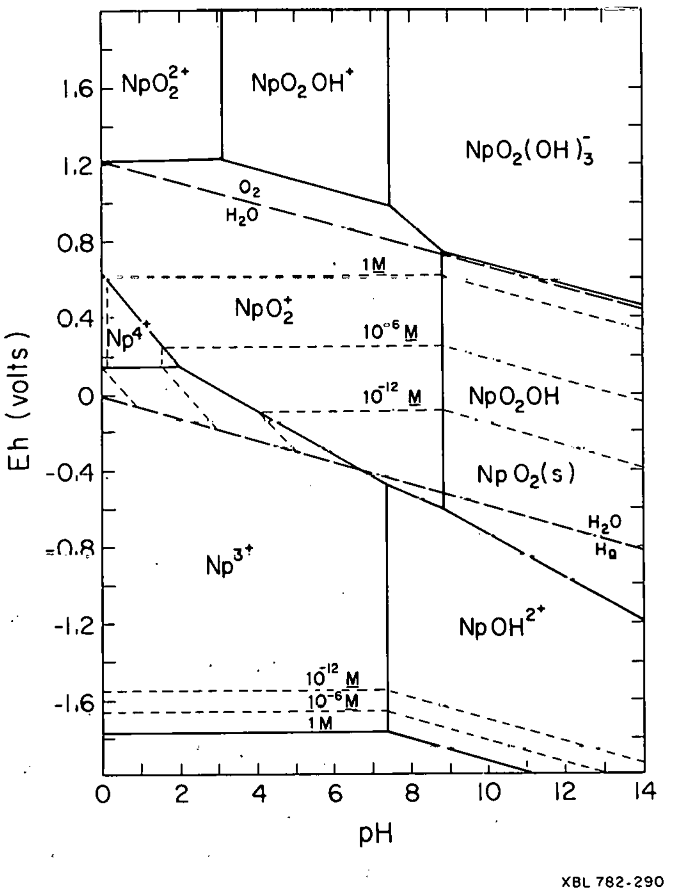

Figure 3-2. Eh-pH diagram for neptunium at 25°C and one atmosphere.

AMERICIUM

Very little data is available on aqueous species of americium, and no information on oxide phases has been found. The Eh-pH diagram for americium is illustrated in Figure 3-3. Equations used in its construction are given below.

$AmO_2^+ + 4H^+ + 2e^- \rightleftharpoons Am^{3+} + 2H_2O$

$\Delta G_R^o = -79.5$ kcal mole^{-1}

$E_o = 1.72$

Eh = 1.72 - 0.118 pH when $[Am^{3+}] = [AmO_2^+]$

$AmO_2^{2+} + e^- \rightleftharpoons AmO_2^+$

$\Delta G_R^o = -37.0$ kcal mole^{-1}

$E_o = 1.60$

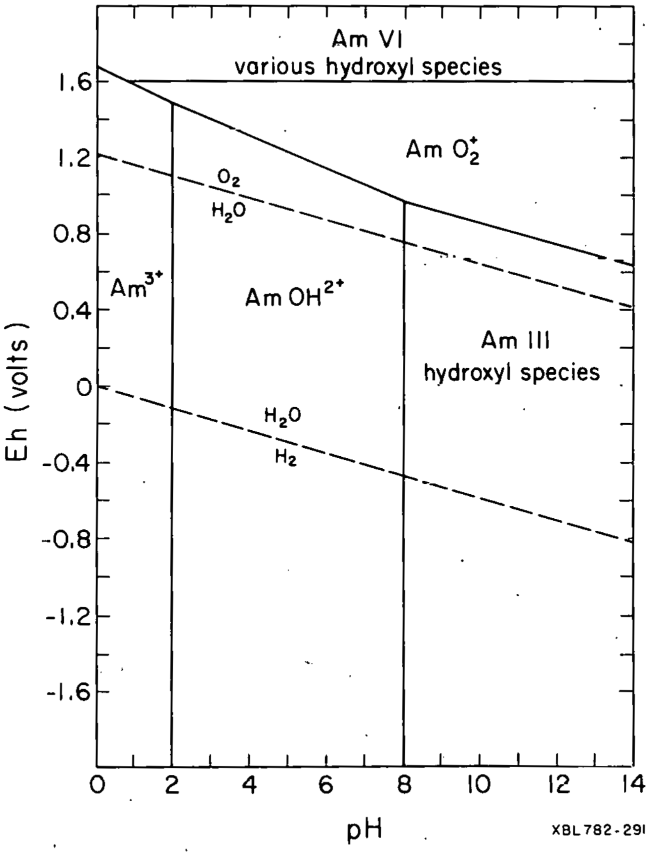

Figure 3-3. Eh-pH diagram for americium at 25°C and one atmosphere.

Data on hydrolysis of americium III is only qualitative. From work done by Korotkin (1975), the first pK_H can be expected to fall between -1 and -3. Schulz (1976) states that americium(IV) exists only in a few complexed states.

CURIUM

The Eh-pH diagram for curium is illustrated in Figure 3-4. The limited data available to construct this diagram are used below to compute the species boundaries given.

$$Cm^0 \rightleftharpoons Cm^{3+} + 3e^-$$

$\Delta G^o_{f,298} = -142.4$ kcal mole^{-1} (Fuger and Oetting, 1976)

$E_o = -2.06$

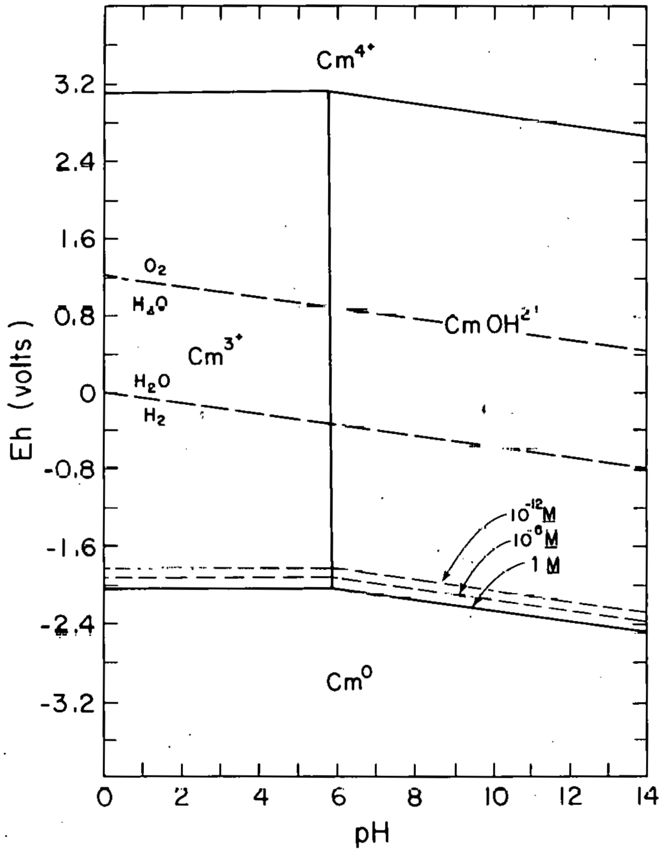

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Figure 3-4. Eh-pH diagram for curium at 25°C and one atmosphere.

$Cm^{3+} + H_2O \rightleftharpoons CmOH^{2+} + H$ (Desire, Hussenois and Guillaument, 1969)

$pK_H = -5.9$

$Cm^{3+} \rightleftharpoons Cm^{4+}$ (Nugent, Baybarz and Burnett, 1971)

$E_o = +3.1$

OXIDATION STATES OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM IN THE NATURAL ENVIRONMENT

The oxidation state and pH range of natural groundwaters have been investigated by Baas Becking, et al. (1960) and are illustrated in Figure 3-5. Most subsurface groundwaters range in oxidation state from -400 to +400 mV and from pH 6 to pH 9. These ranges indicate that plutonium is most likely to be found in the III and V states, neptunium in the V state, and americium and curium in the III state. However, complexing and the effect of temperature may result in other oxidation states becoming significant. In addition, the data used for calculation of the diagrams have not all been corrected to standard state conditions. The effects of ionic strength may have altered some of the species boundaries. The data used in the calculations are also subject to error. Therefore, the Eh-pH diagrams presented should be considered provisional.

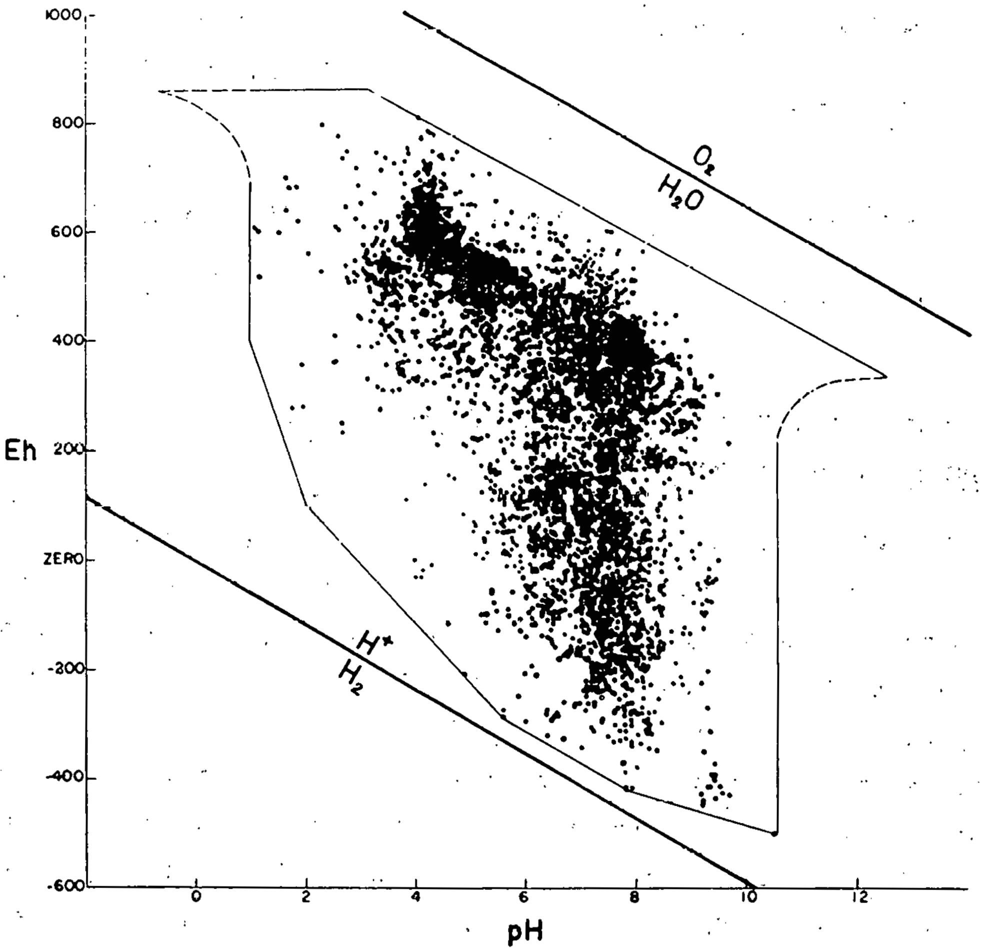

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Figure 3-5. Eh-pH range found in waters in the natural environment. (Source: Bass Becking, et al., 1960, J. of Geology, v. 68, no. 3, p. 276. Copyright 1960 by the University of Chicago.)

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SECTION 4: REVIEW OF THE LITERATURE ON THE DISTRIBUTION COEFFICIENTS OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM

INTRODUCTION

Sorption is one of the mechanisms governing transport of radionuclides by water in porous media. Because distribution coefficients, or K_ds, are a measure of the soil's ability to sorb actinides and other elements, our knowlege of their values is important in assessing the safety of high-level radioactive-waste storage facilities in geological formations. The distribution coefficient is an experimentally determined quantity, and therefore varies with the conditions under which it is determined. There can be as many K_d values as there are combinations of parameters for a given radionuclide such as the kinds of sorbent, the chemical components in the solution, and the temperature. Therefore, wide discrepancies exist in the various K_d values assigned to different radionuclides.

This study reviews all the available literature containing data on K_ds for use in radionuclide transport models and is confined to four actinides--plutonium, neptunium, americium, and curium. The K_d values for these radionuclides are shown in Appendix 4-1, Tables A and B.

THEORETICAL BASIS FOR K_d DETERMINATION

The equilibrium distribution coefficient of sorption, or K_d, is a measure of the moles of nuclide in the sorbed state per unit mass of the geologic medium, divided by the moles of nuclide in the dissolved state per unit volume of groundwater, when the groundwater and the geologic medium are in equilibrium with one another (Routson, 1973).

The K_d in ml/g may be defined (Routson, et al., 1975) as:

$$K_d = \frac{\text{concentration of radionuclide sorbed on the soil } (\mu\text{Ci/g})}{\text{concentration of radionuclide in solution } (\mu\text{Ci/ml})}$$

or

$$K_d = \frac{As/W}{Al/V} \qquad (1)$$

where

As = equilibrium concentration or activity sorbed on the solid phase,

W = weight of solid phase in grams,

Al = equilibrium concentration or activity of the solution phase, and

V = volume of solution in milliliters.

The distribution coefficient is an experimentally determined number and is a practical measure of the relative affinity of ions for the soil. The variables affecting the exchange of radionuclide on the soil are numerous and the process is very complex. Because of its empirical nature, the K_d varies with the conditions under which it is determined (pH of the groundwater, dissolved salts concentration, solution temperature, and kinds of sorbent). K_d is therefore applicable only to specified conditions.

EXPERIMENTAL METHODS

Radionuclide K_ds can be determined from laboratory tests or field tests. Generally, laboratory tests for K_ds are of two types: equilibrium batch tests and column tests.

Equilibrium Batch Tests

In equilibrium batch tests, a known volume of a real or simulated waste solution (that is, a known amount of radiotracer such as ^{239}Pu or ^{241}Am added to an aqueous solution) is mixed (shaken) with a known weight of sorbent (sediment or soil) until equilibrium is attained. The activity of the solution before and after contact is measured by radiometric counting procedures, and the amount of radionuclide adsorbed is calculated. The K_d is then calculated using equation (1).

In a typical batch experiment with simulated waste solution (Prout, 1959), a measured amount of distilled water is poured into a polyethylene bottle and the solution pH is adjusted by adding a measured amount of NaOH or HNO_3. Next, radionuclide is transferred into the bottle by pipet and thoroughly mixed with the solution giving the final radionuclide concentration required. The exact concentration of the radionuclide is determined by removing an aliquot of the solution. A weighed amount of soil is then added to the bottle and the sample shaken on a mechanical shaker until equilibrium is attained. The sample is then centrifuged and an aliquot of the supernatant liquid removed to determine the radioactive constituent concentration. The difference in the solution activity before and after contact with soil gives the amount of the radionuclide adsorbed by the soil. (See Schmalz, 1972, for details on experimental procedure.)

By varying the conditions of the test solution, the influence on K_d of geochemical parameters such as ionic strength, pH, and competing ions (such as Ca^{2+} and Na^+) present in the system can be obtained.

Column Tests

Column experiments are laboratory studies designed to simulate field conditions by packing soil in a glass or metal tube (ion exchange column). In contrast to batch experiments, column tests are open tests in which a liquid containing a radionuclide is pumped or percolated through the column at a flow rate simulating field conditions. The effluent is collected in quantities related to the volume of the column and sampled to determine the breakthrough of any given radionuclide as a function of the throughput volume (Bensen, 1960). The effluent radionuclide concentration (C) is then determined and compared with the influent radionuclide concentration (Co). The ratio C:Co is plotted against the effluent column volumes (V) and an S-shaped breakthrough curve is obtained. The distribution coefficient can be calculated using the following expression (Schmalz, 1972):

$$V_{50} = \frac{K_d \times W}{2} \tag{2}$$

where

V_{50} = the volume required to load a column to the 50% point or the volume at 50% breakthrough, and

W = weight in grams of the soil in the column.

The distribution of a radionuclide can also be represented by an error function plot, that is, by plotting the breakthrough curve on log probability paper, which usually results in a straight line (Reisenauer, 1959).

Small columns have also been used to calculate K_d values for radionuclides (Eliason, 1966, and Glover, et al., 1976). In this method a small volume of sediment is placed in tubes with fritted-disc bottoms and trace solutions are passed through the sediment until the system comes to equilibrium. Equilibrium is attained when the solution activity of the trace ion equals the influent solution activity. K_d values are calculated using equation (1).

Column experiments are subject to dispersion and are expected to yield K_d values representative of field conditions. However, column experiments are very time-consuming, particularly in situations where K_d values are large.

According to Bensen (1960), the results obtained by column experiments are not directly comparable with those of equilibrium experiments when the column influent is equilibrated with the same soil. In passage through a soil column, the influent solution carries away solubilized electrolytes liberated by the soil. In the equilibrium case, the solubilized soil electrolytes remain in the system to inhibit the adsorption of the radionuclides. Soil column data are more directly comparable with those of equilibrium experiments when the soil column influent is adjusted to the same composition as that found in the equilibrium supernatant liquid after equilibration.

Field Tests

Field experiments are the most direct means of obtaining accurate K_d data. Some field experiments have been conducted to measure migration characteristics and breakthrough data of radionuclides, such as ^{90}Sr, ^{137}Cs, ^{106}Ru, ^{99}Tc and others at Hanford (Knoll and Nelson, 1959; Knoll and Nelson, 1962; Brown, 1966). Field investigations at Test Reactor Area, Idaho, gave higher values of K_d for ^{137}Cs and ^{90}Sr than predicted by laboratory techniques (Schmalz, 1972). Field methods may also involve injecting radionuclide-tagged water into the groundwater flow system at the point of interest and then monitoring the movement of the tracer by soil sampling or well or piezometer sampling (Cherry, 1977). However, because of the cost and time required to conduct the experiments, this approach has not been widely used.

A comparison of the experimentally determined K_ds for ^{137}Cs and ^{90}Sr obtained by different methods indicates a wide variation in their values (Table 4-1).

LITERATURE REVIEW

Because this study was confined to plutonium, neptunium, americium, and curium, the literature reviewed includes only publications containing K_d data on these actinides.

Plutonium

Some of the first studies on plutonium distribution coefficient determination in soils were done by Rhodes (1952, 1957a, and 1957b). In laboratory equilibrium studies, soil from the Hanford Project containing

Table 4-1. Comparison of distribution coefficients for ^{137}Cs and ^{90}Sr determined by different methods (Schmalz, 1972).

	K_d (ml/g)	
Determined by	^{137}Cs	^{90}Sr
Laboratory batch technique	285	7.2
Sorption equations	360	10.5
Exchange column experiment	1000	10.5
Field data		
(1968 investigations)	600	--
Field data		
(1970 investigations)	450-950	40

92% sand and 2% free $CaCO_3$ was contacted with a neutral solution containing approximately 4 x 10^{-7} M of plutonium. A soil-to-solution ratio of 1 g to 20 ml was used. The adsorption of plutonium was found to be dependent on contact time, pH, and the concentrations of nonradioactive salts (see Fig. 4-1 and Table 4-2).

In the pH range of 2 to 8.5, about 98% to 100% of the plutonium (K_d > 1980) was sorbed from the solution; the sorption was lowered between pH 8.5 and 12.5. Rhodes concluded that at pH > 2 plutonium polymers were formed and plutonium was adsorbed to soil as positively charged polymers $Pu(OH)_n^{4-n+}$. The adsorption decrease in the pH range 8.5 to 12.5 was believed to be due to change in the characteristics of the polymer, which caused the charge to become negative (plutonium speciation). Rhodes further demonstrated that the high concentrations of inorganic salts (4 M $NaNO_3$ and 2 M di-ammonium phosphate) had no effect on plutonium adsorption on soil (96.5% plutonium sorbed), whereas equal concentrations of organic salts (4 M ammonium acetate) drastically reduced soil adsorption

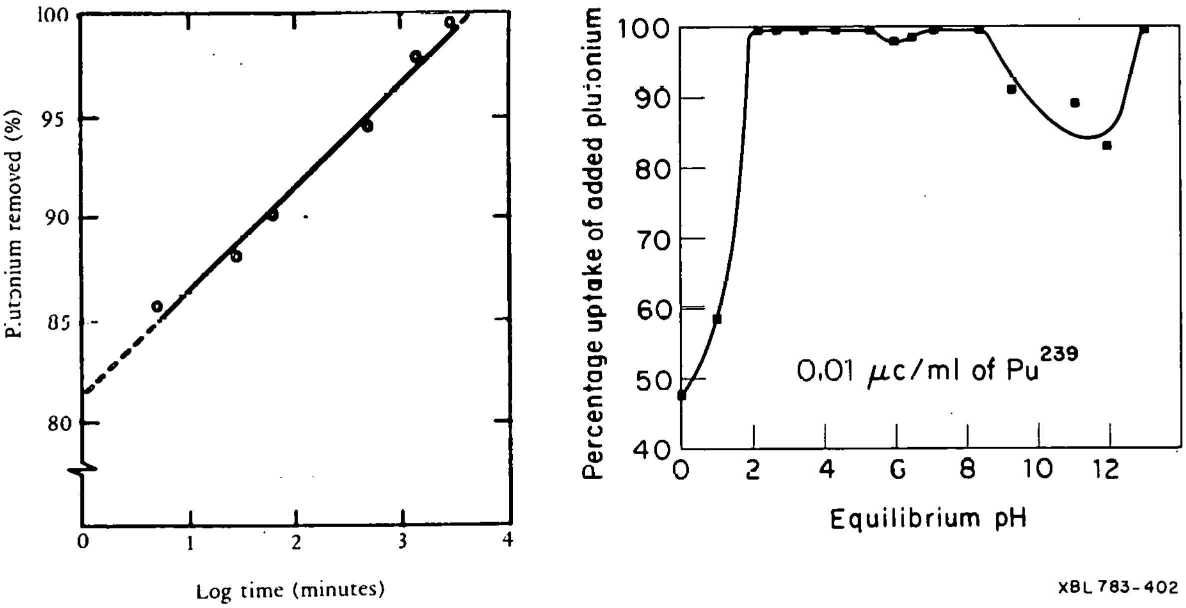

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Figure 4-1. Left: plutonium adsorption by soil as a function of time of contact (Rhodes, 1952). Right: plutonium adsorption by soil as a function of pH (Rhodes, 1952, as cited by Bensen, 1960).

Table 4.2. Equilibrium distribution coefficient values for ^{239}Pu as a function of pH (Rhodes, 1957b).

pH	K_d (ml/g)	pH	K_d (ml/g)
0	18	6.5	1314
1.0	28	7.1	>1980
2.2	>1980	8.4	>1980
2.7	>1980	9.3	200
3.5	>1980	11.1	178
4.4	>1980	12.0	96
5.3	>1980	13.0	1980
6.0	888	14.0	1980

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(58.9% plutonium adsorbed). Rhodes attributed the above data on plutonium adsorption to ion exchange mechanisms. Later, Bensen (1960), reinterpreting Rhodes' data, concluded that precipitation reactions and not ion exchange probably control plutonium sorption on soils.

Prout (1958 and 1959) investigated plutonium adsorption by soil from the Savannah River Plant that contained 20% clay and 80% sand with kaolinite as the dominant clay mineral (Table 4-3). In the equilibrium experiments, K_ds were determined by contacting plutonium-spiked ($\approx 10^{-6}$ $\underline{M}$) solution with soil and using a soil-to-solution ratio of 1 g to 10 ml. Plutonium adsorption was measured as a function of the oxidation state (valence) of plutonium and the pH of the solution. Prout's study substantiated Rhodes' results and showed that the sorption phenomenon is dependent on the plutonium oxidation state and the hydrogen ion activity (pH). Figure 4-2 shows K_d values for plutonium as a function of solution pH for various plutonium oxidation states.

Table 4-3. Exchange capacity and pH of soils (Prout, 1959).

pH	Exchange capacity	
	meq/100 g soil[a]	meq/100 g clay[a]
4	0.012	0.06
5	0.108	0.54
6	0.372	1.86
7	0.504	2.52
8	0.600	3.00
9	0.744	3.72
10	1.24	6.18

[a] Soil contained approximately 20% clay and 80% sand.

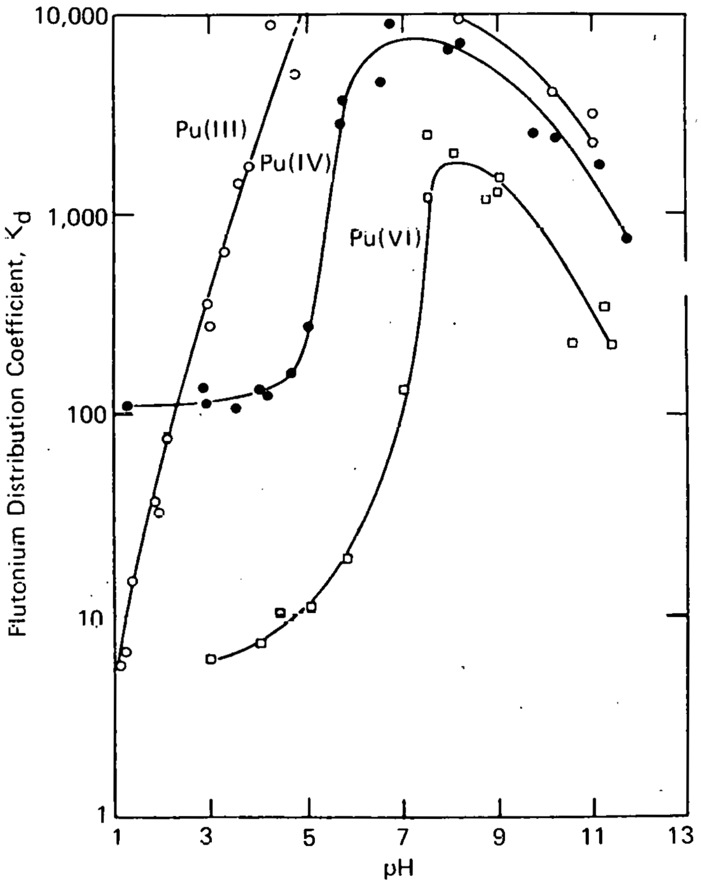

Figure 4-2. Effect of pH and plutonium oxidation state on the adsorption of plutonium by soil (Prout, 1959).

Plutonium adsorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH values of 2.5 and 12, and from solutions of Pu(VI) at pH values greater than 6. Because plutonium ions undergo extensive hydrolysis in alkaline solutions, strong sorption between pH values of 2.5 and about 9 was probably due to a combination of cation exchange and precipitation of hydrolysis products. Above pH 9, formation of negatively charged plutonium complexes probably results in decreased adsorption.

Knoll (1965, 1969) and Hajek and Knoll (1966) did sorption studies using column and batch tests on high-salt wastes (5.4 $\underline{M}$ NO_3^-) spiked with organic contaminants typical of a radionuclide separations plant. The soil used for the study was selected from the samples obtained from two wells at the Z-1A tile field site (subsurface storage cribs) in Richland, Washington. K_d values obtained in batch tests on high-salt wastes from the reprocessing plant are given in Table 4-4.

As seen from Table 4-4, upon neutralization of the waste, plutonium K_d values increased from 2.4 ml/g to 2.9 ml/g. When organic contaminants

Table 4-4. Adsorption of plutonium and americium by soil (Hajek and Knoll, 1966).

Solution	Equilibrium distribution coefficient (ml/g)	
	Pu	Am
Aqueous acid waste (AAW) untreated	2.4	< 1
pH 2 (soil neutralized)	2.7	< 1
pH 3 (NaOH neutralized)	2.9	< 1
Alkaline waste from precipitation		
Supernate--		
aqueous	a	212
aqueous and organic	1.4	42
Sludge leachate	1540	500

[a] Initial plutonium concentration and equilibrium concentration were too low for confident analysis.

(20% by volume) were added to this neutralized waste, the K_d value decreased to 1.4. The K_d value for plutonium increased to 1540 ml/g when water leachates of the sludge, produced on neutralization, were contacted with soil. In other experiments (Knoll, 1969) tap water spiked with plutonium was percolated through columns of soil. Various organic solutions were then percolated through the columns and the quantity of plutonium leached was measured by sampling the effluent at intervals. When the plutonium and americium are added to the organics and then percolated through the soils, the K_d values given in Table 4-5 are observed (Ames, et al., 1976). A column bulk density of 1.5 g/ml is assumed.

Using the batch method, Tamura (1972) measured K_d values for plutonium for selected sorbents. In his study, 0.1 g of sorbent was mixed with 25 ml of water spiked with plutonium ions. The original spike was of Pu^{4+} in 1 $\underline{M}$ HNO_3 and the initial solution pH was adjusted to 7.0 using NaOH. For the anion and cation resins, an equivalent amount of wet resin was used to give 0.1 g of dry weight. The amount of plutonium added was not specified. The K_d values are given in Table 4-6.

According to Tamura, since plutonium can exist in different oxidation states and is subject to hydrolysis in the pH range normally encountered in natural-water systems, its adsorption from a water system is not by normal ion exchange but more likely by "scavenging" of the hydroxide or oxide precipitates. Table 4-6 shows that with the exception of anion resin, bone charcoal, and quartz, the amount of plutonium removed appears to depend on the pH of the suspension. This suggests that the higher pH favors formation of hydroxides that are scavenged by the clays, resulting in greater plutonium adsorption.

Schneider and Platt (1974) estimated distribution coefficients for movement of selected radionuclides through a typical western desert soil in contact with typical nonsaline ground water. The typical soil used was a sand of moderate cation exchange capacity (CEC; about 5 meq/100 g) to sandy loam containing about 1 mg of free $CaCO_3$ per gram of soil. The soil pH ranged between 7.0 and 8.2. The K_d value determined for plutonium for the above soil was 2000 ml/g. No details were given either about the experiment or about the method used.

Table 4-5. Distribution coefficients of americium and plutonium as a function of organic solution (Ames, et al., 1976).

Organics	K_d (ml/g)	
	Am	Pu
Tributylphosphate (20%): CCl_4 (80%)	1.6	5.4
Dibutylbutylphosphonate (30%): CCl_4 (70%)	0.6	0
di-(2-ethylhexyl) phosphoric acid in hydrocarbons	0	0

Table 4-6. Removal of plutonium from pH 7 water by selected sorbents (0.1 g sorbent/25 ml; Tamura, 1972).

Material	Removal (%)	Distribution coefficient (ml/g)	Suspension pH
Attapulgite	94.6	4,370	9.60
Montmorillonite	71.6	630	9.20
Alumina (activated)	75.1	755	8.35
Kaolinite	58.5	352	6.25
Illite	34.0	129	5.90
Quartz	0.0	--	6.35
Dowex 50W-XI	4.2	11	1.82
Dowex I-XI	12.9	37	7.60
Bone charcoal	99.6	62,000	6.65
Coconut charcoal	99.0	25,000	6.80
Apatite	99.7	83,000	6.70

Duursma and Parsi (1974), using a ^{237}Pu tracer in valence states 3+, 4+, and 6+, conducted a series of experiments to determine distribution coefficients of plutonium onto marine sediments with oxic and anoxic sea waters at pH 7.8 to 8.0. Water-column and thin-layer methods were used to determine the K_ds. All three valence states showed K_d values of the order of 10^4 for both oxic and anoxic conditions (Table 4-7).

Experiments on radionuclide migration through soil and on distribution coefficient determination were conducted at Savannah River, South Carolina, with radionuclides containing synthetic, high-salt basic wastes (E. I. Du Pont de Nemours and Company, 1975). Batch equilibrium tests were performed with various resins. In one test, 1 g of resin was shaken overnight with 10 ml of synthetic waste supernate containing 1.75 x 10^7 dis/min·ml of ^{238}Pu. Distribution coefficient values for plutonium varied from 1 to 240 on various resins and are given in Table 4-8.

The migration of solvent-complexed plutonium from separations-process waste through dry and moist soils was determined. Laboratory column tests with dry soils using short columns (2.6 in.) and long columns (5.8 in.) yielded a plutonium K_d (ml/g) value of 6000 for the short column and 3000 for the long column. Column tests with moist soils yielded a plutonium K_d value of ≈ 0.4 for the solvent phase, and $K_d > 30$ for the aqueous phase.

The above test showed that dry (ground-surface) soil effectively sorbs and immobilizes small volumes of solvent-complexed plutonium, but moist (subsurface) soil allows extensive migration of large volumes of solvent-complexed plutonium.

Hamstra and Verkerk (1977) reported distribution coefficient measurements for plutonium and americium using different soil materials taken from boreholes surrounding salt formations in the northeast Netherlands. In batch equilibrium studies, they used stock solutions of the radionuclides in the form of 90% saturated NaCl solutions and a soil-to-solution ratio of 1 g to 150 ml. Equilibrium pH of the solutions was mostly between 7 and 8. The amount of radionuclide (plutonium or americium) added was not specified. The measured distribution coefficients for various soil materials and clay samples taken

Table 4.7. Plutonium-237 sorption by Mediterranean sediment (Duursma and Parsi, 1974).

	Oxic conditions pH = 7.8-8.0					Anoxic conditions pH = 7.8-8.0				
	Sedimentation		Thin Layer			Sedimentation		Thin Layer		
Valence	K	R	K	R'	$T_{1/2}$	K	R	K	R'	$T_{1/2}$
III	$1.6x10^4$	10%	$2.1x10^4$	30%	3	$1.9x10^4$	2.5%	-	-	-
IV	$1.8x10^4$	9%	$1.9x10^4$	50%	1	$1.3x10^4$	8.0%	$>9.4x10^4$	39%	2.4
			$1.5x10^4$	31%	1			($>9.3x10^3$	35%	1.3[a])
VI	$1.3x10^4$	11%	$5.7x10^4$	9%	4	$2.2x10^4$	9.0%	-	-	b

K = distribution coefficient; R = % reduction in water/day without sediment;
R'= glasswall adsorption after three weeks; $T_{1/2}$ = half uptake time to apparent equilibrium in days.

[a] Paper filters rather than millipore filters used as blanks; paper filters strongly adsorbed Pu(IV) and reduced sediment uptake, therefore K is probably low.

[b] Precipitation of Pu on the blank millipore filters with the thin-layer experiments decreased from 50% for Pu(III) to 12% for Pu(VI) and 3% for Pu(VI).

Table 4-8. Resin-supernate distribution coefficients for plutonium. (E. I. Du Pont de Nemours and Co., 1975).

Resin	K_d (ml/g)
"Duolite" ARC-359	240
Linde AW-500[a] (Zeolite)	24
"Chelex" 100	7
"Dowex" 50W-X8	~1
HZO-1 (hydrated zirconium oxide gel)	100

[a]Product of Union Carbide.

at various depths are given in Tables 4-9 and 4-10. Clay samples consisting mainly of illite and kaolinite had plutonium distribution coefficients of ~10^4; river sand had a K_d of 200 ml/g.

Fried, et al. (1974, 1976a, 1976b), in their studies on the migration of actinides in the lithosphere, measured plutonium and americium surface-absorption and migration coefficients on the rock samples found in the vicinity of disposal sites.

In the experiments on the surface-absorption coefficient of plutonium and americium on limestones and basalts, disks of the rock were immersed in solutions of 4×10^{-5} $\underline{M}$ $^{238}Pu(NO_3)_4$ and 10^{-7} $\underline{M}$ $Am(NO_3)_3$. Small aliquots (0.05%) were removed at 12-hr intervals, dried, and measured for alpha counts (or gamma counts for americium) until the attainment of equilibrium. After equilibration the activity in the solutions was measured again. Initial pH of the solution used was 7.0 and the final pH ranged between 7 and 8.

Sorption on the rocks was measured in terms of surface-absorption coefficient, K, which was defined as:

$$K = \frac{\text{(activity of actinide/ml of solution)}}{\text{(activity of actinide/cm}^2\text{ of rock)}} \cdot$$

The results of the experiment showed that on a surface-area basis, basalts sorbed more plutonium than limestone. The surface-absorption

Table 4-9. Distribution coefficients for plutonium and americium for different soil materials (Hamstra and Verkerk, 1977).

Soil material	Distribution coefficient (ml/g)	
	Pu	Am
Clay (mainly illite and kaolinite)	10^4	5×10^4
Sandstone (certain amount of clay)	1×10^3	1×10^4
Caprock (mainly gypsum, no clay)	5×10^2	3×10^3
River sand (mainly quartz, no clay)	2×10^2	4×10^2

Table 4-10. Distribution coefficients for plutonium and americium measured for clay samples taken at various depths (Hamstra and Verkerk, 1977).

Depth of sample (m)	Distribution coefficient (ml/g)	
	Pu	Am
20-30[a]	10^4	8×10^4
55-60[b]	5×10^3	6×10^4
100-125[b]	6×10^3	5×10^4
120-130[b]	5×10^3	6×10^4
120-160[c]	7×10^3	2×10^4
200-225[c]	6×10^3	9×10^4
245-275	8×10^3	4×10^4
300-325	9×10^3	4×10^4
328-348	8×10^3	5×10^4

[a] Quaternary clay (mainly montmorillonite).

[b] Young tertiary clay (mixture of illite and kaolinite).

[c] Older tertiary clay (mixture of illite and kaolinite).

coefficient (K) for pure solution of $Pu(NO_3)_4$ at 4×10^{-5} M was 0.10 ± 0.02 for limestone and 0.07 ± 0.02 for basalts. The effects of salt solutions of Na^+, Ca^{2+}, La^{3+}, and Zr^{4+} at various concentrations on the surface absorption coefficient were also studied (see Figs. 4-3, 4-4, and 4-5). The salts displaced some of the plutonium from the rocks and the displacement became easier with increasing salt concentration and increasing valence.

In determining migration coefficients of plutonium for flow through porous limestone and basalt, Fried, et al. (1976a) used a high-pressure chromatographic absorption apparatus (Fig. 4-6). A small amount of $^{238}Pu(NO_3)_4$ tracer in neutral aqueous solution was placed on the surface of the rock disk and was allowed to dry at room temperature. Water

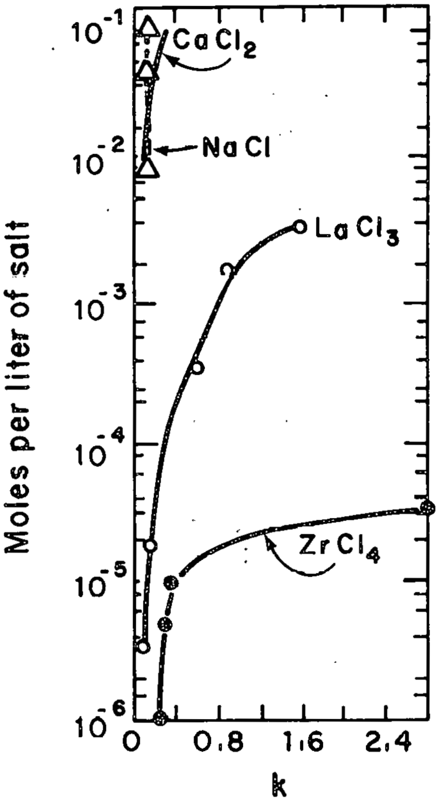

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Figure 4-3. Surface absorption coefficients of plutonium as a function of the concentration of other salts (i.e., $ZrCl_4$, $LaCl_3$, $CaCl_2$, NaCl) for limestone (Fried, et al., 1976a).

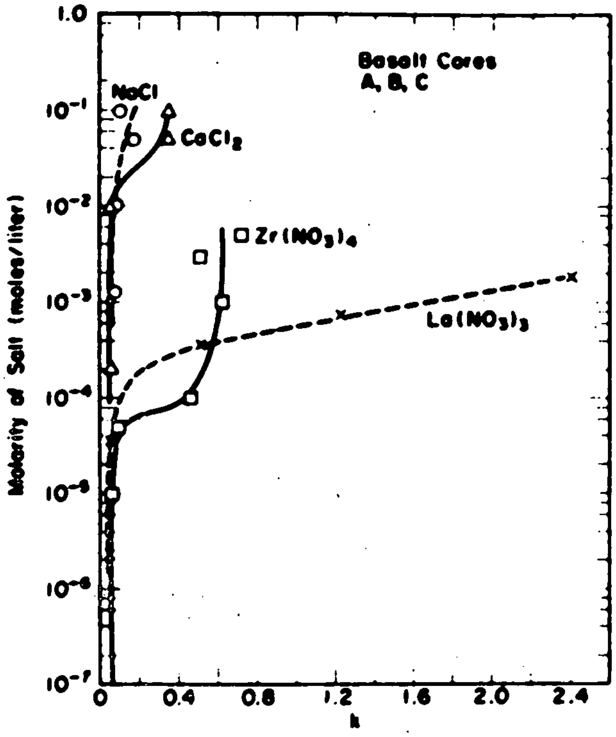
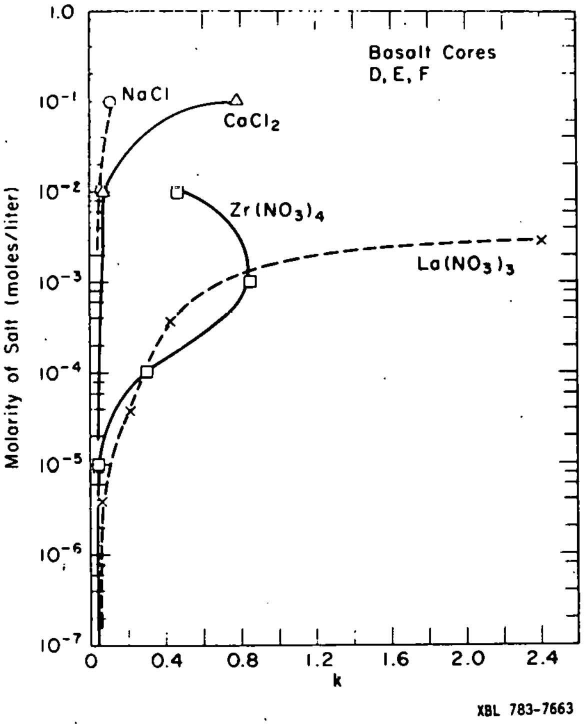


Figure 4-4. Surface adsorption coefficient of plutonium as a function of the concentration of other salts for dense basalt cores (Fried, et al., 1976a).

Figure 4-5. Surface adsorption coefficient of plutonium as a function of the concentration of other salts for porous basalt cores (Source: Fried, S., Friedman, A. M., and Weeber, R., 1976. The distribution of plutonium in a rock containment environment, in Campbell, M. H., ed., High-level radioactive waste management, Advances in Chemistry Series No. 153. Washington, D.C.: American Chemical Society.)



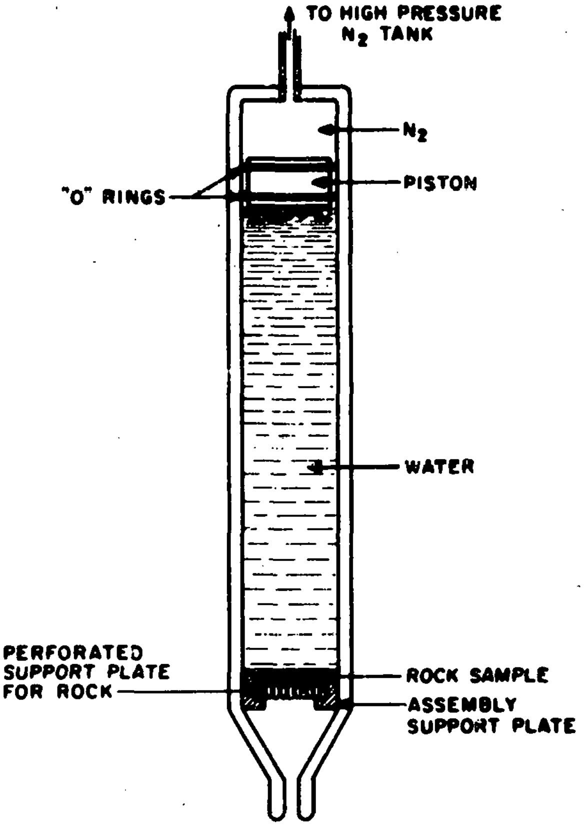


Figure 4-6. Schematic diagram of the high-pressure stainless-steel chromatographic column (Fried, et al., 1976a).

was then forced through the limestone disk in increments by means of a piston, which exerted pressure on the water isolating it from the pressurizing gas. The depth of penetration of the plutonium tracer was measured using an x-ray absorption technique. The results of these experiments yielded a migration coefficient M of 30 ± 10 μm/m of water flow for the limestone and 61 ± 8 μm/m of water flow for the basalts, where M = the average distance traveled by the plutonium atoms for every meter traveled by the water molecules.

Noshkin, et al. (1976) collected seven plutonium-contaminated soil samples from Eniwetok Atoll and equilibrated them separately with uncontaminated sea water. Water was filtered at intervals through an 0.4-μm filter and soil and water were analyzed for plutonium at equilibrium. The mean K_d value for these samples at equilibrium was 8×10^4 ml/g. Field results from particulates in the groundwater vs the groundwater itself gave an average K_d value of 2.5×10^5 ml/g (Table 4-11). The two laboratory and field values are quite close.

Bondietti, et al. (1976) determined plutonium distribution coefficients for Ca-saturated clays separated from Miami silt loam soil and for a reference montmorillonite. They used 5×10^{-3} $\underline{M}$ calcium solutions [Ca-acetate and $Ca(NO_3)_2$] at pH 6.5 and determined K_d values for two plutonium valence states. K_d values as a function of plutonium valence states are given by Table 4-12.

According to Bondietti, et al. (1976), the high sorption of Pu(VI) to the soil clay compared with montmorillonite indicates that plutonium reduction by clay components must have occurred, yielding sorption values similar to those for Pu(IV). Pu(VI) also appears to adsorb less than the tetravalent Pu.

Bondietti and Reynolds (1976) in later work studied the sorption of plutonium when Pu(IV) was added at about 0.6 ppm (Pu mass/clay mass) to treated clays separated from Miami silt loam soil using ^{238}Pu as the tracer. A solution of 5×10^{-3} $\underline{M}$ $Ca(NO_3)_2$ at pH 4.0 was used and K_d values were determined as a function of time and treatment of the clay fraction. The clay fraction was first equilibrated with organic matter present; then the clay was treated to remove organic matter and the resultant material equilibrated again. Next, free iron oxide was also removed and the clay equilibrated. These procedures were repeated after equilibrating for 3 weeks, 18 weeks, and 52 weeks. The K_d values obtained for different treatments and equilibration times are given in Table 4-13. According to Bondietti and Reynolds (1976), the results shown in Table 4-13 suggest that sorption studies using Pu(IV) should be carefully examined because the soluble species that do not sorb may be in a different oxidation state than that initially added.

Glover, et al. (1976) using 17 selected soils of wide-ranging physical and chemical characteristics (Table 4-14), studied their equilibrium sorption and elution characteristics with plutonium and americium nitrates as the source of the actinides. Complete chemical and physical

Table 4-11. Concentrations of ^{239,240}Pu: groundwater particulates in May 1974 (Noshkin, et al., 1976).

Island	Well	Depth (m)	Particulate (mg/l)	^{239,240}Pu (%σ)[f] (fCi/l)[a]	^{239,240}Pu (%σ)[f] (fCi/mg)	ln K_d (d)	Fraction in particulates[e]	K_d
Janet	XEN2	Surface	10.4	21.0 (9)[b]				
				3.79(14)[c]	2.38	13.85	0.92	1.04×10^6
	XEN4	Surface	2.5	2.9 (30)	1.16	12.08	0.31	1.76×10^5
	XEN1	Surface	15.0	47.0 (9)[b]				
				0.95(13)[c]	3.20	13.19	0.87	5.35×10^5
		7	7.8	6.0 (18)[c]				
				0.26(33)[b]	0.80	13.33	0.82	6.15×10^5
	AEN1	7	7.5	1.5 (16)	0.2			
		10.8	26.3	1.3 (50)	0.05			
	AEN3	Surface	5.1	1.3 (60)	0.25	11.23	0.28	7.54×10^4
		7	3.1	0.9 (40)	0.30	12.08	0.35	1.76×10^5
		10	13.8	2.1 (25)	0.15	11.66	0.62	1.16×10^5
	AEN5	Surface	30.2	1.8 (90)	0.06			
		7	2.9	0.9 (70)	0.31			
	AEN9	Surface	0.8	2.4 (23)	3.0	13.12	0.29	4.99×10^5
	AEN2	10	12.8	25.0 (7)	1.95	12.87	0.83	3.88×10^5
Belle	ABM1	Surface	157	206 (2)	1.31	9.56	0.69	1.42×10^4
Elmer	APA1	Surface	4.4	0.2 (40)[b]				
				0.14(53)	0.08			
		10	19.6	0.4(100)[b]				
				0.2 (30)[c]	0.03			

Mean ln K_d = 12.42 ± 1.27
Mean K_d = 2.5×10^5

---

[a] 0.4- and 1-μm filters were processed together except where indicated

[b] 1.0-μm filter only

[c] 0.4-μm filter only

[d] The distribution coefficient is the dimensionless ratio of the quantity of Pu per gram of suspended material (dry weight) to that per gram of water: K_d is calculated by the equation:

$$\ln Kd = \ln \frac{(\text{fCi/mg particulate}) \times 10^6}{\text{fC/l water}}$$

[e] Fraction of ^{239,240}Pu in total particulates >0.4 m

[f] (%σ) values in parentheses are 1σ counting errors expressed as percentages of listed values.

Table 4-12. Effect of valence on plutonium distribution coefficient to Ca-saturated clays, pH 6.5[a] (Bondietti, et al., 1976).

Material	Tracer	Initial actinide valence	% unabsorbed to clay	K_d (ml/g)
Clay separated from				
Miami silt loam soil	^{237}Pu	IV	0.40	10.4×10^4
	^{238}Pu	IV	0.25	16.8×10^4
	^{239}Pu	VI[b]	0.62	7.5×10^4
Montmorillonite	^{239}Pu	IV	2.0	2.1×10^4
	^{239}Pu	VI	63.0	2.5×10^2

[a] Aqueous phase 5 $m\underline{M}$ in Ca^{2+}.

[b] Ca-acetate; remaining studies conducted in $Ca(NO_3)_2$.

Table 4-13. Sorption of $^{238}Pu(IV)$ to treated clays: pH 4.0, 5×10^{-3} $\underline{M}$ $Ca(NO_3)_2$ (after Bondietti and Reynolds, 1976).

Time and treatment	Percent sorbed	Evidence of Polymer or Pu(VI)[a]	K_d (ml/g)
3 weeks			
Clay	99.86	-	2.9×10^5
-O.M.[b]	50.0	-	4×10^2
-Fe + O.M.	99.8	-	2×10^5
Blank[c]	71	-	-
18 weeks			
Clay	99.8	No	-
-O.M.	61.5	Yes	3.5×10^2
-Fe + O.M.	99.9	No	-
Blank	71.7	Yes	-
52 weeks			
Clay	99.9	< 20% (VI)	1.9×10^5
-O.M.	99.8	50% (VI)	8.1×10^4
-Fe + O.M.	99.8	< 20% (VI)	8.1×10^4
Blank	78.6	25% (VI)	-

[a] By thenoyltrifluoroacetone extraction, PrF_3 precipitation (holding oxidant method) and hexone extraction.

[b] O.M. = organic matter.

[c] No clays present.

Table 4-14. Physical and chemical characteristics of soil (Glover, et al., 1976).

Source	Soil code	CEC (meq/100 g)	Soluble salts (mmhos/cm)	Soluble carbonate (meq/1)	Inorganic carbon (% $CaCO_3$)	Organic matter (%)	pH	Sand (%)	Silt (%)	Clay (%)	Texture
Colorado A (Rocky Flats)	CO-A	20.0	3.6	5.97	0.4	2.4	5.7	44	20	36	Clay loam
Colorado B (Sugar Loaf)	CO-B	17.5	0.4	0.97	0.3	3.4	5.6	64	14	22	Sandy clay loam
Colorado C (Rocky Flats)	CO-C	29.6	0.4	1.98	2.4	0.7	7.9	5	31	64	Clay
Idaho A (ERDA)	ID-A	15.5	0.5	2.71	17.2	0.8	7.8	16	50	34	Silty clay loam
Idaho B	ID-B	13.8	0.8	2.51	7.9	0.2	8.3	44	24	32	Clay loam
Idaho C	ID-C	8.2	1.0	2.52	5.2	0.3	8.0	66	41	23	Sandy clay loam
Idaho D	ID-D	17.5	1.2	4.90	0.0	0.1	7.5	38	32	30	Clay loam
Washington A (Hanford)	WA-A	6.4	0.9	2.60	0.6	0.3	8.0	74	12	14	Sandy loam
Washington B	WA-B	5.8	0.4	2.30	0.0	0.1	8.2	74	12	14	Sandy loam
Tennessee (Oak Ridge)	TN	20.5	0.4	0.30	0.0	1.0	4.8	32	32	36	Sandy loam
South Carolina (Barnwell)	SC	2.9	0.4	0.50	0.2	0.7	5.4	78	2	20	Sandy loam-silty
New York (West Valley)	NY	16.0	1.2	1.40							Clay loam
New Mexico (Los Alamos)	NM	7.0	1.7	2.80	0.0	2.7	5.4	32	32	36	Clay loam
Arkansas A	AR-A	34.4	0.5	0.10	0.2	0.7	6.4	48	48	18	Loam
Arkansas B	AR-B	3.8	0.4	0.10	0.9	3.2	6.2	10	34	56	Silty clay
					0.7	0.6	4.8	82	9	9	Fine sand
Arkansas C	AR-C	16.2	0.3	0.10	0.6	2.3	2.3	9	54	37	Silty clay loam
Illinois	IL	17.4	0.5	0.10	0.7	3.6	3.6	31	53	16	Loam

analyses of all but four soils were done. Three standard plutonium solutions containing initial plutonium concentrations of 10^{-8} $\underline{M}$, 10^{-7} $\underline{M}$, and 10^{-6} $\underline{M}$ (or 9,600 dis/min/10 μl, 103,000 dis/min/10 μl, and 972,000 dis/min/10 μl, respectively) were used for sorption measurements. A soil-to-solution ratio of 1 g to 5 ml was used and 10 μl of the required concentration of the standard plutonium solution were added to this mixture. Depending on the experiment, from 5 to 48 hours were required for equilibrium sorption. The distribution coefficients for each of the 17 soils are given in Table 4-15. Tables 4-16 and 4-17 give the same K_d values obtained by Glover, et al. (1976) along with pH and Eh data of the system.

Results shown in Table 4-15 show a wide range of K_d (ml/g) values obtained from a low of 35 to a high of 14,000. This indicates the great sensitivity of K_d values to changes in plutonium concentration, especially at high levels of plutonium sorption.

In plutonium column elution studies by Glover, et al. (1976) with three different soils, 24 g of soil were added to a 1-cm-internal-diameter, 4-cm-long glass column. One gram of the same soil was mixed with 10 μl of 10^{-3} $\underline{M}$ plutonium nitrate solution and then distributed evenly on top of the soil in the column. After packing, the column was washed with one liter of distilled water and the effluent collected and analyzed for plutonium. The K_d values for plutonium obtained by this elution study are given in Table 4-18.

Regression analyses are being performed to determine whether or not relationships exist between plutonium sorption and soil characteristics such as cation exchange capacity, particle size and distribution, and sand and clay content.

Neptunium

Very little work has been done on the distribution coefficient determination of neptunium in sediments and soils. Only two references indicate K_d value determinations for neptunium. A K_d value of 15 ml/g for neptunium between water and a typical western desert soil has been estimated by Schneider and Platt (1974). The soil characteristics

Table 4-15. Mean $K_{d(m)}$ values[a] + statistical error (ml/g) for plutonium at equilibrium sorption (Glover, et al., 1976).

	Initial Pu concentration (M)		
Soil code	10^{-8}	10^{-7}	10^{-6}
CO-A	2200 ± 460	2700 ± 170	1200 ± 190
CO-B	200 ± 24	130 ± 6	40 ± 3
CO-C	1900 ± 110	1800 ± 100	2000 ± 3
ID-A	1700 ± 70	4300 ± 160	5000 ± 290
ID-B	320 ± 26	330 ± 12	140 ± 11
ID-C	690 ± 110	4100 ± 150	4000 ± 23
ID-D	2100 ± 640	1500 ± 80	310 ± 42
WA-A	100 ± 7	100 ± 3	35 ± 1
WA-B	430 ± 27	600 ± 44	680 ± 16
TN	2600 ± 640	1200 ± 100	14000 ± 2700
SC	280 ± 5	870 ± 52	1000 ± 20
NY	810 ± 130	1100 ± 45	870 ± 57
NM	100 ± 5	200 ± 8	220 ± 12
AR-A	710 ± 36	660 ± 33	760 ± 45
AR-B	80 ± 3	230 ± 9	260 ± 35
AR-C	430 ± 23	570 ± 44	870 ± 30
IL	230 ± 10	630 ± 95	320 ± 130

[a] Glover, et al. (1976), use a different notation--$K_{d(m)}$ rather than the conventional notation K_d--to imply that because of the complex chemistry of polyvalent radionuclides, the experimentally measured sorption coefficient may be related to a summation of a number of different mechanisms rather than any specific sorption mechanism.

Table 4-16. Sorption of plutonium in soils; distribution coefficients for soils in basic solutions (Polzer and Miner, 1976).

Soil	Initial Pu conc. (M)	$K_{d(m)}$ (b)	pH	-Eh(V)	Pu_m/Pu_c (a)
WA-A	10^{-8}	100	7.9	0.41	0.4
	10^{-7}	98	7.9	0.42	3.2
	10^{-6}	35	7.9	0.44	40
WA-B	10^{-8}	430	7.8	0.46	0.0004
	10^{-7}	590	7.8	0.46	0.2
	10^{-6}	110	7.8	0.41	7.9
ID-D	10^{-8}	2100[e]	7.8	0.44	0.008
	10^{-7}	1500	8.0	0.41	0.4
	10^{-6}	310[c]	7.9	0.41	5.0
ID-C	10^{-8}	690[c]	8.4	0.45	0.03
	10^{-7}	4100	8.0	0.43	0.06
	10^{-6}	4000	8.0	0.44	0.3
ID-A	10^{-8}	1700	8.4	0.45	0.0005
	10^{-7}	4300	8.0	0.44	0.03
	10^{-6}	5000	7.8	0.45	0.2
ID-B	10^{-8}	320	8.8	0.44	0.05
	10^{-7}	300	8.9	0.41	1.6
	10^{-6}	140	8.6	0.40	63
CO-C	10^{-8}	1900	8.0	0.49	0.0001
	10^{-7}	1800	7.8	-	-
	10^{-6}	2000[c]	8.2	0.44	1.0

[a] Ratio of Pu concentration measured in the water phase at sorption equilibrium (Pu_m) to the Pu concentration calculated to be present if the water were in equilibrium with $Pu(OH)_4$ (Pu_c). Pu_c is based on a solubility product for Pu(OH) of $10^{-51.9}$ in basic solutions.

[b-e] The standard error of the mean is: b, 8% or less; c, between 11% and 16%; d, between 20% and 25%; and e, 31%.

Table 4-17. Sorption of plutonium in soils; distribution coefficients for soils in acid solutions (Polzer and Miner, 1976).

Soil	Initial Pu conc. (M)	$K_{d(m)}$ [b]	pH	Eh(V)	Pu_m/Pu_c [a]
SC	10^{-8}	280	5.5	0.48	20
	10^{-7}	870	5.2	0.53	14
	10^{-6}	1,000	5.2	0.53	100
NM	10^{-8}	100	6.9	0.48	20
	10^{-7}	200	6.0	0.47	600
	10^{-6}	320	6.2	0.51	1,000
TN	10^{-8}	2,600[d]	4.9	-	-
	10^{-7}	1,200	4.0	-	-
	10^{-6}	14,000[d]	5.0	0.53	8.0
AR-B	10^{-8}	80	5.6	0.58	1.0
	10^{-7}	230	5.3	0.55	9.0
	10^{-6}	260[c]	5.0	0.64	3.0
CO-A	10^{-8}	2,220[d]	6.5	0.49	2
	10^{-7}	2,700	6.2	-	-
	10^{-6}	1,200[c]	6.8	0.43	16,000
CO-B	10^{-8}	190[c]	5.8	0.53	6
	10^{-7}	130	5.8	0.53	60
	10^{-6}	40	5.8	0.53	3,200
AR-C	10^{-8}	430	5.9	0.40	100
	10^{-7}	570	5.9	0.42	680
	10^{-6}	870	6.0	0.57	13
IL	10^{-8}	230	5.8	0.61	0.1
	10^{-7}	630[c]	5.4	0.65	0.06
	10^{-6}	27	5.7	0.64	26

Table 4-17. Continued.

Soil	Initial Pu conc. (M)	$K_{d(m)}$ [(b)]	pH	Eh(V)	Pu_m/Pu_c [(a)]
AR-A	10^{-8}	710	6.7	0.51	1.6
	10^{-7}	660	6.5	0.54	5.8
	10^{-6}	760	7.0	0.50	200
NY	10^{-8}	810[c]	6.0	-	-
	10^{-7}	1100	6.0	0.54	6.0
	10^{-6}	870	6.1	0.49	600

[a] Ratio of Pu concentration measured in the water phase at sorption equilibrium (Pu_m) to the Pu concentration calculated to be present if the water phase were in equilibrium with $Pu(OH)_4$ (Pu_c). Pu_c is based on a solubility product for $Pu(OH)_4$ of $10^{-55.2}$ in acid solutions.

[b-e] The standard error of the mean is: b, 8% or less; c, between 11% and 16%; d, between 20% and 25%; and e, 31%.

Table 4-18. Distribution coefficient values for plutonium as a function of soil as obtained by column elution method (Glover, et al., 1976).

Soil	$K_{d(m)}$ (ml/g)
ID-B	144
CO-A	1180
ID-A	5020

are described in the earlier reference to Schneider and Platt in the section on plutonium, above. Routson, et al. (1975 and 1976), using batch tests, determined K_d values for neptunium and americium as a function of calcium (Ca^{2+}) and sodium (Na^+) ion concentration for eastern Washington and South Carolina subsoils. Batch tests were conducted with a soil-to-solution ratio of 1 g to 25 ml and influent solution pHs of 2.5 and 3.1. The system was equilibrated for 24 hours. The K_d values were found to decrease with increasing solution concentrations of Ca^{2+} and Na^+. Properties of soil samples and the results of adsorption studies are given in Tables 4-19 and 4-20 respectively.

Americium

The distribution coefficients of americium have been measured by several investigators. Between water and a typical western desert soil a K_d value of 2000 ml/g for americium has been estimated by Schneider and Platt (1974).

In americium adsorption studies, Hajek and Knoll (1966) used acidic high-salt wastes (5.4 M NO_3^-) spiked with organics typical of a fuel reprocessing plant. K_d values obtained in batch tests are given in Table 4-4. When comparing K_d values for americium with K_d values for plutonium (Table 4-4), in most cases $K_d(Am) < K_d(Pu)$. The K_d values for americium as a function of organic solution from a column study are given in Table 4-5.

Table 4-19. Soil sample properties (Routson, et al., 1975).

Soil	$CaCO_3$ (mg/g)	Silt (%)	Clay (%)	CEC (meq/100g)	pH
Washington	0.8	10.1	0.5	4.9	7.0
South Carolina	<0.2	3.6	37.2	2.5	5.1

Table 4-20. Distribution coefficient values for neptunium and americium as a function of soil and solution Na and Ca ion concentration (Routson, et al., 1976).

	South Carolina		Washington
Solution ($\underline{M}$)	K_d(Am) (ml/g)	K_d(Np) (ml/g)	K_d(Np) (ml/g)
Na			
3.00	1.0 ± 0.1[a]	0.43 ± 0.16	3.19 ± 0.22
0.75	2.9 ± 0.2	0.45 ± 0.09	3.28 ± 0.33
0.30	6.3 ± 0.7	0.51 ± 0.09	3.28 ± 0.13
0.030	130 ± 2.0	0.57 ± 0.03	3.51 ± 0.19
0.015	280 ± 24.0	0.66 ± 0.08	3.90 ± 0.12
Ca			
0.20	1.0 ± 0.04	0.16 ± 0.06	0.36 ± 0.07
0.10	2.2 ± 0.2		0.62 ± 0.04
0.05	3.6 ± 0.6		0.78 ± 0.16
0.02	8.4 ± 1.0		0.93 ± 0.07
0.002	67 ± 5.0	0.25 ± 0.0	2.37 ± 0.04

[a] Standard deviation.

Hamstra and Verkerk (1977) reported distribution coefficient measurements for Dutch subsoils using 90% saturated NaCl solution at pH 7 to 8. A soil-to-solution ratio of 1 g to 150 ml was used. Clay samples consisting of mainly illite and kaolinite had a K_d of 5 x 10^4 ml/g; river sand had a K_d of 400. Clay- and gypsum-bearing sandstones had intermediate K_d values (Tables 4-9 and 4-10).

Fried, et al. (1974, 1976a and 1976b) determined the sorption of americium onto a basalt. The value of the surface-absorption coefficient, K, for 10^{-7} M solutions of $Am(NO_3)_3$ was 0.041 ± 0.02 for basalts (see the earlier reference to Fried, et al. in the section on plutonium, above, for the definition of K and other details). The effect of other ions on the absorption constant was also studied. Addition of salts to the solution lowered americium adsorption. Higher valence cations (La^{3+} and Zr^{4+}) lowered the americium adsorption much more than lower valence cations (Na^+ and Sr^{2+}). See Figure 4-7.

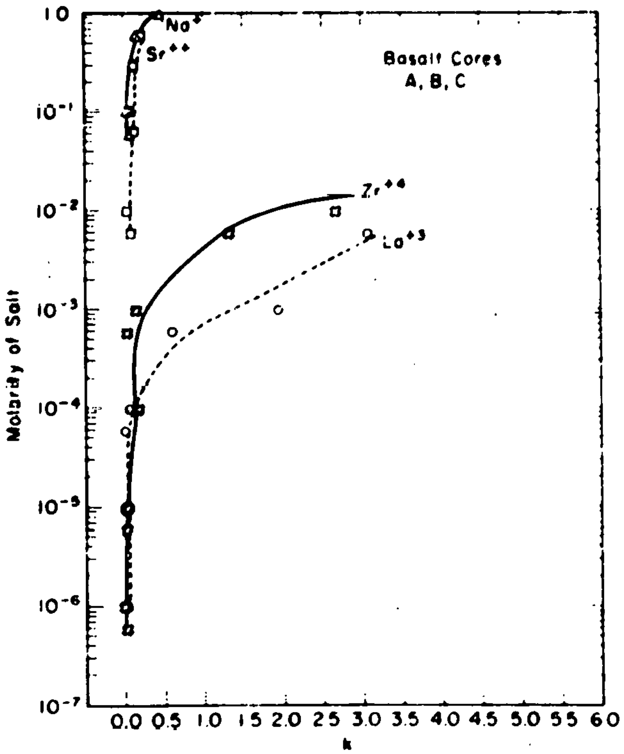


Figure 4-7. Surface absorption coefficient of americium as a function of the concentration of other salts for basalt cores (Fried, et al., 1976a).

Routson, et al. (1975, 1976) used batch sorption experiments to determine K_d values for South Carolina subsoil (sandy clay) as a function of calcium and sodium ion concentration. They used a soil-to-solution ratio of 1 g to 2.5 ml at an initial solution pH of 2.5 and 3.1 and equilibrated the system for 24 hours. The americium K_d values are given in Table 4-20. For Washington subsoil, americium K_d was found to be greater than 1200 ml/g for all concentrations of calcium.

Glover, et al. (1976) used basically the same procedure for americium sorption measurements as was used for plutonium experiments (see the earlier reference to Glover, et al. in the section on plutonium, above). Initial americium concentrations were 10^{-10} $\underline{M}$ and 10^{-8} $\underline{M}$. From 24 to 48 hours were required for equilibrium sorption. The K_d values for americium are given in Tables 4-21, 4-22, and 4-23. Table 4-21 shows that K_d values for americium are very sensitive to changes in americium concentration, especially at high levels of americium sorption.

Curium

Only one reference in the literature indicated distribution coefficient values for curium. Schneider and Platt (1974) gave an estimated K_d value of 600 ml/g for curium between water and typical western desert soil. No details were given either about the experiment or about the method used.

Table 4-21. Mean distribution coefficient values ± statistical error (ml/g) for americium at equilibrium sorption (Glover, et al., 1976).

Soil code	Initial Am concentration (M) 10^{-10}	10^{-8}
CO-A	2500 ± 210	2600 ± 110
CO-B	600 ± 24	840 ± 20
CO-C	5200 ± 970	8100 ± 400
ID-A	5900 ± 230	510 ± 8
ID-B	300 ± 10	610 ± 86
ID-C	820 ± 43	1300 ± 31
ID-D	10000 ± 15000	8500 ± 660
WA-A	120 ± 7	200 ± 14
WA-B	230 ± 5	430 ± 28
TN	2600 ± 470	9700 ± 1100
SC	82 ± 1	190 ± 9
NY	920 ± 79	2300 ± 330
NM	400 ± 11	420 ± 7
AR-A	2900 ± 1800	3300 ± 240
AR-B	390 ± 20	760 ± 72
AR-C	1800	2300 ± 50
IL	1600 ± 190	1900 ± 22

Table 4-22. Sorption of americium in soils; distribution coefficients for soils in basic solutions (Polzer and Miner, 1976).

Soil	Initial Am concentration (M)	$K_{d(m)}$	pH	-Eh(V)
WA-A	$10^{-9.4}$	120	8.0	0.43
	$10^{-7.4}$	200	7.8	0.46
WA-B	$10^{-9.4}$	230	8.0	0.44
	$10^{-7.4}$	430	7.9	0.44
ID-D	$10^{-9.4}$	10,000[b]	7.8	0.45
	$10^{-7.4}$	8500	7.9	0.44
ID-C	$10^{-9.4}$	820	8.4	0.47
	$10^{-7.4}$	1,300	8.2	0.47
ID-A	$10^{-9.4}$	6,200[d]	8.1	0.44
	$10^{-7.4}$	514	8.4	0.42
ID-B	$10^{-9.4}$	300	8.7	0.43
	$10^{-7.4}$	610[b]	8.5	0.42
CO-C	$10^{-9.4}$	5200	8.0	0.42
	$10^{-7.4}$	8100	8.0	0.44

[a-d] The standard error of the mean is: a, 10% or less; b, between 12% and 20%; c, 32%; and d, 60%.

Table 4-23. Sorption of americium in soils; distribution coefficients for soils in acid solutions (Polzer and Miner, 1976).

Soil	Initial Am concentration ($\underline{M}$)	$K_{d(m)}$	pH	-Eh(V)
SC	$10^{-9.4}$	82	6.1	0.54
	$10^{-7.4}$	190	5.9	0.55
NM	$10^{-9.4}$	400	6.9	0.49
	$10^{-7.4}$	420	7.3	0.48
TN	$10^{-9.4}$	2000^{b}	5.2	0.49
	$10^{-7.4}$	9700^{b}	5.1	0.49
AR-B	$10^{-9.4}$	390	6.6	0.57
	$10^{-7.4}$	760	6.5	0.56
CO-A	$10^{-9.4}$	2500	6.6	0.41
	$10^{-7.4}$	2600	6.4	0.43
CO-B	$10^{-9.4}$	600	6.4	0.52
	$10^{-7.4}$	840	6.4	0.43
AR-C	$10^{-9.4}$	1800	5.9	0.57
	$10^{-7.4}$	2300	6.0	0.60
IL	$10^{-9.4}$	1600^{b}	5.9	0.56
	$10^{-7.4}$	1900	5.8	0.56
AR-A	$10^{-9.4}$	820^{c}	6.6	0.57
	$10^{-7.4}$	3300	6.5	0.56
NY	$10^{-9.4}$	920	6.2	0.45
	$10^{-7.4}$	2300^{b}	6.0	0.50

[a-d] The standard error of the mean is: a, 10% or less; b, between 12% and 20%, c, 32%; and d, 60%.

SUMMARY AND RECOMMENDATIONS

Published literature concerning the sorption distribution coefficients of plutonium, neptunium, americium, and curium on soils and sediments was reviewed and the K_d data for the four radionuclides were compiled in tabular form. Very few studies for K_d determination have been conducted for neptunium and there is only one reference in the literature for curium K_d. The available sorption data show a wide variation in radionuclide K_d values.

The recommendations for future studies are as follows:

1. A detailed investigation should be done of the mechanisms (such as ion exchange, precipitation or formation of complex anions), involved in the uptake of the polyvalent radionuclides (such as plutonium and americium) by soil.
2. In future adsorption studies, multiple regression analysis techniques should be employed to determine the combination of soil properties (such as particle size distribution, soluble salt, silt, clay, organic carbon, CEC, or pH) that best account for the retention of radionuclides in soils.
3. Tests should be done under conditions that are close to those existing in the field, that is, with undisturbed samples. Most tests in the literature for K_d determination have been conducted either on artificially prepared soil samples or on field samples that were highly disturbed (exposed to the atmosphere and disaggregated).
4. Studies should be done to understand and identify the radionuclides species or element valence states [such as Pu(IV) or Pu(V)] that are adsorbed in the soil.
5. Studies are needed on the anion species that combine with polyvalent radionuclides to form complex anions and thus inhibit nuclide uptake by soil.

6. Because the ultimate secondary container in a repository for disposal of high-level radioactive waste will be some rock stratum, sorption data on rocks are required. Experiments should be conducted to determine the distribution coefficients on rocks.

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APPENDIX 4-1: SUMMARY TABULATION OF DISTRIBUTION COEFFICIENT

Table A. Review of the literature on radionuclide K_ds. Batch

Tracer element	Actinide valence	Equilibrium distribution coefficient K_d (mℓ/g)	Solution/waste composition and pH	Actinide concentration in solution before contacting with soil	Soil-to solution ratio (g/mℓ)	Shaking time
^{239}Pu	not specified	From 18 to $\geqslant$ 1980 (see Fig. 4-1 and Table 4-2).	Solution prepared using distilled water; pH adjusted by adding NaOH or HCl.	0.01 μCi/mℓ	1:20	Three hours
Pu	III, IV, VI	From 6.0 to $\geqslant$ 10,000 (See Figure 4-2).	Solution prepared using distilled water; pH adjusted by adding NaOH or HNO_3.	0.05 μCi/mℓ	1:10	Two hours
^{239}Pu and ^{241}Am	not specified	For Pu, from 1.4 to 1540; for Am, from < 1.0 to 500; (see Table 4-3).	Synthetic waste prepared by mixing high-salt, acidic aqueous phase (5.4 M NO_3^-) with organic compounds.	Synthetic waste spiked with actual chemical processing waste containing Pu and Am.	not specified	not specified
Pu	IV	From 11 to 8.3 X 10^4 (see Table 4-6).	Solution prepared using distilled water; solution pH adjusted initially with NaOH to 7.0.	Original spike of Pu^{4+} in 1 M HNO_3	1:250	not specified
Np, Pu, Am, Cm	not specified	K_d for Np = 15, K_d for Pu = 2000, K_d for Am = 2000, and K_d for Cm = 600.	Typical nonsaline groundwater pH = 6.8-8.2 . (See p. 3.55 of this reference for groundwater composition.)	not specified	not specified	not specified
^{237}Pu	III, IV, VI	For oxic conditions: from 1.3 X 10^4 to 5.7 X 10^1; For anoxic conditions: from 9.3 X 10^3 to 9.4 X 10^4 (see Table 4-7).	Sea water, pH = 7.8-8.0 for both oxic and anoxic conditions.	Pu added to sea water in III, IV, and VI valence states.	not specified	not specified
^{238}Pu	not specified	From 1.0 to 240 (see Table 4-8).	Simulated plant waste supernate (5.75 M Na^+, 0.5 M AlO_2^-, 0.75 M OH^-, 2.2 M NO_3^-, 1.1 M NO_2^-, 0.3 M CO_3^{2-}, 0.3 M SO_4^{2-}, and 0.0002 M Cs^+)	Supernate contained 1.75 X 10^7 dis/(min)(mℓ)^{238}Pu	1:10	Resin shaken overnight with synthetic supernate
$^{239\text{-}240}Pu$ and ^{241}Am	not specified	For Pu, from 200 to 10,000; for Am, from 400 to 50,000; (see Table 4-9 and 4-10).	90% saturated NaCl solution, pH = 7-8.	not specified	1:150	not specified

DATA FOR PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM

equilibrium test data for plutonium, neptunium, americium, and curium.

Initial soil pH	Soil cation exchange capacity (meq/100g)	Soil/material type and content	Particle size and distribution	Observations/comments	Reference
8.6	5.0	Subsurface soil from Hanford Project. Unconsolidated, unweathered sediments having silt, clay, and ≈ 2% free $CaCO_3$. Clay fraction contains montmorillonite and kaolinite in the ratio of 3:1.	As percent by weight: > 2 mm diam, 6% 2 to 0.2 mm, 67% 0.2 to 0.02 mm, 19% 0.02 to 0.002 mm, 6% < 0.002 mm, 2%	K_d values in Table 4-2 suggest existence of a Pu polymer in solution at pH > 2 with the exception of pH range 8 to 12. Apparently the polymer formed carries a positive charge that enables it to be taken up rapidly by the soil.	Rhodes 1952, 1957a, 1957b
not specified	Ranged from 0.012 for soil pH 4 to 1.24 for soil pH 10 (see Table 4-3).	Soil samples from water table at Savannah River Plant contained 20% clay and 80% sand. Dominant clay mineral – kaolinite.	not specified	Adsorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH 2.5 and 12 and from solutions of Pu(VI) at pH > 6.	Prout, 1958, 1959
not specified	not specified	Soil from various depths between the surface and groundwater from wells at Z-1A tile field site, Richland, Wash., air-dried and sieved to < 2 mm diameter.	not specified	Adsorption from strongly acid or partially neutralized waste was minor. Adsorption from alkaline waste from precipitation was high. Introduction of a slug of organic reduced the K_d of both Pu and Am.	Hajek and Knoll, 1966
not specified	not specified	Study conducted with different minerals (see Table 4-6).	not specified	The amount of radionuclide removed (adsorbed) from the solution appears to depend on the pH of the suspension; the higher pH favors greater removal by formation of nuclide hydroxides which are scavenged by the clays (see Table 4-6).	Tamura, 1972
7.0 to 8.2	5.0	Typical western desert soil–sand or sandy loam containing ≈ 1 mg of free $CaCO_3$ per gram of soil.	not specified		Schneider and Platt, 1974.
not specified	not specified	Study conducted on marine sediments from Mediterranean Sea using sedimentation (water column) and thin layer methods.	not specified	K_d values for both oxic and anoxic conditions appear similar for all three valence states	Duursma and Parsi, 1974
not specified	not specified	Synthetic ion exchange resins (see Table 4-8).	not specified	Out of the five resins tested, sorption of Pu was maximum by "Duolite" ARC-359.	E. I. DuPont de Nemours & Co., 1975
not specified	not specified	Various soil materials (clay, sandstone, caprock and coarse river sand) from boreholes surrounding salt formations in NE Netherlands.	not specified	K_d values for caprock and river sand were lower than clay containing material due to the absence of clay material in them.	Hamstra and Verkerk, 1977

Table A. Review of the literature on radionuclide K_ds. Batch equilibrium test

Tracer element	Actinide valence	Equilibrium distribution coefficient K_d (mℓ/g)	Solution/waste composition and pH	Actinide concentration in solution before contacting with soil	Soil-to solution ratio (g/mℓ)	Shaking time
^{238}Pu and ^{241}Am	IV for Pu, III for Am	Equilibrium surface absorption constant K(cm^2/mℓ): For 4 X 10^{-5} $\underline{M}$ solution of $Pu(NO_3)_4$= 0.10 ± 0.02 for limestone, 0.07 ± 0.02 for basalts. For 10^{-7} $\underline{M}$ solution of $Am(NO_3)_3$= 0.041 ± 0.02 for basalts. (See Figures 4-3, 4-4, 4-5 for the effect on K of other ions.)	Tracer solutions prepared using aliquots of small solutions of the tracer and evaporating them to dryness with HNO_3. Am and Pu brought into solution with distilled water; original solution pH = 7.0, *final pH ranged between* 7 and 8.	Disks of limestone and basalt immersed in solutions of 4 X 10^{-5} $\underline{M}$ $Pu(NO_3)_4$ or 10^{-7} $\underline{M}$ $Am(NO_3)_3$	not specified	Alpha or gamma counting rate of aliquots counted at 12-hr. intervals until equilibrium.
$^{239\text{-}240}$Pu	not specified	Mean K_d for seven samples = 8 X 10^4. Mean K_d for field particulates in the groundwater = 2.5 X 10^5 (see Table 4-11).	Pu-contaminated soil samples equilibrated in the laboratory with uncontaminated sea water.	not specified	not specified	not specified
^{237,238,239}Pu	IV, VI	For soil clay fraction, K_d = 7.5 X 10^4 to 16.8 X 10^4; for reference montmorillonite K_d = 2.5 X 10^2 to 2.1 X 10^4; (see Table 4-12).	Studies conducted in Ca-acetate and Ca-nitrate solutions.	not specified	Varied, not specified.	not specified
^{238}Pu	IV	From 3.5 X 10^2 to 2.9 X 10^5 (see Table 4-13).	Study conducted in 5 X 10^{-3} $\underline{M}$ $Ca(NO_3)_2$ *solution.*	^{238}Pu added at about 0.6 ppm (Pu mass/clay mass).	not specified	Equilibration time = 3 weeks to 52 weeks.
Pu and Am	IV for Pu, III for Am	For Pu: from 35 to 14,000 (see Tables 4-15, 4-16 and 4-17). For Am: from 82 to 10,000 (see Tables 4-21, 4-22, and 4-23).	Solutions prepared by diluting in 0.5 HNO_3 standard solutions of plutonium and americium, respectively. Solutions were kept acidic to prevent hydrolysis and polymerization of plutonium.	Initial Pu concentrations of 10^{-8} $\underline{M}$, 10^{-7} $\underline{M}$ and 10^{-6} $\underline{M}$, respectively. Initial Am concentrations of 10^{-10} $\underline{M}$ and 10^{-8} $\underline{M}$.	1:5	Equilibration time: = 5 to 48 hours for Pu; = 24 to 48 hours for Am.
^{237}Np and ^{241}Am	not specified	K_d = 0.16 to 3.9 for Np; = 1.0 to 280 for Am (see Table 4-20).	Study conducted in varying concentrations of $Ca(NO_3)_2$ and $NaNO_3$ solutions. Initial solution pH = 2.5 for E. Washington; = 3.1 for S. Carolina	Influent activity = 3.7 μCi/25 mℓ for E. Washington; = 1.0 μCi/25 mℓ for S. Carolina.	1:2.5	20-30 minutes; equilibration time = 21 to 24 hrs.

data for plutonium, neptunium, americium, and curium (continued).

Initial soil pH	Soil cation exchange capacity (meq/100g)	Soil/material type and content	Particle size and distribution	Observation/comments	Reference
not specified	not specified	Thin wafers or disks (25 mm diam. and 1.5 mm thick) of dense Illinois Niagra limestone and basalt from EBR-II site (Idaho National Engineering Laboratory).	not specified	The surface absorption coefficients are affected by the types and concentrations of other salts. For example, all curves for both Pu and Am in Figures 4-3, 4-4 and 4-5 show the same trend, i.e. displacement of the actinide ions from the rock lattice by higher concentrations of other metallic ions.	Fried, et al., 1974, 1976a, 1976b
not specified	not specified	Pu - contaminated soil samples from the islands of Eniwetok Atoll	not specified	K_d values from field results (from particulates in the groundwater) and laboratory tests are very close.	Noshkin, et al., 1976
6.5 (aqueous phase 5 m$\underline{M}$ in Ca^{2+})	not specified	Ca-saturated clay from Miami silt loam soil and montmorillonite as reference clay.	not specified	Sorption of Pu (VI) to montmorillonite was substantially less (37%), whereas sorption of Pu to Miami silt loam clay was always above about 99.4%, regardless of initial valence.	Bondietti, et al., 1976
4.0	not specified	Ca-saturated clay from Miami silt loam soil. The clay fraction was treated to remove organic matter and free iron oxides.	not specified	After 18 weeks of equilibration, the presence of a significant fraction of the soluble Pu in the solution (soluble Pu species which do not sorb) suggested the formation of a different Pu oxidation state than that initially added i.e., formation of a polymer (Pu VI or Pu V). Pu valence state identification in experimental systems is therefore necessary for adsorption studies.	Bondietti and Reynolds, 1976
Ranged from 2.3 to 8.3. (see Table 4-14).	Ranged from 2.9 to 34.4 (see Table 4-14).	17 soil samples from various present and probable future Pu-handling areas in the U.S (see Table 4-14).	See Table 4-14.	K_d values are very sensitive to changes in Pu and Am concentration, especially at high levels of Pu and Am soprtion (see Tables 4-15 and 4-21).	Glover, et al., 1976 Polzer and Miner, 1976
For E. Washington soil = 7.0; for S. Carolina = 5.1	For E. Washington soil = 4.9; for S. Carolina = 2.5	Subsoils from East Washington and South Carolina (see Table 4-19).	not specified	Distribution coefficients measured on subsoils as a function of equilibrium solution concentration of Ca^{2+} and Na^{+} decreased for both neptunium and americium. For South Carolina subsoil: $K_d(N_p) = f(Ca^{2+}) = 0.43$ to 0.66; $= f(Na^{+}) = 0.16$ to 0.25 $K_d(Am) = f(Ca^{2+}) = 1.0$ to 67; $= f(Na^{+}) = 1.6$ to 280 For East Washington soil: $K_d(N_p) = f(Ca^{2+}) = 0.36$ to 2.37; $= f(Na^{+}) = 3.19$ to 3.90 $K_d(Am) > 1200$	Routson, 1975, 1976

Table B. Review of the literature on radionuclide K_ds. Column test

Tracer element	Equilibrium distribution coefficient K_d (mℓ/g)	Soil/material type and content	Soil cation exchange capacity. (meq/100g)	Solution/waste composition and pH
^{239}Pu and ^{241}Am	See p. 7 of this reference for breakthrough curves.	Surface soil (< 20′) from wells at Z-1A tile field site, Richland, Wash., sieved to < 2 mm diameter.	not specified	Synthetic waste prepared by mixing ing high salt, acidic aqueous phase (5.4 M NO_3^-) with organic compounds. (See p. 2 of this reference for waste composition.)
^{239}Pu and ^{241}Am	For $TBP\text{-}CCl_4$:[a] K_d = 5.4 for Pu and 1.6 for Am For $DBBP\text{-}CCl_4$: K_d = 0 for Pu and 0.6 for Am For D2EHPA-TBP: K_d = 0 for both Pu and Am (see Table 4-5).	Soil from the bottom of the excavation for 241 AX tank farm, Hanford, sieved to < 2 mm diameter.	not specified	Various organic wastes from Hanford radionuclide separations plant ($TBP\text{-}CCl_4$, $DBBP\text{-}CCl_4$, Fab Oil, 0.4 M D2EHPA-0.2 M TBP in NPH.)
Pu	With dry soils: K_d = 6000 for short column = 3000 for long column With moist soils: K_d = 0.4 for solvent > 30 for aqueous phase instead of solvent.	Dry (ground-surface) and moist (subsurface) soils from Savannah River plant waste burial ground.	not specified	Separations process (radioactive) solvent from underground tanks. (See p. 53 of this reference for chemical composition.)
Pu	From 144 to 5020 (See Table 4-18).	Three soil samples from various present and probable future Pu-handling areas in the U.S. (see Table 4-14).	Ranged from ≈14 to 20 (see Table 4-14).	Column elution study done using Pu nitrate solution.

[a] TBP = tributylphosphate
DBBP - dibutylbutylphosphonate
D2EHPA - di-(2-ethylhexyl) phosphoric acid
Fab Oil - "fabrication oil," a commercial mixture of Lard oil and CCl_4 (25-75 vol. %)
NPH - "normal paraffin hydrocarbons," a commercial mixture of straight chain hydrocarbons including decane, undecane, dodecane, tridecane, and tetradecane.

data for plutonium, neptunium, americium, and curium.

Actinide concentration in solution	Column length and inner diameter (cm)	Column volumes needed for 50% breakthrough	Permeability/ flow rate	Observations/comments	Reference
Synthetic waste spiked with actual chemical processing waste containing Pu and Am.	10.0; 1.9	Between 1.5 and 4.0 for ^{239}Pu, < 0.01 for ^{241}Am	not specified	Uptake of Pu by the soil was very minor and of Am negligible.	Knoll, 1965
Organic wastes from Hanford separations plant spiked with ^{239}Pu and ^{241}Am.	Length = 5.0 and 10.0 respectively, ID = 0.8	For TBP-CCl_4:[a] 30 for Pu and 9 for Am. For DBBP-CCl_4: 3.5 for Am and no adsorption of Pu by soil. For Fab Oil: erratic results. For 0.4 M D2EHPA - 0.2 M TBP in NPH: No adsorption of Pu or Am by soil from this organic.	See pp. 5,6 of this reference for soil permeability to organic wastes.	Soil removed ^{239}Pu and ^{241}Am slowly from some of the organics and not at all from others.	Knoll, 1969
Migration studies simulated postulated leaks into the ground using solvent-complexed Pu from tanks.	Length = 6.6 and 14.7 respectively	not specified	not specified	Tests showed that small volumes of solvent-complexed Pu will not migrate significantly through dry surface soil, but large volumes in moist subsurface soil would be more mobile.	E. I. Dupont de Nemours & Co., 1975
Column packed with 24 g of soil, 1 g of which was mixed with 10 µl of a 10^{-3} M Pu nitrate solution and distributed evenly on top of the soil in the column.	4.0; 1.0	Column washed with 1 ℓ distilled water and effluent collected in 20 ml fractions and analyzed for Pu.	Flow rates = 15 min, 90 min, and 180 min per 20 ml respectively.	The soil with the lowest K_d retained the least amount of Pu while the soil with the highest K_d retained the most.	Glover, et al., 1976

APPENDIX 4-2: GLOSSARY

adsorption	The observed decrease in the initial solution concentration of a nuclide in which the most probable mechanism is identified as a coulombic attraction of the nuclide to the surface of the adsorption solid (Bensen, 1960).
alpha	Used with respect to radiation--a positively charged particle consisting of two protons and two neutrons (ASME, 1957).
basalt	Dark grey to black, dense, fine-grained, igneous rock consisting of plagioclase, augite, and magnetite (G. & C. Merriam Co., 1965).
beta	Used with respect to radiation--a negatively charged particle emitted from the nucleus of an atom and having a mass and charge equal in magnitude to those of an electron (ASME, 1957).
breakthrough	The first detectable concentration of a nuclide in a column effluent (Bensen, 1960).
C/C_o	The amount of a nuclide in the effluent of a soil column divided by the amount of that nuclide added in the influent (Bensen, 1960).
cation exchange capacity	The concentration of an exchangeable cation adsorbed by a soil at pH 7 determined by a standard method (Bensen, 1960).
count	A radiation measurement or indication of a device designed to enumerate disintegrations or events. It may refer to a single detected event or a total registered in a given period of time. It should not be confused with disintegration, as the two terms do not mean the same. The relationship between count and disintegration must be established by a calibration procedure (ASME, 1957).

curie	A measure of radioactivity meaning the quantity of a nuclide disintegrating at the rate of 3.7×10^{10} atoms per second; abbreviated as Ci; a microcurie (μCi) is one millionth of a curie (3.7×10^4 disintegrations per second); a picocurie (pCi) is one millionth of a microcurie (ASME, 1957).
gamma	Relates to radioactivity and means a ray of short wavelength which is emitted from a disintegrating nucleus (ASME, 1957).
half-life	Refers to the time that a substance is radioactive--the time required for a radioactive element to lose 50% of its activity. Each nuclide has a unique half-life (ASME, 1957).
Hanford soil	Representative soil of the Hanford Works, Richland, Washington (Bensen, 1960).
high-level liquid wastes	Liquid wastes containing greater than 100 μCi/ml of mixed radioactivity (Beard and Godfrey, 1967).
intermediate-level liquid wastes	Liquid wastes containing between 5×10^{-5} and 100 μCi/ml of mixed radioactivity (Beard and Godfrey, 1967).
ion exchange	The equivalent replacement of an adsorbed ion on a solid adsorbent by another ion from the solution (Bensen, 1960).
isotope	One of several forms of one element having the same number of protons in the nucleus and thus the same atomic number, but having a different number of neutrons and thus a different mass number; e.g., strontium-89, strontium-90 and strontium-91 all with atomic number 38 (ASME, 1957).

K_d	A term representing the equilibrium distribution coefficient of a nuclide, A, between the solid adsorbent and the solution at equilibrium: $K_d = \frac{A_{solid}}{A_{soln.}} \times \frac{cc_{soln.}}{g_{solid}}$ where: A_{solid} is the amount of A that is associated with the adsorbent; $A_{soln.}$ is the amount of A that remains in the solution; $cc_{soln.}$ is the total volume of solution in cc; and g_{solid} is the total weight of adsorbent in g (Bensen, 1960).
leach	To subject to the action of percolating water or other liquid in order to separate and remove soluble compounds (G. & C. Merriam Co., 1965).
leachate	The percolating solution (Schmalz, 1972).
loam	A soil consisting of a friable mixture of varying proportions of clay, silt, and sand (G. & C. Merriam Co., 1965).
loessial	A buff to yellowish brown loamy deposit (soil) believed to have been deposited by wind (G. & C. Merriam Co., 1965).
low-level liquid wastes	Liquid waste containing less than 5×10^{-5} µCi/ml of mixed radioactivity (Beard and Godfrey, 1967).
nuclide	A species of atom chracterized both by number of protons and neutrons; e.g., strontium-90, atomic number 38 and cesium-137, atomic number 55 (ASME, 1957).
percolate	To pass through a permeable substance, to penetrate (G. & C. Merriam & Co., 1965).
surface absorption coefficient	Represented as K and defined as the ratio of radioactivity in a milliliter of solution to the radioactivity absorbed per square centimeter of rock: $K = \frac{\text{(activity of actinide/ml of solution)}}{\text{(activity of actinide/cm}^2\text{ of rock)}}$ (Freid, et al., 1976a).

uptake	The observed decrease from the initial concentration of a solution contacting soil, regardless of the mechanism of removal such as adsorption, precipitation, etc. (Bensen, 1960).
vadose	Of, or relating to, or being in the earth crust above the permanent ground water level (Schmalz, 1972).
water table	The upper limit of the portion of the ground wholly saturated with water--a plain or surface (G. & C. Merriam Co., 1965). The natural water table is different from a perched water table, which is usually caused by the activity of man such as waste disposal or irrigation, etc. Perched water, whether caused by man or other natural causes, is localized in extent at a higher elevation that the natural or regional water table (Schmalz, 1972).

SECTION 5: PRELIMINARY CONSIDERATIONS IN DETERMINING AN EXPERIMENTAL METHOD TO MEASURE RADIONICLIDE TRANSPORT IN WATER-SATURATED ROCKS

INTRODUCTION

One of the most pressing problems in this task was choosing an experimental configuration to measure radionuclide transport in rocks. At first, it seemed reasonable to treat a rock rather like a chromatographic column in which the migration of radionuclides might be examined as a function of time. Water could be forced through a given thickness of rock, and the degree of retardation of the radionuclide measured. In order to test this approach, information on rock physical properties was gathered as a first step. The data obtained were then used to compute the differential pressures needed to force specified volumes of water through a cylindrical rock core of given diameter in an experimentally reasonable length of time.

The calculations showed that for practically all rock types, the pressures required were experimentally unreasonable. In fact, it became obvious that for most host rocks, flow along fractures could be the only means by which radionuclides might migrate significant distances. The experiment should therefore be designed to study radionuclide migration principally along fractures, with diffusion into the rock on either side.

The following subsections contain a brief description of the results obtained from a literature study of the physical properties of rocks and give the calculations used to determine the experimental feasibility of forcing water through solid rock cores.

ROCK PHYSICAL PROPERTIES

The rate of transport of a radionuclide through a porous medium depends on the physical and chemical properties of the medium in question. this section reviews the physical properties of selected rocks that may be candidates for radioactive waste storage repositories.

The ranges of values of these physical properties are presented in Table 5-1. The most abundant data were found on rocks that bear some economic interest, such as oil sands. On such rocks, ample data afford crude statistics of the reproducibility and credibility of the data range. For rocks of low economic association, such as rhyolites, no direct data were found on such physical properties as porosity and

Table 5-1. Rock physical properties.

Rock type	Dry density (g/cm^3)	Water saturated density (g/cm^3)	Water content (%)	Grain size (mm)	Porosity (%)	Permeability (cm^2)	References
Argillite	2.70-2.94			<0.0625	2.69-10	5.68×10^{-12}	Kemp, 1970; Jackson, 1970; Reich, 1973; Schoeller, 1962
Basalt	2.76-2.95	2.763-3.03[a]	1-2.7	<0.1	0.1-11.4	3.35×10^{-20}[b] -1.33×10^{-13}	Kemp, 1970; Fried, et al., 1974; Hyndman and Drury, 1976; Schoeller, 1962; Duncan, 1969; Griffith, 1937; Davis, 1969
Gabbro	2.55-3.12	2.56-3.15[a]	0.37-1.0	>0.5	0.29-3.0	$<9.87 \times 10^{-11}$	Jackson, 1970; Duncan, 1969; Vinayaka, 1965; Hyndman and Drury, 1976; Kemp, 1970; Griffith, 1937; Davis, 1969
Granite	2.52-2.81	2.52[a] -2.81	0.0[a]	0.7-1.3	7-1.3	4.6×10^{-14} -5×10^{-16}	Jackson, 1970; Kemp, 1970; Vinayaka, 1965; Duncan, 1969; Griffith, 1937; Brace, 1968
Limestone	2.21-2.76	2.39-2.77	0.36-7.5[a]	0.0625	1.0-37.6	3.36×10^{-9} -9.86×10^{-12}	Jackson, 1970; Schoeller, 1962; Locke and Bliss, 1950; Murray, 1960; Davis, 1969
Rhyolite	2.32-2.62			<0.05	4-15.5		Jackson, 1970; Kemp, 1970; Schoeller, 1962
Sandstone	1.93-2.50	2.2-2.55	2.0-14[a]	0.0625	5.4-27.1	5×10^{-12} 3×10^{-8}	Jackson, 1970; Vinayaka, 1965; Scheidegger, 1960; Davis, 1969

[a] Calculated in this report from saturated densities.
[b] Calculated in this report from hydraulic conductivity values (in Atlantic Richfield Hanford Co., 1976).

permeability. Permeability values for basalt were calculated from hydraulic conductivity formulas (Davis, 1969) employing statistically averaged literature values of density and viscosity. Hydraulic conductivity data were taken from Atlantic-Richfield Hanford Co. (1976).

DIFFERENTIAL PRESSURE REQUIREMENTS FOR FORCING WATER THROUGH ROCK CORES

Experiments on K_d values and migration rates of ions in geologic formations can be done by at least two methods: (a) forcing a given volume of solution through a column of rock; or (b) allowing solution to adsorb on the surfaces of rock specimens. An intercorrelation of the migration coefficients and surface-adsorption coefficients to the migration through porous rock has been demonstrated by Fried, et al. (1974). The purpose of this section is to determine the differential pressure needed to force a given volume of solution through a column of rock. These calculations should provide valuable insight on how to design experiments to measure migration rates and K_d values.

In order to make the necessary calculations, a conceptual model of a rock was specified. This model assumes that the rock grains are uniform packed spheres, that the radionuclide is adsorbed as a monolayer on the exposed surfaces of the rock mineral grains, and that one atom is adsorbed for each 25Å^2 of surface area. Implicit in the last assumption is an infinitely large K_d. In other words, all of a radionuclide is quantitatively removed from solution, as long as there are available sites upon which the radionuclide might adhere. This represents a limiting case, which is useful in determining experimental constraints.

By using the data on grain size given in Table 5-1 and the assumptions given above, it is easy to calculate the volume of fluid needed to saturate the internal surface of a cubic volume of rock. Thus:

$$\text{volume of liquid needed to saturate} = \frac{\pi d^{N}\underline{m}}{2a}$$

where d = length of one side of a cube,

a = radius of a mineral grain,

N = Avogadro's number, and

$\underline{m}$ = molality of the radionuclide.

The time needed to saturate a given internal volume of rock depends on the permeability, thickness, and exposed surface of the rock, the properties of the fluid, and the pressure applied to the fluid to force it through the rock. In order to calculate the pressure required to saturate the rock in an experimentally reasonable length of time, an expression relating these parameters must be derived.

If v_x is the velocity of the fluid (measured as fluid flux across a unit area of porous medium) in the direction x, and dP/dx is the pressure gradient at the point to which v_x refers, then Darcy's law may be expressed as:

$$v_x = (k/\mu)\frac{dP}{dx} \qquad (1)$$

where k is the permeability of the medium and μ is the viscosity of the fluid. In addition, if A is the cross-sectional area of the column and Q is the volume of liquid passing through it per unit time, then

$$V_x = Q/A \quad . \qquad (2)$$

Furthermore, by combining and rearranging equations (1) and (2), one gets:

$$kdP = (\mu Q/A)\ dx \quad . \qquad (3)$$

Consider a slab of material of thickness, L, with liquid being forced through and with P_1 and P_2 as the terminal pressures. Equation (3) can be integrated over the slab thus:

$$k\int_{P_2}^{P_1} dP = \left(\frac{\mu Q}{A}\right)\int_0^L dx \qquad (4)$$

$$k(P_1 - P_2) = \frac{\mu QL}{A} \qquad (5)$$

$$P_1 = \frac{\mu QL}{AK} + P_2 \qquad (6)$$

Using average values of permeability for six rock types (argillite, basalt, gabbro, granite, limestone, and sandstone), the pressure differential was calculated across 2.54-cm-diameter cores 1-cm long. It was assumed

Table 5-2. Pressure differentials required across rock cores to ensure experimentally reasonable aqueous solution flow rates.

	1 day		5 days		10 days		20 days	
	Concentration		Concentration		Concentration		Concentration	
Rock type	10^{-9} M	10^{-6} M	10^{-9} M	10^{-6} M	10^{-9} M	10^{-6} M	10^{-9} M	10^{-6} M
Argillite								
Volume to saturate (l)	3.34×10^{2}	3.34×10^{-1}						
Pressure (atm)	3.31×10^{4}	3.41	6.62×10^{3}	7.62	3.31×10^{3}	4.31	1.66×10^{3}	2.66
Basalt								
Volume to saturate (l)	2.09×10^{2}	2.09×10^{-1}						
Pressure (atm)	3.51×10^{12} to 8.84×10^{5}	3.51×10^{-9} to 8.84×10^{2}	7.02×10^{11} to 1.78×10^{5}	7.02×10^{8} to 1.78×10^{2}	3.51×10^{11} to 8.84×10^{4}	3.51×10^{8} to 8.84×10^{1}	1.76×10^{11} to 4.42×10^{4}	1.76×10^{8} to 4.42×10^{1}
Gabbro								
Volume to saturate (l)	4.17×10^{1}	4.17×10^{-2}						
Pressure (atm)	2.38×10^{3}	3.38	4.77×10^{2}	1.48	2.39×10^{2}	1.24	1.20×10^{2}	1.12
Granite								
Volume to saturate (l)	1.60×10^{1}	1.60×10^{-2}						
Pressure (atm)	1.81×10^{7} to 1.96×10^{5}	1.81×10^{4} to 1.96×10^{2}	3.62×10^{6} to 3.90×10^{1}	3.62×10^{3} to 1.96×10^{1}	1.81×10^{6} to 1.96×10^{-4}	1.81×10^{3} to 1.96×10^{1}	9.04×10^{5} to 9.83×10^{3}	9.04×10^{2} to 9.83
Limestone								
Volume to saturate (l)	1.04×10^{1}	1.04×10^{-2}						
Pressure (atm)	5.97×10^{2} to 1.8	1.50 to 1.02	1.20×10^{2} to 4.50	1.12 to 1.00	6.0×10^{1} to 2.80	1.06 to 1.00	2.1×10^{1} to 1.9	1.03 to 1.00
Sandstone								
Volume to saturate (l)	1.04×10^{2}	1.04×10^{-1}						
Pressure (atm)	1.18×10^{3}	2.18	2.36×10^{2}	1.24	1.19×10^{2}	1.12	6.0×10^{1}	1.06

that the water required to saturate the core could be forced through in 1, 5, 10, or 20 days. The initial concentration of the radionuclide was assumed to be 10^{-9} and 10^{-6} M/l. Table 5-2 shows the resulting pressure differentials for the different cases being considered.

Pressures were relatively high for rocks with low permeability, leading to the conclusion that any significant flow in those rocks must be along fissures. Measurement of K_d values would have to be made by a surface adsorption method because, if the rocks were homogeneous and free of incipient fractures, solid core studies would require relatively high pressures to force solutions through the rocks.

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SECTION 6: REVIEW OF TRANSPORT MECHANISMS OF RADIONUCLIDES IN WATER-SATURATED ROCKS

INTRODUCTION

Transport of radionuclides in water-saturated rock involves both physical and chemical processes. The physical nature of the system determines the rate of fluid flow, while chemical processes lead to exchange of mass between the fluid and the solid phases. A variety of chemical processes can occur, including dissolution, precipitation, ion exchange, sorption, and ultrafiltration. Physical processes can be grouped into two principal categories of transport--advection and diffusion. Diffusion occurs in solids, along surfaces, and in the aqueous phase. Solid-state diffusion is an extremely slow process and may be ignored in all but exceptional situations in natural systems having temperatures less than 100°C. Diffusion in the aqueous phase (or longitudinal diffusion, which is taken to mean three-dimensional diffusional processes) is not a rapid process compared with the speed of certain chemical reactions, such as hydrolysis reactions. However, diffusion in the aqueous phase may proceed at a rate comparable with the rate of advection in many natural systems. The nature of the porous media also leads to a process known as dispersion or eddy-diffusion. As the mobile phase flows around obstacles in its path it encounters regions where flow is hindered and those where flow is relatively unimpeded. Because the fluid avoids obstacles along the path of least resistance, the velocity fluctuates over wide limits. Thus velocity varies from channel to channel because of the viscous constraint of the containing walls. The phenomenon of eddy-diffusion is caused by such point-to-point variations in flow velocity. A molecule in a fast streampath will take a step forward to the center of mass (zone), while a molecule in a slow streampath will take a step backwards relative to the center of mass. As a molecule follows its original streampath, it is carried into a part of the channel network that has a velocity differing from the velocity of the original streampath. Lateral diffusion will also cause a molecule to enter a new velocity regime. As a result of these processes, zone spreading occurs and the chemical front "flattens."

CHEMICAL RETARDATION AND THE DISTRIBUTION COEFFICIENT

In the absence of competitive processes, the center of mass of a solute zone would move at about the same rate as the mobile aqueous phase. However, various physico-chemical processes, such as sorption, tend to retard the passage of solute. Giddings (1965) has generalized the dynamics of zone migration. A zone migrates smoothly at some fraction R of the mobile phase velocity. Thus the zone velocity is Rv, where v is the average velocity of the mobile phase. If R is the fraction of solute in the mobile phase, then 1 - R is the fraction in the stationary phase or the amount adsorbed. The term R/(1-R) is thus the ratio of the solute in the mobile phase to solute in the stationary phase, and

$$\frac{R}{1 - R} = \frac{C_m V_m}{C_s V_s} \qquad (1)$$

where C_m is the concentration in the mobile phase, V_m is the volume of the mobile phase, C_s is the concentration of the stationary phase, and V_s is the volume of the stationary phase.

The distribution coefficient, K_d, is defined as

$$K_d = \frac{C_s}{C_m} \quad . \qquad (2)$$

Therefore, equation (1) reduces to

$$\frac{R}{1 - R} = \frac{V_m}{V_s K_d} \quad . \qquad (3)$$

Because the velocity of the solute is given by

$$v_i = vR \qquad (4)$$

the relative velocity of the solute species i with respect to the mobile phase yields the classical expression of Martin and Synge,

$$R = \frac{v_i}{v} = \frac{V_m}{V_m + K_d V_s} \qquad (5)$$

which reveals the relation between retardation and the distribution coefficient.

QUANTITATIVE TREATMENT

Measurements of distribution coefficients have been done principally by two methods, batch experiments and column experiments. The theoretical treatment of column processes can be roughly divided into two groups, rate theories and equilibrium theories (Helfferich, 1962).

In rate theories, calculations are based on continuous flow through the column and finite rates of ion exchange or adsorption. These theories are predictive but are also mathematically complex. Therefore, rate laws and assumptions about equilibrium are often simplified. Such theories (for example, Giddings, 1965, pages 119-193) fail to bring out the self-sharpening effects of favorable equilibrium.

In equilibrium theories, local equilibrium between the liquid and bed is assumed. In practice this assumption is usually not valid and deviations from local equilibrium are accounted for by introducing the concept of "effective plates." In this concept, continuous column processes are approximated by fictitious discontinuous processes. Unfortunately, this formulation is semiempirical in nature and is not predictive.

Rate Theories

One of the most general approaches to column processes can be found in the material balance treatment of Glueckauf (1949). The natural balance for an infinitesimal layer for an arbitrary species i (see Fig. 6-1) is:

$$\left(q\,\frac{\partial X_i}{\partial V}\right)_z + \left(\frac{\partial C_i}{\partial z}\right)_V - \frac{\Delta z}{2}\left(\frac{\partial^2 C_i}{\partial z^2}\right)_V - \frac{D\beta}{v\sqrt{2}}\left(\frac{\partial^2 C_i}{\partial z^2}\right)_V = 0 \qquad (6)$$

where q is the column cross section; X_i is the amount of species i in sorbent and solution per unit volume of bed; C_i is the concentration of species i in the interstitial solution; V is the solution volume, which has passed the layer since the experiment was initiated; z is the space coordinate downstream; D is the effective diffusion coefficient; β is the fractional void volume; and v is the linear flow rate.

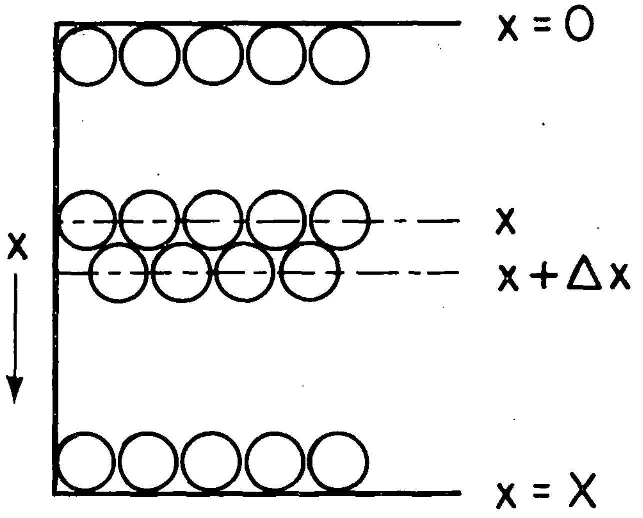

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Figure 6-1. Schematic representation of a packed bed. The material balance is set up for the "plate" between x and x+Δx (from Helfferich, 1962).

The material balance is quite general since no assumptions about local equilibrium and ion exchange or sorption isotherms have been made. Local equilibrium is a limiting case in which X_i is a function of C_i only; this function is given by the isotherm. For nonequilibrium conditions, the functional relationship between X_i and C_i must be obtained by combining equation (5) with the rate equations of ion exchange or sorption (Helfferich, 1962). It should also be noted that source and sink terms are needed to describe dissolution and precipitation reactions.

Equilibrium Theories

Although local equilibrium is difficult to achieve in column experiments, it can be achieved in batch experiments. Therefore, X_i as a function of C_i can be obtained in batch experiments and substituted into equation (6). A rigorous formulation of the thermodynamics of ion exchange was first done by Gaines and Thomas (1953). Laudelout et al. (1967) and van Bladel and Laudelot (1967) have shown how the theoretical formulation of Gaines and Thomas could be used experimentally to derive the thermodynamic equilibrium constant K for any ion exchange reaction. The beauty of the thermodynamic approach is that with a limited number of experiments, the distribution coefficient can be predicted as a function of solution concentration. The drawback to the thermodynamic approach is that it assumes a homogeneous substrate having only a single type of site.

TRANSPORT IN NATURAL SYSTEMS

In order to apply experimental data to natural systems, the experimental conditions must closely approximate those in natural environments.

Local Equilibrium

Fluid flow rates in basalt and granite environments are thought to be on the order of a few centimeters per year. Longitudinal diffusion may, in this case, dominate advection as a means of transport. Under these conditions local equilibrium probably exists between ions in exchange sites and ions in the aqueous phase. It follows that experiments should also be performed under equilibrium conditions. Certain types of batch tests, including the equilibrium dialysis method, fulfill the requirement. However, column experiments are often run at unnaturally high rates of fluid flow. In such experiments, nonequilibrium effects may dominate and the results may not be transferable to natural systems.

Geometry of the Medium

In certain natural systems, such as granite and basalt systems, fluid transport occurs primarily along fractures. These fractures are often coated with alteration products such as clays and zeolites. Other avenues of preferred flow occur along void systems that were formed subaerially when the rocks were exposed to weathering processes, which enabled clays to form. These observations suggest that clays and zeolites should be the subject of laboratory experiments.

Chemical Processes

Natural environments host not only ion exchange and sorption phenomena but also dissolution and precipitation reactions. Invariably geologic environments contain phases that were originally found under conditions of higher pressure and temperature. These metastable phases dissolve slowly over time, gradually enriching the aqueous phase in their component species. Continued dissolution leads to saturation with respect to product phases such as clays and zeolites. The precipitation of these phases provides additional substrate for ion exchange and sorption and additional solute species, which compete with radionuclides for surface sites. Laboratory experiments should reflect these interacting processes.

CONCLUSION

Transport of radionuclides in natural systems is accompanied by reactions at solid-liquid interfaces. Existing chromatographic theory cannot be used to adequately describe these processes. Extensions of chromatographic theory should include the effect of nonequilibrium and equilibrium interfacial processes. The rate of fluid transport in subsurface environments is slow. Thus, diffusional transport may be of the same order as advection transport; and fluid flow algorithms must be designed to minimize numerical dispersion. Transport occurs primarily along fracture systems in igneous terraines and the fractures are commonly coated with secondary phases such as zeolite and clays. Thus secondary, not primary, mineral phases should be the subject of sorption-desorption experiments.

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SECTION 7: COMPUTER SIMULATION OF MASS TRANSFER INVOLVING ACTINIDES IN WATER-SATURATED ROCKS: PRELIMINARY CONSIDERATIONS

INTRODUCTION

To understand radionuclide transport it is important to know the chemical behavior of the radionuclide in the environmental conditions found in the saturated rocks surrounding the waste storage repository. In general, we can expect that ground water saturating rocks fractures and pores has reached partial or complete equilibrium with respect to the mineral phases composing the rock. Alteration of the rock is also expected to have taken place where the rock minerals were in contact with an aqueous fluid not in initial equilibrium with the rock minerals. The composition of the groundwater therefore reflects the host rock and its interaction with the groundwater. If a terminal storage repository is leached by this groundwater, the groundwater composition will be modified by reaction with the waste product. Subsequent transport of the waste by groundwater movement away from the storage site will lead to a renewed attempt by the modified groundwater to reestablish equilibrium with the host rocks.

Several questions must be answered before we can establish what happens to a given radionuclide under the conditions described above. First, is it true that the groundwater achieves final equilibrium with respect to the host rocks? To what extent do bicarbonates or chlorides influence the overall composition of the groundwater? Second, what are the reactions that take place between the waste product and the groundwater? Third, what degree of complexing of the radionuclide will occur and what solid phases, if any, will precipitate? Fourth, what kind of reactions take place that lead to the removal of the radionuclide from solution? Is it adsorption, ion exchange, or precipitation? How are these reactions described?

In the introduction to this report, we emphasized that these factors can all have a critical bearing on the magnitude of the K_d value to be assigned to a particular environment. Their significance must therefore be established before more extensive computer simulations of radionuclide transport in groundwater can be made. Not all the questions posed can be addressed by the present project. For example, the leaching behavior of the waste product form is the subject of separate study under task 2 of the Waste Isolation Safety Assessment Program. However, the nature of the groundwater composition and the resulting interactions among the ground water, the radionuclide, and the host rock are relevant to this study.

COMPUTER SIMULATION OF MASS TRANSFER

During the last ten years, a powerful technique has been developed which allows for the computer simulation of complex chemical reactions between groundwater or hydrothermal fluids and rocks. This technique, originally developed by H. C. Helgeson and his coworkers at Northwestern University and described in several papers (Helgeson, 1968; Helgeson, et al., 1970), has subsequently been modified and refined by others such as the staff of the Kennecott Computing Center in Salt Lake City, C. Herrick of the Los Alamos Scientific Laboratory, T. Wolery of Northwestern University (Wolery, 1978), and T. Brown of the University of British Columbia.

The technique permits us to calculate the progressive mass transfer between solids and an aqueous phase as a function of reaction progress, ξ, which was conceived by De Donder and Van Rysselberghe (1936) to describe the changes in the mass of a species undergoing chemical reaction. They originally called this reaction progress the "degree of advancement" of a reaction. In order to understand what is meant by this term and how it is used we will give a simple, specific example followed by reference to a more general, complex case.

A SIMPLE CASE IN WHICH LIME REACTS WITH SULFURIC ACID

Consider a beaker containing one kilogram (~1 liter) of approximately 0.1 molal sulfuric acid (H_2SO_4) having a specified initial pH of 1.0. Into this beaker are added small increments of slaked lime $Ca(OH)_2$. The sulfuric acid will react with and dissolve the slaked lime as it is added according to the following reaction:

$$H_2SO_4 + Ca(OH)_2 = CaSO_4\ aq + 2H_2O \quad .$$

Eventually, so much slaked lime will be added that saturation will be reached with respect to the mineral gypsum which will then precipitate:

$$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O \quad .$$

With continuing additions of slaked lime, nearly all of the sulfate ion will precipitate as gypsum and the slaked lime itself will become saturated. From then on, addition of more slaked lime will only result in its accumulation on the bottom of the beaker and no further chemical changes will occur in the solution.

The chemical changes taking place during this experiment can be studied in terms of the amount of slaked lime added to the beaker, where the addition of each mole (74 g) of slaked lime added represents the degree of advancement or one unit of reaction progress, ξ. This relationship can be represented as shown in Figure 7-1.

What happens in the beaker can also be studied as a function of reaction progress. Thus, we can plot how much gypsum or slaked lime precipitates, or what happens to the distribution of aqueous species

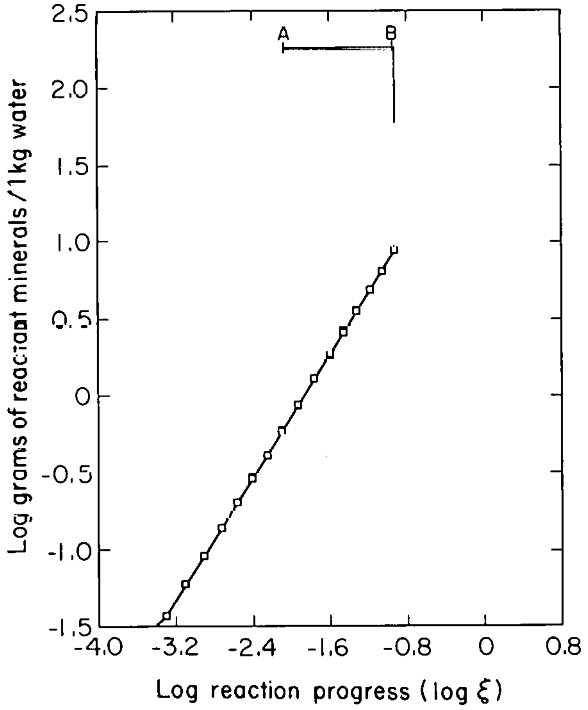

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Figure 7-1. Correlation between reactant consumed and reaction progress. (A = gypsum, B = portlandite.)

in solution as a function of ξ. Schematic diagrams illustrating precipitation and speciation are given in Figures 7-2 and 7-3, respectively.

DEVELOPMENT OF A GENERAL CASE

Now consider a more complicated case in which one kilogram of surface water is allowed to react with the surrounding country rock. In this case, the water contains carbonates, sulfates, chlorides, and other dissolved constituents. The rock is also made up of several minerals. A granite, for example, may contain quartz, orthoclose, albite, muscovite, and biotite in varying proportions. In this case, we react the mineral constituents according to their molar ratios in the rock and identify one ξ unit of reaction progress as having taken place when an aggregate mole of minerals has reacted with the water. The chemical reactions that take place as a function of reaction progress are far more complex. There are many more potential product minerals

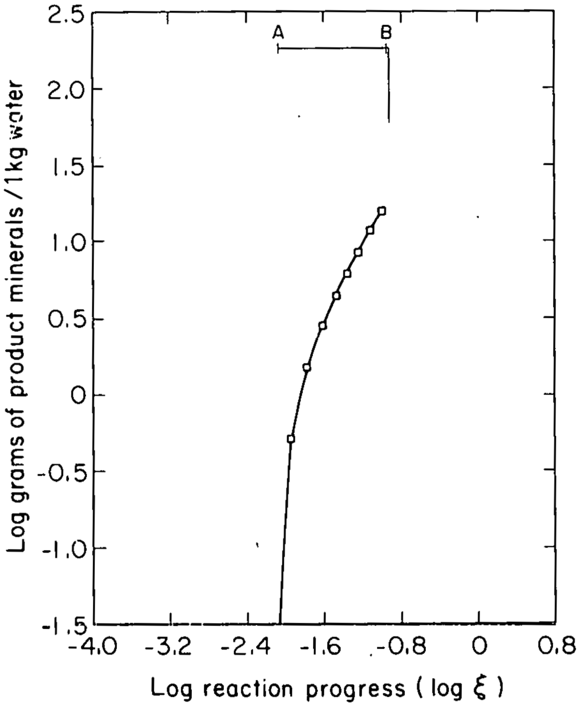

Figure 7-2. Relationship between product phases and reaction progress, ξ. (A = gypsum, B = portlandite.)

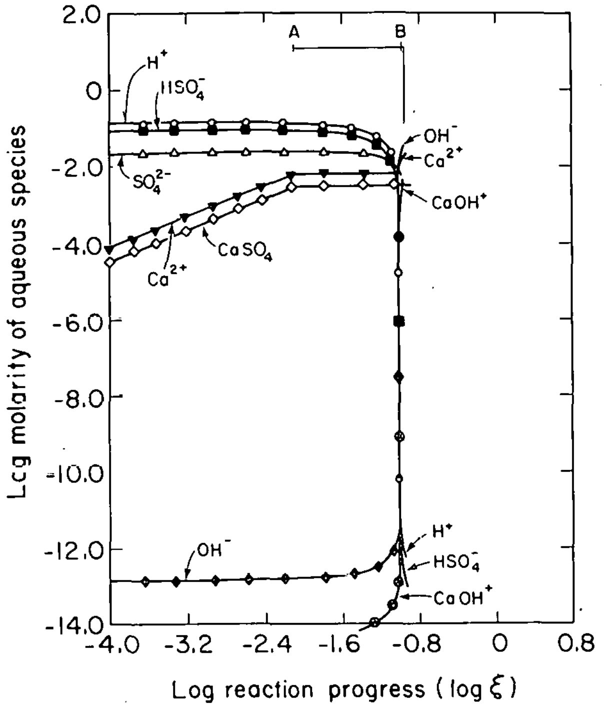

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Figure 7-3. The variation in the concentration of aqueous species as a function of ξ. (A = gypsum, B = portlandite.)

to take into account and many more aqueous species to monitor in the solution. Furthermore, chemical changes may occur in solution, which lead to the dissolution of already precipitated phases, and equilibrium between the water and the country rock may never be achieved.

To examine the progressive chemical changes which would take place in such a complex system over space and time, we would normally require detailed knowledge of the thermodynamic properties of the precipitating phases, their alteration products, and the chemical species in the solution. We would also need to understand the rates and mechanisms of the heterogeneous chemical reactions that proceed during mineral dissolution and precipitation, and the influence that the rock structure (grain size, micropores, and connecting fractures) has on reaction rates. With our present knowledge, we are in no position to model the kinetic behavior of such complex chemical reactions between rocks and groundwater. However, by making a few simplifying assumptions, we can model the behavior of a complex chemical system, such as that described above, which provides a fair representation of what is actually observed to happen.

The assumptions are as follows.

1. The reaction proceeds isothermally.
2. Reactions are studied as a function of ξ rather than time. This eliminates the need to know the reaction rate or mechanisms of the participating reactions.
3. Reactant minerals dissolve in the aqueous phase in proportion to their molar ratios.
4. Thermodynamic equilibrium is always maintained both within the aqueous phase and with respect to the product minerals.

For relatively long time periods (about 10^3 to 10^8 years), the above statements are assumed to be valid. Their validity is based on comparative observations with natural systems and has not been tested in any formal way. For periods of less than 10^3 years, deviations can occur and care must be taken in interpreting the results of a computer simulation.

The mathematical algorithms developed to permit study of a complex chemical system as a function of reaction progress have been fully documented elsewhere (see Helgeson et al., 1970). All computer codes subsequently developed employ the same basic principles, so that the choice of code depends on its availability and suitability for the solution of a particular problem.

All codes depend on an extensive thermodynamic data base, consisting of solubility products for solids and dissociation constants for aqueous species given at discrete temperatures (usually at 25-50°C intervals). Because of the magnitude of the task required to collect the needed thermodynamic data, the data are usually obtained from the literature without critical review. Therefore, the data are of variable quality and are rarely, if ever, internally consistent. Recent efforts by Helgeson and his students to develop an internally consistent set of data of naturally occurring solids and aqueous complexes have culminated with the development of SUPCRT. This code permits calculation of solubility and dissociation constants of well-characterized minerals and aqueous species over a range of temperatures and pressures that encompases most conditions expected in the earth's crust.

FUTURE PLANS

Given sufficient thermodynamic information, it should also be possible to predict the behavior of actinides in the presence of groundwater modified by the host rock composition. During fiscal year 1977, available thermodynamic data were collected on the actinides plutonium, neptunium, americium and curium as described in Section 2 of this report. This information will be incorporated in the existing data base of FASTPATH, the code developed by Kennecott Copper Corporation staff, and simulation of the chemistry of the actinides will be made in the presence of typical groundwaters in representative host rock environments. Results of such computer runs will provide tentative answers to the following uncertainties: (a) the relationship between groundwater composition and the environment; (b) the effect of bicarbonates and chlorides on overall groundwater composition; (c) the degree of complexing of actinides under subterranean conditions; (d) the effect of oxidation potential and pH on actinide solubility; (e) to what extent the K_d of a given radionuclide will be affected by complexing; and (f) the limits of solubility of actinides as determined by known phases.

Providing answers to these uncertainties will not solve all of the problems identified at the beginning of this section. Nevertheless, they do provide insight and quantify the effects on radionuclide K_ds caused by the environmental conditions in waste-repository host rocks. This information is vital in order to properly design experiments to measure K_ds and will also serve to interpret the differences in K_ds measured by different laboratory techniques.

In addition to the collection of actinide data, work has proceeded on updating the data base and debugging the code, which developed mysterious and obscure problems when modified to run on the CDC 7600 at LBL. The problems have been partially resolved, although further work remains to be done.

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DISCUSSION--JOHN A. APPS

Definition of K_d (Figure 1-1)

Q. What do you mean by "definition of K_d"?

A. We use the standard definition found in the literature: the ratio of a mass of radionuclide that is adsorbed on 1 g of solid to the concentration of that radionuclide in the equilibrium solution.

Q. Then why is it at the right of Figure 1-1, rather than at the left?

A. Because, at this stage, we don't know which are the significant parameters that affect the commonly accepted term of K_d--the underlying factors, such as surface area or chemistry. All of these variables are being turned out at separate times; yet all must be taken into account to understand what K_d in fact means in a practical sense.

Q. What is the completion time for each of these tasks?

A. We hope to get the experimental program well under way and the detailed models organized in the latter part of FY 1978, continuing into FY 1979.

Literature Reviews

Q. Several of the subcontractors are doing literature reviews; is there a plan for collecting and collating the results--for example, with respect to K_d values?

A. There seems to be a great deal of dispute over how to define K_d values. According to our review of the literature on transport modeling, much of the work done to date does not take into account the complexities of mineralogy or chemistry of the host rocks. The whole rationale behind this project is to determine what kinds of problems arise from this simplistic approach. It is clear, for example, that if changes in oxidation state and pH can result in variations in K_d over six orders of magnitude, then use of a constant K_d in a transport model can lead to large errors. It may be that, if a transport model is to lead to realistic values, it will have to incorporate some of the chemistry or some understanding of the crystal configuration of the rock being used.

Q. Did your literature survey include the early classified work of the military projects? Some of it might provide a useful data base.

A. We only looked at material that has been published. I don't know how much of the classified material has been declassified and published.

Oxidation State and pH of Plutonium (Figure 3-1)

Q. Where did you find these data? We've been looking for a year for good thermodynamic data on plutonium.

A. These data come from Fuger and Oetting, *Chemical Thermodynamics of Actinide Elements and Compounds*, published by the International Atomic Energy Authority in 1976.

Q. Aren't your limits for environmental Eh somewhat high?

A. Yes, especially for subsurface environments. I expect that, when we finish the modeling work for the characteristic rock types--basalts, granites, and sandstone, for example--we will find most of them bunched fairly tightly toward the basic end. Also, since the whole goal of a terminal storage facility is to isolate these elements subsurface, it becomes a matter of philosophy and opinion as to how intensely one should look at transport under highly oxidized conditions.

Q. The literature has already delineated a range of oxidation reduction potentials that are considered to be typical of the normal environment. Can we now go further and say that the typical oxidation reduction potentials in a deep storage location would be in the lower quarter or half of that range?

A. We've tried with Pu(IV), at a temperature of 75°C (the expected temperature of a 1,000 m repository). The Pu which was in an essentially neutral solution with traces of ferrous ion, was reduced to Pu(III), regardless of the speciation shown on Figure 3-1. Similarly, Np(V) was reduced to Np(IV) in the presence of a small amount of ferrous ion.

Q. How accurately can your modeling techniques predict oxidation reduction potential?

A. We can, for any actinide, automatically compute the oxidation state of the system, taking into account implicitly any reactions between the actinide and other substances, such as ferrous ion.

Q. But your technique is only as good as the thermodynamic data that you use. The data in the literature are seriously in doubt; we have no good data for the kinds of conditions typical of repositories.

A. What we need to do is to complete our analysis of the available data. If this analysis indicates that serious holes exist, then we'll need to begin an experimental program to find out what they are. We need to try to bridge these gaps by FY 1979. Perhaps the Division of Physical Research could address itself to this question with funding support or with more fundamental work on actinide chemistry.

Q. Perhaps it would be more helpful to view these techniques not as a rule or method for calculating radionuclide concentrations, but rather as a means of identifying some important variables that affect these concentrations.

A. That's a good point. Developing insights as to what in fact is controlling the chemistry of the environment can be more important than trying to quantify factors.

Q. Do diagrams such as this one work for very low concentrations, where there is no polymerization of the aqueous phase?

A. They are concentration-independent. The boundaries represent the concentrations on either side.

Q. But won't the concentration influence the results? For example, won't there be a substantial difference between a valence state that polymerizes at a high concentration and one that does not?

A. Yes, there could be. I'm hoping that Battelle will look at the leaching of the waste product forms and will be able to provide us with information as to the kinds of concentrations that can be expected from radionuclides that are leaching away from the terminal storage repository. I would expect that we won't see supersaturations, but rather concentrations that are close to the saturation of the oxides or the more stable phases of the solid, stemming from interaction between groundwaters and the waste product form.

Q. Does anyone have any guesses on rule-of-thumb Eh values for underground environments?

A. The problem is that it is very difficult to measure the oxidation potential of a rock. When you drill a hole, you perturb the system, exposing it to air. It is easy to obtain reproducible Eh readings for well waters and springs; for low-permeability rocks, however, in which it can take 10 years for a cavity to fill with groundwater, it is very difficult experimentally to take measurements. I haven't seen any measurement of Eh in low-permeability host rocks.

Q. Is it a known fact that the conditions in such rocks will be anaerobic?

A. These systems are the antithesis of the high-permeability geothermal brine systems. We know that the oxidation reduction potential is very low. I can't cite exact figures, however, because what we've measured is the true election potential, which is different in terms of M/1--it's down in the region of 10^{-60}.

Q. Does everyone feel that a meaningful Eh measurement can be made?

A. It depends on the system and on the elements that are present. If sulfide is present, for example--as it is in many groundwaters--and a platinum electrode is used, the results may tell you the solubility of platinum sulfide, but they won't give a meaningful Eh. In general, the species that controls the electrode reaction depends on what puts out the fastest exchange current, and may not really reflect the Eh. (One participant noted that Bob Berner at Yale has demonstrated that a platinum electrode does work in sulfide bearing waters; his results will be published soon in the American Journal of Science.)

Pressure Differentials (Table 5-2)

Q. What do you mean when you say you have a monolayer?

A. I'm assuming that the actinide is adsorbed as a monolayer on the surface of whole mineral grains--that there are no points of contact.

Analytical Techniques to be Used in Future Experimental Work

Q. When you refer to techniques for determination of the mineral phases onto which actinides are preferentially adsorbed, to which techniques are you referring?

A. I can only think of autoradiography at the moment, though there may be other techniques.

Q. Would Auger spectroscopy be one?

A. It might, but I would be somewhat hesitant to use it, since we don't really know what happens to the solution when it penetrates the rock and transports the actinide. Auger spectroscopy might work for depths of 500 Å or less, but we may be talking about penetration depths of several millimeters.

Q. Would some type of X-ray excitation give you depths in millimeters?

A. Yes, that's another possibility. The selection of a detection method depends to a great extent on the particular isotope of the actinide that is under study.

Q. At high concentrations, wouldn't you have to take into account the effects of radiation damage?

A. Yes, that could potentially be a problem--but here we're talking generally about low concentrations; I don't know if radiation damage would cause problems at these concentrations.

Q. We found that measuring the ratio of the L X-rays works well; we can see penetration from 15 μ to about 1 mm into the rock.

A. Yes, that is a technique that we've briefly discussed ourselves.

"TRANSPORT PROPERTIES OF NUCLEAR WASTES IN GEOLOGIC MEDIA"

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TRANSPORT PROPERTIES OF NUCLEAR WASTES IN GEOLOGIC MEDIA

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ABSTRACT

Laboratory experiments were performed with nuclides of cesium, plutonium, neptunium, and americium to examine the migratory characteristics of long-lived radionuclides that could be mobilized by groundwaters infiltrating a nuclear waste repository and the surrounding geologic body. In column infiltration experiments, the positions of peak concentrations of cesium in chalk or shale columns, plutonium and americium in limestone, sandstone, or tuff and neptunium in a limestone column did not move when the columns were infiltrated with water. However, fractions of all of the nuclides were seen downstream from the peaks, indicating a large dispersion in the relative migration rates of the trace elements in the lithic materials studied.

The results of static absorption experiments indicate that plutonium and americium are strongly absorbed from solution by the common rocks studied and that their migration relative to groundwater flow is thereby retarded, a conclusion that is consistent with results from the column infiltration experiments. In addition, the reaction rates of these dissolved elements with rocks were found to vary considerably in different rock-element systems.

Following a sorption step in batch experiments with granulated basalt and americium-bearing water, plutonium and americium were desorbed from rock and repartitioned between rock and solution to an extent comparable to their distribution during absorption. In contrast, when tablets of various rocks were allowed to dry between absorption and desorption tests, plutonium and americium were not generally desorbed from the tablets.

In batch experiments with plutonium- and americium-bearing water and granulated basalt of several different particle sizes, the partitioning of americium and plutonium did not correlate with the calculated area of the fracture surfaces nor did the partitioning remain constant (as did the measured surface area). Partitioning is concluded to be a bulk phenomenon with complete penetration of 30-40 mesh and smaller particles.

I. INTRODUCTION

The Waste Isolation Safety Assessment Program (WISAP) being managed by the Pacific Northwest Laboratory was set up to provide technical support for the National Waste Terminal Storage Program (NWTS). The overall objective of WISAP is to evaluate potential interactions between emplaced radioactive waste and surrounding rock which might affect the safety of long-term containment. Task 5 of WISAP was formulated to develop quantitative data describing the radionuclide-geologic media interactions that control the transport of radionuclides. The experimental program being conducted at Argonne National Laboratory is designed to meet the objectives of Task 5.

The experimental program has utilized three types of experiments (described in Table 1) designed to give information on the migration behavior of nuclides in aqueous solution-rock systems. The purposes of using different approaches are to establish nuclide behavior under a variety of experimental conditions and to identify the characteristics of nuclide adsorption that are important to understanding nuclide migration in natural systems (recently fractured rock, weathered rock, porous rock, etc.).

II. ROCKS, NUCLIDES, AND AQUEOUS SOLUTIONS

Rocks from geologic formations that may be suitable for siting nuclear waste repositories were selected for study. The rocks were from large, stable formations of low economic value and within the continental United States. The selected rocks were of a variety of chemical compositions and physical characteristics and included rocks of sedimentary, igneous, and metamorphic origin. Silicates such as granites, basalts, and metamorphic rocks common in geologically stable parts of the North American continent and carbonates such as limestone, chalk, and dolomite that are typical of rocks associated with salt formations were used in the study. Salt deposits are seriously considered for waste repositories. However, salt was not included in this first work because its study requires special experimental techniques not needed to study the other less-soluble rocks.

The elements cesium, plutonium, neptunium, and americium in the waste produced during nuclear power generation contain long-lived isotopes and are of concern in the design of nuclear waste repositories. The nuclides cesium-134, plutonium-237, neptunium-239, and americium-241 were selected for study because they emit gamma rays during their decay and can be analyzed by counting of radioactivity without the need to make chemical separations or thin samples. Gamma ray spectra from liquids or rock solids were measured using NaI scintillation spectrometers. In determining nuclide concentration relative to its concentration in the starting solution, counting data was corrected for nuclide decay, background, Compton scattering, and interference from the decay of other nuclides.

Pre-equilibrated solutions were used in this work. Each solution was prepared by equilibrating distilled water with particles of a rock to be studied. Typically, mixtures were stirred for one week, the particles were allowed to settle for one week, and the liquids with dissolved materials were decanted or filtered (through Whatman No. 1 paper) to remove suspended matter. This method of preparation was used to establish mineral contents of the

Table 1. Experimental Methods Used to Investigate Migration Behavior of Nuclides[a]

Method	Material	Method Description	Parameters Measured	Potential Relation to Nuclide Migration
Column infiltration	Solid rock columns	Aqueous solutions are forced through columns of permeable rock.	Dispersion in V_n	Migration behavior in solid rock
	Rock aggregate	Aqueous solutions percolate through crushed rock.	Dispersion in V_n	Migration behavior in fresh regolith
Static absorption and desorption	Rock tablets	Reaction of rock tablets with static solutions of minerals and nuclides.	Kinetics of the reaction, reversibility, and K_D	$V_n = \frac{V_w}{1 + K_D\rho/\varepsilon}$
Batch partitioning measurements	Rock aggregate	Granulated rock is reacted with stirred solutions of minerals and nuclides.	Surface saturation limits; dependence of K_D on grain size, nuclide concentration, and dissolved salts	$V_n = V_n$ (grain size, C_n, f_{Cl^-})

[a] Symbols:
V_n, velocity of nuclide in rock (cm/s).
V_w, velocity of aqueous solution in rock (cm/s).
K_D, partition coefficient, equals nuclide concentration per gram of rock divided by nuclide concentration per milliliter of solution.
ρ, density of rock (g/cm^3).
ε, porosity of rock (fraction).
C_n, concentration of nuclide (ppm).
f_{Cl^-}, fugacity of chloride ion.

solutions comparable to those existing in groundwater in equilibrium with the rock formations. The hydrogen ion concentrations of the pre-equilibrated solutions were measured with an ion probe and are given in Table 2 (expressed as pH values).

Table 2. Hydrogen Ion Concentrations in Pre-Equilibrated Solutions (expressed as pH values)

Rock	Hydrogen Ion Concentration, pH
Shale, Pierre	6.5
Chalk, Selma	8.5
Sandstone, Ohio Barrier	8.0
Limestone, Salem Formation	8.3
Tuff, Nevada Test Site	6.4
Columbia River Basalt	7.4
Georgia White Marble	8.3
Barrier Sandstone	6.8
Soapstone	8.2
Culebra	8.6
Gneiss	8.1
Dolomite	8.2
Chalcopyrite	5.4
Galena	6.1

Solutions of plutonium and americium for all three types of experiments were prepared by evaporating nitrate solutions of the isotopes to dryness and dissolving the residue, or part of it, in distilled water. Small quantities of these solutions (10 μL) were added to water that had been pre-equilibrated with rock or were added directly to rock saturated with the water. It is assumed that 50% of the gamma activities was counted by use of the NaI-well crystals, the activities and concentrations of the plutonium and americium used in static absorption experiments were 2.3 nCi/mL or 8×10^{-13} $\underline{M}$ plutonium-237 and 4.5 nCi/mL or 5.8×10^{-9} $\underline{M}$ americium-241. Plutonium and americium were in solutions prepared in air with no reducing agents and in the final solutions were believed to be in the +4 and +3 valence states, respectively.

Neptunium was extracted in a 0.1$\underline{N}$ HCl solution from a solution where it was present as a daughter product of americium-243. The neptunium was believed to be in the +5 valence state and was used in the experiments without drying to prevent oxidation changes that would result during evaporation of the solution as a result of an increase in acidity.

Cesium was introduced in the column infiltration experiments as a solution of CsCl added directly to rock material saturated with water to about 5.7 μCi/g of dry rock; alternatively, it was added to a pre-equilibrated solution to produce a concentration of 0.01 μCi/mL.

The addition of small quantities of radionuclides to pre-equilibrated water was in analogy to the postulated leaching of radionuclides from solidified waste in the repository. In the experiments, the migratory behavior of the nuclides was studied by reacting the radionuclides with rock--either by contacting rock with the nuclide-bearing solutions or by infiltrating rocks with pre-equilibrated water that contained radionuclides.

III. COLUMN INFILTRATION EXPERIMENTS

Column infiltration experiments were done to determine relative migration rates of nuclides in some geologic media and to examine the effects of different procedures on the experimental results. In these experiments, pre-equilibrated solutions were employed; low-pressurized (0-1 400 Pa or 0-0.2 psi) to moderately pressurized (345,000 Pa or 50 psi) solutions were allowed to infiltrate columns of rock. Prior to infiltration, the nuclides were added to the pre-equilibrated solutions or were placed directly on rock saturated with water. The former method is thought to be typical of conditions hypothesized for a repository from which solutions of low nuclide concentration would continually infiltrate a geologic body. On the other hand, the latter method is simpler because the total activity in the column and eluates was constant with time (when radioactive decay is accounted for).

The water was collected after it passed through the column and was analyzed to determine the amount of nuclide leaving the column. The infiltration experiments are analogous to elution procedures in column chromatography, with the pre-equilibrated water serving as the eluant. Several experimental designs were employed. In one method, a standing tube of water approximately 150 cm high was used as a source of pressurized water. The apparatus, incorporating a standing tube of water and designed to accommodate rock aggregate, is depicted in Fig. 1. In another method, a regulated pressurized air supply was used to provide pressures up to 2.8×10^5 Pa (40 psi). The air was isolated from the water solution by a movable rubber piston in a cylinder; this prevented dissolution of air in the water.

Thirteen experiments with cesium, plutonium, americium, and neptunium nuclides were performed in columns. The rocks and elements studied in the experiments are listed in Table 3.

When cesium solutions at very low concentrations are used, the absorption of cesium on glassware is of concern. To examine this, two glass tubes were filled with cesium-containing waters pre-equilibrated with chalk or shale. The solution activity was monitored for the duration of the infiltration experiments. No adsorption of cesium onto the glass was detected; thus, the glass used in these experiments apparently performed satisfactorily. However, after 250 h, a precipitate did form in the shale-equilibrated water, accompanied by a decrease of 50% in the activity of the solution. The precipitate may be related to the organic content of the shale and may be of biological origin.

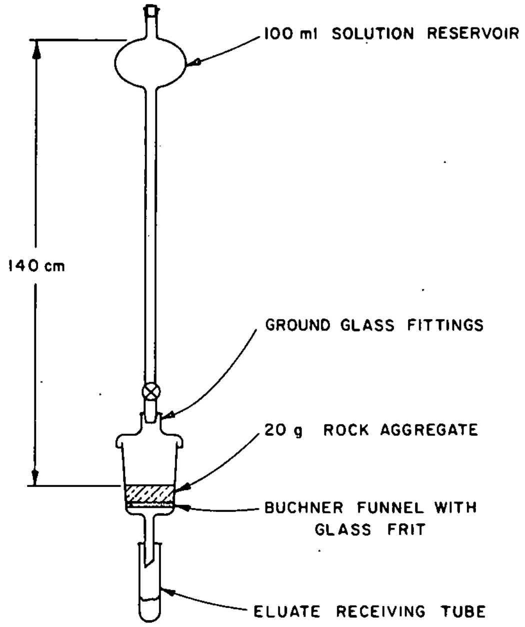

Fig. 1.

Low Pressure Column Infiltration Apparatus for Use with Rock Aggregate

Table 3. Rocks and Elements Studied in Infiltration Experiments

Rock Type	Elements and their Valence States	Density, g/cm^3	Porosity,[a] % by Volume
Shale, Pierre Front Range	Cs^+	1.2	27
Chalk, Selma	Cs^+	1.0	40
Limestone, Salem Formation	Am^{+3}, Np^{+5}, Pu^{+4}	2.3	13
Sandstone, Ohio Barrier	Am^{+3}, Np^{+5}	2.1	19
Tuff, Nevada Test Site	Am^{+3}, Np^{+5}, Pu^{+4}	1.7	27

[a] Porosity measurements were performed by weighing a sample before and after its saturation with water. The difference in weight is indicative of the pore volume of the sample.

Five column experiments (1 through 5, Table 4) were performed with Selma chalk or Pierre shale. The chalk or shale was crushed and sieved to 18 mesh and then ground for 10 min in an automatic mortar and pestle; the material (rock aggregates) was then used to form the rock columns. This treatment was chosen to separate the particles of shale or chalk without fracturing a large fraction of the individual grains. In two experiments (Expt. 1 with chalk and Expt. 4 with shale), cesium was added to the mineral water. In the other three experiments, small volumes of solution containing cesium were added directly to the water-saturated rock columns.

In each experiment, eluates consisting of selected numbers of column volumes, were collected and each eluate was analyzed for nuclide activity. Figure 2 gives the activity in the eluate (adjusted for volume) versus the

Table 4. Relative Migration Rates of Cesium Measured in Crushed Selma Chalk and Crushed Pierre Shale

Expt.	Material	Range of Column Elution Rates, mL/h	Elution Volume, mL	Final Quantity of Cesium on Column, μCi/g	Relative Migration Rate[a] Peak Activity,[b] V_{Cs}/V_w	Relative Migration Rate[a] Maximum Detected, V_{Cs}/V_w
1	Chalk	4.2-20	2 300	1.0	1×10^{-5}	0.16×10^{-2}
2	Chalk	1.9-9	3 500	0.28	0.6×10^{-5}	0.24×10^{-2}
3	Shale	0.7-0.9	560	0.028	9×10^{-5}	0.8×10^{-2}
4	Shale	0.2-0.5	370	0.20	6×10^{-5}	0.2×10^{-2}
5	Shale	0.4-1.1	530	0.28	70×10^{-5}	50×10^{-2}[c]

[a] The relative migration rate is the velocity of the nuclide divided by the velocity of the infiltration water. The calculation of relative migration rate uses the porosity values given in Table 3 and assumes that all porosity is subject to fluid flow.

[b] These values represent maximum migration rates for the peak of the activity. Although no evidence of migration of the activity in the peak was detected, the peak migration rates were estimated by assuming that the activity had traveled the thickness of the sample that was taken from the top surface.

[c] Rapid migration of some cesium occurred through large cracks in the crushed material in Expt. 5.

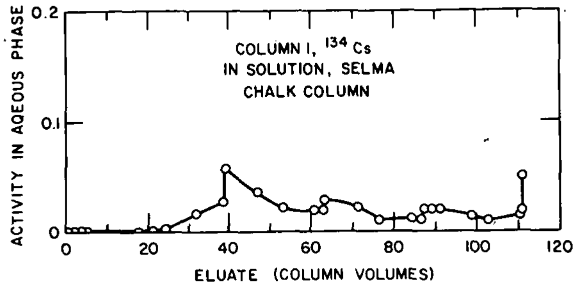

Fig. 2.

Activity in the Eluate Versus Cumulative Eluate Volume. Expt. 1

cumulative volume of eluate for Expt. 1. Activity was not detected in the first 25 column volumes of eluate that passed through the column. Measurable activity occurred in subsequent eluates for the duration of the experiment, remaining a small fraction of the activity of the infiltrating solution.

In Expt. 5, activity was detected in the initial eluate obtained; this is believed to be a consequence of a wetting and drying sequence that preceded application of cesium solution and produced fissures in the shale material. The fissures closed after application of the radioactive eluant. The concentration of cesium in the eluate decreased gradually over the duration of the experiment.

Each experiment was terminated by stopping eluant addition. The ground-rock column was then sampled at various depths to determine how far the cesium had penetrated. The activity levels determined in the four columns in which no cracking occurred are plotted in Fig. 3. A small top sample was taken from each column in order to locate the position of maximum concentration (*i.e.*, peak activity) within the column. The top samples contained the highest concentrations of cesium, indicating that the activity did not move perceptibly within the columns. However, all samples analyzed contained measurable concentrations of cesium. The resulting distribution of cesium in the columns is strongly skewed, with the maximum near the surface of the column and a long tail of activity extending in the direction of water flow. The presence of cesium at the bottom of the columns implies a spread in relative migration rates for the cesium. Data are given in Table 4 on the infiltration experiments and the migration rates based on (1) the position of the peak activity and (2) the detection of cesium in the eluate or in the bottom of the columns.

Eight experiments were done in columns to investigate the migration of plutonium, americium, and neptunium through limestone, sandstone, and tuff. Cylindrical rock columns were cut from rocks and sealed in polyethylene tubes with epoxy in a manner to prevent water bypassing. The rock columns were wetted with mineral water, and nuclides were added to the top surface of the columns in small volumes (1 mL) of water. After the radioactive water soaked into the rock, the columns were pressurized with pre-equilibrated water. The eluates from each experiment were collected and were analyzed for the amount of nuclide that had passed through the column. The relative migration rate was calculated as the distance the nuclide traveled, divided by the distance the water front traveled (Table 5). For nuclide in the eluate, the distance traveled was the thickness of the entire rock column. The results are expressed as percentages of nuclides transmitted with migration rates greater than the relative migration rate given in column 4. For the first experiment listed

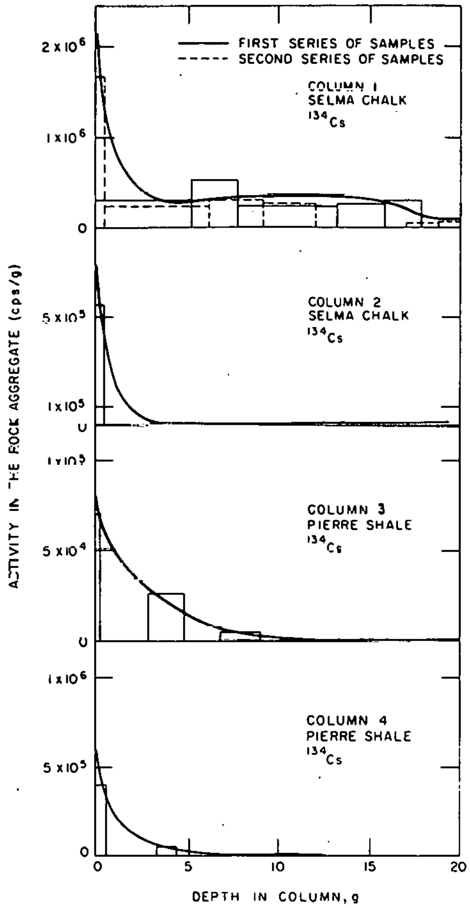

Fig. 3.

Column Infiltration Experiments. Plot of the activity in the rock versus depth in the columns. All columns had measurable ^{134}Cs concentrations at the bottom (20 g) level. Column numbers correspond to experiment numbers.

in Table 5, as an example, it can be seen that 2.6% of the plutonium nuclide was eluted from the column at a migration rate at least 0.001 times the travel rate of the water front. At this migration rate, 2.6% of the nuclide passed from the top to the bottom of the column in an eluate volume 1000 times the pore volume of the column.

IV. STATIC ABSORPTION EXPERIMENTS

Static absorption experiments were run on a series of rock types (*i.e.*, all rocks listed in Table 2 except the first three). In an experiment, a tablet of rock was suspended by a platinum wire inside a polyethylene tube and was immersed in a solution containing radionuclides of either plutonium or americium or both. After immersion, the rock tablet was removed from the solution at various intervals, and the activity remaining in solution was monitored by gamma counting. After monitoring of the radioactivity, the rock tablet was reimmersed in the solution to continue the experiment. Generally, the activity associated with the solution decreased very rapidly during the first few hours or days of contact with the rock, and the activity remained constant for the remainder of the experiment. Figure 4 is a typical plot of reaction time versus the amount of nuclide remaining with the solution. The amount of nuclide with the solution is expressed relative to the amount of nuclide in solution at the start of the experiment. After the activity had

Table 5. Cumulative Percentage of Nuclide (Column 5) with a Velocity Greater than the Stated Migration Rate (Column 4) as Determined in Column Infiltration Experiments

Sample	Expt.	Nuclide and Valence	Migration Rate[a] of Nuclide Relative to Water Front Travel Rate	Nuclide Passing Through the Core, % Cumulative
Limestone, Salem Formation	6	Pu^{4+}	1	0.007
			0.5	0.01
			0.006	0.11
			0.001	2.6
Limestone, Salem Formation	7	Am^{3+}	0.3	0.002
			0.05	0.005
			0.01	0.024
			0.007	0.031
Limestone, Salem Formation	8	Np^{5+}	1.0	0.030
			0.5	0.053
			0.02	0.092
			0.009	0.69
Limestone, Salem Formation	9	Am^{3+}	0.42	0.000 4
			0.008	0.008
			0.003	0.068
			0.001	0.28
Limestone, Salem Formation	10	Np^{5+}	0.4	0.04
			0.1	0.11
			0.003	1.1
			0.001	6.1
Sandstone, Ohio Barrier	11	Am^{3+}	0.3	0.000 2
			0.05	0.002
			0.04	0.024
			0.011	0.033
Sandstone, Ohio Barrier	11	Np^{5+}	1	1.3
			0.10	12.3
			0.01	61.3
			0.005	69.7

(contd)

Table 5. (contd)

Sample	Expt.	Nuclide and Valence	Migration Rate[a] of Nuclide Relative to Water Front Travel Rate	Nuclide Passing Through the Core, % Cumulative
Sandstone, Ohio Barrier	12	Np^{5+}	0.4	0.45
			0.09	12
			0.03	28
			0.06	45
Tuff Nevada Test Site	13	Am^{3+}	0.3	0.000 3
			0.15	0.001
			0.09	0.004
			0.06	0.002

[a] The relative migration rate, V_n/V_w, was calculated from the eluate volume, V_e, by the equation

$$V_n/V_w = T(\varepsilon A)/V_e$$

where ε is the porosity of the rock given in Table 2 and A and T are the cross-sectional area and the thickness of a column, respectively.

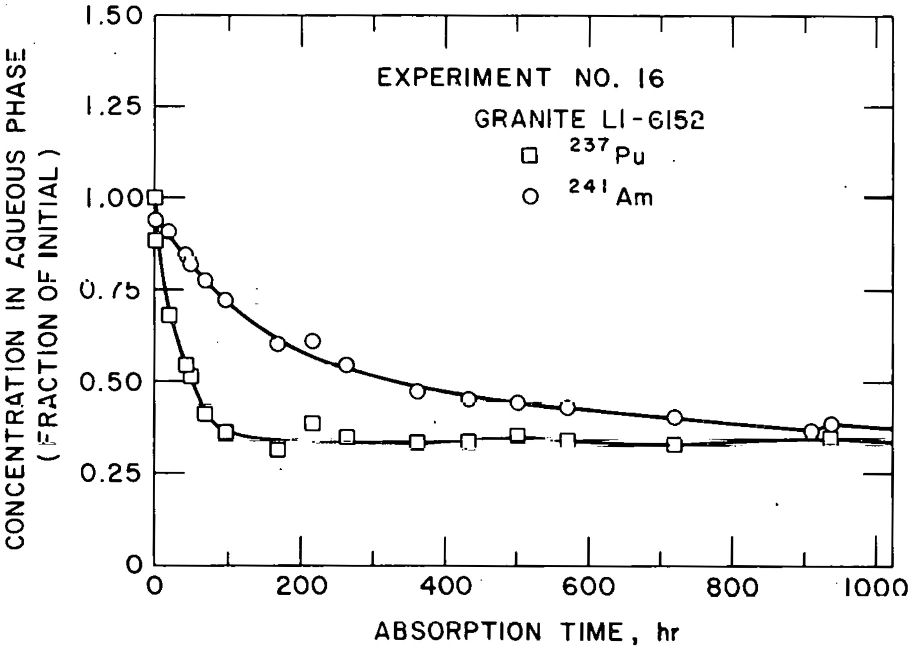

Fig. 4. Static Absorption Experiment. Activity of plutonium and americium in solution versus contact time with a rock tablet

attained a constant value, tubes having two nuclides were emptied, lightly rinsed, and counted to determine the activity that adhered to the polyethylene tubes. The amount of radionuclide, A, remaining with a solution as a function of time, t, that the solution and rock were in contact was approximated by the equation

$$A = A_f + (1 - A_f)e^{-(t/t_r)} \tag{1}$$

where A_f is the final amount remaining with the solution and t_r is the characteristic time of reaction. The exponential decrease in the amount of nuclide in solution suggests that the reactions of both plutonium and americium with the rocks proceed with first order kinetics.

Some of the nuclides were absorbed on the polyethylene tubes used in the experiments. After the rocks were withdrawn, the amounts in the empty tubes were subtracted from the total amounts in the solution-containing tubes to obtain the amounts in the solutions, A_s. The latter amounts were used to determine K_D, ratio of nuclide in the solid to nuclide in solution, by the equation

$$K_D(\text{mL/g}) = \frac{A_r/\text{g of rock}}{A_s/\text{mL of solution}} \tag{2}$$

where A_r is the amount of nuclide absorbed by the rock and is equal to 1.0 minus the fraction of the nuclide associated with the solution.

In experiments with some rocks, the radionuclides were strongly absorbed by the rock tablets and the amount absorbed on the polyethylene tubes was a large fraction (>50%) of the total activity remaining in the tubes. This effect resulted in large corrections to the nuclide concentrations of the solutions and in subsequent errors in the calculated ratios of nuclides in the rocks to nuclides in solution.

Results from the experiments with two isotopes applied simultaneously are listed in Table 6. Nearly all of the experiments (20 out of 31) exhibited the behavior expressed by Eq 1, for which a characteristic time of reaction, t_r, and a distribution coefficient, K_D, could be determined. The values of t_r were estimated from absorption curves and the values of K_D were calculated from the counting data. These values are listed in Table 6.

The characteristic times of reaction for different nuclides and rocks shows a considerable spread in these experiments, varying from about 1 h to in excess of 600 h. However, the time of reaction appears to be constant and well defined for a particular nuclide and rock, as indicated by the consistency of results from duplicate experiments. With some rocks (*e.g.*, gneiss), the reaction times were long and precluded attaining steady-state behavior, even in the 1000-h experiments.

In most experiments, the plutonium and americium nuclides were absorbed by the rock. This effect is indicated by partition coefficients in excess of one. Often, the isotopes were strongly fractioned, leading to partition coefficients in excess of 100.

Table 6. Static Absorption Experiments with Plutonium and Americium at Ambient Temperature. Plutonium and americium were applied simultaneously. The experiments were run for 900 h or more.

Rock Type	Expt. No.	Characteristic Reaction Time, h		Partition Coefficient, K_D	
		Pu	Am	Pu	Am
Salem Limestone	13	40	10	>150[a]	∼160[a]
Granite, LI-6152	16	25	160	30[a]	5
Columbia R. Basalt	19	60	150	230[a]	320
Tuff, Nevada Test Site	22	180	5	39	370[a]
Metamorphic	25	450	∼20	130	2.6
Magenta	28	50	400	41[a]	47
Georgia Marble	30	5	5	77[a]	162[a]
Georgia Marble	31	5	5	180[a]	160[a]
Georgia Marble	32	8	5	51[a]	220[a]
Oolitic Limestone	33	5	<5	540[a]	415[a]
Oolitic Limestone	34	5	<5	710[a]	520[a]
Oolitic Limestone	35	5	<5	210[a]	690[a]
Barrier Sandstone	36	50	25	8.2	11
Barrier Sandstone	37	n.d.[h]	15	20	12
Barrier Sandstone	38	50	15	6.4	7.7
Soapstone	39	15	10	8.4[a]	23[a]
Soapstone	40	15	15	23[a]	67[a]
Soapstone	41	20	25	28[a]	105[a]
Culebra	42	<5	<5	16[a]	58[a]
Culebra	43	1	1	19[a]	84[a]
Culebra	44	1	1	20[a]	59[a]

(contd)

Table 6. (contd)

Rock Type	Expt. No.	Characteristic Reaction Time, h		Partition Coefficient, K_D	
		Pu	Am	Pu	Am
Gneiss	45	75	$\gtrsim 600$	10	18[c]
Gneiss	46	150	$\gtrsim 600$	17	8.3[c]
Gneiss	47	150	$\gtrsim 600$	16	4.4[c]
Dolomite	48	<5	<5	3.4[a]	10[a]
Dolomite	49	<5	<5	34[a]	150[a]
Dolomite	50	<5	<5	13[a]	26[a]
Chalcopyrite	51	100	75	25	0.6
Chalcopyrite	52	150	n.r.[d]	3	0.3
Chalcopyrite	53	200	n.r.	4.7	0.5
Galena	56	n.d.	n.r.	3.9[a]	0.1

[a] In these experiments, a considerable amount (>50%) of the radionuclide associated with the solution was retained on the walls of the polyethelene tube. The activity in the solution was determined by subtracting the activity on the walls from the activity of the tube plus solution. The corrections are large and may have led to errors in the calculated partition coefficients.

[b] "n.d." indicates that the activity curve did not fit the behavior indicated by Eq. 1.

[c] Partition coefficients were measured after a 1000-h experiment and do not represent equilibrium conditions.

[d] "n.r." indicates that reaction was insufficient to allow the characteristic reaction time to be measured.

For experiments in which plutonium was the initial nuclide in solution and in which americium was added after 1000 h of contact of the solutions and rocks, the absorption behavior seen for the plutonium and americium is consistent with that seen for experiments listed in Table 6. However, in the experiments in which americium was the initial nuclide, the addition of plutonium after 1000 h of contact time often had a significant effect on the behavior of the americium. In three of five experiments, the absorption of americium on the rock was enhanced by the addition of plutonium. In one experiment, addition of plutonium resulted in transfer of americium from the rock to the solution. In another experiment, addition of plutonium had no effect on the behavior of americium.

From the experimental results, the presence of synergistic effects was seen to be confined to cases in which a plutonium spike was added to solutions containing americium. This suggests that something associated with the plutonium affects the absorption equilibrium of americium. It is unlikely that the plutonium itself is the source of the synergistic behavior because the concentration of plutonium is low. A possibility that will be examined is that the agent for the synergistic behavior is an auxiliary chemical used in the preparation of the plutonium-237 and still present in the spike. The agent may affect the absorption of plutonium as well, a point that would not be apparent from these experiments.

V. BATCH PARTITIONING EXPERIMENTS

Two sets of batch partitioning experiments are described. The first set of experiments was performed to test the reversibility of the sorption process. The second set was performed to determine whether sorption increases with decreasing particle size of the rock.

The migration behavior of nuclides depends sensitively on whether adsorption processes are reversible. Ion-exchange models used to predict nuclide migration generally assume that the sorption process is reversible. To test whether this assumption is valid for americium in a common rock, batch experiments were done with granulated Columbia River basalt of graded mesh size and americium-bearing solutions. Rock samples of 0.1 to 0.3 g were agitated with 2 or 3 mL of solution in glass test tubes for 500 h. One or two milliliters of solution was then removed from the test tubes and analyzed for americium-241 activity. The partitioning of americium between solution and rock during absorption was determined from the initial and final activities of the solution.

The active solution that had been sampled from the test tubes was then replaced with rock-equilibrated water without activity and the water-basalt system was agitated for an additional 500 h. The activity of the solution after this agitation period was determined and is indicative of the partitioning of americium during desorption. The experimental results are given in Table 7. The results indicate that americium desorbed from the basalt and that the reaction is reversible. However, the distribution ratios are higher after desorption, indicating that americium is preferentially retained by the rock. This effect is not large, considering that greater than 90% of the americium activity is retained by the rock in both cases.

The existence of reversibility in these experiments contrasts with results obtained when rock samples were allowed to dry after absorption. In 19 desorption experiments of this type, 11 showed no measurable desorption of plutonium or americium, 6 experiments showed slight desorption of americium, 1 experiment (with marble) showed slight desorption of plutonium, and 1 experiment (with galena) showed complete reversibility of americium during desorption. These results indicate that reversibility of the reactions may depend upon the history of the rock-nuclide system.

Batch absorption experiments were done to determine whether decreasing the particle size of a sample would increase its absorptivity. If absorption is a surface phenomena, the amount of absorption per gram of material may increase as the surface area of the material is increased.

Table 7. Partition Coefficients for Values of Americium in Columbia River Basalt After Absorption and Desorption[a]

Expt.	Mesh Size	Partition Coefficient, K_D, After Absorption	Partition Coefficient, K_D, After Desorption
1	16-20	83	156
4	16-20	70	124
7	16-20	95	121
2	30-40	138	247
5	30-40	148	336
8	30-40	121	164
3	50-70	147	316
6	50-70	164	322
9	50-70	115	215

[a] Equilibration times for adsorption and desorption were each 500 h. The experimental temperature was 24°C.

To test this theory, a fine-grained basalt (Columbia River basalt) was ground and was divided into three mesh size ranges. Basalt was chosen because of its moderate distribution coefficients for plutonium(IV) and americium(III) and its presumed low permeability. The surface areas of the three mesh-size samples were determined, using the B.E.T. (Brunauer-Emmett-Teller) method. These surface area measurements, reported in Table 8, were similar for the three samples and indicated that the basalt may have a fine pore structure yet not be of low permeability. The pore structure may account for the large surface area compared to that calculated for nonporous spheres, and is also presented in Table 8.

In each experiment, between 0.1 and 0.5 g of basalt was allowed to equilibrate under slight agitation with 2 or 3 mL of water solutions to which plutonium(IV) and americium(III) tracers had been added (Table 9). Six measurements were made for each nuclide with each of the three mesh sizes used. The conditions used in these batch partitioning experiments and the measured distribution coefficients in the basalt materials of various particle sizes are given in Table 9. No difference in partitioning was noted (using the Student T Test) with materials of the two smallest mesh sizes (30-40 and 50-70 mesh) for either nuclide. However, the partition coefficient of americium was seen to increase for material in the 16-20 and 30-40 mesh sizes (greater than 90% confidence that they represent different values). This grain-size effect on americium is also evident from the data in Table 7. The partitioning of plutonium was also seen to decrease with increasing

Table 8. Surface Areas of Three Mesh Sizes of Columbia River Basalt

Mesh Size	Opening Width, μm	Surface Area Calculated for Nonporous Spheres, m^2/g[a]	Surface Area from B.E.T. Measurement,[b] m^2/g
16-20	850 to 1180	0.0020 to 0.0028	8.7
30-40	425 to 595	0.00398 to 0.0056	7.3
50-70	212 to 300	0.0079 to 0.0112	7.7

[a] Range of surface areas was calculated from the range of particle sizes (nonporous spheres) presumed to be in each size fraction.

[b] An indication of the sensitivity of the method was a measurement of a powdered sample of $BaCO_3$ giving a surface area of 0.1 m^2/g.

particle size for the two largest mesh sizes but less than for americium (plutonium partitioning values increased from ∿85 to ∿115 when particle size was changed from 16-20 to 30-40 mesh).

VI. DISCUSSION

In most static absorption experiments, the plutonium and americium were seen to be strongly absorbed into the rock. This strong affinity of nuclides for the rock phases would be expected to retard the migration of nuclides during infiltration. In infiltration experiments, nuclides of cesium, plutonium, and americium were seen to migrate much more slowly than did the infiltrating fluid. Much of the cesium moved with low velocity, as evidenced by the peak concentration of cesium being near the top of the columns (Fig. 3). Similarly, from the results in Table 5, most of the plutonium and americium was not eluted from the columns and therefore must have moved only a fraction of the distance of the water front. For example, for the first experiment listed in Table 5, it can be seen that only 2.6% of the activity was eluted from the column with a relative migration rate greater than 0.001 of the water front travel rate. This behavior is consistent with the high partitioning coefficients measured in the batch experiments and substantiates results reported previously.[1]

In order to model the transport phenomena of waste nuclides, simplifying assumptions concerning nuclide-rock reactions have been made.[2-4] These assumptions generally include the following: (1) that exchange reactions of nuclides between rock and solution are reversible, (2) that the nuclide-rock reactions are instantaneous so that the equilibrium of the nuclide between solution and rock is locally maintained within the rock, (3) that a rock formation can be represented as a continous homogeneous medium, and (4) that the concentration of each nuclide is sufficiently low that nuclides react independently of each other and do not affect macroscopic properties of the water.

Table 9. Batch Partitioning Experiments--Conditions and Measured Partition Coefficients in Basalt of Various Particle Sizes

Mesh Size	Sample Number	Sample Weight, g	Solution Volume, mL	Americium		Plutonium	
				Percent Absorbed	Partition Coefficient	Percent Absorbed	Partition Coefficient
16-20	147-1	0.262	2	91.6	83	n.p.[a]	
	147-4	0.561	3	92.9	70	n.p.	
	147-7	0.261	3	89.2	95	n.p.	
	157-1	0.207	2	89.4	81	91.6	106
	157-4	0.265	3	86.6	73	84.3	61
	157-7	0.408	3	93.0	98	91.7	81
	157-11	0.212	2	n.p.		92.7	119
	157-14	0.211	3	n.p.		78.6	52
	157-17	0.323	3	n.p.		92.0	107
30-40	147-2	0.146	2	91.0	138	n.p.	
	147-5	0.120	3	85.6	148	n.p.	
	147-8	0.356	3	93.5	121	n.p.	
	157-2	0.145	2	92.3	165	91.3	144
	157-5	0.248	3	91.8	135	90.8	119
	157-8	0.330	3	91.4	97	89.4	77
	157-12	0.165	2	n.p.		91.7	134
	157-15	0.179	3	n.p.		79.7	66
	157-18	0.333	3	n.p.		94.8	164
50-70	147-3	0.104	2	88.4	147	n.p.	
	147-6	0.151	3	92.5	164	n.p.	
	147-9	0.253	3	90.7	115	n.p.	
	157-3	0.120	2	94.4	280	91.8	187
	157-6	0.179	3	91.8	186	87.8	120
	157-9	0.286	3	94.0	165	92.1	122
	157-13	0.203	2	n.p.		91.6	108
	157-16	0.133	3	n.p.		83.5	114
	157-19	0.303	3	n.p.		91.2	103

[a] "n.p." indicates that the element was not present in the batch partitioning experiment.

Given these simplifying assumptions, a nuclide is expected to migrate down the column with a well-defined velocity. For a nuclide concentrated initially in a narrow band at the upper end of the column, continued elution of the column will move the band down the column. As the band moves down the column, it widens and assumes the shape of a Gaussian curve. The velocity of the peak of the nuclide band, V_n, relative to the velocity of the water front, V_w, is given by

$$V_n/V_w = \frac{1}{1 + (K_D\ \rho/\varepsilon)}$$

where ε is the porosity and ρ the density of the rock and K_D is the ratio of the nuclide between solid and solution as defined in Eq. 2.

Where diffusion is small in relation to the migration rate of the band, the band width due solely to the exchange reactions will be proportional to the square root of the distance the peak had traveled. Nuclide migration has been modeled to include dispersion of the type produced by diffusion of nuclides within the fluid. Diffusion of nuclides within the fluid will increase the width of the peak but will not destroy the Gaussian shape of the band.[5] This model of nuclide migration appears to accurately describe the movement of strontium in a column of glauconite aggregate.[2]

However, the simplified model of nuclide migration does not, in general, accurately describe results of nuclide migration obtained experimentally. From results of the static absorption experiments, the reaction rates appear to be well defined for a particular nuclide-rock system. It is seen from the data, however, that there is considerable variation in the characteristic reaction time for different nuclides and rocks; the reaction time varied from about 1 h for some systems to in excess of 600 h for others. With some rocks (*e.g.*, gneiss), the reaction times were long and steady state behavior was not attained, even in the 1000-h experiments (Table 6).

These results indicated that in different rock-nuclide systems, attainment of local equilibrium would require different reaction times and, consequently, different velocities of an infiltration fluid. Therefore, models of nuclide migration may need to consider conditions other than local equilibrium during fluid flow and the various reaction rates for different rock-nuclide systems.

Based on the distribution of nuclides in the rock columns or in the eluates during infiltration experiments, it is seen that the nuclides do not behave, in general, as predicted by models using simplifying hypotheses. For example, the skewed distributions of cesium seen in rock aggregate columns imply a large dispersion in the relative migration rates of cesium in both chalk and shale. Although a low migration rate of most of the cesium is evidenced by the high cesium concentrations at the top of the column, cesium is also present at the bottom of the columns, which is indicative of much higher migration rates for some of the cesium. The dispersion in migration rates is evident from the variation in migration rates seen in Tables 4 and 5. Similar dispersive characteristics were seen for plutonium, americium, and neptunium in rock columns; in all infiltration experiments with these nuclides, activity was detected in the initial one or two column-volumes of eluate that passed through the columns and was also present in all subsequent eluates sampled. Similar skewed distributions were observed for plutonium migration in tuff; the plutonium concentrations were in the form of tails decreasing exponentially with depth in the direction of fluid flow.[6,7] The experimental results suggest that models involving a single migration rate for these nuclides would not accurately represent their migration behavior in common rocks.

The great range in the observed relative migration rates implies that movement of nuclides, even in a uniform and homogenized material such as the rock aggregate used with cesium, has to be described by a model that accounts for this dispersion. Large field experiments which traced the advancing water front from one well to another[2,8] required a dispersive model of fluid flow to account for the observations. The dispersion was attributed to the channeling of water in the many cracks and subsequently the many pathways in the permeated medium for the water. Similar dispersive effects may exist in the column infiltration experiments due to a void structure in the rocks. Fluids moving through a rock aggregate or within rock pores would be continuously divided into finer offshoots and would be recombined into larger streams at intersecting flow paths. Variations in path lengths and fluid velocities in the different paths from one point to another would result in additional spreading of a peak as it migrates through the column. This type of dispersion, as determined in simply characterized media, increases with the distance the peak has traveled but preserves the peak symmetry.[8] Therefore, it cannot account for the skewed nuclide distributions seen in the infiltration experiments.

Several conditions may have existed in the infiltration experiments that could have contributed to the nonidealized behavior seen. Possibly, for example, the dispersion in nuclide migration was caused by large heterogeneities in the columns. Visible cracks in one column were found to result in greatly increased velocities of cesium. Channeled flow in similar but smaller cracks or in pores within the rock columns may have contributed to the observed nuclide distribution by allowing solutions to pass through the columns with little reaction with the rock.

Alternatively, dispersion may have been due to the flow rates used in the experiments being high enough to prevent equilibration of the solution and rocks. Reaction rates measured in static absorption experiments cannot be used to estimate the extent of equilibrium expected in the column infiltration experiments because the proportion of fluid to rock, and hence the reactant and reaction sites differ considerably in the two experimental techniques. In addition, in static absorption experiments, the nuclides in solution contact the rock by diffusion or advection processes, whereas in the column infiltration experiments the nuclides in solution are forced through the rocks. Nonetheless, the solution residence time in column infiltration experiments (typically 0.4 to 2 h) is often only a small fraction of the characteristic reaction time measured in static absorption experiments (5-1000 h), suggesting that nonequilibrium behavior might be expected in the column infiltration experiments. This effect would allow some of the nuclide to be washed through the column without retardation resulting from partitioning on the solid rock phase. The flow rates used in the column infiltration experiments reported here (calculated from the porosity in Table 3 and column elution rates in Table 4) are comparable to flow rates found for some groundwaters, and effects at these flow rates could be expected in natural systems.

Other factors that may have caused or contributed to the observed dispersive behavior might be the formation of colloids of the nuclides that react only slowly with lithic materials, the migration of clay or other particulate material with radionuclide adherence, and the effect of soluble organics, or bacterial activity. These conditions, except the last, may be present in geologic bodies considered for nuclear repositories.

The dispersive characteristics seen in the column infiltration experiments are likely to be important in assessing nuclide retention in geologic storage facilities. For example, plutonium is considered (on the basis of laboratory experiments) to have a strong affinity for lithic material and therefore a low migration rate relative to the advancing water front. From static partitioning measurements, plutonium in Salem limestone would be expected to have a relative migration rate of 4×10^{-4}. This calculated value is based on the simplifying assumptions stated previously and is consistent with the observation (from column infiltration experiments) that most of the plutonium was retained by limestone, even after continued infiltration. However, it is seen in Table 4 that 2.6% of the plutonium travels at a relative migration rate greater than 0.001. This small but finite amount of activity may present a radiological hazard, and the greater velocity associated with this activity than with the bulk of the activity may be a limiting factor in nuclide retention. This assessment that dispersion of relative velocities is important differs from recent viewpoints which suggest that dispersion is not a governing factor in the confinement of waste.[4]

VII. CONCLUSIONS

In rocks of silicate and carbonate minerals studied in static absorption experiments, plutonium and americium were found to be strongly absorbed by rock tablets. Relative migration rates of plutonium and americium by fluid flow, based on results of the static absorption experiments, are considerably lower than the velocity of the infiltrating water. The experiments also indicate that the reaction rates of nuclides in solutions and rocks vary considerably for different rock-nuclide systems. Therefore, for a solution containing several nuclides and moving through rock, conditions of local equilibrium may exist for some nuclides and not for others. Thus, models of nuclide migration need to consider the reaction rates of the individual nuclides.

In column infiltration experiments with shale and chalk, the peak concentrations of cesium in the columns were seen to move with low velocity, which is consistent with a strong partitioning of the nuclide onto the rocks. However, cesium activity was also seen in a long tail extending through the column from the cesium peak in the direction of water flow; it resulted from relative migration rates up to three orders of magnitude greater than that for the peak concentration. Nuclide activity downstream from the peak activities was also seen for plutonium, americium, and neptunium in solid rock columns of limestone, sandstone, and tuff. Therefore, there is a large difference in the relative migration rates of these elements in the common rocks studied. This needs to be considered if the behavior of these elements in geologic materials is to be described accurately.

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DISCUSSION--MARTIN SFIT7

Rock Studies by Infiltration Experiments (Section III)

Q. Do you have a more detailed breakdown of rock types listed in Table 3?

A. The chalk is quite pure. It's predominantly $CaCO_3$, although it does have some traces of black material in it--probably soot. The shale is quite complex, from both a mineralogical and an organic viewpoint. It has about 2% organic material. The limestone consists mostly of $CaCO_3$; I don't know its magnesium or iron content. The sandstone is much more complex than the limestone. The tuff is also quite complex, and is hard to characterize.

Q. Are the valence states shown for the nuclides in Table 3 those that you initially added to the solution?

A. Yes, we think so. In designing our experiments, we tried to create conditions that would be typical of repository sites in bedrock. We assume that the groundwaters and nuclides will assume characteristics that are comparable to those that would be found in the repositories; however, we have not yet verified that this in fact happens.

Q. Is the tuff zeolitized?

A. It's quite pliable.

Q. Is it from the Nevada Test Site?

A. Yes.

Q. How did you determine porosity?

A. By saturation experiments. We used a knife or saw to cut out a block of material of a certain volume, put that into an evacuator, and evacuated the emergent water. Then we infiltrated it with water and measured the differences in weight. We think this is representative of the kind of porosity we're looking for in infiltration experiments--not the closed type, but the type that is open to the surface and interconnected; and therefore available for infiltrating.

Infiltration Experiment Procedures (Figure 1)

Q. With a small sample like this, how did you avoid wall effects?

A. The walls were made a part of the column by packing the material into the columns. Shale swells quite markedly when it is wet, and chalk swells somewhat. Also, just by observation, we've never seen any removal of the materials from the wall. In addition, we have experimental results that demonstrate that we are not transmitting fluids from top to bottom without interacting with the column.

Q. How did you do the aggregate experiments?

A. Shales and chalk both look solid when dry, but when they are wet they disaggregate very easily. What we did was to lightly grind the material to make an aggregate, and then packed it into columns of this type. We hoped to be able to break them apart, so they would conform to the shape of the funnel, without actually breaking individual mineral grains and forming new types of materials.

Q. You mention that you used a preequilibrated solution. Did you check to see whether the solution going in and the solution coming out had the same composition?

A. No, but we suspect that there is no difference. When the water was equilibrated, it was reacted for periods of weeks, whereas its residence time in the column was only a matter of days.

Q. But wouldn't the rate of equilibration in the packed bed be faster than that in shaking experiments?

A. That's debatable. The experiment we did was to measure the total dissolved solid content in the preequilibrated waters from Day 1, Day 2, Day 3, and Day 4. After Day 1, we saw no increase in total dissolved solids. Shales, for example, stayed at 100 mg/l of dissolved solids after the first day. Given that the reaction appeared to be complete in one day, allowing a week was conservative, and allowing another week for the materials to settle out was still more conservative.

Q. If you have 10 g/l in an equilibration solution and 20 g of rock, doesn't that change your weight/volume ratio?

A. The assumption we made, which is true in most cases, is that the dissolved mineral content in the equilibrated water is sufficiently low that stirring 10 g of material will not change the compositon significantly. This is true in the case of shale. It is not true, however, in the case of salt, where large volumes can be dissolved in equilibrated solutions.

Q. Do you think you were at saturation with respect to the soluble components?

A. I think so, at least with respect to shale, dissolved mineral content did not change after the first day. Some of the experiments, however, were done only for selected situations; consequently, we don't know about all of the minerals to the same degree of definition.

^{134}Cs in Solution (Figure 2)

Q. What percentage of the total load is represented by the amount integrated under the curve?

A. About .01%--a small amount, but a significant one, and certainly measurable.

Q. Was there ^{134}Cs in the influent solution throughout the experiment or did you load the Cs in the first few column volumes and then run equilibrated water without Cs?

A. The solutions initially had Cs in them; as they began to pass out of the column, it was found that they had been stripped of this Cs. Later, some Cs trickled through; most of it, however, stayed in the columns. At a later point in the experiment, because the activity on the column was becoming fairly high, we decided to use groundwaters that did not have Cs in them. Thus, the latter portion of the curve represents solutions without Cs. Two interesting observations can be made in this regard: (1) since there was initially no activity from the solution containing Cs, the solution must have been intimately contacted with the rocks, with no leakage from side effects, chanelling, etc.; and (2) since, when the Cs-containing groundwaters were replaced with waters without activity, the element still had about the same rate of activity, the Cs implanted in the column must have been in dynamic interaction with the groundwaters.

<u>Rock Aggregate Activity (Figure 3)</u>

Q. Is the Cs moving as a soluble form or on a very fine particulate in the top layer of the column?

A. Both are quite possible. I'm not sure whether we have experimental data that will differentiate between these two possibilities.

Q. Since the equilibrated water will have a large quantity of micron-sized particles that will serve as carriers, could you be getting a combination of a physical deposition at the surface of the rock and a soluble component that is ionized throughout?

A. The problem with that view is that, if the Cs were carried along on these small particles that were pushed down the column, we could then expect to see some activity in the initial eluates that pass out of the column. Since we do not see such activity, we can assume that this is not happening.

Q. This kind of curve is sometimes obtained when you have a column that channels. Have you ever tried using a colored solution to determine how the advancing front moves down?

A. I don't think we need to worry about that possibility, since the initial eluant showed no activity.

Q. You could still have channeling, even with a delay of 10-20 column volumes before activity appears, since the effect could be in the form of a jagged front that moves down.

A. I don't eliminate that possibility. Some of the features shown here appear in the experimental results for intact cores, too. Whether they are due to fingering, channeling, or some other phenomenon, they seem to be a common feature of this type of infiltration experiment.

Q. How did you measure peak velocity? (Table 4)

A. I didn't measure peak velocity; I measured the upper limit to the movement of that peak velocity.

Q. Do your results mean that Cs moves faster in shale than in chalk? (Figure 3)

A. No, the differences just represent variations in sample size: I took smaller samples of the chalk.

Q. What kind of curve would you get if you added ^{3}H to your effluent?

A. We never used ^{3}H, but we did use iodine in some of these carbonate or silicate experiments. Iodine is similar to ^{3}H in that it does not react with some rocks. In the rocks with which it does not react, the activity both emerged and diminished quite rapidly. This suggests that fingering is not a dominant effect in this type of experiment.

Q. Is the flow rate constant all this time?

A. The pressure above the column is constant, but we found that the flow rate, which started out fairly high, diminished with time--probably due to packing of the materials. Thus, they went from an equivalent of 50-100 m/yr to about 7m/yr.

Q. Your experiments went on for several days; could you have been getting any biological growth?

A. I don't know. In the control experiment, however, standing tubes of groundwater with Cs in them were measured on a weekly basis for the activity of the Cs that remained in solution. The activity in the chalk remained constant for periods of months. That of the shale did change fairly rapidly after 2-3 weeks, furthermore, a precipitate formed on the bottom of the tubes. These changes could have been due to biological growth.

Q. If you ran the experiment five times as long and put five times as much material through, would the shape of the curve representing the concentration/depth ratio remain the same, or could the peak saturate and then move down?

A. I don't know; we haven't had the time to run longer experiments yet. We've ordered some new equipment, however--items such as peristalic pumps and solvent metering pumps--that will allow us to run these experiments for months at a time in isolated systems; then we should be able to obtain the type of data that you're asking for.

DISCUSSION--PAUL RICKERT

Reaction Times Compared (Table 6)

Q. What were the reaction times with galena?

A. They were almost nonmeasurable. The K_d shows that very little was absorbed from solution. We didn't get a curve that dropped down and leveled off, so we didn't measure the reaction rate.

Q. Did you run blanks, too?

A. No, we did not. However, after the experiment was finished, we took the solutions out of the test tube and determined the amount of activity that had been absorbed by the test tube walls. Often, we found that up to 20% of the activity that seemed to be associated with the solution was actually associated with the test tube walls. To correct for this factor, we subtracted the wall activity figures from the original figures obtained before determining K_d values.

Q. What was the composition of the solution in which you ran the equilibrations?

A. These were rock-equilibrated waters; that is, distilled water was allowed to equilibrate with ground-up samples of rock.

Autoradiographs Planned (Section IV)

Q. Did you look at the tablets after you finished the experiment, to try to determine whether the bonding was a chemical bonding, a physical adsorption, or some other factor?

A. No, but we plan to do autoradiographs in the near future.

Further Tests of Pu, Am

Q. Did you run duplicate experiments for comparison?

A. The experiments with Pu and Am in combination were done in triplicate.

Q. How well did the replicates check out with one another?

A. Initially, we ran three tablets of each rock type. In the first case, the solution was just spiked with Pu; in the second, with Pu and Am; and in the third, with just Am. After the first set of reactions had been completed, we noticed that the reaction rates for Am were different when the rock was equilibrated with Am alone from those in which it was equilibrated with Am and Pu. Then we added the complementary nuclide to each of the experimental solutions, both to see if the amount of the initial nuclide that had been adsorbed by the tablet would be altered, and to check the reaction rate of the complementary nuclide. We found that, if we added Am to a solution that already contained Pu, Am was adsorbed in the same way as it had been in the two nuclide experiments. However, when we added Pu to a solution that already contained Am, we saw a rapid decrease of both Am and Pu in solution, at a rate comparable to that of Pu in the single-nuclide experiment. We are not sure whether Pu is causing the synergistic effect, or whether it is some other factor, such as a contaminated solution; however, we are currently planning experiments to try to answer this question.

Q. Did the samples dry out between immersions?

A. No, they did not.

Q. How do you add the ^{237}Pu?

A. We took nitrate solutions of the tracers to dryness, then dissolved them in distilled water, and took a spike of that--about 10λ of

^{237}Pu--and added it to 2 ml of solution. It did not change the overall volume of the solution significantly.

Q. Did it change the pH?

A. We are not sure whether drying the nitrate solutions to dryness results in an alteration of pH when they are redissolved, but we think that it does not change pH very much.

Comparison of Experimental Methods

Q. How do the various experimental methods compare? Did you reach any conclusions about them?

A. We compared batch, static, and column infiltration experiments run in sandstone and tuff from the Nevada Test Site. We found a wide difference in Pu adsorption between static and batch adsorption experiments--a K_d of 11 for the static and 326 for the batch. In general, we found that the tablet experiments gave more conservative K_d values than did the batch adsorption experiments. In some cases, however, the batch experiment did not give as large a value as the static adsorption experiment. With column infiltration experiments, when water is pressurized and forced through a column of sandstone, we found that about 70% of the activity came through in approximately 203 column volumes. Approximately 3% came through in the first three column volumes, and then it diminished to 2%, etc., eventually leveling off at a few tenths of a percent. It continued to elute at that rate for a total period of 203 column volumes. These data seem to suggest that, for certain rocks and certain systems, ion exchange is not the mechanism.

Q. I agree with that, but I don't agree with the way you're interpreting your column infiltration data. Could some of the mathematicians in the group give us some insight on that question during the open discussion?

(No answer given)

Q. What if the K_d values were related on a surface-area basis rather than a weight basis?

A. I don't know. With granulated basalt and several other rock samples, we measured surface areas. We didn't see a change in surface area with decreases particle size, although the BET measurements may not have been applicable in this particular case. We also failed to see a large change in nuclide adsorption with decreased particle size. Therefore, we cannot be sure that surface area is a governing factor.

Characterization of Minerals

Q. I still have a problem with the fact that the systems do not appear to be characterized well enough.

A. We know what limestone is: it is $CaCO_3$, with a little Fe and some Mg. We can characterize all we want, but we'll still see the same phenomena.

Q. I've seen a wide range of limestone types in the field; some are only 10% $CaCO_3$.

A. I still think limestones can be characterized in a generic way, and this characterization will be representative of 90% of all limestones. Furthermore, since the phenomenon occurs with a variety of nuclides and a variety of rock types, it appears to be a general one rather than one specific to certain minerals; therefore, such specific characterization does not appear to be particularly important in this case.

Applicability of Ion Exchange

Q. Before you conclude that the ion exchange modeling efforts are no good, you should also address the question of possible side effects--e.g., scaling or channeling.

A. We will be doing experiments in the near future to see the effects of increasing the column length. With the increased time that this change will provide, it is possible that ion exchange will take place and we will see a larger percentage of activity coming out of the first few column volumes.

Q. Isn't it incorrect to talk about whether the ion exchange mechanism holds or does not hold? The theory holds; but, for it to work, you have to change the ion concentration; which you have not done. You are using a single ion concentration and obtaining a single set of data. Therefore, you should be saying that your measurements are not in equilibrium or are not comparable.

A. I agree. In the laboratory, we can artificially create a system in which we obtain very good ideologic behavior. Our point is that, in general, this is not the kind of behavior that we see.

"SYSTEMATIC STUDY OF NUCLIDE SORPTION ON SELECT GEOLOGIC MEDIA"

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Abstract

Various methods are being employed to systematically measure the distribution of solutes of interest in radioactive wastes on a few selected compounds typifying adsorptive components of natural formations from aqueous solutions over a wide range of ionic strength at controlled pH. These methods include conventional "shaking" experiments, column methods, and axial filtration. The need for an enormous number of measurements in a systematic investigation dictates that these methods will have to be as rapid as possible, as well as reproducible and accurate. We are, therefore, testing these techniques and modifying them to meet these goals. Their utility is being evaluated both by the internal consistency of results obtained for adsorbent-adsorbate systems over a range of experimental conditions and by agreement of results by different methods under the same conditions.

Early emphasis has been upon measuring adsorption functions with samples of montmorillonite obtained from various sources. We are examining these clays by various analytical methods and have spent considerable time investigating various methods of treatment and purification.

We have determined values of the distribution coefficient for Cs^{+}, Sr^{2+}. and K^{+} in exchange with Na^{+}. The adsorption functions for Cs^{+}/Na^{+} exchange with a number of samples of montmorillonite were surprisingly ideal. Ideality of exchange with Sr^{+} and K^{+} has not been observed so far, but large decreases of the distribution coefficient with increasing ionic strength have been observed.

Introduction

An important criterion in selection of geological formations as disposal sites for wastes from the nuclear power industry is the degree to which the radioactive substances can be immobilized by the storage environment. The retention depends on the very complicated chemistry of the minerals and on their interaction with the widely different compositions of ground water which may pass through; distribution of species between solid and liquid phases will be a strong function of both. The complexity of making choices can be inferred from Table I, a listing of minerals of priority interest which has been provided us, and Table II, a tabulation of nuclides whose isolation appears of particular importance. It would probably be prohibitive to try to accumulate the quantity of information which would be necessary for anything close to an optimal choice from the vast number of plausible possibilities. Further complications arise from the effect of temperature, variations of which can be expected both from the heat generated by radioactivity and from the diversity of temperatures in potential repositories.

The situation would be more manageable if systematic information were available on various classes of formation components, particularly those of high ion-exchange activity. Since the minerals listed in Table I can be ordered in relatively few classes, it is reasonable to hope that there will be parallels in dependence of adsorption on ionic strength and other variables, which will decrease the number of measurements necessary to define properties adequately. Barring synergistic effects, which appear unlikely (though the possibility of them must be checked), suitability of geological formations could be screened from data on model components.

We are, therefore, systematically measuring the distribution of solutes of interest in radioactive waste on a few selected compounds typifying adsorptive components of natural formations, from aqueous solutions over a wide range of ionic strength at controlled pH and also at controlled Eh, when necessary. In later stages, adsorption from more complex brines and the effect of temperature variations will be investigated, and the predictability of adsorptive properties of complex natural minerals from those of key constituents will be determined.

Methods and Materials

1. Methods: In view of the wide variations in results from studies of adsorption on minerals in the literature from different laboratories, development of methods is an essential component of our activities, especially in the early stages. The need for an enormous number of measurements in a systematic investigation dictates that the methods will have to be rapid, as well as reproducible and accurate. We are testing several techniques and modifying them for present purposes. Their utility is being evaluated both by the internal consistency of results obtained for adsorbent-adsorbate systems over a range of experimental conditions and by agreement of results by different methods under the same conditions.

Attainment of reliable results also requires attention to the kinetics of adsorption. The rates of adsorption are also, of course, pertinent to the applications of interest here.

Three methods are so far being used to obtain adsorption information: conventional "shaking" experiments, column methods, and axial filtration. There are different modes of operation with some of these methods favorable for different situations.

In our shaking experiments, weighed amounts of purified and properly pretreated clay are shaken with known volumes of solution and, usually, the reduction of concentration of the adsorbate in the solution is determined after separation of solid and solution by centrifugation or other means. An appropriate analytical technique, atomic absorption or counting of radiometric tracers, for example, is used to determine concentration. 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.

Columns made from montmorillonite alone have insufficient flow rate, for efficient rapid determination of exchange equilibria. We have, therefore, been experimenting with various methods of bringing throughput to reasonable levels by mixing clays with other materials which are expected to have low adsorbability. We have tested columns containing montmorillonite and various proportions of a number of materials, including glass beads (100 to 150 microns in diameter), sand, asbestos, and Celite (a diatomite filter aid).

Satisfactory flow rates have been obtained under gravity flow with columns that are about 2 cm long and 0.5 cm in diameter. Distribution coefficients have been determined for Cs^+/Na^+ exchange with columns containing montmorillonite and Celite, and the results are given below in the results section.

We have begun using an axial filter to determine values of $\underline{D}$ with montmorillonite. This system, illustrated schematically in Fig. 1, uses a cylindrical filter rotating about its axis which is enclosed in a coaxially-mounted cylindrical pressure vessel. Solution is introduced into the outer chamber and then flows through the filter into the cylindrical space within the filter and finally out through a tube mounted on the axis of rotation. The adsorbent can build up on the filter at low rpm; in this mode, the filter acts as a shallow bed, high area, multiplate column. At sufficiently high rpm (typically several thousand) the adsorbent may be uniformly suspended in the pressure chamber. The device then acts as a (single-plate) stirred-tank reactor. It is this mode which we are at present modifying for distribution coefficients lower than those previously measured. If adsorbate is introduced into the slurry, the concentration of the adsorbate in the filtrate (under the proper conditions) will build up to the initial concentration as the adsorbent reaches equilibrium with the particular solution used. The equation describing the change in concentration is

$$\ln(1 - (C/C_o)) = -V/(V_f + m\underline{D}) \tag{1}$$

where C is the concentration of the effluent,

C_o is the initial concentration,

V is the volume of the effluent,

V_f is the volume of the solution contained within the outer chamber of the filter,

m is the weight of the adsorbent, and

$\underline{D}$ is the distribution coefficient

If $\ln(1 - C/C_o)$ is plotted vs V, a straight line is obtained from whose slope the expression $(V_f+m\underline{D})$ can be calculated. Since m and V_f are known, the value of the distribution coefficient can then be calculated. The distribution coefficient could also be calculated from any point on the curve such as C/C_o equals 1/2 or by determining the total amount of adsorbate on the adsorbent by integration of the curve shown in Fig. 2. The reversibility of exchange may be checked by eluting the adsorbate with the adsorbate-free solution. The principal advantage of this method is the ease and rapidity with which series of determinations of D may be made and exchange kinetics can be checked.

After some selection of filtering surfaces, satisfactory flow rates with montmorillonite in the pressure chamber and with solutions of high ionic strength have been obtained, at moderate pressure (< 20 psi) and at 2500 rpm rotation velocity. The results for Cu(II)/Na(I) exchange, (chosen primarily for convenience) are shown in Figure 2. No Cu(II) was initially in the chamber. The ratio of effluent concentration C to feed concentration C_o as a function of volume passed through the system lags behind that computed for no adsorption. For the example shown in Figure 2, a value of (V_f+mD) of 235 cc was obtained from the slope of a plot of $\ln(1-C/C_o)$ vs V. Since m is 4.4 grams and V_f equals 185 cc, a value of D equal to 11.4 was obtained. For a batch experiment under comparable conditions, D was 12 cc/gm at 0.6M NaCl, 16 at 1.1M, 16 at 2M, and 14 at 4.1M.

Note that the adsorption and elution curves are symmetrical and cross at $C/C_o = 0.5$. This implies that there are no significant kinetic difficulties.

2. Materials: Our samples of clay minerals include the following:
   - A. Source clays, Dept. of Geology, University of Missouri.
     1. STx-1 Ca-Montmorillonite (White), Gonzales County, Texas.
     2. SWy-a Na-Montmorillonite, Crook County, Wyoming.
   - 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).

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 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 NaAc-HAc pH 5 reagent to remove carbonates, then with 30% H_2O_2 to remove organic matter, and finally with sodium dithionite to remove hydrous iron oxides.

We have also examined some of our clays with x-ray and scanning electron microscope techniques. Figures 3 and 4 show some of the results of these measurements for the Na-montmorillonite obtained from the University of Missouri. The Ca x-ray maps in Figure 3 correspond to the pictures above them and show that Ca-containing impurities are present as discrete particles corresponding to the bright spots in the x-ray map. In Figure 4, the same clay is shown after purification, and in this figure, the Ca x-ray maps show that esentially all discrete particles containing Ca and Fe impurities were removed by the purification procedure. The general spectrum is also shown in Figure 4. The chlorine shown is from a small amount of NaCl left in the clay that was not removed by the washing step prior to drying.

Besides montmorillonite, we also have obtained samples of kaolinite, attapulgite, dickite, halloysite, illite, and sand.

Results and Discussions

In our initial experiments on the determination of adsorption functions, our emphasis has been on the determination of the ideality of exchange at low loadings of the adsorbent. Consider the ion exchange equilibrium represented by the following equations:

$$M^{n+} + n\overline{A}^{+} \rightleftharpoons \overline{M}^{n+} + nA^{+} \tag{2}$$

$$K = \frac{(\overline{M})\ (A)^{n}}{(M)\ (\overline{A})^{n}} \cdot G \tag{3}$$

where the bars over the concentration terms represent adsorbed species, K is the equilibrium constant, G is the product of the activity coefficients of the various species, and A represents a singly charged ion such as Na^{+}. If the capacity of the adsorbent is C, then assuming no invasion of co-ions,

$$(\overline{A}) = C - n\overline{M} \tag{4}$$

If $\overline{M}$ is present at trace loading, i.e. at only a few per cent of capacity, then

$$(\overline{A}) \approx C \tag{5}$$

so that

$$\frac{K}{G} \approx D.\ \frac{(A)^n}{(C)^n} \qquad (6)$$

where D, the distribution coefficient equals $(\overline{M})/(M)$. Assuming K/G to be constant (ideal conditions), rearrangement of Equation 6 and differentiation yields

$$\frac{d \log D}{d \log A} \approx -n$$

A plot of log D vs log A should therefore be a straight line of slope equal to -n under the ideal conditions of trace loading and constant K/G.

Adsorption functions have been determined for Cs^+/Na^+, $K^+/Na^+/$ and Sr^{2+}/Na^+ exchange, and the results are shown in Figure 5 and Tables III & V. Before an exchange experiment, the clay was washed several times with concentrated salt solution to convert it entirely into the desired form, e.g., with NaCl to convert it to the Na^+ form. In each series pH was controlled with either bicarbonate or acetate buffers.

The results of a series of experiments for Cs^+/Na^+ exchange with a number of montmorillonites are shown in Figure 5. (See listing of montmorillonite given above. The symbols Na and Ca under the "code" heading refer to the sodium and calcium montmorillonites from the University of Missouri.) These clays were purified by the methods described above. For the Na-montmorillonite, experiments were conducted both before and after iron removal with insignificant changes in D. Slopes of log D vs. log c_{NaCl} were similar for all samples, and not greatly different from minus 1, the value predicted for low Cs(I) loading and constant ratios of activity coefficients in the solid and solution phases. Absolute values of D at a given NaCl concentration fell within a factor of ~5, a range narrow enough to encourage us that useful predictions can be made of properties of natural materials from measurements on individual samples. The effect of pH between 5 and 8 is not great. In these experiments clay to solution ratios were varied in order to obtain maximum analytical accuracy (see the example for K^+/Na^+ exchange given in Table 3). Equilibration times were 24 hours.

The results for K^+/Na^+ exchange are given in Table 3. For these experiments, equilibration times were three days. Table 4 shows results for Sr^{2+}/Na^+ exchange. In this case, duplicates are shown and experiments were run with and without the acetate buffer. Solution to clay ratios varied from about 75 to 7.5 cc/gm depending on the concentration of Na^+. Loadings varied from 15×10^{-3} moles per kg clay at 0.2M Na^+ to 0.4×10^{-3} at 5.5M Na^+. Equilibration times were five days. For these and most of our experiments, 10 ml tapered-tip polypropylene centrifuge tubes were used for the equilibrations.

The results for potassium and strontium exchange when plotted as log D vs log A do not give the expected slope of -n. However, in both cases, there are large decreases in the value of D as the concentration of sodium ion is increased. We are somewhat concerned about our atomic absorption analytical procedure for strontium, and we therefore plan to check Sr^{2+}/Na^+ exchange results by other procedures.

Table 5 shows the results of a comparison of Cs^+/Na^+ exchange for adsorption functions obtained with both batch and column experiments. The columns were constructed of Celite (a diatomite filter aid) and montmorillonite. Elution curves from 20% clay columns, when operated at 60°C, were quite symmetrical at NaCl concentrations of 4 and 2 moles/liter. At lower concentrations, some tailing was observed. In these experiments, small amounts of solution containing 5×10^{-3}M tracer were introduced into the top of the column and eluted by a NaCl solution of the same concentration as that containing the exchanging ion. The agreement between column and batch methods is quite satisfactory, and we plan to continue using this type of column for other exchange systems.

We have also been concerned with the possible effects that would be observed if two different adsorbents with different values of K/G (cf. Eqs. 2-6) were mixed together. By solving simultaneously two equations of the form of Equation 3, but with different values of K/G, we were able to construct theoretical log D vs log A plots for the mixed adsorbent but with the same adsorbate. Because a great number of calculations were involved, especially for the quadratic equations with 2/1 exchange, a computer was used to make the calculations and plot the results. Examples are given in Figures 6 and 7. In Figure 6, K/G for component one is 1 and for component two is 100, and the value of M, the concentration of the adsorbed ion, is 10^{-4} M at equilibrium. In this case, plots of log D vs A are linear but displaced according to the percent of component two, and loadings of both components one and two are low. For the case shown in Figure 7, all conditions are the same except that K/G for the second component is 10,000 and M is 10^{-3}M. Under these conditions, the equilibrium constant is very high and the concentration of M is relatively large. The loading of component two is therefore high and linear plots are not obtained.

Conclusions and Recommendations

With regard to methodology, we are fairly satisfied that our "shaking" and axial filtration methods can give us the reproducible, accurate sets of data which we need. However, additional work will be done on the axial filter in order to speed the acquisition of data. We are less satisfied with our column methods, and because we believe that development of these column methods is important because of their speed and convenience for systems with low distribution coefficients, we shall continue to spend time in their development.

We have spent a great deal of time in investigations of purification procedures for clays, because we believe it is of particular importance to obtain reproducible measurements with relatively pure materials so that we shall have a good starting point for the examination of mixtures. We feel that our purification procedures are now sufficiently developed that we may now proceed with determinations of adsorption functions on pure materials. Because we have spent much more time than originally planned on these procedures, we have not yet begun as many adsorption measurements as we had planned at this date, particularly with low capacity adsorbents. However, we are encouraged by results such as those shown in Fig. 5. The linearity of the slopes and the near negative unity slope show that the behavior of these adsorption functions is surprisingly ideal. These plots also illustrate the wide variation in distribution coefficients that can occur when the ionic strength is changed.

TABLE I

A Mineral Classification Scheme, with Approximate Empirical Formulae

I. Silicates	
A. Feldspars	
1. Orthoclase	$KAlSi_3O_8$
2. Plagioclase	
Albite	$NaAlSi_3O_8$
Anorthite	$CaAl_2Si_2O_8$
B. Pyroxene	
1. Augite	$CaMg(SiO_3)_2$ with $(Mg,Fe)(Al,Fe)_2SiO_6$
C. Amphibole	
1. Hornblende	Complex silicate of Ca, Al, Mg, Fe(II), Fe(III)
D. Mica	
1. Muscovite	$H_2KAl_3(SiO_4)_3$
2. Biotite	$H_2K(Mg,Fe)_3\ (Al,Fe)(SiO_4)_3$
E. Others	
1. Quartz	SiO_2
2. Olivine (Chrysolite)	$2(Mg,Fe)O \cdot SiO_2$
3. Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
Illite	$(K_2O)_{1/2}Al_2O_3 \cdot (SiO_2)_3 \cdot 7H_2O$
Montmorillionite	$(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2(H_2O)_{5to7}$
II. Other Oxides	
1. Gibbsite	$Al_2O_3 \cdot 3H_2O$
2. Limonite	$2Fe_2O_3 \cdot 3H_2O$
Hematite	Fe_2O_3
Magnetite	$FeO \cdot Fe_2O_3$
3. Amorphous (Fe, Al, Mn) Hydrous Oxides	
III. Carbonates	
1. Calcite	$CaCO_3$
2. Dolomite	$CaCO_3 \cdot MgCO_3$
IV. Sulfates	
1. Gypsum	$CaSO_4 \cdot 2H_2O$
2. Anhydrite	$CaSO_4$
V. Phosphate	
1. Apatite	$CaF \cdot Ca_4(PO_4)_3$

TABLE II

Nuclides in Wastes Most Critical for Immobilization

1st Priority	Pu, Am, Cm, Np, U, Ra, Tc, I, Sr, Cs
2nd Priority	Eu, Sm, Zr, Ni, ^{14}C

Table III

Distribution Coefficients for K^+/Na^+ Exchange

pH 5 Acetate Buffer 3 Day Equilibration

Conc. Na^+ Molarity	Wt. Clay gm	Solution Volume cc	D cc/gm
4	1.5	4	0.9
2	1.5	4	1.6
1	1	4	2.6
0.5	0.5	4	3.2
0.25	0.25	4	5.0
0.1	.1005	4	14.7

Table IV

Distribution Coefficients for Sr^{2+}/Na^+ Exchange

5 Day Equilibration

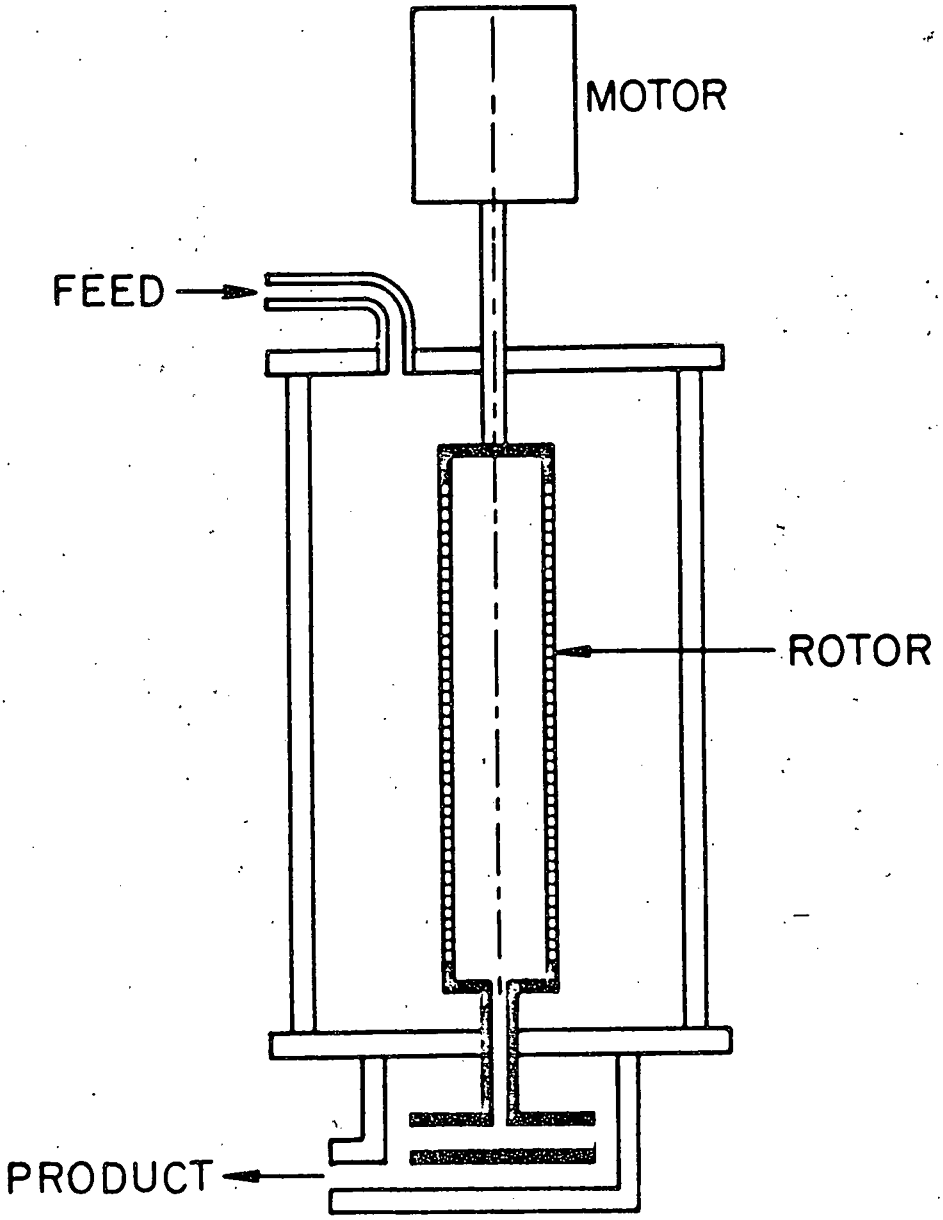
Without Buffer pH ∿ 7.6		With Acetate Buffer, pH 5	
Conc. Na^+ Molarity	D cc/gm	Conc. Na^+ Molarity	D cc/gm
0.2	113.5	0.2	52.9
	108.4		52.9
0.6	33.6	0.6	28.4
	33.0		30.3
2.1	8.7	2.1	13.0
	8.7		12.2
5.5	3.52	4.7	1.3
	3.48		1.3

Table V

Comparison of Batch + Column Methods for Cs^+/Na^+ Exchange

Conc NaCl (moles/ℓ)	4	2	1	0.5
D (Batch) 22°, cc/g	2.0	5.0	10	20
D (Column) 60°, cc/g	∿2	5.8	13	20

ORNL-DWG. 74-4005



AXIAL FILTER

Fig. 1

ORNL-DWG 77-12619

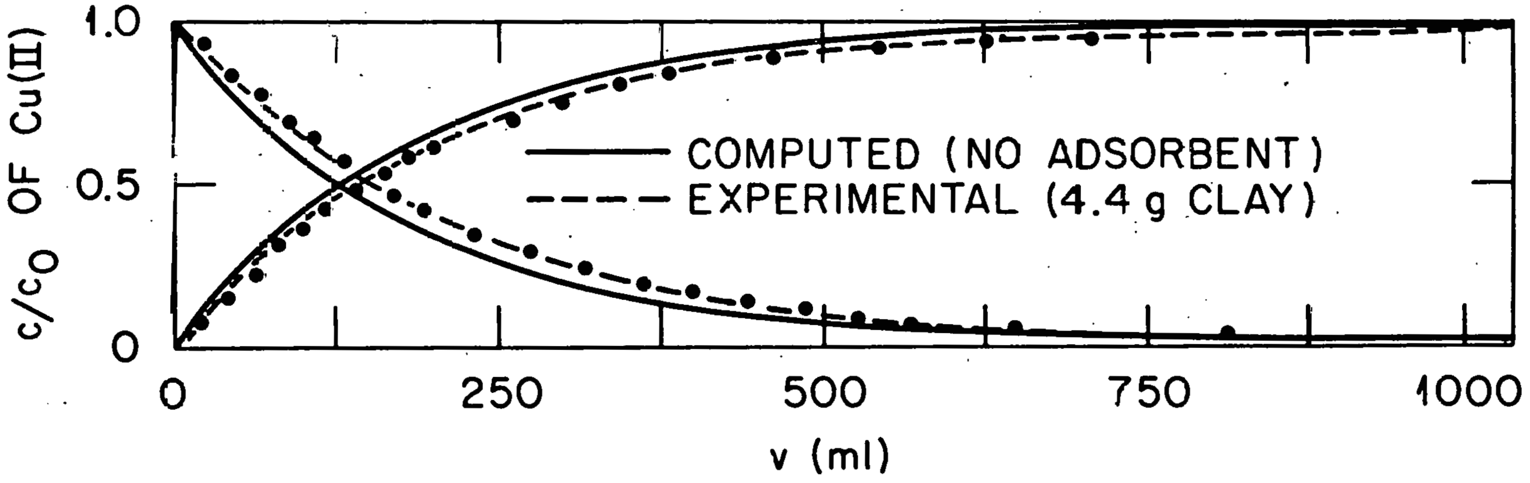
Na MONTMORILLONITE

(NaCl + BUFFER pH 5) 1.0 *M*

$CuCl_2$ $1 \cdot 10^{-4}$

2500 rpm T = 28°C

CHAMBER VOLUME ~185 cm^3



Use of Axial Filter to Measure Adsorption and Elution

(Low Distribution Coefficients)

FIG. 2

OAK RIDGE NATIONAL LABORATORY
Analytical Chemistry Division
Physics Methods Laboratory
Building 4500N Room E-10 Phone 3-0155
PM Number 2429

ORNL-Photo 3885-77

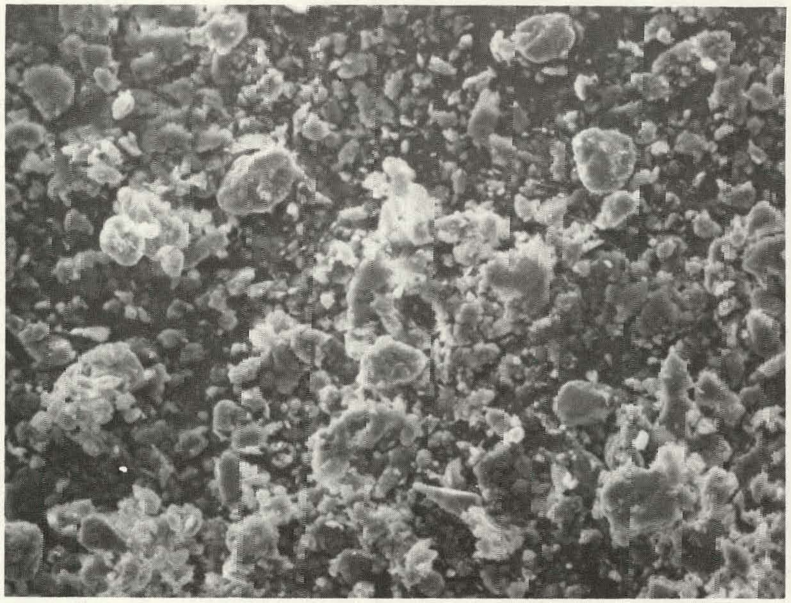
Date: 17 Aug 1977

Name: R. E. Meyer

Specimen: Na - Montmorillonite

Comments: X-ray maps of calcium-containing particles
S-6549 is an expanded view of central particle in S-6548

Sample
S- 6548 Mag: 350X



Sample
S- 6548 (Ca Kα Map) Mag: 350X

Sample
S- 6549 Mag: 3500X

Sample
S- 6549 (Ca Kα Map) Mag: 3500X

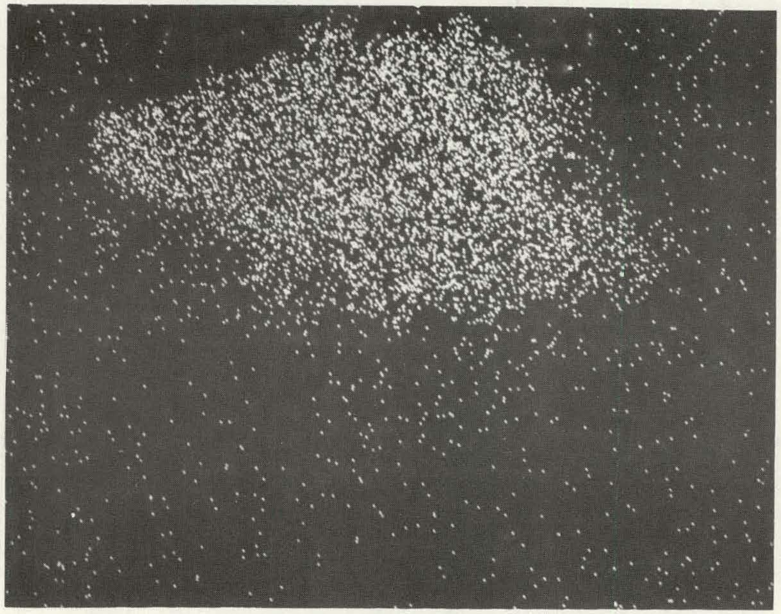


Fig. 4

Date: 23 Aug 1977

ORNL-Photo 3882-77

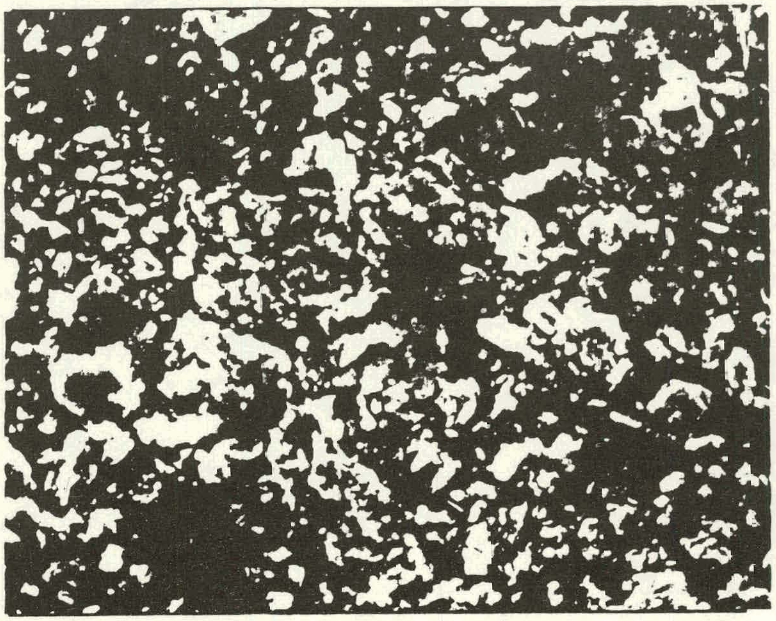
Name: R.E. Meyer

Specimen: Purified "RT" Na-Montmorillonite (Fine)

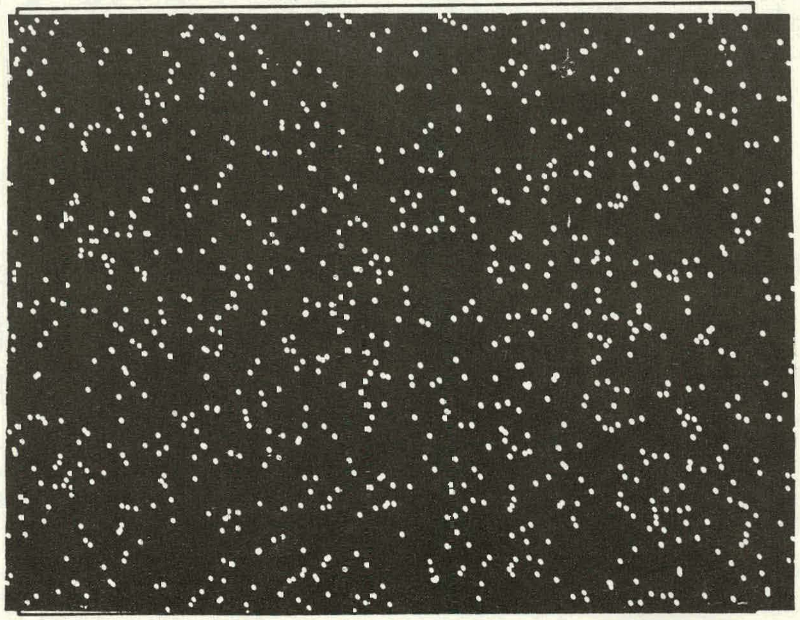
Comments: Photograph, General Spectrum, Fe and Ca Maps of finely divided Na-Montmorillonite - Purified by "RT" process

OAK RIDGE NATIONAL LABORATORY
Analytical Chemods Division
Physics Methods Laboratory
Building 4500N Room E-10 Phone 3-0155
PM Number 2513

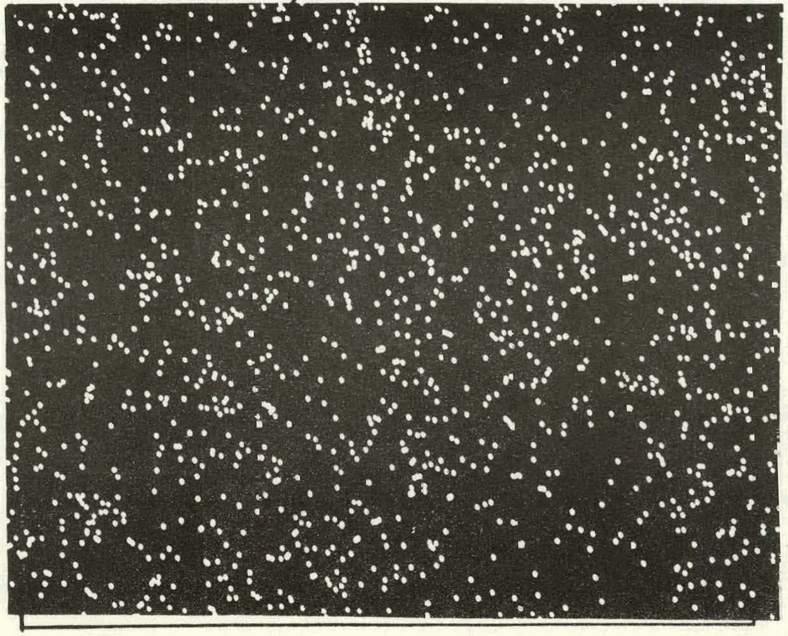
Sample
S- 6552
Mag: 700 X



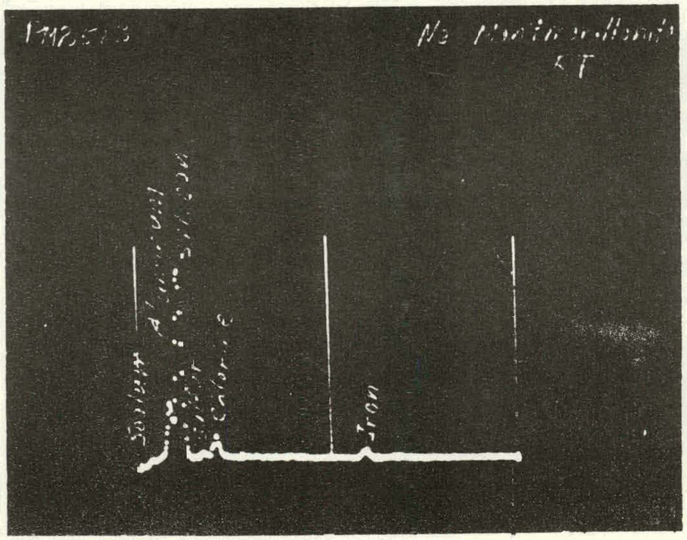
Sample
S- 6552 - Ca Map
Mag: 700X

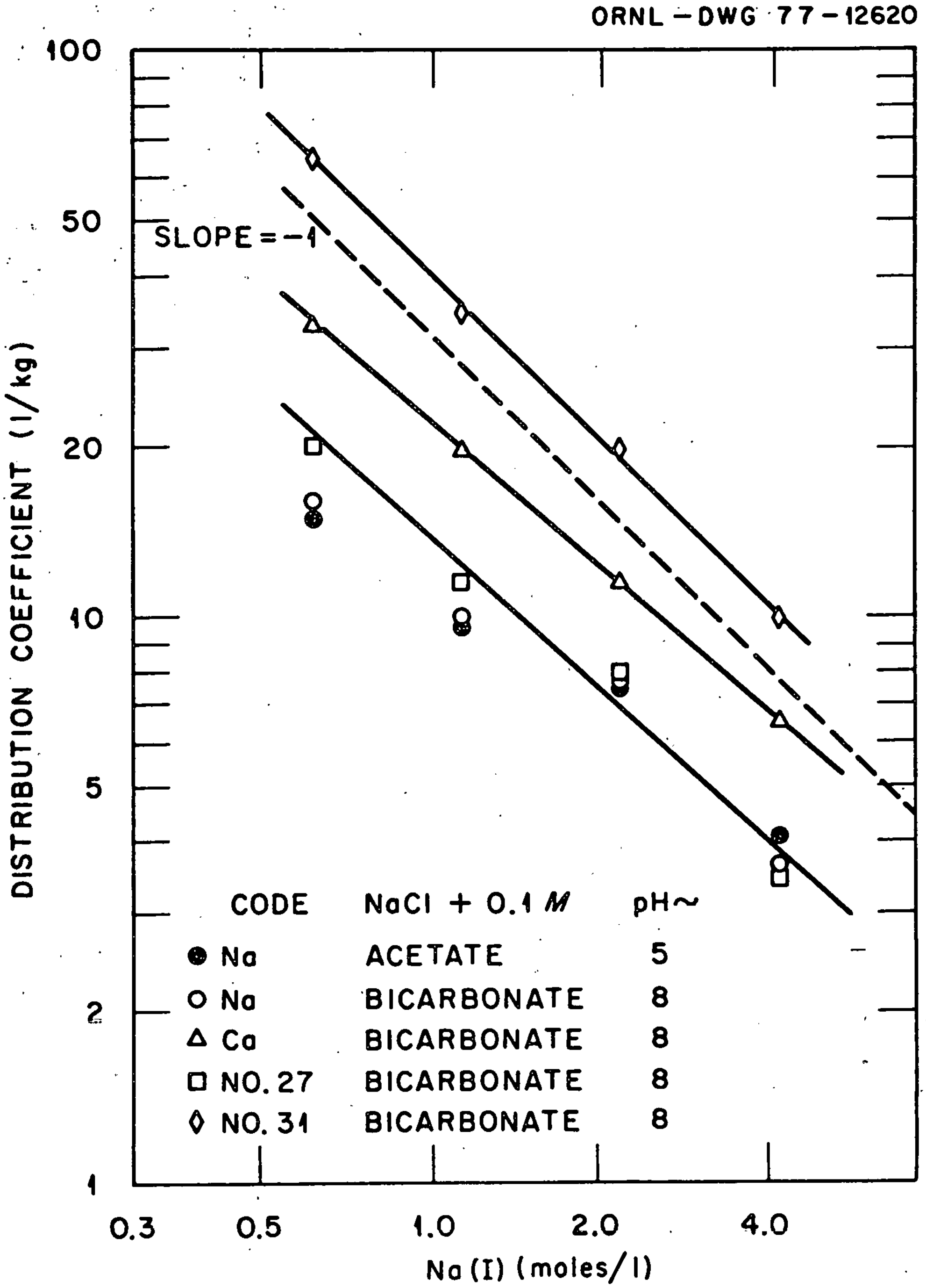


Sample
S- 6552-Fe Map
Mag: 700 X



Sample
S- General Spectrum of S 6552
Mag:





Distribution of Cs (I) Between Aqueous NaCl Solutions and Montmorillonite from Several Sources $[\sim 10^{-3}\ M\ \mathrm{Cs(I)}]$

FIG. 6

Log D vs. Log A for 1–1 exchange

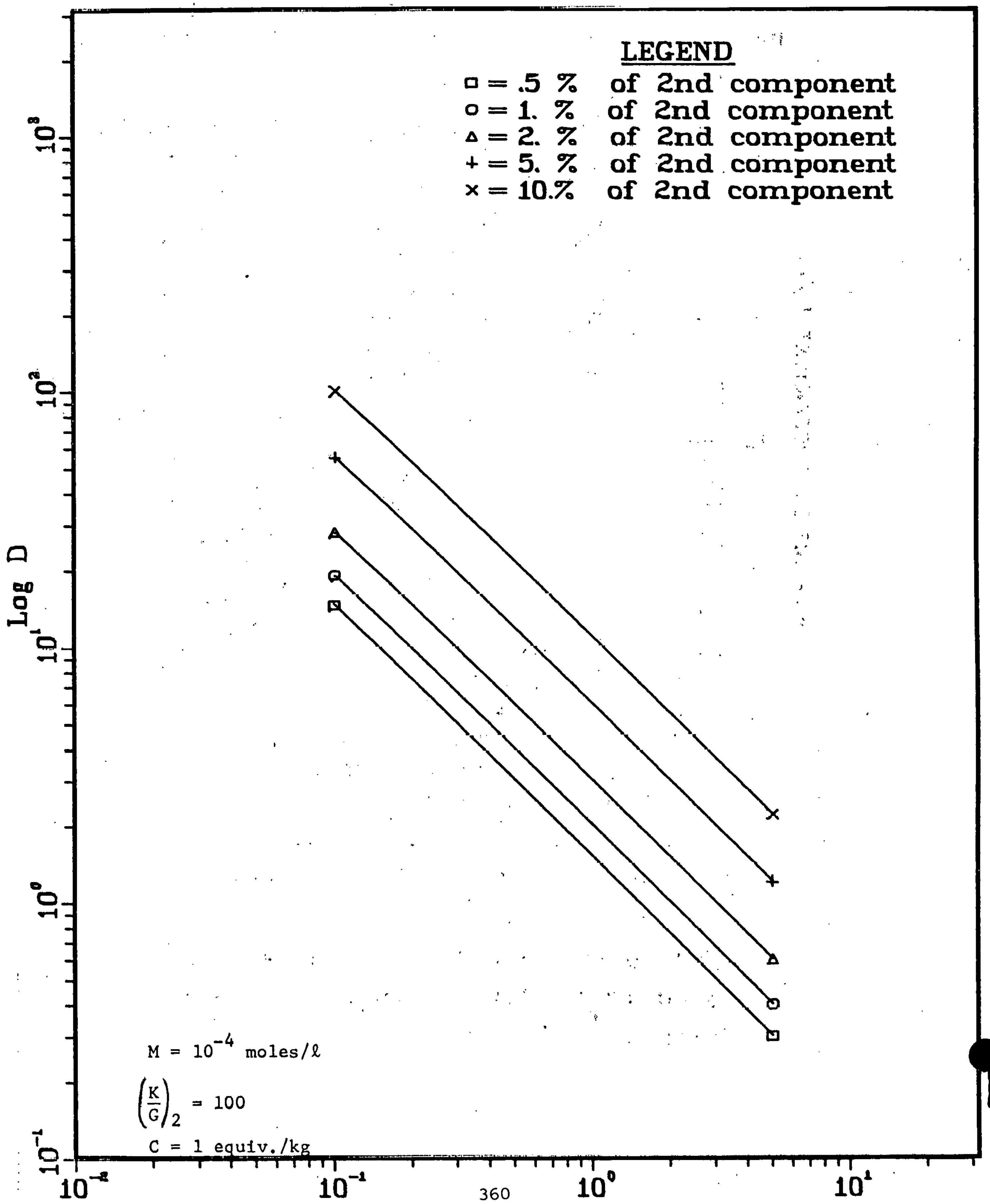
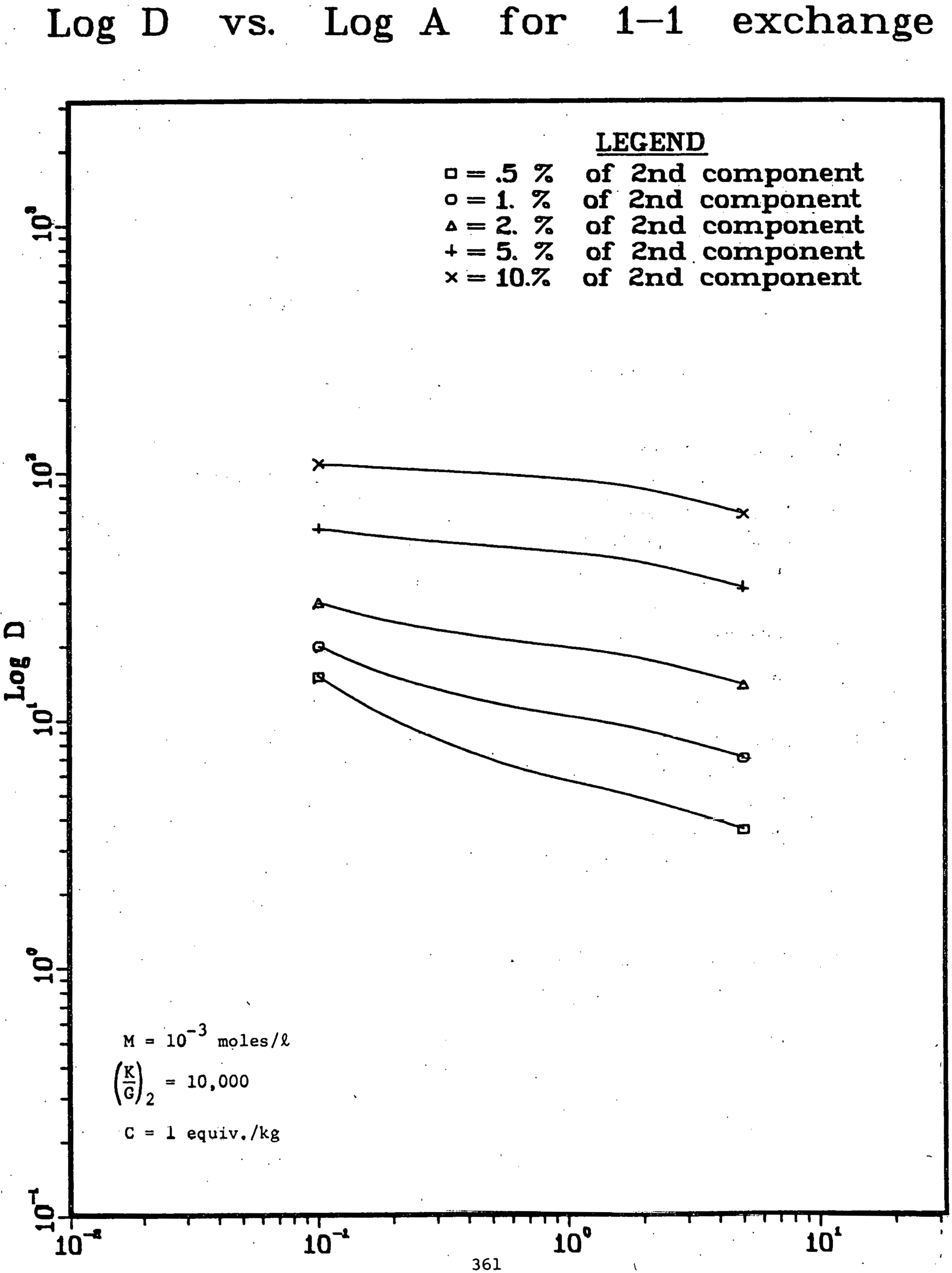


FIG. 7



$M = 10^{-3}$ moles/ℓ

$\left(\frac{K}{G}\right)_2 = 10{,}000$

C = 1 equiv./kg

DISCUSSION--R. E. MEYER

Distribution of Sr (II) between Aqueous NaCl Solutions and Ca-Montmorillonite (Table 4)

Q. Has this been through the Jackson treatment procedure?

A. Yes, all of the data I've shown are for samples that have been through the Jackson procedure.

Q. What does the distribution coefficient of Sr look like when you lower its concentration to very trace levels.

A. We have some experiments that show the effects of loading, but we haven't done much experimentation with very low concentration levels. Wahlberg, however, who went all the way down to carrier-free Sr, found that, as long as Na concentration remained the same, the distribution coefficient stayed roughly the same.

Q. Have you had any problem replicating these experiments?

A. In this particular case, we were able to replicate the results one week later. However, these data are only about two weeks old, so we haven't had a great deal of time in which to do replications. We are not sure what would happen with continued attempts at replication, particularly since we discovered the presence of an unexpected loading effect that caused the distribution coefficient to change more than we had anticipated with respect to the percentage of loading on the clay.

Theoretical Calculation (Figures 6, 7)

Q. What do the different curves represent?

A. These are plots of the distribution coefficient vs. the concentration of the electrolyte that we've exchanged with small amounts of another substance. The amount of this second substance has been gradually increased from 1% to 2% to 5%, etc. Even when it was loaded up to 50%, however, no significant differences in plotting curves emerged.

Q. Is the usual concentration up to 5% of the ionic concentration of the second phase?

A. If we're working with a clay material, for example, which includes 1% of one component and 5% of another, we'll want to know how the shape of the curves will change if we load up one of the components. Conversely, if we observe a nonlinear behavior, we'll want to know how much of a particular component was present and whether this presence explained the anomalous behavior.

Q. Do you have two solid phases?

A. Yes, there are two different clays mixed together. We assume that they don't affect each other.

Q. What if you have more than one type of site?

A. As long as they do not affect each other, we would expect the behavior to be the same. Since there could be some interaction between them, however, we could not use two different equilibrium coefficients as we have done here.

Q. What do the different intercepts mean?

A. The actual position of the line is determined by the value of K that we have to choose (see equation 3).

Q. Is there any physical significance to the different intercepts?

A. Not particularly. They are fairly arbitrary, depending mainly on where the concentration is selected.

Q. But your intercept at 1M is given by the assumed constant. Doesn't this, in fact, explain the nonlinearity of the tail on elution curves? In other words, could you have two different materials with different elution characteristics superimposed on each other, which could resolve into two peaks overlying one another?

A. If a column is not in true equilibrium, you could obtain such a separation. However, if it is in equilibrium--if there is no change in distribution coefficient as the material moves down the column--then there will be just a single velocity: namely, the average velocity of the average distribution coefficient. I should also add that we are just getting started with column experiments and do not have a great deal of data yet.

Scheduling of Additional Experiments

Q. What kind of schedule do you have set up for additional work? For example, when do you plan to move into the actinides?

A. We are somewhat behind right now in terms of the schedule set up in our proposal; however, if all goes well, we expect to move from Sr into one of the +3 ions--perhaps Eu (III) or Am (III)--within the next couple of months. We plan to begin with these relatively easy cases before tackling some of the more complex ones.

Methodology

Q. I support your approach to the problem. Don't you feel, however, it is difficult to understand the process involved unless it's built into the experiment at the very beginning?

A. We feel that the development of methodology is very important--as are the methods of treating the clay minerals. I'd like to hear some discussion of what is the best way to treat these minerals. For example, is the Jackson procedure really the best?

Size Control

Q. Do you use anything to control size, such as mesh?

A. There shouldn't be much of a size effect.

Q. I would think that you would find a sizable difference in distribution coefficients between particles that are 2 μ in size and those that are much smaller.

A. If there were a strong surface area effect, I could understand such a difference. In the case of montmorillonite, however, there is not much of a surface area effect. With other minerals, particle size could be more of a factor.

Effect of Salt Concentration

Q. Do your distribution coefficients approach zero as the salt concentration increases?

A. They do not approach zero, but they do become quite low. This causes additional problems, as it is difficult experimentally to measure distribution coefficients when they are so low.

Synthetic and Pretreated Materials

Q. What about using synthetic materials--e.g., synthetic clays or silicates--to determine the idealized behavior of one supporting material?

A. We've been giving some thought to that. If you know where we can obtain some good, pure synthetic clays, please let us know.

Q. With synthetic clays, you usually end up with large amounts of amorphic almuninum silicate component. Wouldn't this have a significant effect on your results?

A. It probably would. However, after natural materials have been cleaned, they also can include amorphous or other extraneous materials. The Jackson procedure was designed to purify systems for X-ray diffraction analysis: it removes unoxidized organics, acid-soluble carbonates, and reducible iron and manganese. It was not designed to purify materials for chemical analysis, and therefore leaves behind components such as amorphous silicate materials. Thus, there is no way of being sure that a given material is chemically pure.

Q. Isn't the procedure generally used for all sorts of purification?

A. Yes, but only because no one else has tried to develop a procedure using different criteria.

Q. I've found that the peroxide treatment results in high retention of Sr, which is irreversible against Ca exchange. I think we don't really know what we're doing to clays when we purify them.

A. All of the methods have their limitations: peroxide reactions are not good because of their pronounced effect on site-specific charges; the Jackson method is not adequate to explain such phenomena as the exchange reaction between montmorillonite and Cs. Because of problems such as these, I feel that the best method is to determine the adsorption properties of a material in its natural state, and then to look at it later, by the Jackson procedure or other methods, to find out what phase in the soil, sediment, or rock was responsible for the adsorption reaction. This method, besides avoiding side effects from the treatment procedure, provides distribution coefficient that is based on all of the perturbing factors actually found in the field.

Q. Can you dissolve the components, look at their behavior, and then characterize their behavior of assemblage?

A. That's a reasonable way to approach the problem. We do have plans for a year and a half from now to treat mixtures of components, first investigating them singly and then putting them together to see what happens. It's a complex question, given the differing degrees of purity of natural materials; however, our present column infiltration experiment, which contains a small hint of mixtures, represent a step in the right direction. The columns are made from two adsorbable components. At present, one is hoped to be very small in terms of its extent of adsorption, and the other very large. So far, although the minor component was adsorbed, it did not appear to affect the distribution coefficient of the major component. I am still unsure of the validity of these results, however, because the curves do not look ideal enough; they should not have any tail. Nevertheless, once we do learn how to mix and maintain two components in the desired proportion, we can begin to do more complex experiments of the type you describe.

Natural-Material vs. Pure-Component Approach

Q. I feel that it is important to start with natural components. If you do not know what the material looks like in its natural state, you won't be able to determine the degree to which you've perturbed the system in purifying its components.

A. There are two basic avenues of approach: one starts with the basic building blocks and works back to the original material; the other begins by characterizing the original material and then slices it into its components. The end product of both approaches is the same, and, although WISAP accentuates the generic, rather than the site-specific approach, it feels that both avenues are valid and both should be followed.

Q. But what if you disturb key factors in the slicing, e.g. if you crack the mineral or change the weathering pattern?

A. That could be a problem. If you begin with the natural material and then fractionate it chemically to determine where the sorption occurred, as you remove one layer you could be affecting another. It is traditional, of course, to begin with the least harsh treatment and to work down from there; still, the problem is not really resolvable. There is no such thing as a perfectly clean slice. Similarly, with the building-block method, you may have the problem of determining that the subsamples tested in the laboratory are representatives of the natural material in the field unless you can show that a variety of subsamples all give the same results.

Q. Another problem with the natural-material method is that such materials are site specific, so that results obtained from one montmorillonite subsample may not be representative of montmorillonite subsamples found at other sites. On the other hand, studying pure materials will not help much if we don't know in the end the components of the natural material. I think the question can be argued either way, but, to my mind, the crucial point is the degree to which a particular material is representative of all subsamples.

A. That's why we've looked at montmorillonite from other sources: we want to get a feeling for the range of behavior.

Q. Don't you also need to look at it in the context of time schedules? We don't have a great deal of time in which to set up a repository. Working with the rocks themselves is the quickest way to obtain the answers we need--even though synthesizing them from pure materials may be better science.

A. That is true, but we also are responsible for providing information that will enable predictions to be made in many orders of magnitude of both time and space. What we may have to do is to question seriously the time frame in which the repository is to be set up. It may be that, within the next few years, we simply cannot obtain sufficient data on which to base a risk analysis. We need to perform the best science we know how: we cannot make million-year extrapolations on the basis of poor science.

Q. Is what we are doing science--or is it empiricism?

A. That's a good question. Empiricism has its place: both a cathedral and a model-T Ford can be, and have been, built empirically by people who have no understanding of the basis of what they are doing.

Q. I think that both the natural-materials and the building-block approach should be followed simultaneously. However, it should be stressed that there are not just one, but _two_ variables of concern: the composition of the solid phase and the composition of the liquid phase. The latter is very important: simply changing the ionic strength of the solution can result in changes over orders of magnitude. Thus, whatever approach is followed, both phases need to be examined.

(No answer given.)

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"STUDIES OF RADIONUCLIDE AVAILABILITY AND MIGRATION AT THE NEVADA TEST SITE RELEVANT TO RADIOACTIVE WASTE DISPOSAL"

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INTRODUCTION

Information on the interaction of radionuclides from underground nuclear tests at the Nevada Test Site (NTS) with the local ground water system has been accumulating for 20 years. The purpose of the present research is to obtain data from the NTS and draw conclusions relevant to radioactive waste disposal. The NTS is a unique laboratory for waste-isolation studies. There large amounts of radioactivity have been "stored" underground for nearly two decades, and, at over 75 sites, the radioactivity has been exposed to ground water for years (Borg et al., 1976).

This project of the Waste Isolation Safety Assessment Program (WISAP) is an adjunct to a weapons-related research program "Radionuclide Migration in the Ground" (RNM) at the NTS. This WISAP project was established to carry out studies that would otherwise not be done because of their lesser importance to the weapons program. Four major areas of investigation were proposed for FY 1977:

1. Field measurements involving injection and recovery of tracers, analysis of large-volume water samples from nuclear test locations, and analysis of the feasibility of sampling operations at various old test locations.

2. Sorption studies, principally laboratory measurement of the distribution of specified radionuclides between the liquid and solid phases of rock-water systems representative of nuclear test sites.

3. Experiments with leaching of radioactive material.

4. Analysis of the problems arising from the differences between intergranular and fracture flow, with particular attention to the relevance of laboratory measurements, such as K_d, to field migration models.

This report will cover primarily items 1 and 2 above. During FY 1977, all work on item 3 was funded by the RNM project. Therefore, only a brief summary of the leaching apparatus will be included here. We have not started work on item 4.

This project was funded at LLL in March 1977. Staffing was complete and a stable level of effort obtained by May. Thus the reported results represent about six months of effort at the originally proposed level of 2 FTE per year.

FIELD STUDIES

As the project began we had two basic goals for field studies: (1) to conduct field tracer experiments that would be compared with laboratory experiments, and (2) to obtain, concentrate, and analyze large-volume pumped water samples from the sites of underground nuclear explosions in order to determine the <u>in situ</u> availability of radionuclides (especially Pu) to ground water.

During the year there have been three changes in the original plan. First, the fact that our field experiments depended on drilling performed for the RNM project proved to be a major inconvenience. Therefore some effort was directed at developing an independent program. Second, there was clearly a need to evaluate the feasibility of field work at nuclear test sites outside of NTS, which we did. Third, we obtained large-volume water samples from several locations not originally included in our plans.

The Basic Field Program

During FY 77, LLL evaluated several options for meeting our original goals.

Single-well tracer tests: To obtain information about the velocity of ground water flow at NTS, the U. S. Geological Survey (USGS) is developing a technique for single-well tracer tests. A tracer is injected into a well and allowed to drift for several months. It is then pumped back, and inferences on the rate of ground water flow (drift of the tracer) are made based on the time it takes to pump the tracer back to the well.

Considerable effort has been expended by the USGS in finding tracers that are not sorbed. (Use of tritium as a tracer is not allowed at NTS because of possible confusion with tritium from nuclear explosions.) Our original idea was to add other radionuclides to the USGS tracer slug and thus obtain data on their retardation or sorption relative to the non-sorbed tracer monitored by the USGS. A severe technical problem is that the USGS injects only 50 ml of tracer into the well. This is a reasonable amount if the tracer is not sorbed. However, the tracers of interest to us would be strongly sorbed, and therefore we would probably be unable to get measurable quantities of tracer in the pumped water. For this reason primarily, we decided to look at a two-well tracer test.

Two-well tracer tests: The USGS has developed and operates a well field known as the Amargosa Tracer Site southwest of NTS. The tests are carried out in a dolomite which is part of the lower carbonate aquifer which is the principal flow path to offsite for groundwater in the eastern half of NTS. We have obtained USGS permission to operate a two-well tracer test at the Amargosa site and are currently preparing an application for a permit from the Nuclear Regulatory Commission and the Nevada Bureau of Environmental Health.

Because this site is predominantly a fracture flow system, we will be interested in comparing retardation factors measured in the field with those calculated from lab measurements on bulk rock. One hypothesis is that the fractures will be coated with minerals more sorptive than the bulk dolomite and hence show greater retardation.

Bilby cavity/chimney sampling: The first nuclear test detonated below the water table at the NTS was code-named Bilby. It was detonated in 1963, and a well was drilled and completed within the collapsed zone at and above the point of detonation. The USGS originally planned to pump from several vertical zones which had been perforated to obtain infill data, but a partial collapse of the casing at the top of the perforated section prevented pumping individual zones. Pumped samples from the entire 200 m section were obtained in 1964 by the USGS and determinations for ^{144}Ce, ^{137}Cs, ^{60}Co, ^{106}Ru, ^{125}Sb and ^{3}H were made on a few samples. During this time the chimney was continuing to fill.

Our plan was to use the pump already in the well to collect samples for complete radiochemical analysis, including low level counting and a specific search for Pu. We also planned to test a field apparatus for water-sample concentration.

Unfortunately, the pump no longer worked. Further effort seemed justified because a significant improvement in the NTS data base can be obtained through high quality radiochemical analyses at the Bilby site. Furthermore, no other site at NTS with water containing fission products and possibly Pu could be pumped for testing of a field water-concentration apparatus.

Therefore, we wrote a work plan, obtained a cost estimate, worked out joint funding with the Weapons Program, and refurbished well U3cn-PS2 at the Bilby site. A total of 5000 gallons were pumped, and LLL took eleven 1-gallon samples and one 55-gallon sample for low-level analysis. These samples will be analyzed in FY 1978. The well will be available for testing the field water concentration apparatus when it is completed.

Other sites: There are other sites at NTS where the opportunity to pump water contaminated by fission products and Pu may arise. Two, Cambric and Almendro, have been developed by the Weapons Test Program. Cambric has been pumped in the past and is currently blocked by packers. Almendro has been drilled but not perforated because of slow in-fill of water. If the opportunity arises to take large-volume pumped samples, we will do so. At present there are no operations planned until FY 1978.

Field Water-Concentration Apparatus

At present, large-volume water samples are being returned in 250 ℓ (55 gal) drums to LLL for concentration and analysis. We are planning to buy or build a field distillation unit something like that shown in Figure 1. Such a device would concentrate up to 4000 liters (880 gal) of

NTS well water to about 2 Kg of salts. This concentration would improve the sensitivity of our well water analyses by several orders of magnitude. Such an increase in sensitivity would be an aid to the understanding of underground radionuclide movement at NTS.

Evaluation of Nuclear Test Sites in Crystalline Rock and Salt

As noted earlier, we evaluated nuclear test sites in media other than standard NTS alluvium and tuff. There are two sites in salt, three in granite, and three in basalt. We find that additional field studies at one salt site and one granite site are feasible and might produce data of interest to waste isolation. Field studies at the rest are significantly less likely to be productive, or else would be economically prohibitive.

Basalt sites: Although there have been some tests above the water table at NTS, all three nuclear tests in basalt below the water table were at Amchitka Island, Alaska. No post-shot reentry was attempted for the first two (code-named Longshot and Milrow) but there was post-shot reentry for the third (the Cannikin test). Small volume thief samples were obtained, but no pump tests were carried out. The island is essentially deactivated now and the cost of further sampling operations would be prohibitive.

Granite sites: There have been three U. S. nuclear explosions in granite. The two at NTS (Hardhat and Piledriver) were conducted above the regional and local water table in an unsaturated zone.

There are therefore no water samples to collect at these sites.

The third test in granite (the Shoal event) was conducted below the water table in the Sand Springs granite 48 km (30 miles) southeast of Fallon, Nevada. The depth of burst was 367 m (1205 ft) below the land surface and 91 m (300 ft) below the pretest water table altitude. Hydrologic studies before the test showed a low storage capacity in the rock, and the estimated time required for chimney infill was 10 years. Following infill, it was estimated that there would be a 9-m/yr (30 ft/yr) water migration rate to the southeast.

The Shoal site is a good place to study and document leaching and transport of radioactive materials deposited in granite below the water table. Measurements at Shoal could be directly correlated to crystalline rock repositories.

At the Shoal site, one drill hole (PS-1) penetrated the apex of the chimney and went out the bottom of the cavity. If reentered, this hole would provide water samples from the chimney/cavity region. Because the amount of the radioactive species deposited is known or can be calculated, a comparison can be made with the amount of radioactivity in the water. Although the amount in the water is a result of a two-stage process of leaching and resorption,leaching can be estimated by using laboratory values to calculate resorption.

Because of the low permeability, low storage capacity, and low flow rate within the Shoal granite, measurements outside the chimney area do not appear practical. At present, we are still trying to verify the manner in which the post-shot hole was plugged so that we can write a proposal for re-entry and sampling.

Salt sites: There have been three nuclear tests at two sites in salt. The first (code-named Gnome) was located about 48 km (30 mi) SE of Carlsbad, New Mexico. It was a 3.1-kt explosion in December, 1961 at a depth of 361 m (1184 ft) in the Salado bedded salt.

The second site, the Tatum salt dome near Hattiesburg, Mississippi accomodated two tests. The first, Salmon, was a 5.3 kt explosion in October 1964, at a depth of 828 m (2717 ft). The standing open cavity was reentered and used for the 0.4-kt Sterling nuclear explosion, which was a test of seismic decoupling.

Our conclusion is that, of the two sites, the better opportunity for work useful to the Waste Isolation Program exists at the Gnome site in New Mexico. There are clean-up operations planned prior to deactivation, and it is possible that some work might be combined with these operations.

Definitive research on migration below the cavity would likely be very expensive, as it would be necessary to sink a shaft and mine a drift under the base of the cavity to obtain unequivocal data. However, a sample of brine from the cavity could probably be obtained during site cleanup operations. During these operations, DOE-NV plans to drill a reentry hole and pour nuclide-contaminated soil down this hole into the cavity. Prior to emplacement of the soil, it would be possible to set a bridge-casing across the cavity to sample brine in the lower part of the cavity.

During previous operations, about 100,000 liters of water were put into the cavity. This water should now be in approximate equilibrium with the cavity material, having dissolved about 30 metric tons of contaminated salt. Thus there is here a unique opportunity to obtain field data on the availability of radionuclides to a brine solution.

During clean-up operations prior to deactivation of the Salmon site, a slurry of contaminated mud was injected into the cavity. The mineralogy of the mud is such that a completely unnatural environment now exists within the cavity. Were samples of brine recovered it would be difficult if not impossible to relate the data to the natural mineralogy of the salt. Therefore, attempts to sample at this site are technically infeasible if the purpose is to obtain information relevant to waste isolation in salt formations.

Other NTS Sampling:

Wells have been completed at two other nuclear test sites that have potential for studies related to this project: the Nash site in dolomite and the Bourbon site in limestone. Pumping at the well near Nash established the presence of tritium in the water, and LLL took a large-volume sample which will be concentrated for low-level counting for nuclides other than tritium. We plan to take another large volume sample at the Borbon site when pumping is done there.

At both of these sites pumps have been left in the holes, however it has not yet been established that nuclides other than tritium are present in the water. After construction of the field water concentration apparatus we will use it at these sites.

HIGH PRESSURE CORE
SORPTION STUDIES

Sorption studies are done by three methods; static, column, and core. Core measurements are relatively rare, but they most closely simulate intergranular flow under field conditions. Preliminary work at LLL (Tewhey, 1976) indicated the feasibility and utility of the core method. The apparatus we are building for core measurements is designed to operate under higher confining pressures than the earlier experiments, and control of temperature is possible. Thus, *in situ* conditions can be simulated. There will also be a considerable variety of rock material available due to the small core size. With this equipment, the following objectives will be pursued:

1. Comparison of static and core methods of sorption ratio determination.
2. Investigation of phenomena such as dispersion and desorption by injection of pulses of tracer into a steady-state flow through the rock core.
3. A systematic investigation of sorption as a function of time, pressure, temperature, and composition of the carrier liquid (including effect of competing ions).
4. Measurements relevant to specific field sites at NTS.

During FY 1977 the apparatus was designed (Fig. 2), and at the end of September:

- The high pressure source and sample injection system were available.
- The sample mold was available.
- The sample holder was available.

- The receiver design was deferred until completion of initial tests on the pressure source, sample holder, and rock samples.

The apparatus is designed for longitudinal driving pressures up to 3.4 MPa (500 psi) and radial confining pressures up to 40.8 MPa (6000 psi). The rock samples are 13 or 26 mm diameter and 26 mm in length; they are covered along the sides by cast plastic jackets which also seal them to the end fittings and prevent leakage of the confining pressure fluid. Brass and stainless steel have been specified for the prototype sample holder since they have mechanical properties which are quite adequate for the initial tests and they are more quickly and cheaply fabricated than high pressure steel.

The driving pressure of 3.4 MPa (500psi) is determined by the nominal pressure rating of the radionuclide spike injection valve. The other components have higher ratings: 68.0 MPa (10kpsi) for the supply pump and 6.8 MPa (1kpsi) for the supply line between injection valve and high pressure cell. The injection valve and supply line are made of teflon to minimize sorption effects. To increase the driving pressure, we must either operate the injection valve above its nominal rating at the cost of shortened valve life, or switch to a stainless steel injection valve. The brass high pressure sample chamber is rated for confining pressures up to 40.8 MPa (6kpsi) which correspond to a depth of 1.7 km (5700 ft) in media with a density of 2.4 Mg/m^3 and should therefore be large enough for a simulation of reasonable waste repository depths.

The adapters which hold the ends of the cylindrical sample have been designed in both 13 mm and 26 mm sizes, with the 13 mm size being used for initial pressure and jacket fabrication tests. The smaller size minimizes sample support problems, but the larger size tends to average out sample inhomogeneities. We plan to use the larger size wherever possible.

We have obtained large samples of well-characterized tuff, the Trailridge member of the Thirsty Canyon Tuff from a locality at Pahute Mesa, Nevada Test Site. It is a partially welded silicic ash-flow tuff with moderate sorptive characteristics and millidarcy-range permeability. It is not strongly zeolitic, but we have found that very clay-rich or zeolitic tuffs either lack mechanical strength (tend to disintegrate in the apparatus) or else are highly impermeable. We are in the process of obtaining other samples from known stratigraphic horizons.

During the year, we have developed a collection system to be used with both the high pressure K_d system and the leaching system. Effluent from these systems is fed into bottles lined with 4 in. x 2 in. x 12 in. polyethylene bags. The bottles are then placed inside of a forced air oven whose temperature is held at a constant 85°C. Experiments have shown that it takes 30-40 hours for evaporation to be complete. Each bag is then rolled so that the residual salts are at the center of the roll. This rolled bag is placed in a 1" steel die and pressed to a pellet shape at 20.6 MPa (3000psi), while a heating jacket then raises the temperature to 150°C. When this temperature is reached, the die is rapidly cooled and the pellet removed.

The pellet is then gamma-counted with a low-level Ge(Li) gamma-ray spectrometer. Experiments (Table 1) have shown that the precision of pelletizing and counting these bags is about 4%. The accuracy is about 5%. The precision of just the gamma counting is about 0.4%.

Depending on the particular sample, after gamma counting, selected pellets are ignited in platinum beakers and radiochemically separated and purified for $^{239+240}$Pu and ^{238}Pu analysis. This requires addition of a ^{242}Pu tracer, lengthy purification procedures, and electrodeposition with subsequent alpha-pulse height analysis. We had not completed tests of this collection system using Pu solutions at the end of FY 77.

Static sorption studies

We have obtained a suite of samples from a drill hole near the site of the Cambric experiment. The reason for interest in the Cambric site is that extensive measurements have been made in the cavity-chimney area (Hoffman et al., 1977), and pumping is ongoing in a well located 91 m (300 ft) away. Therefore, we are attempting to obtain laboratory data useful in the interpretation of these field measurement

We selected samples that were equal in depth to the cavity-chimney zone below the water table. These samples have been analyzed by X-ray diffraction for their mineralogic content. Samples from 287 to 308 m (940 to 1010 ft) depth have been crushed, screened to recover the 44 to 150 µm particle size range, and are to be composited into a large sample for static K_d studies.

We have already used samples of water from Well 5B in Frenchmen Flat for other K_d studies, and have obtained a fresh supply of that water. We have also replenished our stocks of fission product tracers, including Sb, Ru, Y, Sr, Ce, and Co. We will start a series of static K_d measurements on Cambric material during the fall of 1977.

LEACHING STUDIES

During FY 1977, as part of the RNM Program, we designed, built, and tested, a single-pass leaching system in which the solution contacts the solid only once (Figs. 3 and 4). Leaching studies are commonly carried out either in closed vessels under static conditions, or in a recirculating system with continuous leachate removal (multiple pass). Under static conditions, the solid and liquid phases tend to equilibrate with each other. With our single-pass leaching system we hope to simulate a non-equilibrium situation where new solution is constantly in contact with the solid, and where the maximum possible leach rate is attained. Also, this single-pass system will allow study of resorption by the leached material through the use of tracers in the leach solution.

This apparatus has 20 channels, which can be operated in one to four flow-rate groups. Each metering pump (10 channels each, Fig. 5) is continuously variable in flow rate, and each channel can be operated in either a high or low flow position, giving a range of flow rates from 9 to 279 m/yr (Table 2). By comparison, the flow rate in the lower carbonate aquifer at the Yucca Flat test area, Nevada Test Site, has been estimated to lie between limits of 1.8 to 180 m/yr, and elsewhere at 18 to 410 m/yr (Borg, et al, 1976, pp. 47-51).

There are also estimates of flow velocity beneath the Pahute Mesa test area of 2-76 m/yr (ibid, p. 53). Therefore, the equipment is designed for realistic NTS flow rates.

The single-pass leaching system is designed to allow variation in (and control of) flow rate, temperature, leaching solution composition, and solid particle-size. The range of operating conditions is given in Table 2.

In theory each channel could receive a different leaching solution, although we will start with a single solution for all channels. Up to three solutions may be studied simultaneously later.

Details of the sample holder are shown in Figs. 6 and 7. The purpose of the side filler plug is to allow introduction of the solid sample after assembly and pressure-testing.

During FY 1978, the apparatus will be used to leach melt glass samples from nuclear events selected for age, quality of samples available, and variety of rock types. This work will be under the sponsorship of the RNM program. We also plan to construct a second apparatus and use it to leach simulated doped reprocessed reactor waste as part of Task 3, WISAP, activities.

The most important advantages of this one-pass leaching apparatus are:

- Control of resorption effects.
- Provision for a large number of simultaneous experiments.
- Ability to handle concentrated Cl^- leachant solutions if necessary.

SUMMARY

The LLL project in the WISAP Program has four areas of investigation:

- A field measurement program
- Sorption studies, with emphasis on development of techniques that more realistically represent field migration than standard static K_d measurements
- Experiments in leaching of radioactive material, with emphasis on kinetic data.
- Analysis of the problems arising from the differences between intergranular and fracture flow, with particular attention to the relevance of laboratory measurements to field migration models.

During FY 1977 we worked in the first three areas, with leaching funded by another program. In the first two areas, the principal technical results of the LLL effort were:

- Recommendations regarding the feasibility of field studies at nuclear explosion sites in granite, basalt, and salt.
- Evaluation and planning for field tracer studies at the Nevada test site.
- Design and partial fabrication of a system for sorption study in rock cores at elevated pressure.
- Design and testing of a laboratory system for collection and analysis of water samples from the rock sorption and leaching systems.
- Design of a field concentration apparatus for collecting large-volume samples for low level counting.

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TABLE 1

PRECISION AND ACCURACY OF γ-COUNTING PLASTIC PELLETS.......

EXPERIMENT	PRECISION (1 σ FROM $\bar{x}$)	ACCURACY (COMPARED TO LIQUID STANDARD)
5 SEPARATE PELLETS	4%	+ 5.%
PELLET #6 COUNTED 6 TIMES - SAME DETECTOR	0.4%	+ 3.%
PELLET TURNED OVER AND COUNTED 6 TIMES	0.2%	- 3.%
3 ALIQUOTS OF ^{137}Cs TRACER COUNTED IN STD LIQUID GEOMETRY	0.4%	-----

TABLE 2

CHARACTERISTICS OF THE ONE-PASS LEACHING SYSTEM

NUMBER OF TYPES OF SOLUTIONS, FOR EACH PUMP: UP TO 10

FLOW RATES:

	LOW SPEED	HIGH SPEED
VOLUME, CM^3/DAY	13 -158	26 -460
LINEAR, M/YR:	9 114	18 -331

SAMPLE HOLDER FILTER:

DIAMETER: 25.4 MM
PORE SIZE: 1 μM

OPERATING TEMPERATURE: 20 - 85°C

VOLUME OF POWDER 2.1 CM^3 MAXIMUM

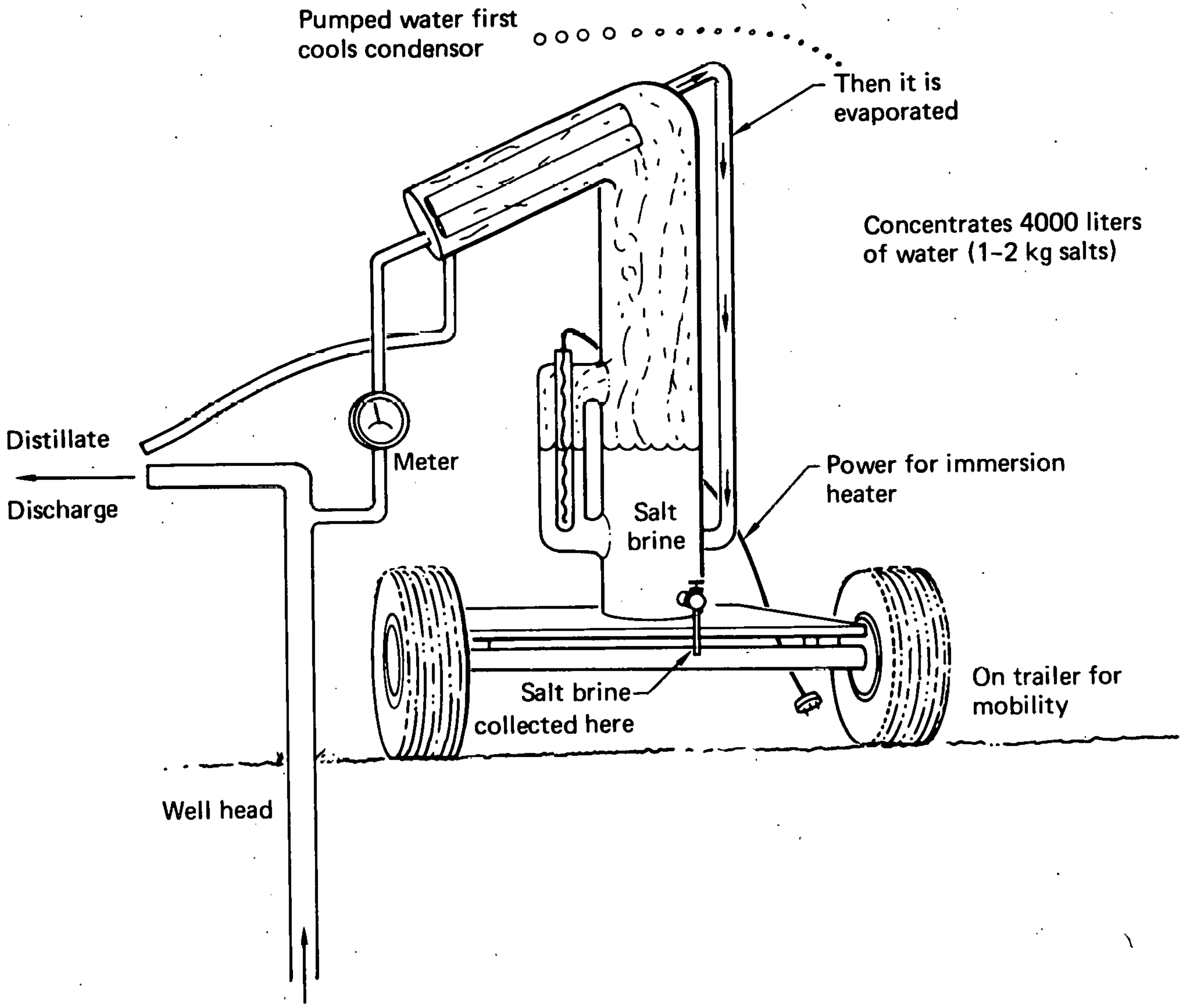

Fig. 1. Field Distillation Apparatus*

*Sketch is a modified version of a Barnstead Thermodrive Still.

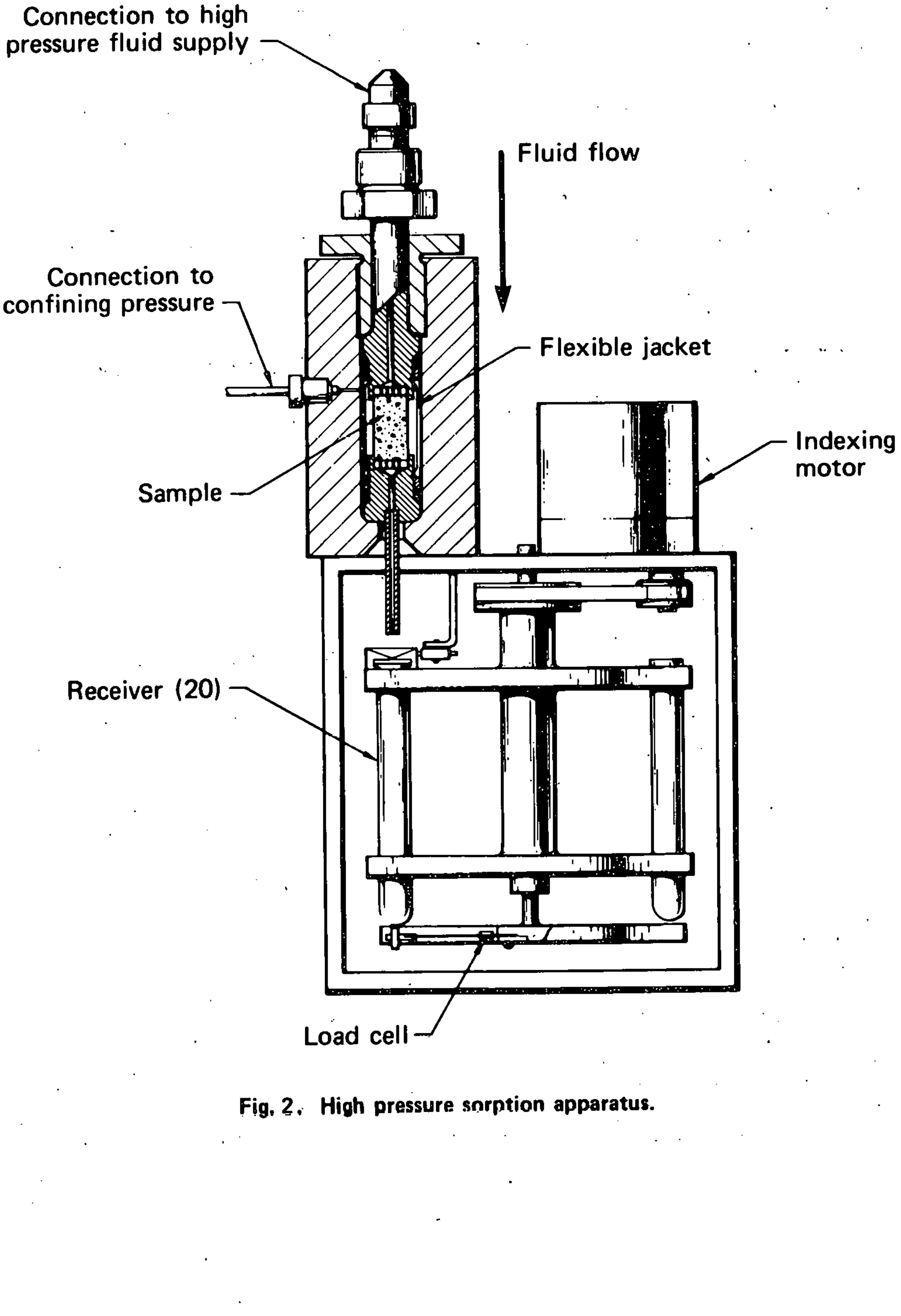

Fig. 2. High pressure sorption apparatus.

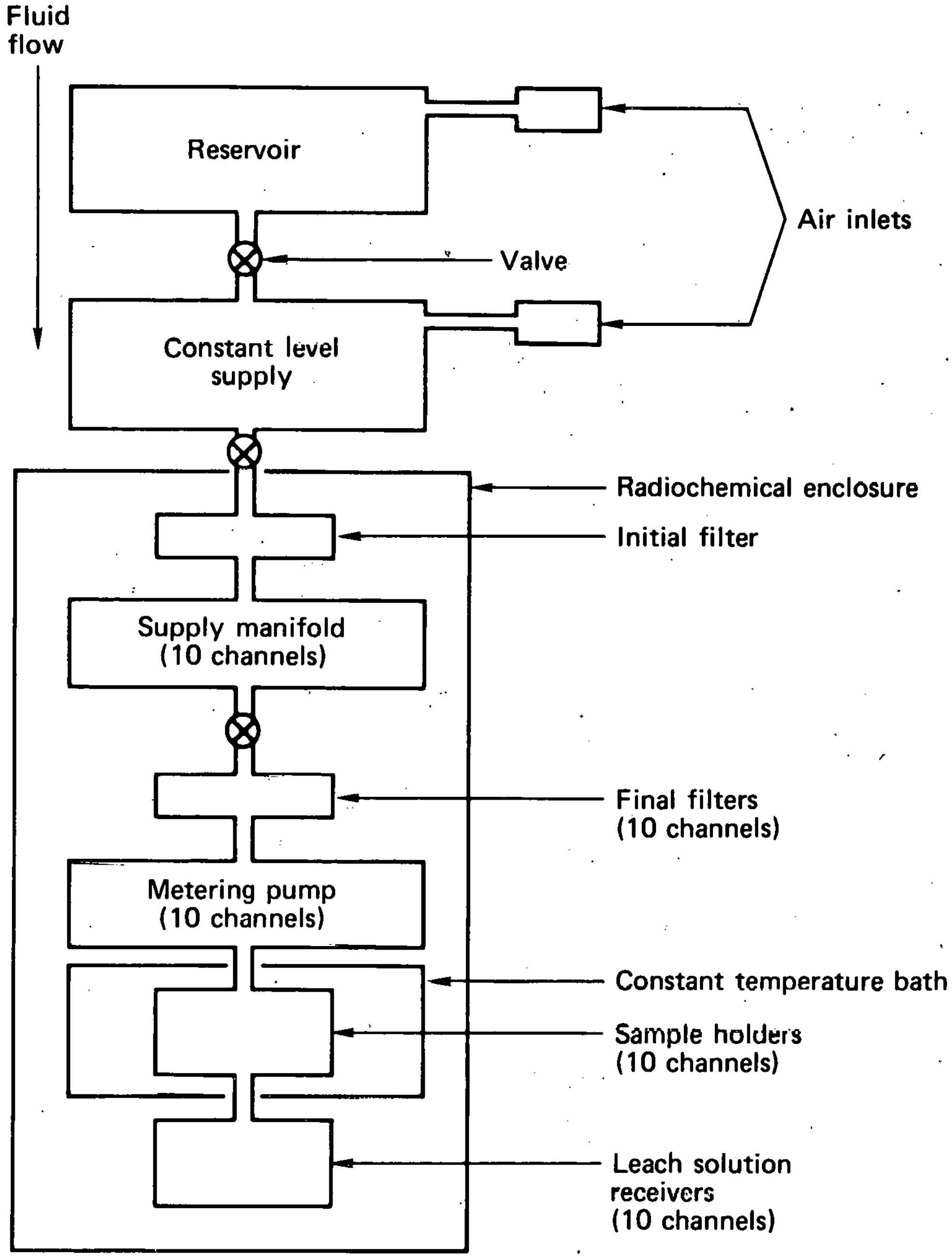

Fig. 3. Functional diagram, one-pass leaching system.

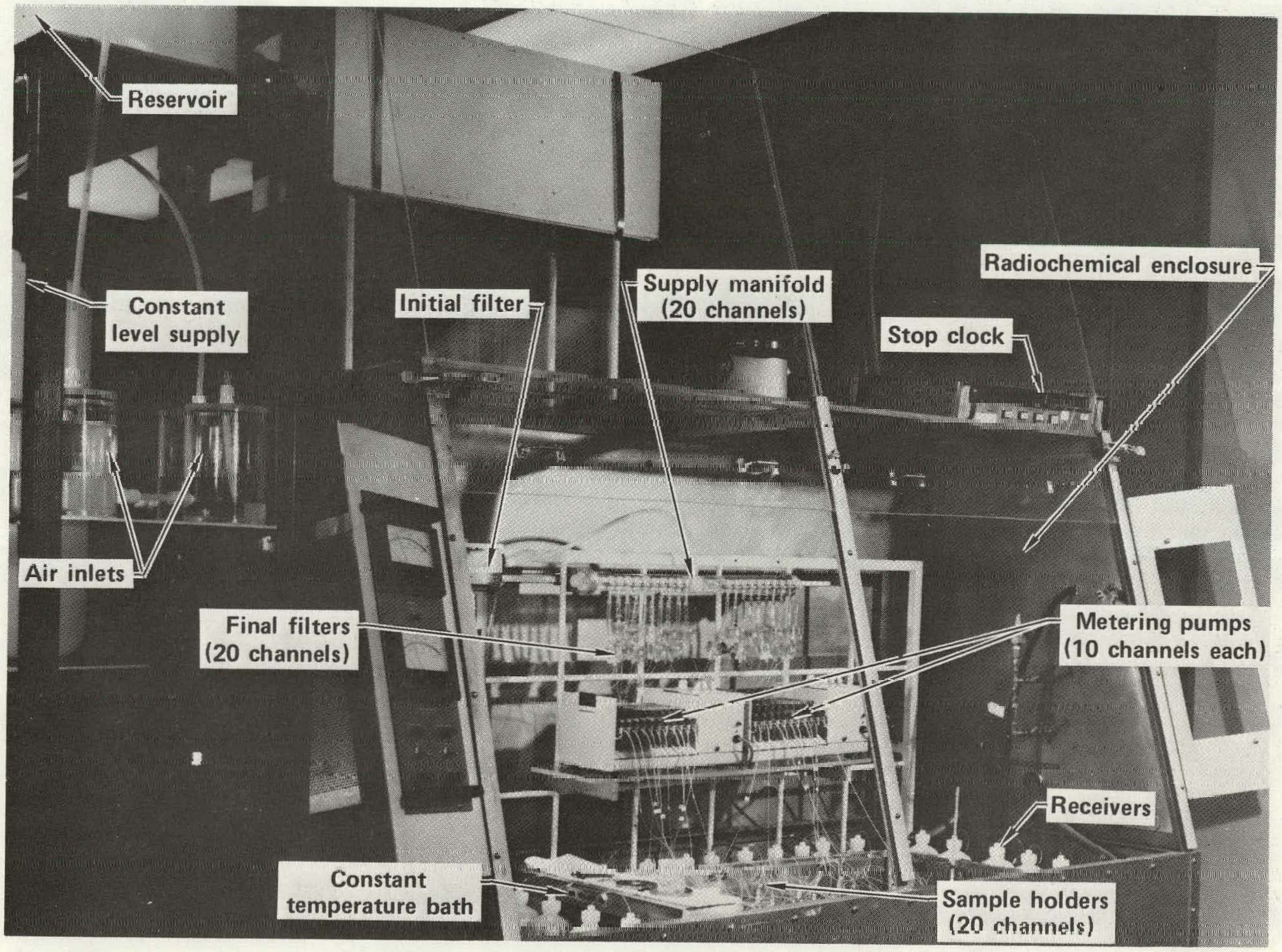

Fig. 4. One-pass leaching system – general view

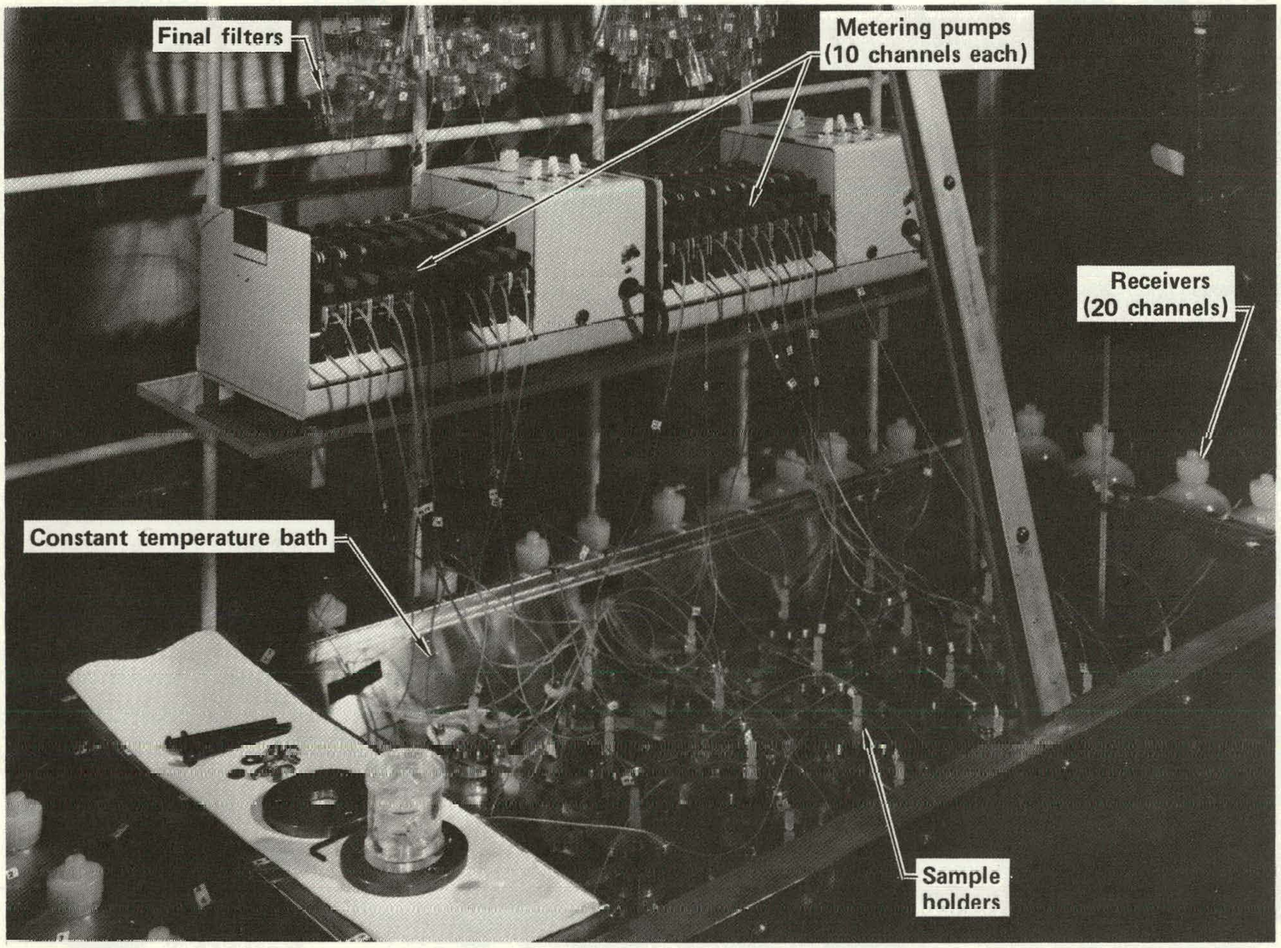

Fig. 5. One-pass leaching system – details of pumps, sample holders, and receivers

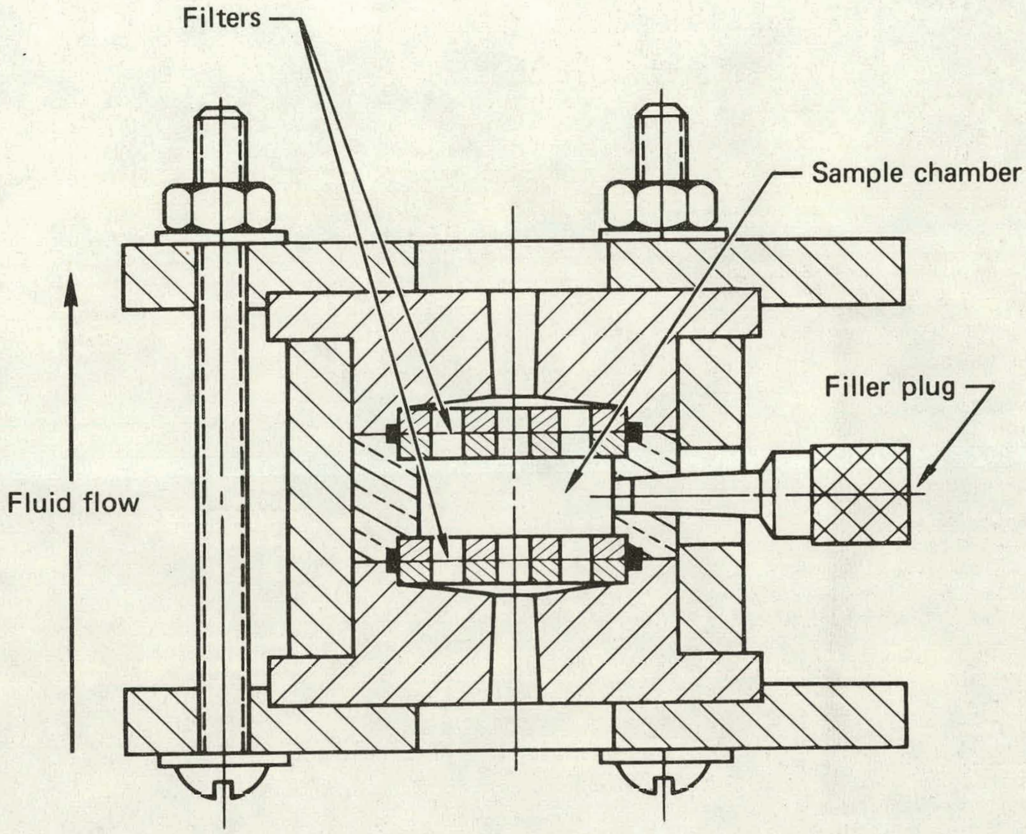

Fig. 6. Sample holder, one-pass leaching system.

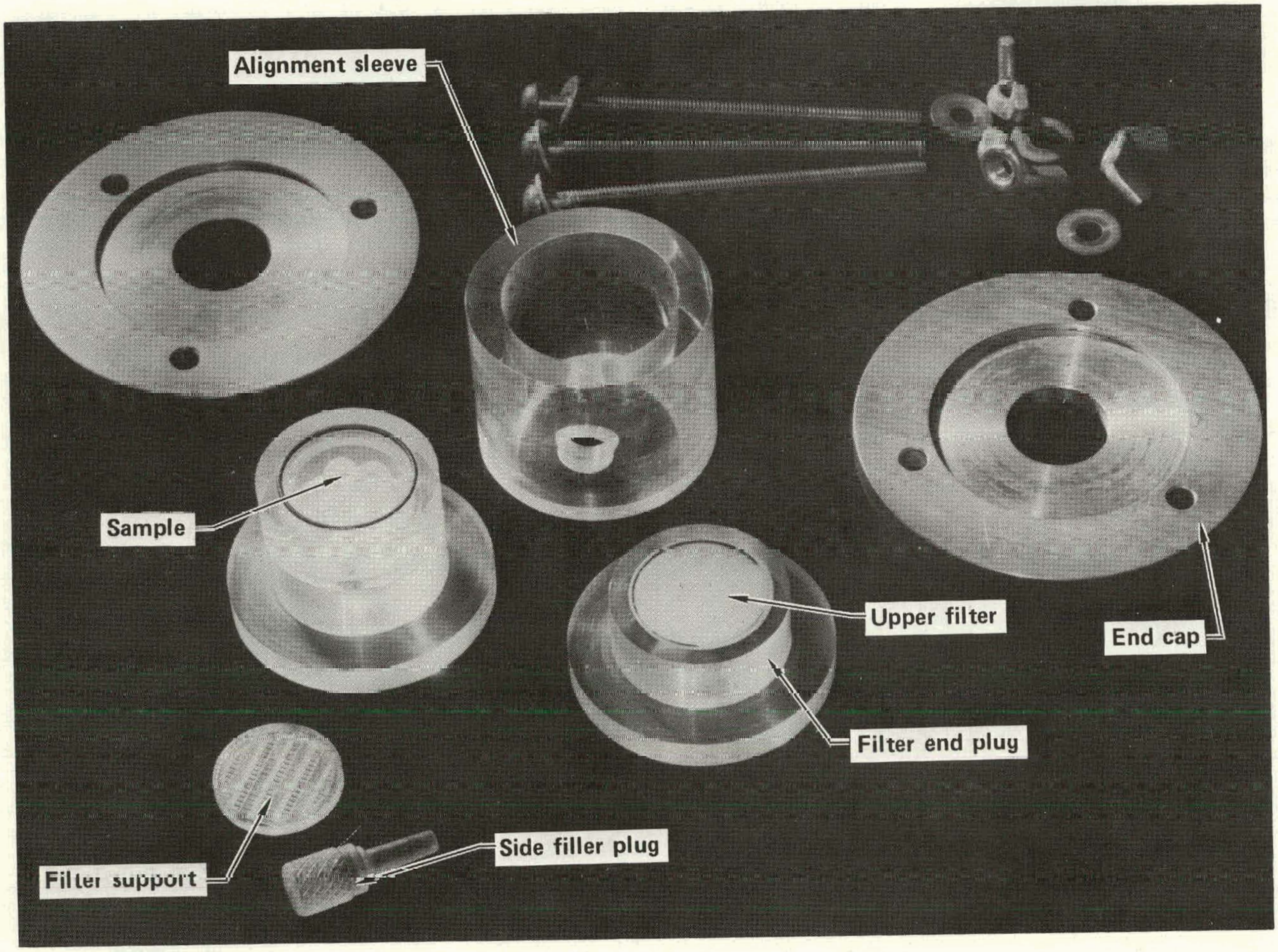

Fig 7. Sample holder assembly

DISCUSSION--LAWRENCE D. RAMSPOTT

Potential Sampling of Gnome Event

Q. What is the size of the gnome event cavity?

A. It is about 361 m across and 100 m high.

Q. How much would it cost to drill a couple of vertical holes outside of the cavity, to determine horizontal migration?

A. I don't know that there is any evidence that there would be any horizontal migration. There are some observation wells that have already been drilled, but these are 300-400 m away. However, even if there were migration, it would take several hundred years for the migrating material to reach these wells. One could drill through the cavity, case it, and try to take water samples from below, but the data would always be suspect: there would be no way to assure that contamination was not pushed down from above.

Q. Is your hydraulic gradient definitely down in that area?

A. That's not known. The area is essentially a dry formation into which 100,000 l of water were placed by the drilling process. The rocks consist of 2% water, but it is tied up with the other minerals. In this particular area, there is no evidence that, in the salt itself, there is any hydraulic gradient or any migration of water.

Cost of Sample Wells

Q. You implied that the cost-per-foot of a sample well was a function of the depth required. Do you have a formula for that relationship?

A. No, I don't, although there are standard oil field figures. It cost us about $10,000/day to operate the test site and to drill a few 1,000-ft. holes, and it took from 10 to 30 days to perform the required hydraulic tests.

Two-Well Recirculating Tracer Test

Q. What is the horizontal distance that you would have to pump at the Armargosa site?

A. About 400 feet.

Q. Are you going to add tracers to monitor water flow?

A. We can use ^{3}H.

Q. Have dispersion tests already been done there?

A. Yes, with ^{3}H and ^{35}S. That's one attractive feature of this site: a great deal of work has already been done.

Q. What is the residence time along the 400 feet?

A. In a 20-day test conducted by the Water Resource Division, the first appearance of ^{3}H came at 1,000 gal./min. in one day. All of the ^{3}H that had been injected was recovered within the 20-day period.

Q. Do you have a list of chemical tracers that you prefer to use?

A. We had hoped to use the tracers with short half-lives, such as ^{58}CO, ^{85}Sr, ^{95m}TC, ^{103}Ru, ^{124}Sb, ^{134}Cs, ^{141}Ce, and ^{237}Pu rather than chemical tracers.

High Pressure Adsorption Apparatus

Q. How do you insure that the water goes through the sample and not around it?

A. The sample is jacketed, and pressure is applied outside of the jacket. Since the confining pressure is always greater than the driving pressure, the jacket is held tightly against the sample's surface.

Q. Are you looking for hydraulic variations in pressure?

A. No, we are looking for chemical variations resulting from pressure conditions similar to those found in actual sites. We want to increase the pressure to the point where fractures and cracks close up. We expect this procedure to produce changes in flow paths and permeability, but we also want to determine whether changes in pressure produce chemical changes.

Q. In the high-pressure flow experiment, are you planning to perform a rock sample characterization after the experiment, as well?

A. I'm not sure what benefit would be derived from such a procedure.

Difficulty of Low-Level Sampling (Field Water Concentration Apparatus)

Q. The ultimate objective of low-level sampling is to be able to detect a substance in quantities as low as one atom. The procedures are very difficult to perform correctly and require many years of practice. If your sampling team doesn't have about 20 years of experience in obtaining the very lowest limits possible, I would guess that they would not be able to perform this procedure correctly. In such a case, I would recommend seeking the assistance of a team that does have the expertise since, with the time crunch, you cannot really afford not to do it right the first time.

A. I'm not sure I can answer your question. At Livermore we have one of the best low-level analytical capabilities there is, and the samplers are certainly aware of the problems involved.

Q. The problem is that what most laboratories would call low-level is not the lowest that could be obtained.

A. All we are trying to do is to increase our sensitivity. If we don't detect anything, there is no problem. The problem would be in our obtaining erroneous data--for example, due to contamination. It is to avoid problems such as this that we have developed our field distillation apparatus.

Program Similarities

Q. I'd like to comment on the similarities between the radionuclide migration (R.N.M.) program and OWI's migration program. Essentially, the programs share both the same goal--to quantify the movement of the same nuclides--and the same experimental problems. OWI is looking forward to the possibility of verifying the models it introduces--either through simulation of the field situation with pumping tests, or by means of a geological precedent, such as Oklo. The problem is in the expense of such work and the fact that neither group can assume the other's budget.

A. Yes, field work is very expensive; that's one of our main problems.

"SOIL CHROMATOGRAPH K_d VALUES"

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R. S. Fisher, and B. A. Smith

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SOIL CHROMATOGRAPH K_d VALUES

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INTRODUCTION

The transport of radionuclides by groundwater in porous media is governed by convection, dispersion and sorption processes. Of the three processes, sorption of the radionuclide to the surrounding geological media probably plays the greatest role with regard to how far any particular radionuclide will be transported. Historically, this sorption process has been characterized by a distribution coefficient (K_d) empirically determined for a specific radionuclide, geological media, and ambient conditions (pH, concentration of competing ions, etc.). Sorption is often considered to be a reversible phenomenon (ion exchange); however, with some radionuclides, i.e., Cs-137 and Pu-239 (IV) it is well established that irreversible sorption and precipitation reactions take place. Conventionally, K_d values are determined under "equilibrium conditions" using either a batch method or columns under saturated flow. In the batch method convection and diffusion processes are eliminated as far as influencing the K_d measurement. In columns under saturated flow moisture-flow processes apparently affect K_d measurements. A possible explanation is coupling of the sorption mechanism to the flow mechanisms. This would mean that the equilibrium state itself, should it be attained locally, would depend on such variables as the flow rate and the dispersivity of the saturated porous system.

Geological media selected for nuclear waste repositories certainly are not water saturated although as in most underground formations water is universally present. Thus, initial conditions of a repository will likely be unsaturated flow, and if a repository is breached by free flowing water, the initial flow conditions through the geological media will be unsaturated flow. In unsaturated flow, the quantity of water within the pore space is considerably less than that under saturated conditions. Thus, because of the soluble salts present in most porous media, the ionic strength of the solution phase is greater in unsaturated conditions. Because of the higher concentration of competing ions in the solution phase, K_d values for trace concentrations of radionuclides will be lower than those values determined under saturated flow conditions if sorption is controlled by ion exchange mechanisms. Soil chromatography is a technique which simulates the distribution of radionuclides between solid and aqueous phases in unsaturated as well as saturated conditions.

One of the most important advantages, however, of the chromatographic technique is its differentiation. If more than one species of the radionuclides exists (either due to the difference in oxidation states of the radionuclide or the formation of a soluble stable complex), then differences in their sorption properties can be resolved from their different migratory patterns within the chromatograph. This is not the case if the conventional batch technique is used to determine K_d values. Species differentiation is of particular importance in the assessment of the potential movement of the actinides from geological repositories as their valence state depends on the ambient environment. For example, Pu (VI) is much more mobile than Pu (IV). Thus any environmental condition that favors production or stability of Pu (VI) will enhance the mobility of Pu.

MODELING

Perhaps the most important disadvantage of soil and thin-layer chromatography in the past has been its lack of an adequate quantitative theory. The basic chromatographic equation, which has been used in the past, is a simplified solution to the transport equation which neglects dispersion, competing-cation, and variable moisture-saturation effects. Such a model predicts sharp rectangular fronts, which are not attained experimentally. Consequently some subjectivity must be introduced to compare such theoretical profiles with the experimental shapes that are actually obtained. To close this gap between theory and experiment we have been developing computerized numerical models. Our initial effort consisted of solving a water-transport equation and a mass-transport equation and automatically optimizing the fits to experimental data (Quantitative Analysis of Soil Chromatography, I. Water and Radionuclide Transport. M. Reeves, C. W. Francis, and J. O. Duguid, ORNL-5337). This first approach included the effects of dispersion and variable saturation but, like the basic chromatographic equation, it neglected the influence of a competing cation, such as Ca or Na, on the radionuclide movement.

During the past fiscal year coupled mass-transport equations have been implemented in order to alleviate this deficiency. At the same time the basic chromatographic equations has been rederived analytically to improve its characterization of variable saturation and competing ions. The latter model is still incapable of fitting the different experimental profile shapes. However, it does provide a simple check on the uniqueness of the numerical model, which has been critized as being "too complicated".

The basic objective of the modeling effort is to determine the selectivity coefficient between a given radionuclide and a dominant cation like Ca or Na relative to a particular type of geologic media, such as Conasauga shale. From this selectivity coefficient, one can then easily obtain the distribution coefficient as a function of the concentration of the dominant species. The required experimental data for such an analysis are water-content distributions (Fig. 7, for example) and trace-radionuclide and dominant cation distributions (Fig. 8, for example).

Experimental Chromatography:

Channel chromatographic (CLC) plates were used instead of the conventional TLC plates. These plates are 20 by 20 cm with nine channels or columns measuring 10 mm in width and 2 mm in depth. Soils or finely ground rock material are slurried with water until moderately fluid and then applied to the plates using a conventional TLC spreader. Strips of blotter paper, approximately 0.7 mm wide and 2 cm long, are used as wicks for transporting the eluting solution to the soil layered in the channels. The wicks are held in place by clamping a 20 by 20 cm conventional TLC plate on top of the CLC plate. By using these wicks, the soils in the CLC plates may be eluted again after drying. If wicks are not used, soil will slough off during immersion in the eluting, or feed solution since the CLC plates are positioned at 68 degrees relative to the surface of the eluting solution.

The radionuclide to be considered may be introduced into the column chromatograph either through the feed solution or by spotting the radionuclide directly onto the soil or other geological media used. In the latter case a spot containing 10^4-10^5 dpm is placed 4 cm from the base of the chromatographic column. The wicks are then submerged in the feed solution.

In some of the earlier work, autoradiography and a dissection method were used to determine distribution patterns. Medical X-ray film was used for the autoradiography. The film was enclosed in thin sheets of plastic to prevent its contamination. It was then clamped securely between the TLC plate and the CLC plate and exposed for periods ranging from 48 to 72 hours. Measuring the movement of radionuclides in this manner sufficed only in that it gave the general characteristics of the mobility of one radionuclide to another. Another method for obtaining distribution patterns consisted of dissecting each column into 1.5 cm increments of soil. The radioactivity of each increment was then counted separately with a suitable detector. Although this technique was capable of quantitative measurement, it was extremely laborious and its resolution was limited to the lengths of the soil increments. Currently, a radiochromatographic scanner (Berhold Model LB 276) equipped with a gas-flow or NaI detector is being used for measuring the movement of the various radionuclides.

RESULTS

Analytical Model:

In most transport models, K_d values are used to determine a retardation factor $R_d = 1 + pK_d/n$ where p and n are bulk density and porosity of the soil. The similarities between this equation and the basic chromatograph equation, $1/R_f = 1 + W_aK_d/V_s$ where W_a and V_s are quantities in the liquid (g/ml) and solid phases (g/g), respectively, is the basis of the analytical model. The assumption here is that $1/R_f$ should be equivalent to R_d and thus K_d values can be determined directly from R_f values knowing the bulk density and effective porosity of the soil.

To determine the R_f value, the radionuclide is spotted at the 4 cm mark on the chromatograph. After drying, the plate is scanned with the radiochromatographic scanner and then eluted with the selected eluting solution. The plate is removed from the eluting solution when the wetting front has traveled approximately 10 cm. After recording this distance, the plate is dried and then scanned to compare the distribution of the radionuclide to that before elution (Figs.1-4). Because the distribution of the radionuclide along the chromatograph, before and after wetting, closely resembled a normal distribution pattern, the position of the radionuclide was established at the mid-points of the curves. The R_f values were calculated using the distances between these points. Distribution coefficients were calculated using the R_f, the respective bulk density, and porosities of the soils (Table 1).

The resolution of the scanner is 0.2 cm; therefore, for a water front moving 6 cm beyond the spotting position the R_f value cannot be less than 0.033. This in turn limits K_d values to less than 15 for most soils.

The distribution coefficient calculated from the R_f values agreed quite well for Sr-85, but for Na-22 the K_d by the chromatograph method was considerably smaller than by the batch method. Comparing column K_d's to the batch K_d's at an equilibrium concentration of 0.1 $\underline{N}$ calcium is probably not justified as the concentration of calcium in the soil solution at the 4 cm mark on the chromatograph is likely closer to 0.05 $\underline{N}$ than 0.1 $\underline{N}$ calcium. Thus, column K_d's would be considerably smaller than batch K_d's if batch K_d's were calculated at soil solution concentrations of calcium. Actual values for calcium or for that matter the cation displaced from the soil sites by calcium cannot be calculated without benefit of the coupled-equations model. This is one of the most important reasons for developing the coupled-equations model.

Selectivity Coefficients:

Selectivity coefficients for the various radionuclides are required for comparison with the coupled-equations results. Selectivity coefficients should be determined for the radionuclide of interest using trace concentrations of the radionuclide ($< 10^{-6}$ $\underline{M}$) in the presence of macromolar concentrations of the dominant cation in the solution and sorbed on the solid matrix. The selectivity coefficient is defined as follows:

$$K_{(i)/(j)} = \frac{(\bar{x}_i/x_i)^j}{(\bar{x}_j/x_j)^i} \qquad (1)$$

where $\bar{x}_i$ is the concentration of the radionuclide (i) on the solid matrix,

x_i is the concentration of the radionuclide (i) in the equilibrium solution,

$\bar{x}_j$ is the concentration of the dominant cation (j) on the solid matrix,

x_j is the concentration of the dominant cation (j) in the equilibrium solution,

j is the cationic charge of (j), and

i is the cationic charge of (i).

Because (i) is the radionuclide and present in trace quantities, $\bar{x}_i/x_i = K_d$ of the radionuclide. Thus equation (1) can be rearranged to the following

$$\log K_d = \frac{i}{j} \log K_{(i)/(j)} + \frac{i}{j} \log \bar{x}_j - \frac{i}{j} \log x_j \ . \qquad (2)$$

A log-plot of K_d versus the concentration of x_j should give a straight line with a slope of i/j and an intercept equal to $\frac{1}{j} \log K_{(i)/(j)} + \frac{i}{j} \log \bar{x}_j$. Because the concentration of (j) >> (i), the term log $\bar{x}_j$ is constant and equal to the cation exchange capacity of the solid exchanger.

Selectivity coefficients of Ni, Sr, and Na were determined relative to macroconcentrations of Ca (equilibrium concentrations ranging from 10^{-4} to 1 M) for the Muscatine silt loam soil. Approximately 1 gram sample of this soil were saturated (by repeated washings in Oak Ridge type centrifuge tubes) with 20 ml of 1 N $Ca(NO_3)_2$ containing tracer quantities of Ca-45. The calcium solution concentrations were varied by diluting with distilled water so that equilibrium calcium concentrations in the solution phase ranged from 1 to as low as 10^{-4} $\underline{N}$. Tracer quantities ($< 10^{-6}$ $\underline{M}$) of Ni-63, Sr-85, and Na-22 were added to these suspensions and equilibrated by shaking overnight. Adsorption of Na-22 and Sr-85 was complete after overnight shaking, however, adsorption and desorption of Ni-63 was time dependent (Tables 3 and 4). The log-log plots of the K_d values obtained for each of these radionuclides (Ni-63, Na-22, and Sr-85) at various calcium solution concentrations are presented in Fig. 5. A reasonably good fit (all $r^2 > 0.90$) to a straight line was found for all radionuclides considering that the range of calcium concentrations was nearly 10^4. The slope of each curve, however, did not represent "ideal" behavior, viz, the slopes for Sr-85 and Ni-63 should have been -1 while the slope for Na-22 should have been -0.5.

The K_d's of sodium and nickel in the presence of various calcium concentrations were obtained with Conasauga shale.

For sodium

$$\log K_d = 0.51 - 0.24 \log (\mathrm{Ca}) \qquad r^2 = 0.760, n = 12$$

$$\text{when } 1.0 \leq (\mathrm{Ca}) \leq 7.1 \times 10^{-4}$$

and for nickel

$$\log K_d = -.06 - 0.81 \log (\mathrm{Ca}) \qquad r^2 = 0.905, n = 12$$

$$\text{when } 1.0 \leq (\mathrm{Ca}) \leq 1.3 \times 10^{-2}; \text{ (Ca) in meq/ml.}$$

These regression equations can be subtracted from equation (2) and the selectivity coefficients can be expressed in terms of calcium concentrations (Fig. 6) by simple power laws of the form

$$K = ax^b \tag{3}$$

where a and b are constants and x is the calcium concentration in the solution phase.

Movement of Radionuclides in Conasauga Shale Relative to Calcium:

Conasauga shale (< No. 35 mesh) was dry-sieved into channel chromatographs using a TLC spreader. Instead of inclining the chromatographic plate at 68 degrees, the following data were obtained while the plate was in a horizontal position. The radionuclides were introduced into the columns via paper wicks (10 cm) dipped in 10 ml of 1 N $Ca(NO_3)_2$ contained in polyethylene test tubes. Each tube contained tracer levels ($<10^{-6}$ M) of a radionuclide (H-3, Na-22, Ni-63, Sr-85, Ru-106, Cd-109, Ce-144, and Sb-125) and Ca-45 to monitor Ca movement. Thus, in this manner, the profiles (concentration versus distance along the chromatograph) of water, the displacing cation (Ca) and each radionuclide can be evaluated in a single wetting. After wetting to 10 cm, the columns were removed in 1 cm increments. The columns containing H-3 and Ca-45 were dissected immediately after removing the TLC plate covering the chromatograph to avoid loss of H-3. The cations were displaced from the shale increments using three 10 ml washing of 1 N $Ca(NO_3)_2$ in 0.1 N HCl and DTPA (1.3 g/l). From the distribution of water, calcium and the radionuclides along the chromatograph (Figs. 7 and 8) K_d values and selectivity coefficients will be determined using the coupled-equations model. Distribution patterns in Figs. 7 and 8 expose an important problem for these analyses. The dominant cation such as calcium, has a spacially variable concentration over the length of the chromatograph. Both the distribution and selectivity coefficients are functions of this concentration, and hence they also vary as a function of distance along the chromatographic column. These two coefficients should, therefore, not be determined directly from the chromatograph, but rather from sorption parameters which do not vary. Quantities a and b of equation (3) which resulted from analyses of the batch measurements fit this criterion very well. These constants, a and b of the equation $K = ax^b$, are also easily obtained from the numerical analyses of the distribution patterns of the various radionuclides along the chromatograph. In this manner, equations (2) and (3) can be used to determine selectivity and distribution coefficients as functions of the concentrations of the dominant cations.

SUMMARY

The objective of the project is to calculate distribution coefficients (K_d's) of radionuclides in chromatographic columns filled with soil or other porous geological media. Values calculated will then be compared to K_d's determined in the conventional batch method. Last year, a water transport and a mass-transport equation were optimized to fit the experimental data. This year, initial efforts were directed at assessing the theoretical sensitivity of these models. Because no significant differences could be detected in the movement of the radionuclides between wettings using distilled water as an eluting solution, it became apparent that the models were of little use unless they were coupled to a competing-ion mass transport equation. This equation coupled with the water and mass transport equations describe radionuclide movement using eluting solutions of various ionic strengths. The model has been developed and is being used to determine K_d's and selectivity coefficients from experimental data. Once the uniqueness of the model has been verified, these coefficients in turn will be compared to those that have already been determined in conventional batch procedures over ranges of calcium concentration (1 to 10^{-3} meq/ml).

Table 1. Distribution coefficients (K_d) in soil chromatographs.[1]

	Calcium concentration in eluting solution meq/ml	
	0.10	0.01
	Muscatine silt loam	
Ca-45	2.6	>15
Sr-85	3.0	>15
Na-22	0.23	1.2
Ni-63	>15	>15
I-129	0.0	0.0
Tc-99	0.13	0.09
	Fuquay sand	
Ca-45	0.23	1.23
Sr-85	0.46	1.48
Na-22	0.26	0.15
Ni-63	0.85	5.4
I-129	0.02	0.0
Tc-99	0.11	0.02

[1] $1/Rf = 1 + p\,K_d/n$ where p and n are bulk density and porosity of the soil. For Muscatine silt loam, $p = 1.21\ g/cm^3$, $n = 0.545$; Fuquay sand, $p = 1.38\ g/cm^3$, $n = 0.479$.

Table 2. Comparison of chromatographic K_d values to those determined by the batch measurement technique.

	Ca Concentration[1] 0.1 meq/ml	
	Chromatograph	Batch
Sr-85	3.0	2.1
Na-22	0.23	4.3
Ni-63	>15	270

[1] Calcium concentration of eluting solution for chromatograph studies and equilibrium concentration for batch studies calculated from the regression equations for

Sr, $K_d = 0.28\ (Ca)^{-0.87}$, $r^2 = 0.99$
Na, $K_d = 2.34\ (Ca)^{-.028}$, $r^2 = 0.93$
Ni, $K_d = 33.9\ (Ca)^{-0.90}$, $r^2 = 0.98$

where (Ca) is calcium concentration in meq/ml.

Table 3. Influence of Time on Sorption of Nickel on <2μm Fraction of a Muscatine Silt Loam[1]

Ca Concentration meq/ml	Time (hr) 2	6	24
	K_d		
1	15.9	27.5	33.9
0.1	132	195	214
0.01	1097	1378	1350
0.001	9126	9757	8515

[1] K_d values determined from regression equation:

For 2 hr

$$K_d = 15.9\ (Ca)^{-0.92} \quad r^2 = 0.980,\ n = 10$$

6 hr

$$K_d = 27.5\ (Ca)^{-0.85} \quad r^2 = 0.990,\ n = 10$$

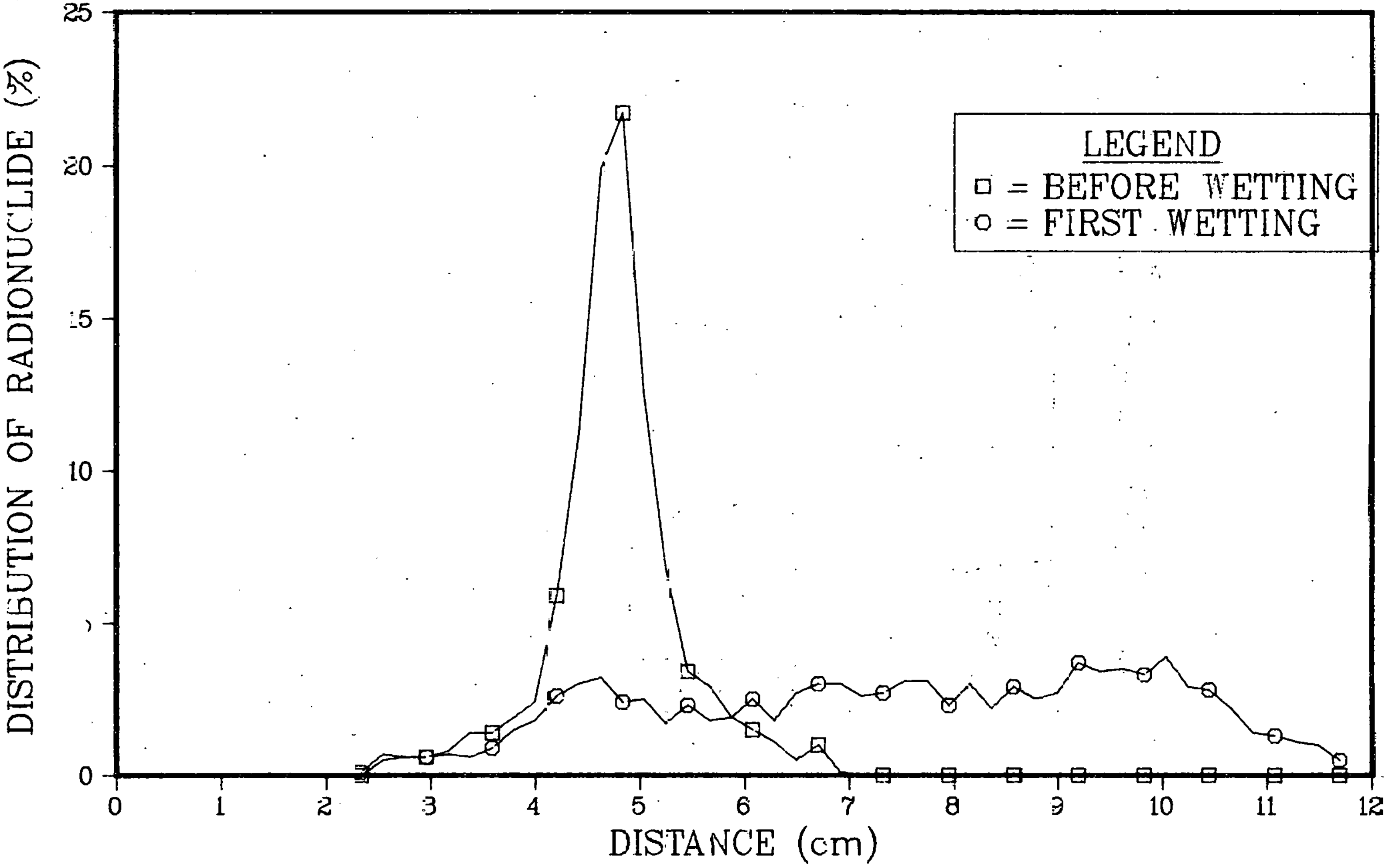
24 hr

$$K_d = 33.9\ (Ca)^{-0.90} \quad r^2 = 0.979,\ n = 10$$

where (Ca) is calcium concentration in meq/ml.

Table 4. Influence of Time on Desorption of Ni-63 from <2μm Fraction of Muscatine Silt Loam.

Sorption after 24 hr		Desorption in 1 N Ca		
		Time (hr)		
		2	6	24
Ca meq/ml	K_d		K_d	
1	34	83	40	20
0.1	214	109	65	46
0.01	1350	111	70	49
0.001	8520	119	65	49



MOVEMENT OF RADIONUCLIDES IN FUQUAY SAND

STRONTIUM-85

ELUTING SOLUCTION - 0.1 N CA

Figure 1

MOVEMENT OF RADIONUCLIDES IN FUQUAY SAND

NICKEL-63

ELUTING SOLUCTION - 0.1 N CA

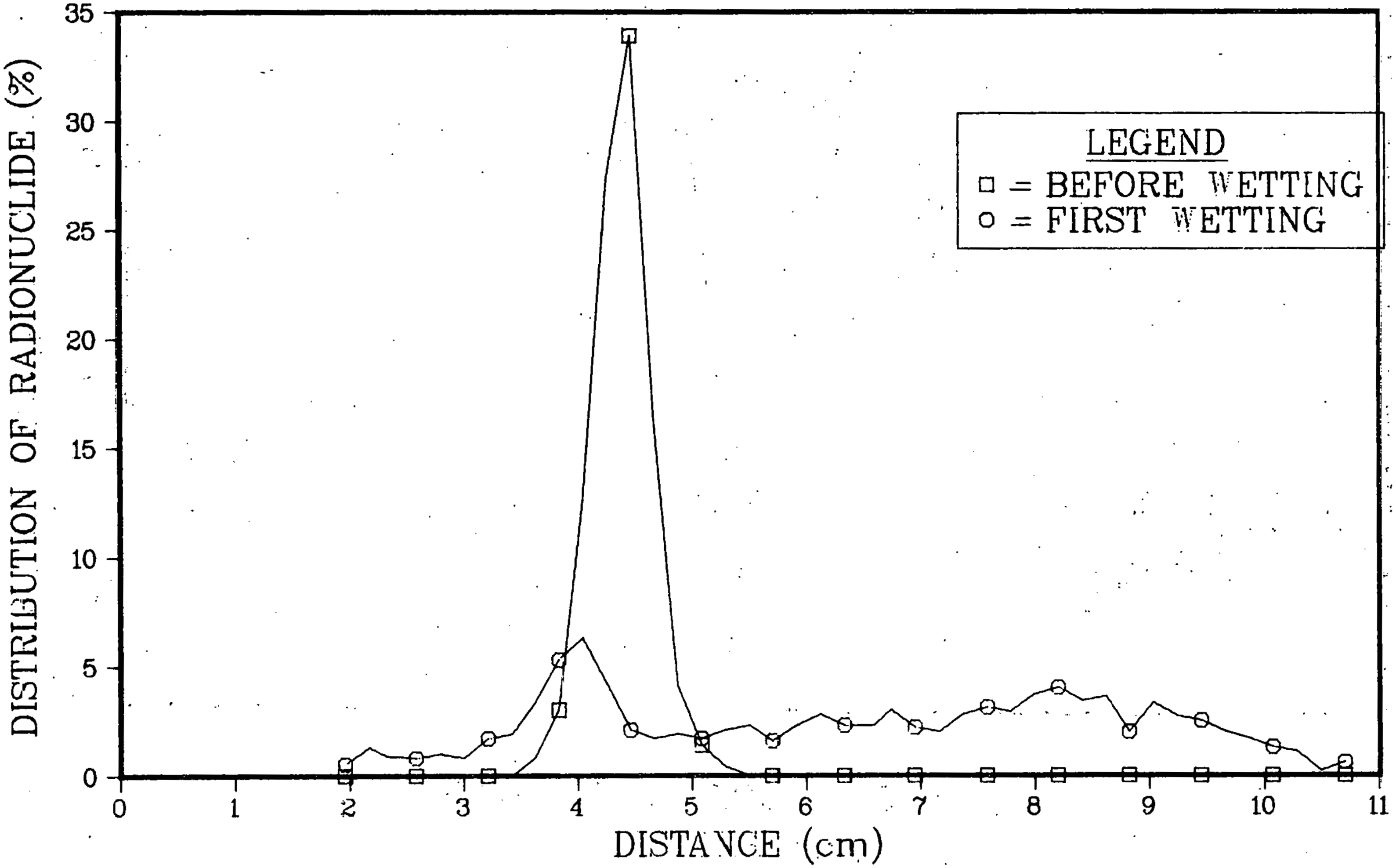
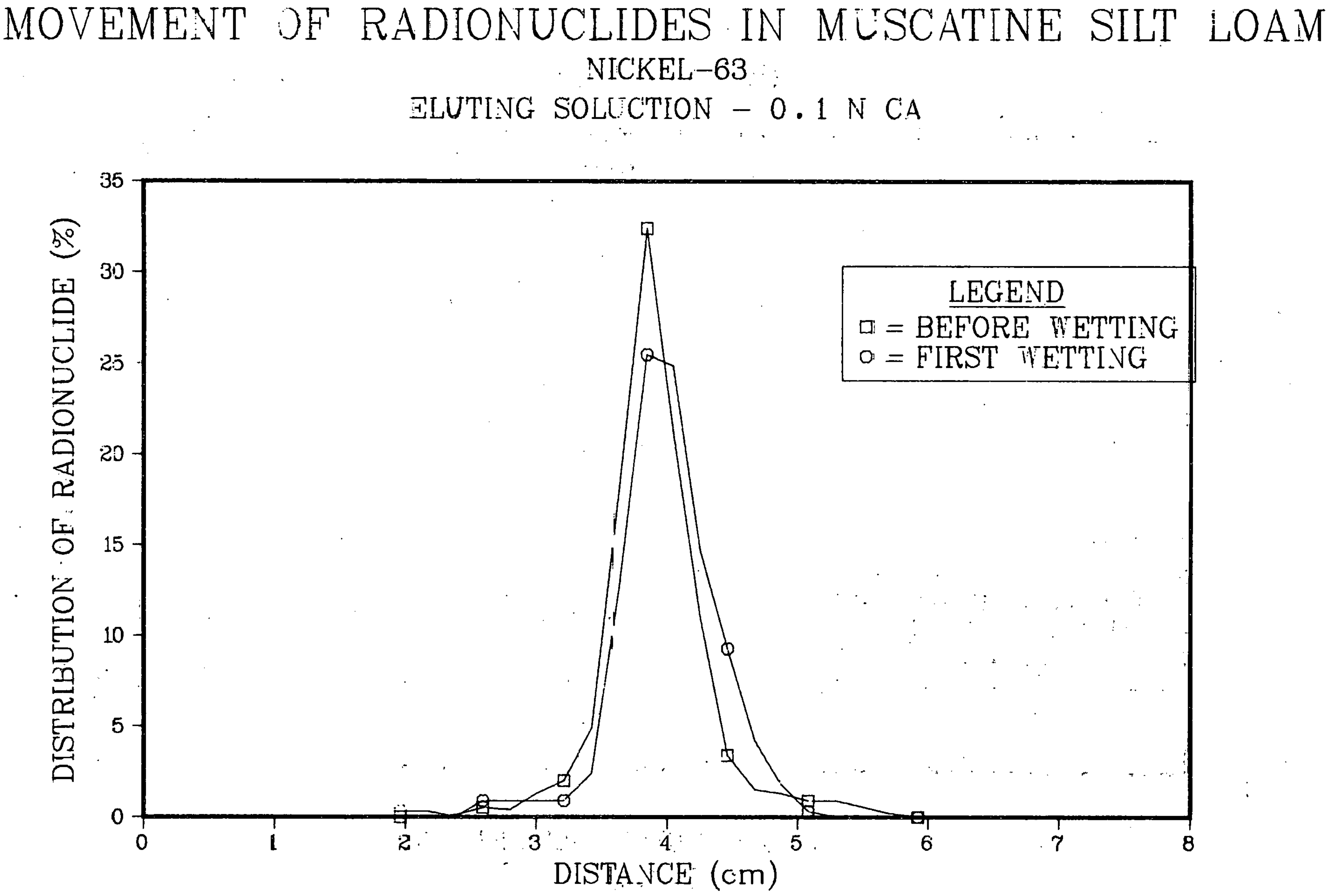
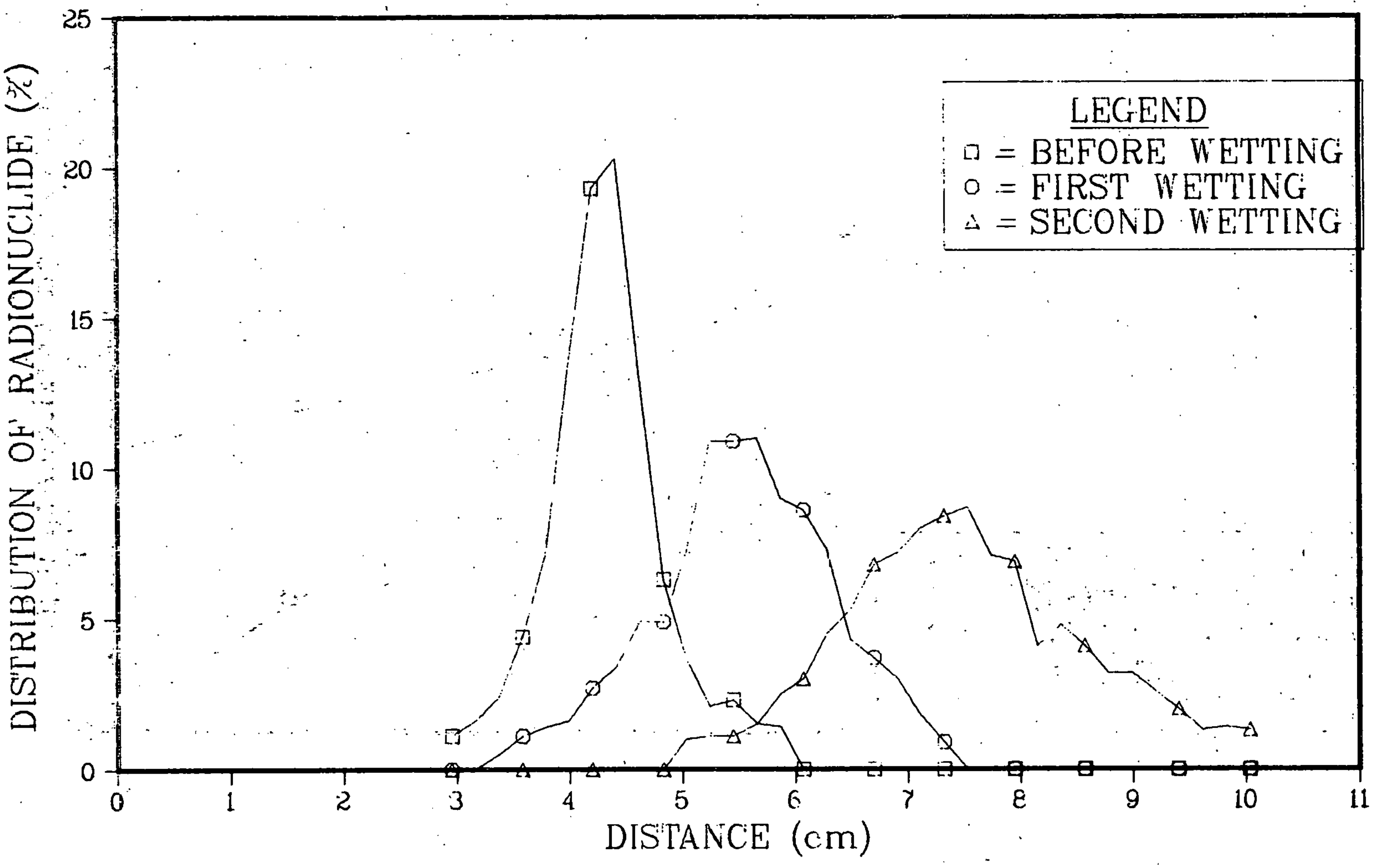


Figure 2



MOVEMENT OF RADIONUCLIDES IN MUSCATINE SILT LOAM
NICKEL-63
ELUTING SOLUCTION - 0.1 N CA

Figure 3



MOVEMENT OF RADIONUCLIDES IN MUSCATINE SILT LOAM

STRONTIUM-85

ELUTING SOLUCTION - 0.1 N CA

Figure 4

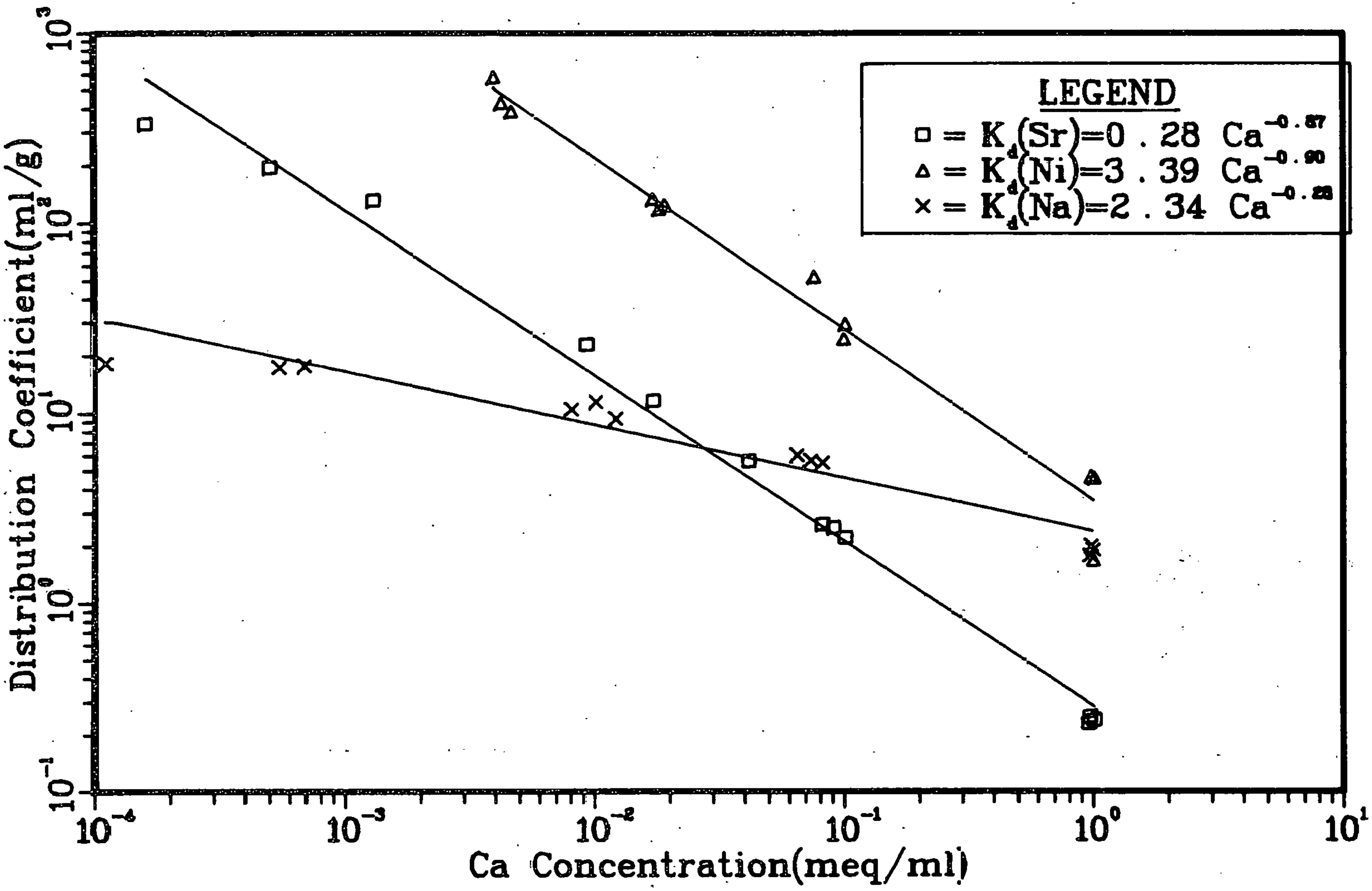


Figure 5. Distribution Coefficients as a Function of Calcium Concentrations in the Solution Phase (Muscatine Silt Loam).

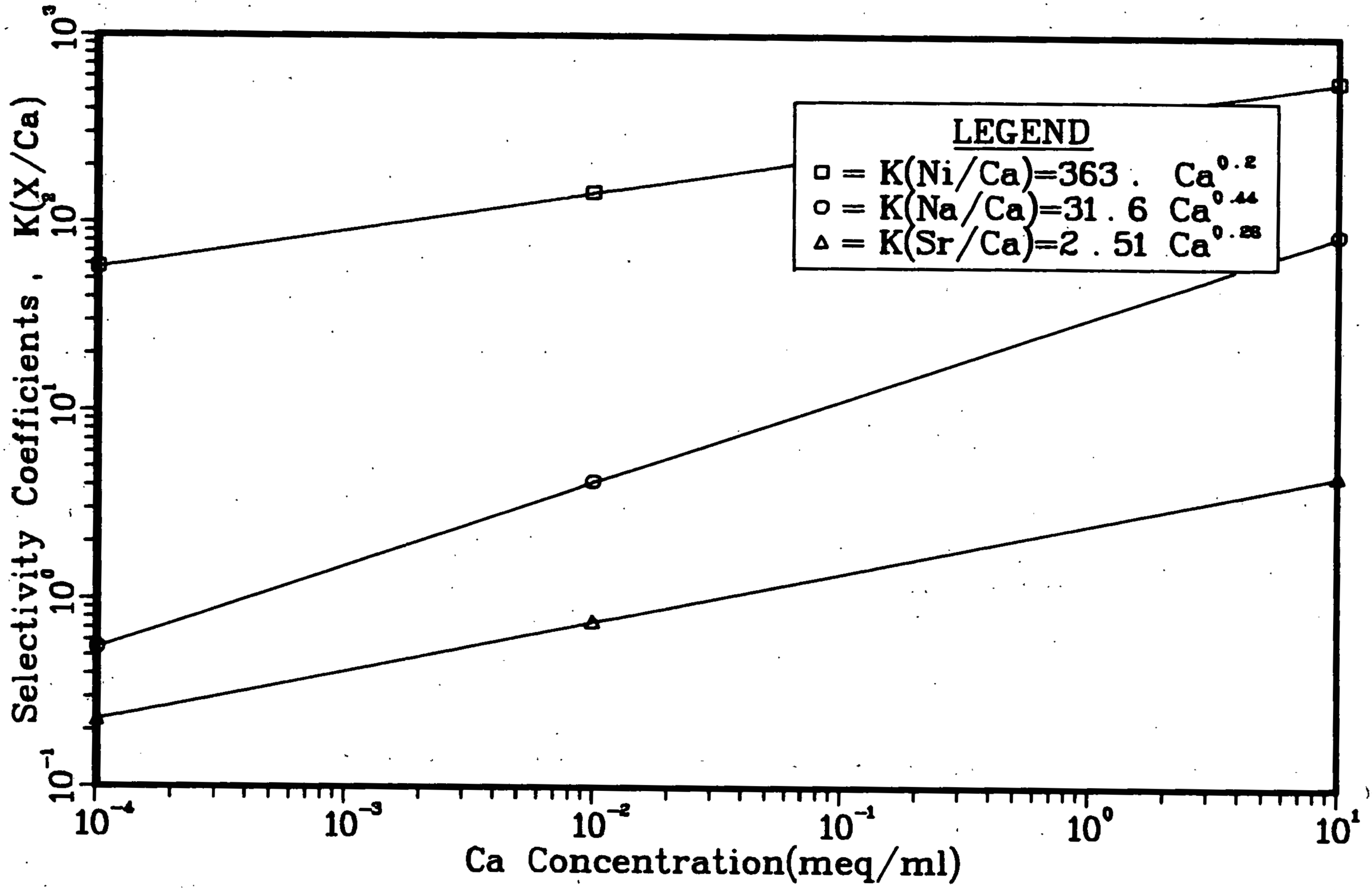


Figure 6. Selectivity Coefficients as a Function of Calcium Concentrations in the Solution Phase (Muscatine Silt Loam).

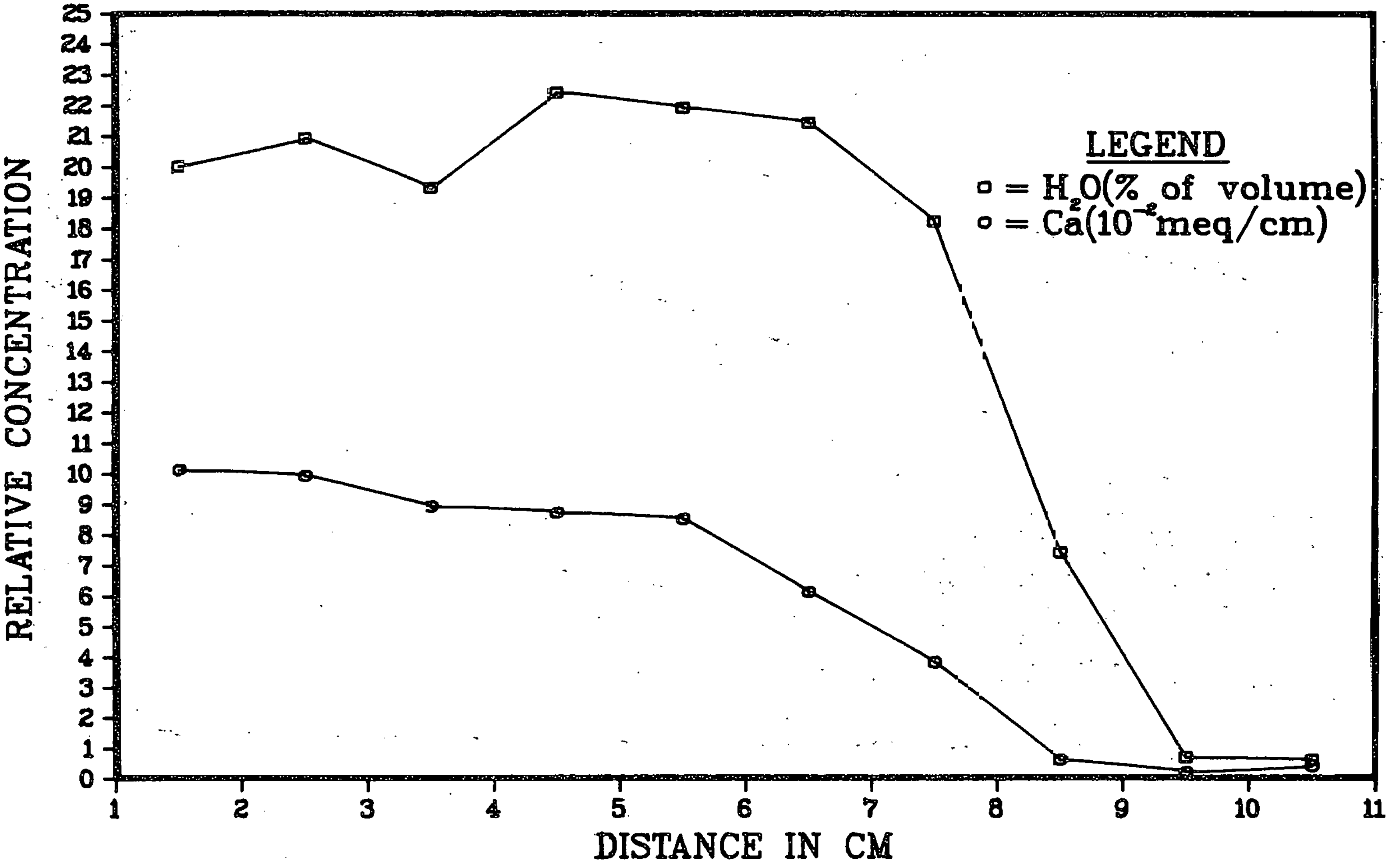


Figure 7. Distribution of Water and Ca in Conasauga Shale after Wetting to 10 cm with 1 N $Ca(NO_3)_2$.

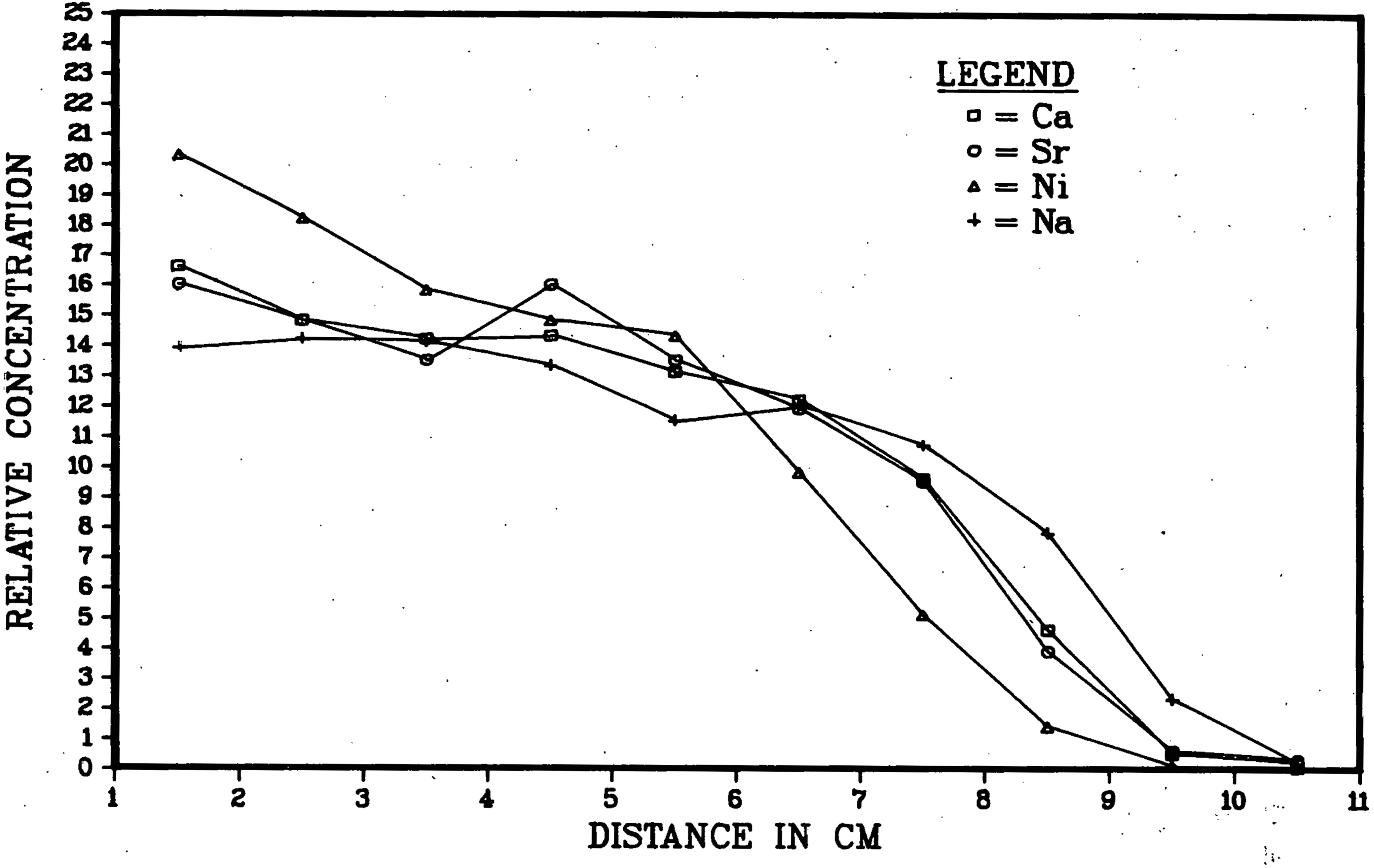


Figure 8. Relative Distribution of Tracer Quantities of Sr, Ni, and Na to Ca after Wetting Conasauga Shale to 10 cm with 1 N $Ca(NO_3)_2$.

DISCUSSION--C. W. FRANCIS

Experimental Chromatography

Q. Is the solvent aqueous?

A. In this case, it was water. We can use different Ca concentrations, different Na concentrations--whatever we need to do, to detect mobility.

Q. Are the plates protected against evaporation?

A. Yes. After we put in the soil slurry and let it dry, we cover the chromatograph with plastic up to the 5 cm line, and then clamp a conventional TLC (thin layer chromatograph) plate on top. Also, all of these experiments are carried out in a closed system.

Q. Does muscatine silt loam have a low iron content?

A. We didn't purify it. It's a good agricultural soil, high in organic material. I would guess that it has less than 2% Fe (II) or (III).

Q. What is the size fraction of the soil that you're using?

A. Everything less than 500μ.

Q. Did you perform any tests to determine the effects of spotting?

A. Yes, we've tried it just about every way possible. It cannot be done upside down, as this will result in streaking along the side; but it can be done in a number of other ways.

Q. Did you get any particle size fractionation from top to bottom when the slurry settles out?

A. I don't know. When we elute in a sandy soil, we might simply be moving very fine, submicron-sized particles from the bottom to the end of the column. To correct for this, in some Pu experiments performed last year (see ORNL-5337, "Quantitative Analysis of Soil Chromatography. I Water and Radionuclide Transport" by M. Reeves, C. W. Francis, and J. O. Duguid) we eluted fuquay sand several times and then spotted it. We still saw a Pu spot at the end of the column. However, fuquay sand is an unusual type of soil in that organic matter can be dispersed very easily. Consequently, the Pu at the end of the column could be a soluble organic matter complex.

Q. If you had particle fractionation due to size, with fine particles on the top and coarse ones on the bottom, wouldn't the water move faster on the bottom, next to the glass?

A. It could be.

Q. When you load the plates, is it sufficient to slurry the soil in water and let it dry?

A. Yes. At first, we thought this method would just work with sandy soil. When we tried it with muscatine silt loam, however, even though the loam cracked during the drying process, we obtained more uniformity of water-front movement than we had with the fuquay sand; with the sand, the water movement is so fast that it results in some variability.

Q. What do you do if a crack develops in the soil?

A. If there is a large crack, the water won't be able to move up the column; to solve this problem, we just push on the end of the column to close up the crack.

Q. Do you rely on settling or do you vibrate the column?

A. We just rely on settling. In fact, with the conasauga shale, we didn't even wet it. We simply dry-sieved it into the columns, making sure that the columns were vertical. I think this is the direction we should be taking, since it is closest to the actual situation likely to be found in the field--a water front coming into an unsaturated salt dome.

Q. How thick are the samples as far as the beta emitters are concerned?

A. We do see some self-absorption; however, we're not really interested in quantity but rather in how far a particular radionuclide moves.

Q. What about Sr? I think you're just measuring the surface.

A. We use gamma Sr, not beta.

Q. After drying radionuclides (e.g., Pu and Am) on the crushed rocks, have you found it difficult to get them back off the rocks?

A. We've tried to determine whether there is retention after drying. In the case of Pu, I can't be sure. We did not have our NaI detector on our chromatographic scanner for those experiments, and therefore would have had difficulty in picking up low concentrations. For the other radionuclides that we've used, I've seen no evidence of retention after drying. In the case of Cs, however, we don't even use it; it's my opinion that it will not migrate very far.

Q. I wouldn't say the same thing about your data. It doesn't seem like anything has stopped at the 4 cm mark; everything seems to be moving.

(No answer given)

DISCUSSION--MARK REEVES

Modeling

Q. Is the unsaturated distribution coefficient that you use the same as one for a saturated system?

A. The model assumes that the distribution coefficient is proportional to the degree of saturation--i.e., to the water content divided by the total porosity. (See ORNL-5337, "Quantitative Analysis of Soil Chromatography. I Water and Radionuclide Transport" by M. Reeves, C. W. Francis, and J. O. Duguid.)

Q. Do the Xi's and Xj's in your equations represent activities or concentrations?

A. They are concentrations--meq/g.

Q. Was the equation you used for the selectivity coefficient dependent on a homoionic exchange?

A. No, the valences are taken into account in the equation. The P's represent the valence.

Q. What happens if you have more than one competing ion--for example, Ca and Na competing with Sr?

A. The program is set up in a general manner so that it can handle any number of competing species.

Q. Would your setup still be based on binary selectivity coefficients iterating through to simulate simultaneous situations?

A. Yes, that's right.

Radionuclide Movement in Shale (Figure 7, 8)

Q. Is there any reason why the liquid concentration and the activity on the shale should fall off at the same distance?

A. It has to do with the equation for the selectivity coefficient, which requires that the liquid and active solid concentrations for the minor constituent be the same as those for the major constituent.

Q. Are these computer-generated curves?

A. Yes, they are.

Guarding Against Error

Q. How sensitive are your calculations to possible errors in those exponents on the Ca concentrations (Figures 5, 6)?

A. We will have to input experimental errors and use those inversely to weight our parameters that we optimize. I suspect that we will need to input relatively large errors and emphasize that less in our optimization, since, for experimental reasons, we are not planning on preequilibrating the crushed rocks or soil. What we will be doing instead is to put a dominant cation into the soil, which, in a sense, equilibrates it, and then allow the trace material to elute into it. Also, we will be doing a sensitivity analysis on the final results.

Q. Do you have any feeling as to whether your optimization schemes for the dispersivity and for the selectivity coefficient will be unique?

A. We are attempting to guard against the possibility that they will not be unique by using both comparable batch measurements and simplified analytical formulas. There is a slight physical distinction between them, however: the dispersivity refers only to the liquid phase as it flows through the solid, whereas the selectivity coefficient refers to both solid and liquid phases. However, I'm not sure whether this distinction is sufficient to assure uniqueness.

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"THE KINETICS AND REVERSIBILITY OF RADIONUCLIDE SORPTION REACTIONS WITH ROCKS"

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THE KINETICS AND REVERSIBILITY OF RADIONUCLIDE SORPTION REACTIONS WITH ROCKS – PROGRESS REPORT FOR FISCAL YEAR 1977

INTRODUCTION

The work described in this report is part of the Waste Isolation Safety Assessment Program (WISAP) managed by the Pacific Northwest Laboratory for the Office of Waste Isolation. Progress in fiscal year 1977 is reported (the project was begun in March 1977).

Assessment of the safety of radioactive waste storage in rock formations requires a knowledge of radionuclide sorption on the rock. Sorption data is used in predicting migration from the storage site to the biosphere. Radionuclide sorption is described in terms of equilibrium sorption coefficients (K_d's). Since K_d values obtained in the labroatory depend on the methods used to obtain them, reliable, reproducible data are difficult to find. To avoid this problem, it is necessary to define a method or methods which will yield reproducible and useful data for predicting sorption. The effects of experimental variables on K_d values must be understood if a useful measurement method is to be defined. The specific goal of this program is to determine the effects of irreversible sorption reactions and rates of sorption on measurement of K_d. This information will help to define a specific method for K_d measurement and will provide a significant amount of site-specific sorption data.

Some sorption reactions have been shown to be irreversible. An example is the replacement of cations by cesium ion in mica-like minerals. Cesium ion is essentially "fixed" in the sorption sites of these minerals and cannot be recovered by ion exchange reactions. Irreversible sorption reactions will 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.

There are two types of reactions that result in changes in K_d with time. The first is a sorption-desorption reaction with the rock. This type of reaction will probably be diffusion-controlled and is relatively rapid (on the order of days or weeks). The second is the reaction of geologic media with macro-components of the groundwater. Possible reactions are: (1) mineral transformation, (2) mineral dissolution, and (3) precipitation of dissolved minerals and other groundwater components. This type of reaction is expected to be slow.

The work completed thus far emphasizes a thorough characterization of the rocks chosen for study, determination of the precision of K_d measurements using the batch equilibration method, and accelerated "weathering" experiments by leaching the rocks.

MATERIALS AND METHODS

ROCKS

Four rock types were selected, each representing a possible location of a deep geologic waste repository. These rocks are basalt, quartz monzonite porphyry ("granite"), argillite, and rocksalt. The sampling location and the geologic formations from which these samples were obtained are given in Table I.

TABLE I

SOURCE OF ROCK SAMPLES

Rock Type	Sampling Location	Geologic Formation
Basalt	Sentinal Gap, Washington Outcropping	Umtanum Flow
Quartz Monzonite Porphyry ("Granite")	Nevada Test Site Sample UE15e7	Climax Stock
Argillite	Nevada Test Site Sample VE17e (2200')	Eleana
Rocksalt	Carlsbad, New Mexico ERDA Drill Hole #9 (2621.2-2621.8')	________

GROUNDWATERS

Groundwater analyses were obtained for the four sampling sites listed above. Synthetic groundwaters with compositions approximating those of the above sites were prepared. A thoroughly analyzed water from a well near Paterson, Washington(1) 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 were chosen for experiments with granite and Eleana argillite. They are, respectively, a sodium-calcium-bicarbonate-sulfate water(2) and a calcium-magnesium-bicarbonate water.(3) A nearly saturated brine solution obtained by dissolving salt core from the Carlsbad, New Mexico site in deionized water is the "groundwater" associated with the salt. The compostions of the synthetic groundwaters are given in Table II.

TABLE II

COMPOSITION OF SYNTHETIC GROUNDWATERS*

Basalt	Granite	Argillite	Salt
295 mg/ℓ $NaHCO_3$	620 mg/ℓ $CaSO_4 \cdot 2H_2O$	112 mg/ℓ $CaCO_3$	287 g/ℓ $NaCl$
	302 mg/ℓ $NaHCO_3$	76 mg/ℓ $MgCO_3$	6.0 g/ℓ Na_2SO_4
		135 mg/ℓ $NaHCO_3$	16 mg/ℓ $Na_2B_4O_7 \cdot 10H_2O$
			14 mg/ℓ $NaHCO_3$
			520 mg/ℓ $NaBr$
			29 mg/ℓ KCl
			13 mg/ℓ KI
			40 mg/ℓ $MgCl_2$
			3.3 g/ℓ $CaCl_2 \cdot 2H_2O$
			6 mg/ℓ $FeCl_3$
			33 mg/ℓ $SrCl_2 \cdot 2H_2O$
			1.6 mg/ℓ Rb_2SO_4
			1.3 mg/ℓ $CsCl$

*As prepared.

RADIONUCLIDES

The radionuclides chosen for study are those which appear to be of most importance in radioactive storage safety (i.e., present in significant quantities in the wastes, possess long half-lives, and have high toxicity). These radionuclides are: cesium-137, strontium-90, ~~technetium-99~~, ruthenium-106, ~~promethium-147~~, ~~neptunium-237~~, plutonium, and americium-241.

METHODS

Equilibrium radionuclide distributions were measured using batch experiments. Five grams of crushed rock were pre-equilibrated overnight with thirty milliliters of the appropriate unspiked groundwater in sealed pretared polycarbonate centrifuge tubes (50 ml). The tubes were centrifuged and the supernate discarded. This pre-equilibration was repeated to ensure minimal changes in the groundwater composition when the spiked groundwater solution was added. The tubes were then weighed so that the residual volume of unspiked groundwater not decanted could be measured. This volume was used to correct the initial concentration of tracer since the tracer solution is diluted by it. Thirty milliliters of groundwater spiked with a single radionuclide were then added to the tubes and the tubes were shaken for 48 hours and centrifuged. The supernate was decanted from the crushed rock and analyzed for tracer concentration and pH. The tracer concentration was determined by standard counting techniques. Blank experiments were run to measure sorption of the tracer on the centrifuge tubes.

Both pH and Eh were allowed to vary in these experiments. The crushed rock buffered both the pH and Eh of the groundwater solutions. Measurement of these quantities were made for each rock-groundwater composition after the equilibration.

Equilibrium K_d values were calculated from tracer analyses of the groundwater solutions before and after equilibration with the crushed rocks. Five repetitions of each rock-groundwater-radionuclide equilibration were made to determine the precision of the K_d measurements.

The effect on K_d of transformation ("weathering") of the rock over long time periods is being studied. Accelerated weathering of basalt, granite, and argillite is being attempted by continuous leaching with hot, distilled water in a soxhlet apparatus. The effect of leaching on the microstructure and chemical composition of rock surfaces and K_d values is being studied.

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE ROCKS

Each of the four rock types was characterized as follows: (1) bulk elemental analysis, (2) qualitative mineralogy, and (3) surface area of crushed samples. Thorough characterization was necessary so that effects of sample characteristics on K_d measurements could be determined. Additional characterization work is needed (i.e., carbonate and water content, ion exchange capacity, quantitative mineralogy, and organic content) and will be completed in fiscal year 1978.

Elemental Analysis

Samples of basalt, granite and argillite were dissolved in dilute, aqueous hydrochloric acid after fusion with lithium metaborate. These solutions were immediately analyzed using an inductively coupled argon plasma source spectrometer (Applied Research Laboratories). This instrument measures the concentration of 29 elements simultaneously. Aqueous filtered solutions of the New Mexico rocksalt were also analyzed with this instrument.

Ten elements of measurable concentration were detected in the basalt, granite, and argillite samples. Results of these analyses are given in Table III. Averages of at least three analyses are given. Carbonate and water were not determined.

TABLE III

CHEMICAL COMPOSITION* OF BASALT, GRANITE, AND ARGILLITE

Oxide	Basalt	Granite	Argillite
SiO_2	56.7	68.4	57.3
Al_2O_3	12.0	15.9	20.7
$FeO^{\dagger}$	11.2	2.62	5.62
MgO	3.55	0.86	2.33
CaO	6.73	3.37	1.41
Na_2O	3.19	3.37	0.92
K_2O	1.69	3.61	1.29
TiO_2	1.53	0.29	0.79
BaO	0.06	0.09	0.02
P_2O_5	0.47	0.23	0.30
Total	97.12	98.74	90.36

*Given in weight percent.

†Only ferrous iron is assumed to be present.

Partial analysis of the soluble fraction of the salt (>99 percent) gave the following results.

TABLE IV

CHEMICAL COMPOSITION OF THE SALT

Element	Weight Percent
Na	33.3
K	0.3
Mg	0.09
Ca	0.18
Sr	0.01
Cl	ND*
Br	ND
SO_4	ND

*ND = Not determined

Mineral Content

The mineral content of each rock type was determined using X-ray diffraction and scanning electron microscope-microprobe techniques. X-ray diffraction patterns for the crushed rock samples are shown in Figure 1. The minerals which can be identified from these diffraction patterns are given in Table V.

TABLE V

MINERALS IDENTIFIED BY X-RAY DIFFRACTION

Basalt	Granite	Argillite	Salt
Labradorite	Anorthite	Quartz	Halite
Augite	Quartz	Chlorite	Sylvite
	Biotite	Stilbite	
	Albite		
	Brookite		

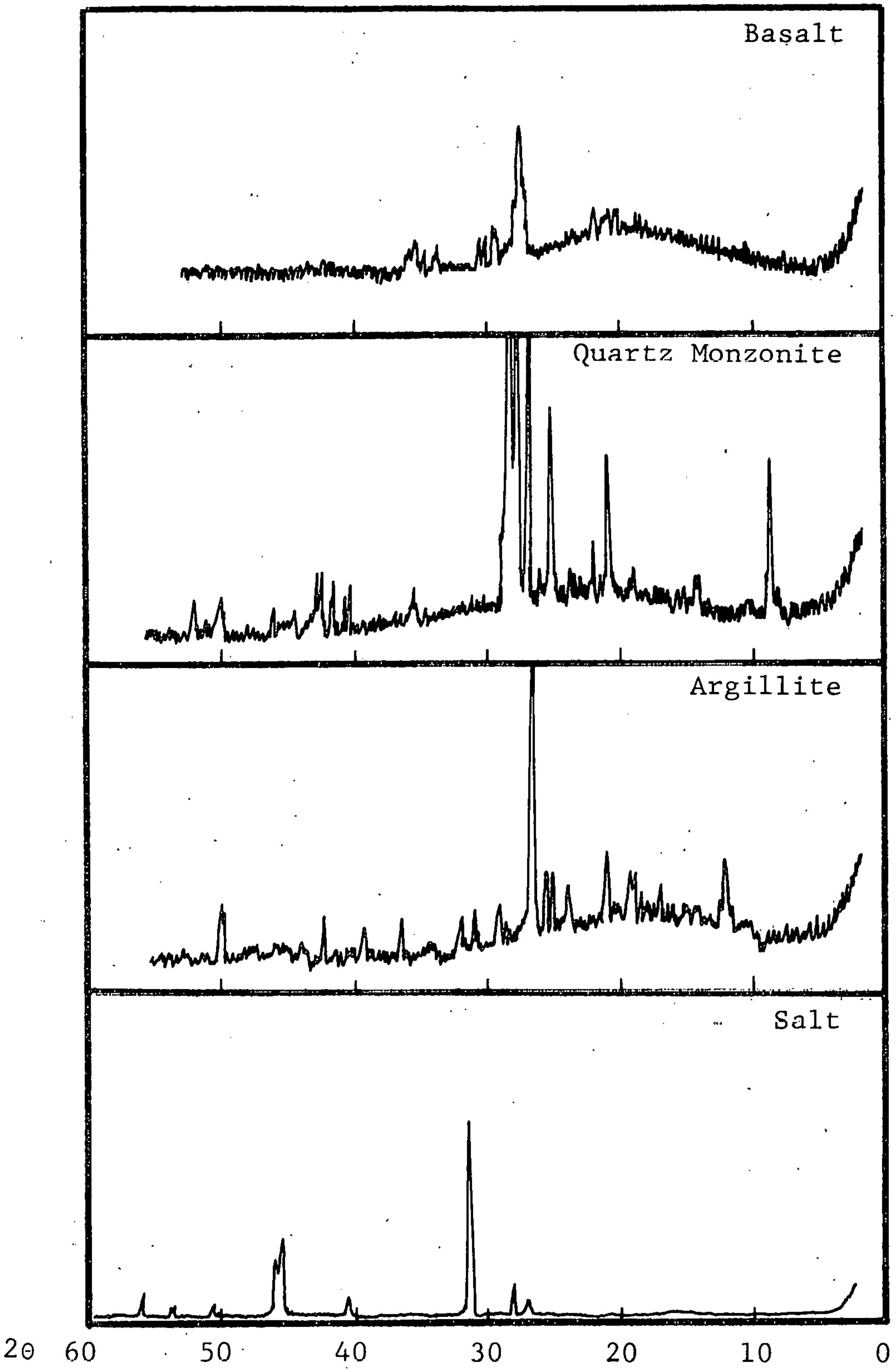

FIGURE 1

X-RAY DIFFRACTION PATTERN (COPPER SOURCE)
OF BASALT, GRANITE, ARGILLITE, AND SALT

Polished sections of the rocks were examined with an SEM-microprobe to measure grain size and identify mineral phases. Element maps and spot analyses were compared with secondary photomicrographs of the rock surfaces and were used to identify mineral phases. The results of analyses of different areas on the polished surface of each rock type are shown in Figures 2 through 20 in the Appendix. The abbreviations for the mineral phases shown in the photomicrographs are given below.

Q = quartz - SiO_2
Or = K-feldspar - $KAlSi_3O_8$
Ab = albite - $NaAlSi_3O_8$
An = anorthite - $CaAl_2Si_2O_8$
Py = pyroxene - $Ca(Mg,Fe)Si_2O_5$ or $(Mg,Fe)SiO_3$
Mt = magnetite - Fe_3O_4
Il = ilmenite - $FeTiO_3$
Bt = biotite - $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$
Ap = apatite - $Ca_5(PO_4)_3(F,Cl,OH)$
Tt = titanite - $CaTiSiO_5$
Pl = plagioclase - $NaAlSi_3O_8$-$CaAl_2Si_2O_8$
Ha = halite - NaCl
Gy = gypsum - $CaSO_4 \cdot 2H_2O$
Ep = epsonite - $MgSO_4 \cdot /H_2O$
Cy = clay
Ct = calcite - $CaCO_3$

The mineral phases identified in each rock type are summarized in Table VI. The minerals are listed in order of decreasing abundance.

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 (see Figure 1) indicate a large amount of amorphous material is present. Ilmenite exists as dendrites throughout the matrix.

TABLE VI

MINERALS IDENTIFIED BY THE SEM-MICROPROBE

Basalt	Granite	Argillite	Salt
Plagioclase	Plagioclase	Quartz	Halite
Pyroxene	Quartz	Clay	Gypsum
Ilmenite	Albite	Orthoclase	Epsonite
$FeSiO_4$	Orthoclase	Calcite	Clay
	Magnetite	TiO_2	
	Biotite		
	Titanite		
	Apatite		

The "granite" (actually a quartz monzonite porphyry) is very course 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. The salt consists of large halite crystals (1 to 10 mm) with inclusion of fine-grained clay, gypsum, and epsonite.

Surface Area

Measured values of K_d are dependent on the surface area of the crushed rock. The extent of sorption is directly proportional to the surface area since sorption is a surface reaction. Therefore, surface areas must be reported along with K_d values so that data from different investigations can be compared. Alternatively, distribution coefficients can be defined in terms of surface area as follows:

$$K_d' = \frac{K_d}{\text{surface area/gram}} = \text{ml/m}^2$$

where K_d is defined in standard terms (ml/g). The distribution coefficients are reported both as K_d and K_d' in this report.

The surface areas measured by the BET method are given in Table VII.

TABLE VII

SURFACE AREAS OF CRUSHED ROCKS

Rock Type	Surface Area,* m^2/g
Basalt	5.1
Granite	0.9
Argillite	5.4
Salt	ND

*Average of two measurements.

DISTRIBUTION COEFFICIENTS

Equilibrium K_d's for ^{137}Cs, ^{90}Sr, ^{106}Ru, Pu, and ^{241}Am were measured under conditions simulating natural groundwater in contact with the rocks (see Methods section). The crushed rock loaded with radionuclides from these measurements will be used in later experiments to test the reversibility of radionuclide sorption. The loaded rock will be equilibrated with other solution compositions (unspiked groundwater and groundwater spiked with Na^+, K^+, Ca^{+2} and Mg^{+2}) and the resulting K_d values measured.

The precision of the K_d measurements was determined by repeating each equilibration experiment five times. The initial concentrations of tracers were as follows: ^{137}Cs, 52 μCi/ℓ; ^{90}Sr, 750 μCi/ℓ; ^{106}Ru, 70 μCi/ℓ; Pu, 730 μCi/ℓ; and ^{241}Am, 6,500 μCi/ℓ. The measured pH values of the equilibrated groundwater solutions are given in Table VIII. The K_d values obtained in terms of milliliters per gram and milliliters per square meter are given in Tables IX and X, respectively. These values are not yet corrected for container sorption.

TABLE VIII

pH VALUES OF EQUILIBRATED SOLUTIONS

	Basalt	Granite	Argillite	Salt
Cesium-137	8.64	8.00	8.69	7.41
Stontium-90	7.90	7.92	8.74	7.39
Ruthenium-106	8.37	7.97	8.62	7.49
Plutonium	8.61	8.16	8.72	7.37
Americium-241	8.78	8.15	8.69	7.34

TABLE IX

SUMMARY OF K_d VALUES IN MILLILITERS PER GRAM*

	Basalt	Granite	Argillite	Salt
^{137}Cs	296 ± 31	650 ± 64	986 ± 114	0.07 ± 0.09
^{90}Sr	151 ± 18	5.46 ± 0.45	191 ± 44	0.13 ± 0.15
^{106}Ru	38.0 ± 8.1	210 ± 15	1,991 ± 375	3.55 ± 0.30
Pu	19.8 ± 4.0	5,398 ± 1,123	318 ± 49	1,228 ± 627
^{241}Am	231 ± 18	60,436 ± 28,875	2,637 ± 1,345	2,265 ± 285

*The error given is the standard deviation for five replicate experiments.

TABLE X

SUMMARY OF K_d VALUES IN MILLILITERS PER SQUARE METER*

	Basalt	Granite	Argillite	Salt†
^{137}Cs	58.0 ± 6.1	722 ± 71	183 ± 21	--
^{90}Sr	29.6 ± 3.5	6.06 ± 0.50	35.4 ± 8.1	--
^{106}Ru	7.45 ± 1.59	233 ± 17	369 ± 69	--
Pu	3.88 ± 0.78	5,998 ± 1,348	58.9 ± 9.1	--
^{241}Am	45.3 ± 3.5	67,151 ± 32,083	488 ± 249	--

*The error given is the standard deviation for five replicate experiments.

†Surface area was not measured for salt.

The wide range of K_d values obtained shows the importance of mineral content of the rock. The salt has a very low affinity for ^{137}Cs, ^{90}Sr, and ^{106}Ru as expected because of its low ion exchange capacity. Only the small amount of clay present in the salt can act as an ion exchanger and the tracer ions have to compete with a high concentration of Na^+ in the brine. However, both Pu and ^{241}Am sorb strongly on the salt, probably because of precipitation and/or physical sorption.

The granite strongly sorbs ^{137}Cs, ^{106}Ru, Pu and ^{241}Am, but sorbs ^{90}Sr weakly. The K_d for ^{137}Cs is particularly high with granite, possibly because of the strong affinity of Cs ion for mica. The relatively high calcium concentration of the granite groundwater may explain poor sorption of ^{90}Sr since these two cations are known to compete for the same sorption sites. No explanation for the strong actinide sorption can be offered.

The radionuclides are poorly sorbed by the basalt compared to granite and argillite. The two actinides and ^{106}Ru in particular are weakly sorbed. The formation of anionic Pu carbonate complexes in the basic (pH = 8.6) groundwater solution would result in poor Pu sorption since anions are weakly sorbed. The basalt groundwater contains about 0.0034 $\underline{M}$ HCO_3^- so that carbonate is available for complex formation. Americium may also form carbonate/hydroxyl complexes in basic solutions.

Formation of anionic complexes might also explain the relatively poor sorption of Pu in argillite. About 0.0042 $\underline{M}$ HCO_3^- is available for complex formation. As expected, the sorption of ^{137}Cs, ^{90}Sr, and ^{106}Ru is relatively strong because of the high clay content of the argillite.

LEACHING EXPERIMENTS

Samples of crushed basalt, granite, and argillite were leached continuously with hot, distilled water in soxhlet extractors in order to simulate long-term "weathering" effects on the surface of these rocks. The effects of this accelerated "weathering" on K_d's will be examined in later experiments. Dissolution and hydrolysis of the rock surface will likely affect radionuclide sorption.

After one month of leaching, the surface of the basalt sample had turned brown (originally it was black) due to formation of ferric hydroxide. The Fe(II) in the basalt was oxidized by air in the extractor. A significant amount of the sample had dissolved and then precipitated in the boiling flask as a white, colloidal suspension (probably $SiO_2 \cdot xH_2O$). A brown layer also developed in the granite sample due to Fe(II) oxidation and hydrolysis. The boiling flask developed a hard crust on the inside surface due to dissolved material from the granite. No change in the argillite sample was observed, however, large amounts of colloidal silica formed in the boiling flask.

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3. I. Y. Borg, R. Stone, H. B. Levy, and L. D. Ramspott, *Information Pertinent to the Migration of Radionuclides in Groundwater at the Nevada Test Site, Part I: Review and Analysis of Existing Information, Lawrence Livermore Laboratory*, U. S. Energy Research and Development Administration Report UCRL-52076, May 1976.

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APPENDIX

Phase Analyses of Polished Surfaces for Basalt, Granite, Argillite, and Salt

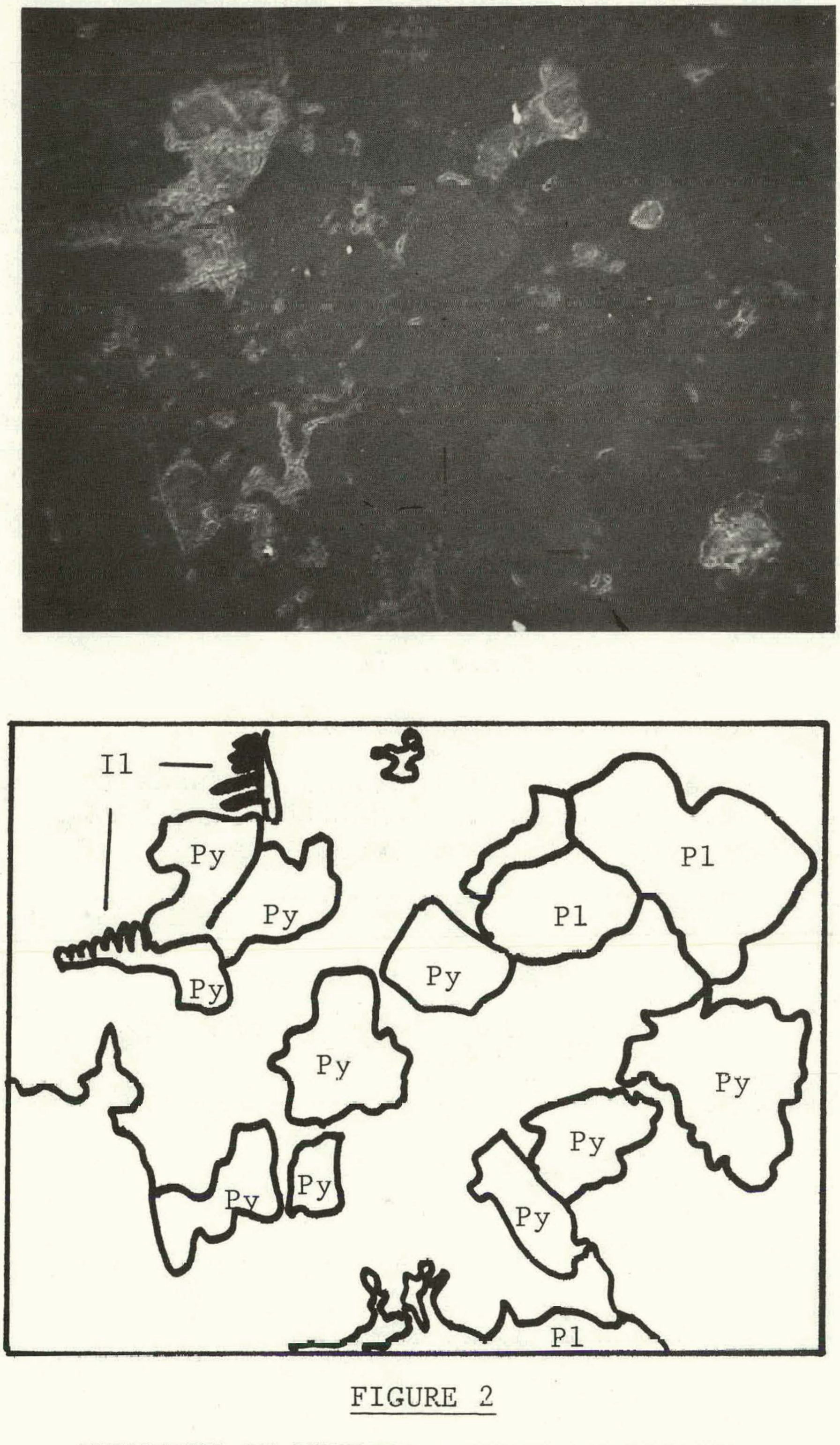


FIGURE 2

IDENTITY OF MINERAL PHASES IN BASALT,
AREA A, 400X

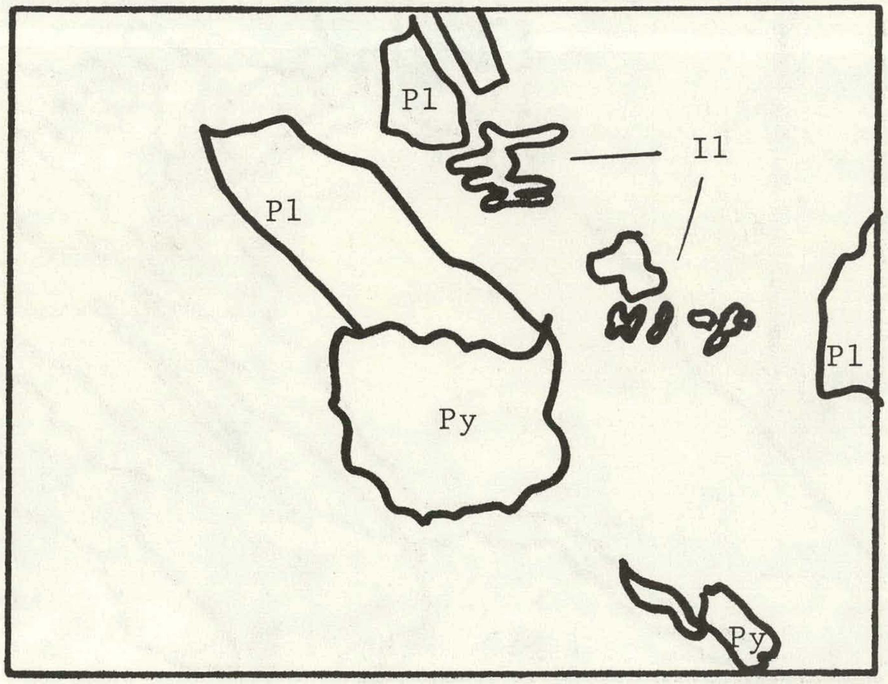


FIGURE 3

IDENTITY OF MINERAL PHASES IN BASALT, AREA B, 700X

FIGURE 4

IDENTITY OF MINERAL PHASES IN BASALT,
AREA C, 1000X

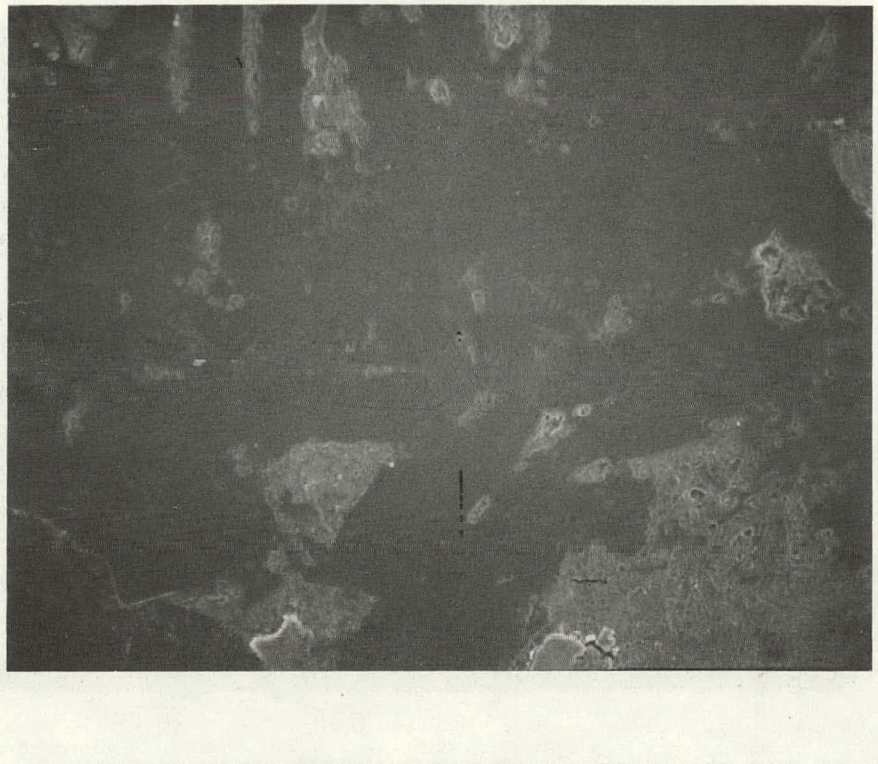


FIGURE 5

IDENTITY OF MINERAL PHASES IN BASALT,
AREA D, 400X

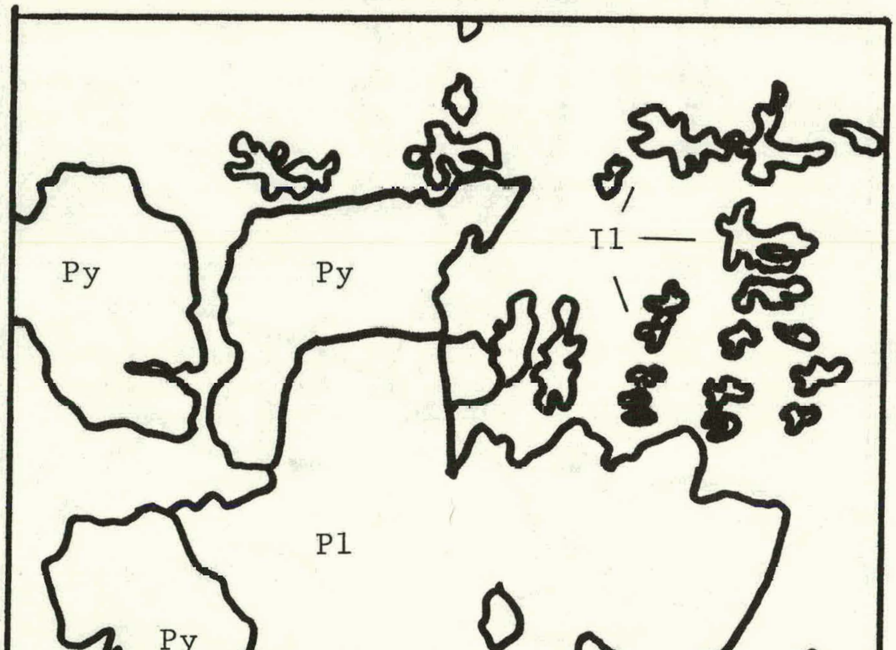


FIGURE 6

IDENTITY OF MINERAL PHASES IN BASALT, AREA E, 1000X

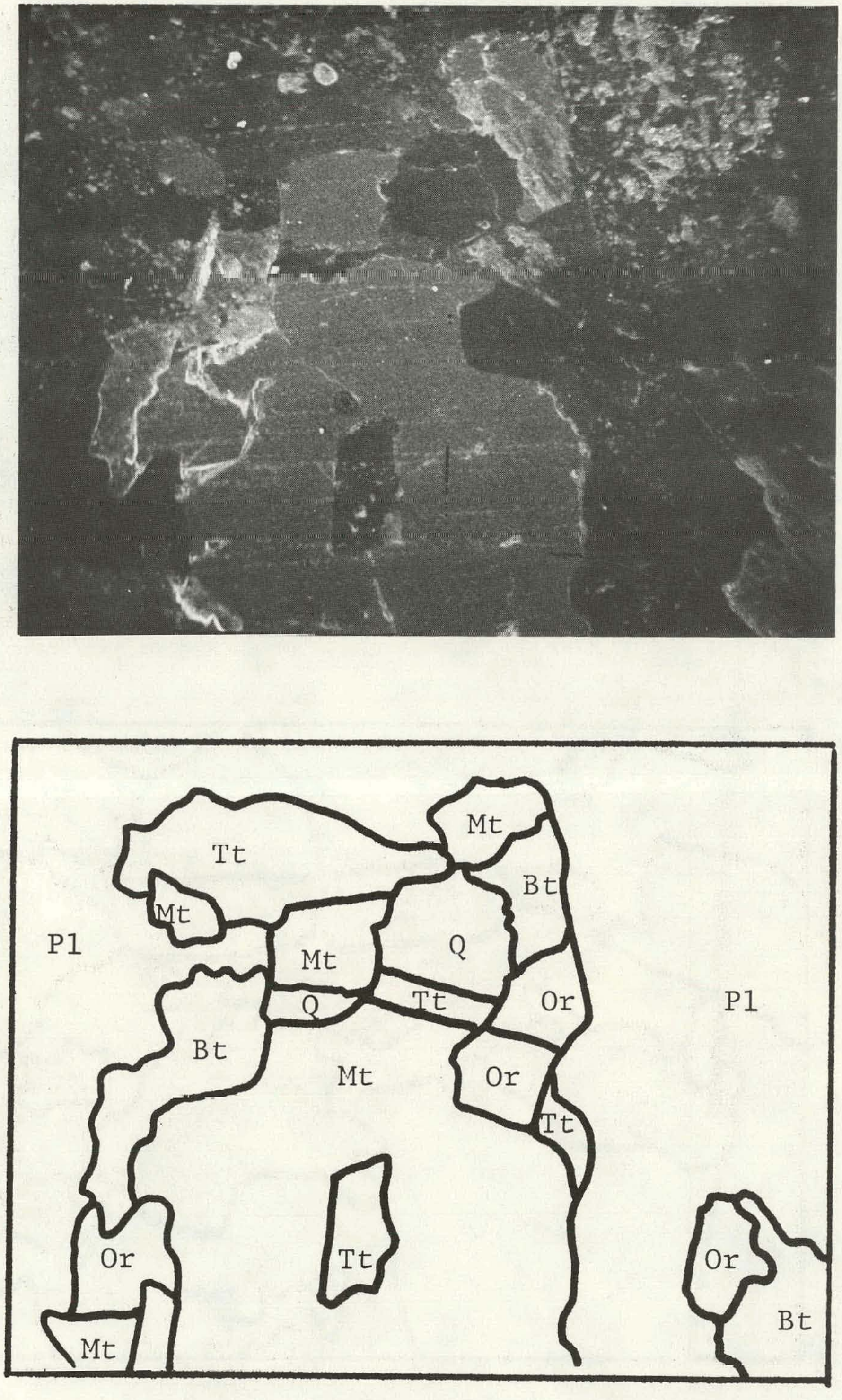


FIGURE 7

IDENTITY OF MINERAL PHASES IN GRANITE, AREA A, 100X

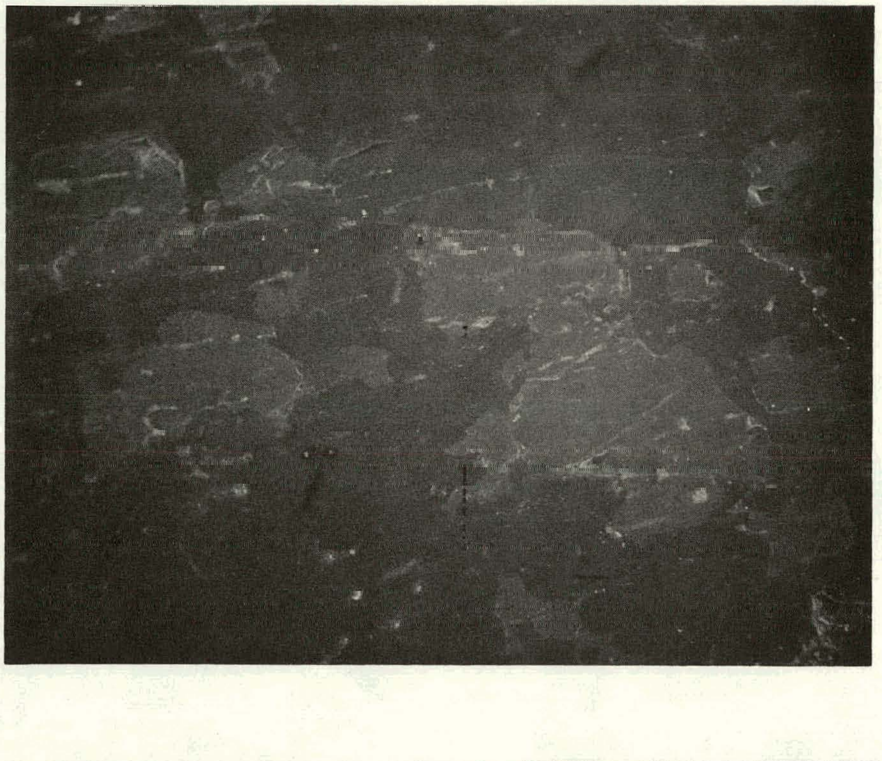


FIGURE 8

IDENTITY OF MINERAL PHASES IN GRANITE, AREA B, 100X

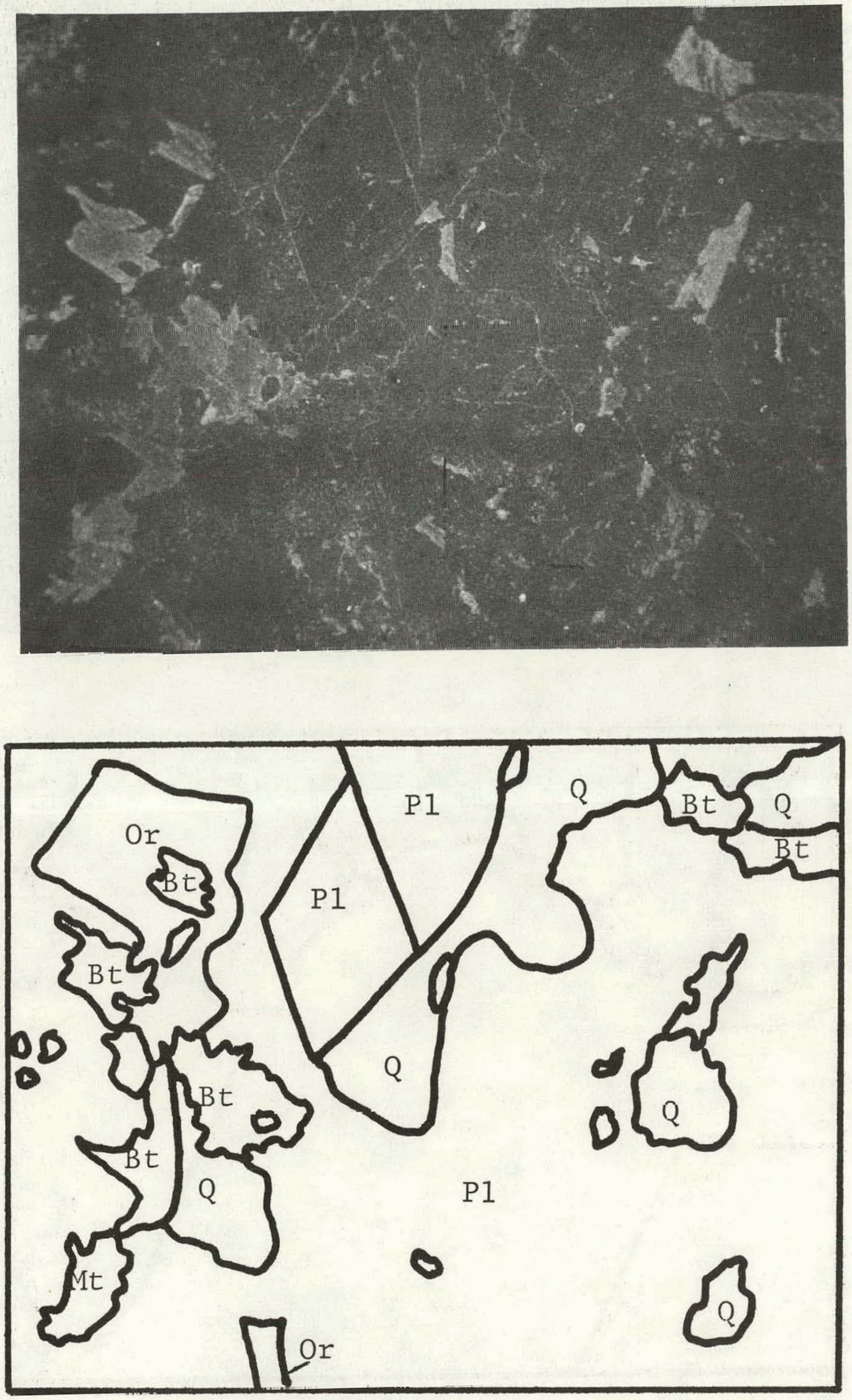


FIGURE 9

IDENTITY OF MINERAL PHASES IN GRANITE, AREA C, 50X

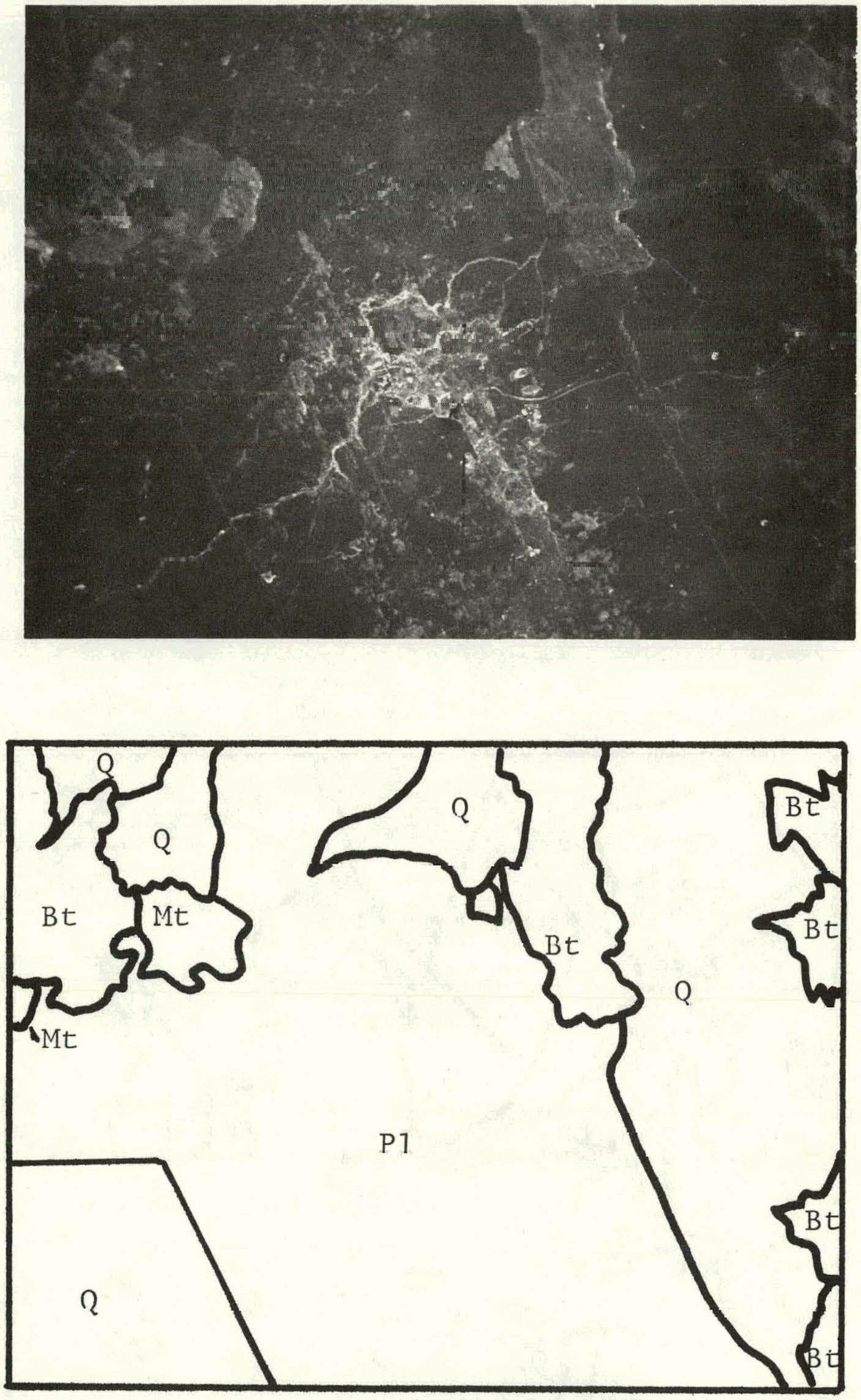


FIGURE 10

IDENTITY OF MINERAL PHASES IN GRANITE, AREA D, 100X

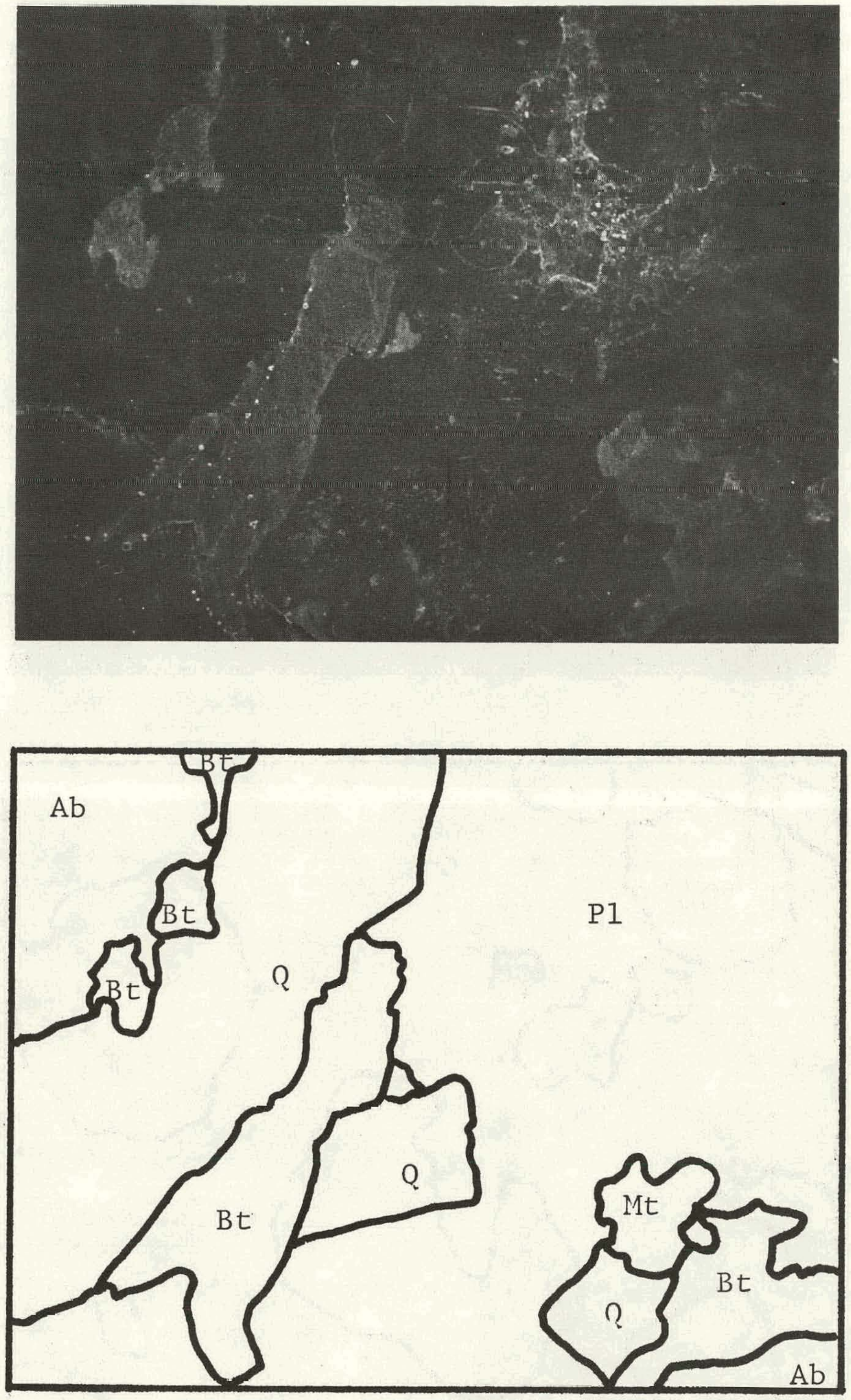


FIGURE 11

IDENTITY OF MINERAL PHASES IN GRANITE, AREA E, 100X

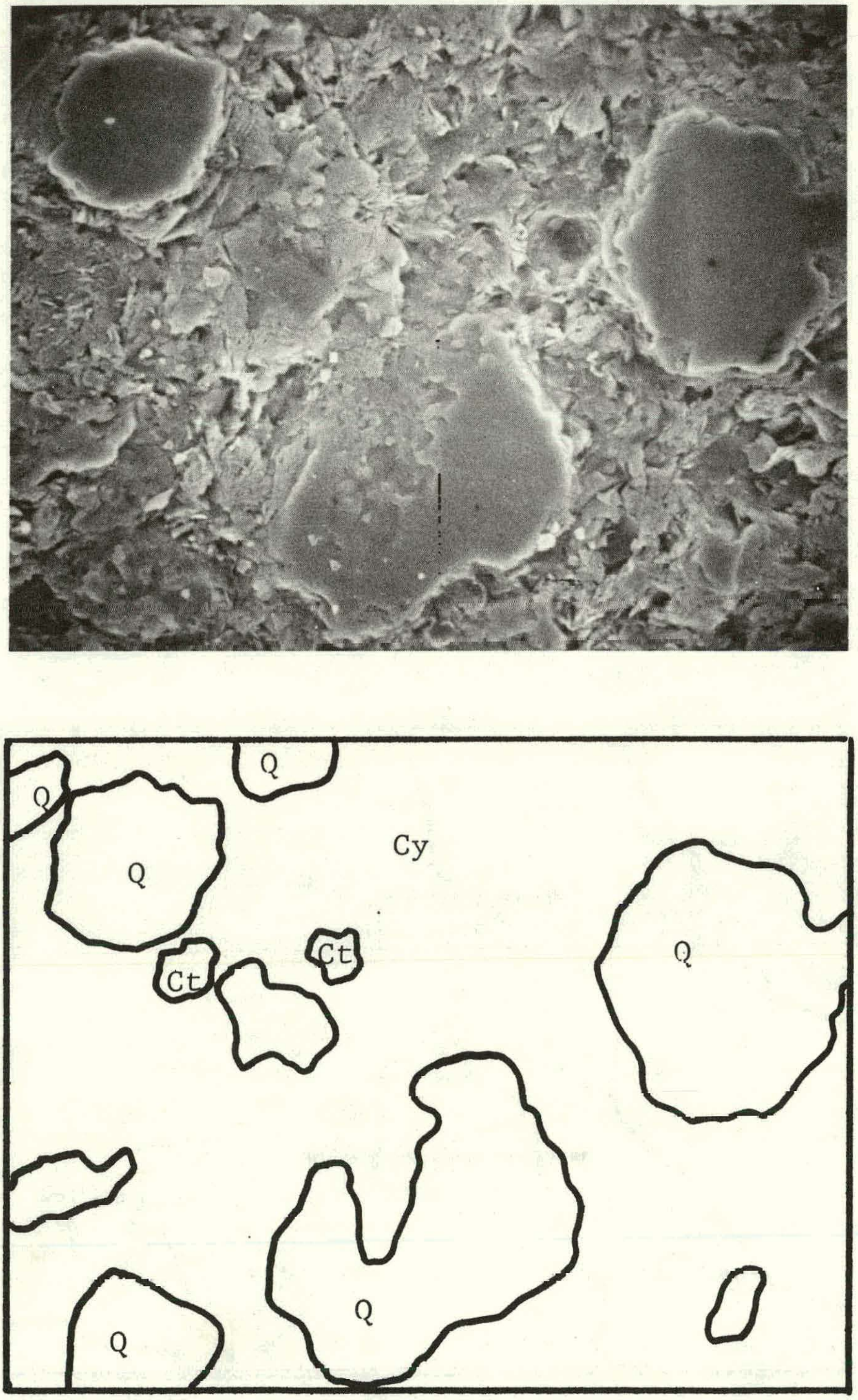
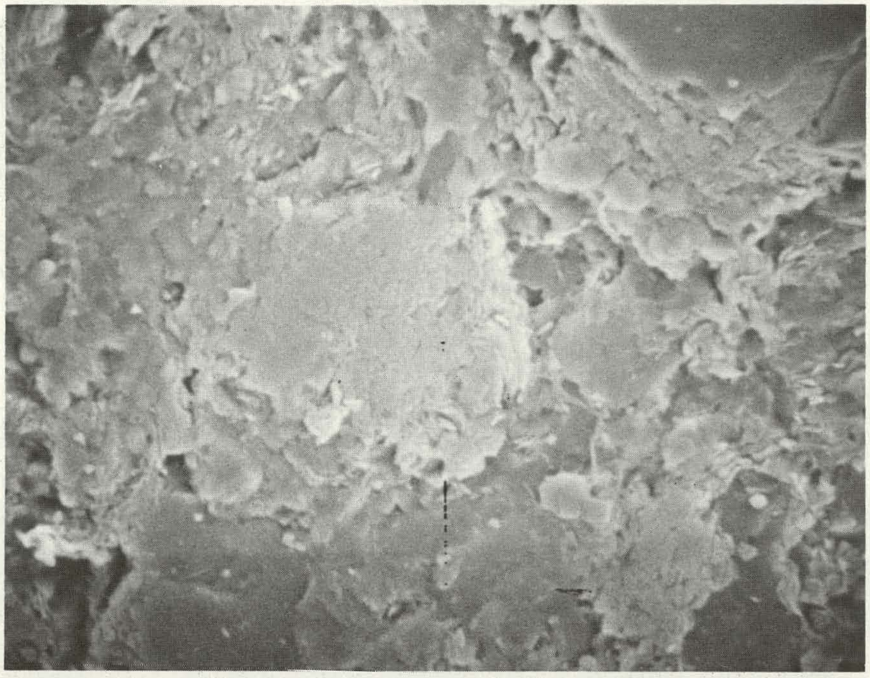


FIGURE 12

IDENTITY OF MINERAL PHASES IN ARGILLITE,
AREA A, 2000X



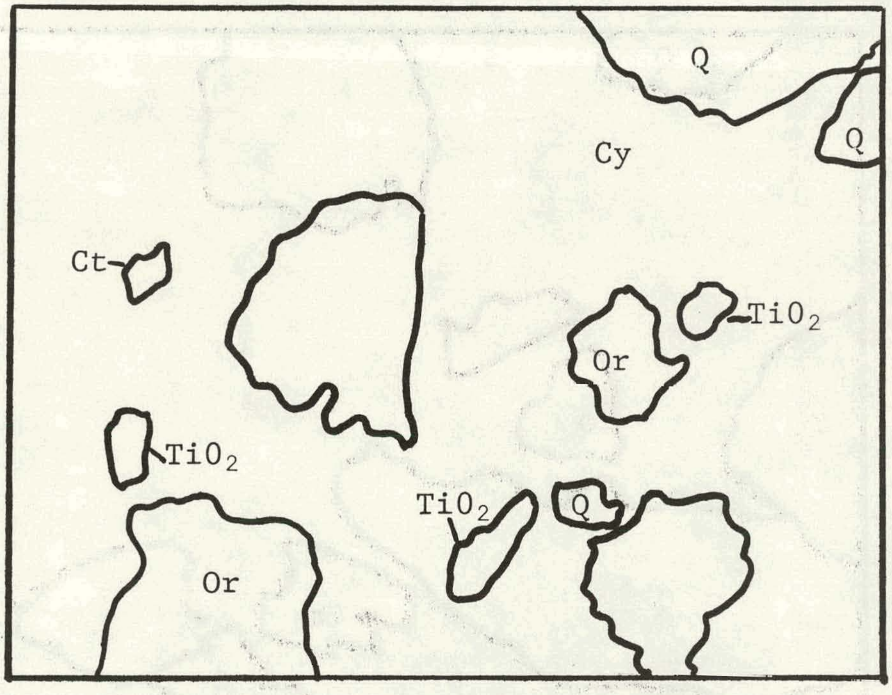


FIGURE 13

IDENTITY OF MINERAL PHASES IN ARGILLITE, AREA B, 2000X

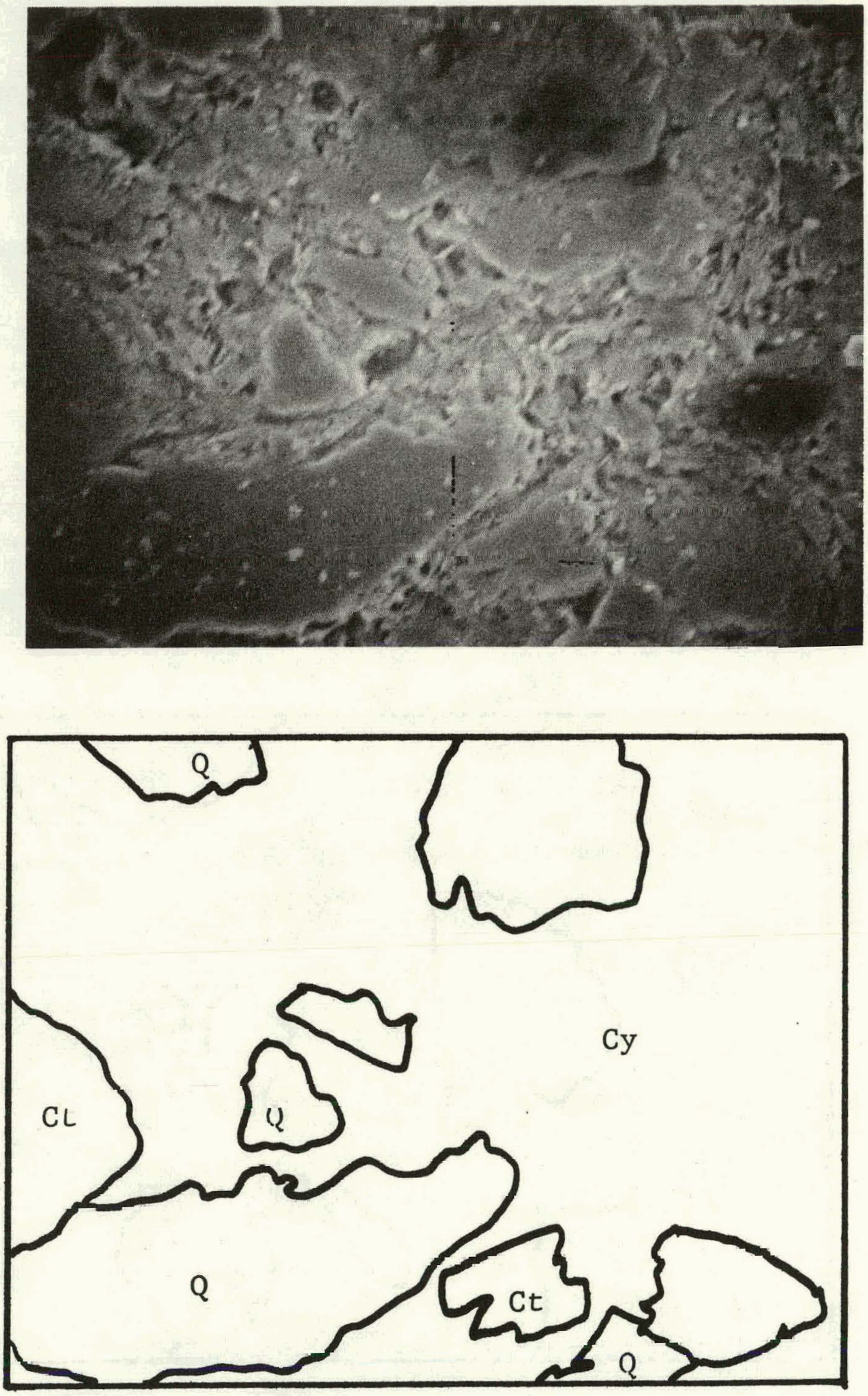
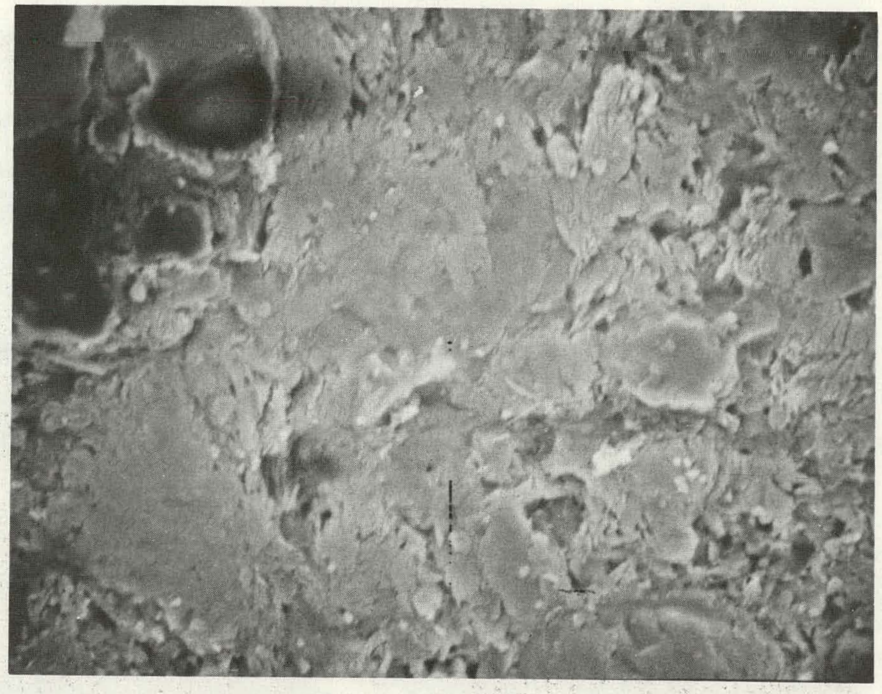


FIGURE 14

IDENTITY OF MINERAL PHASES IN ARGILLITE,
AREA C, 2000X



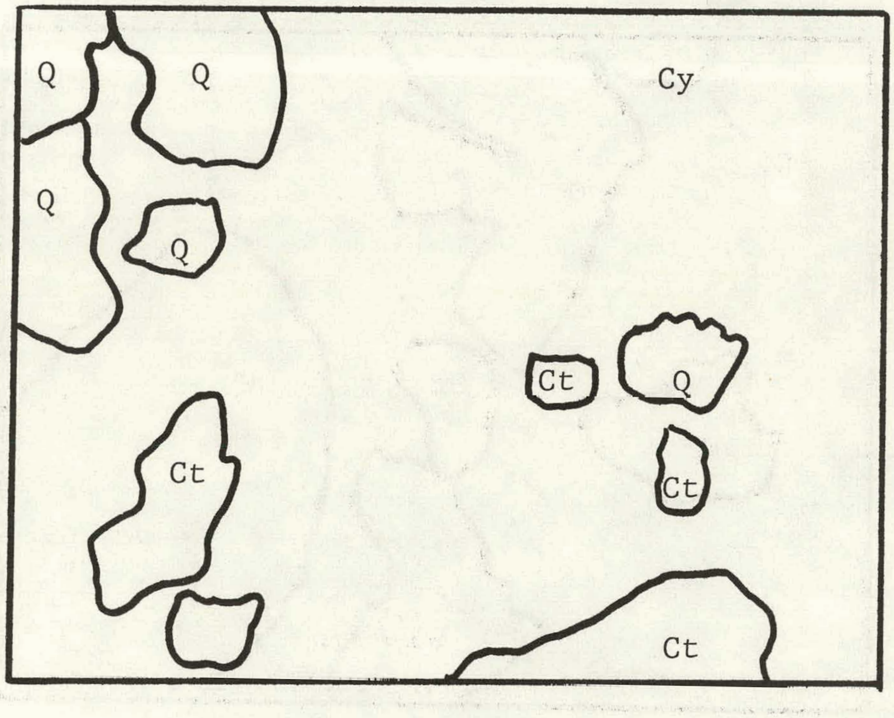


FIGURE 15

IDENTITY OF MINERAL PHASES IN ARGILLITE,
AREA D, 2000X

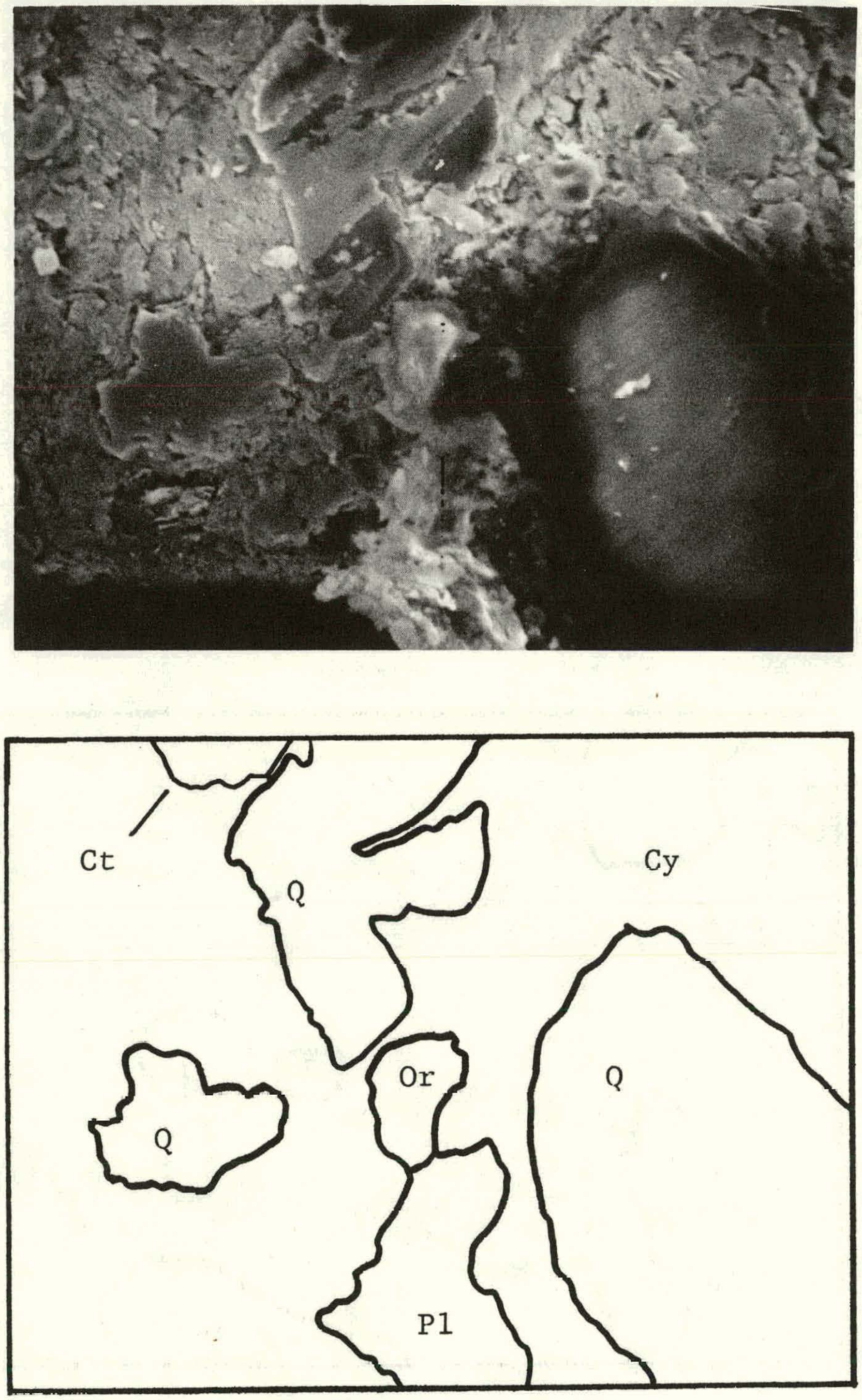


FIGURE 16

IDENTITY OF MINERAL PHASES IN ARGILLITE,
AREA E, 2000X

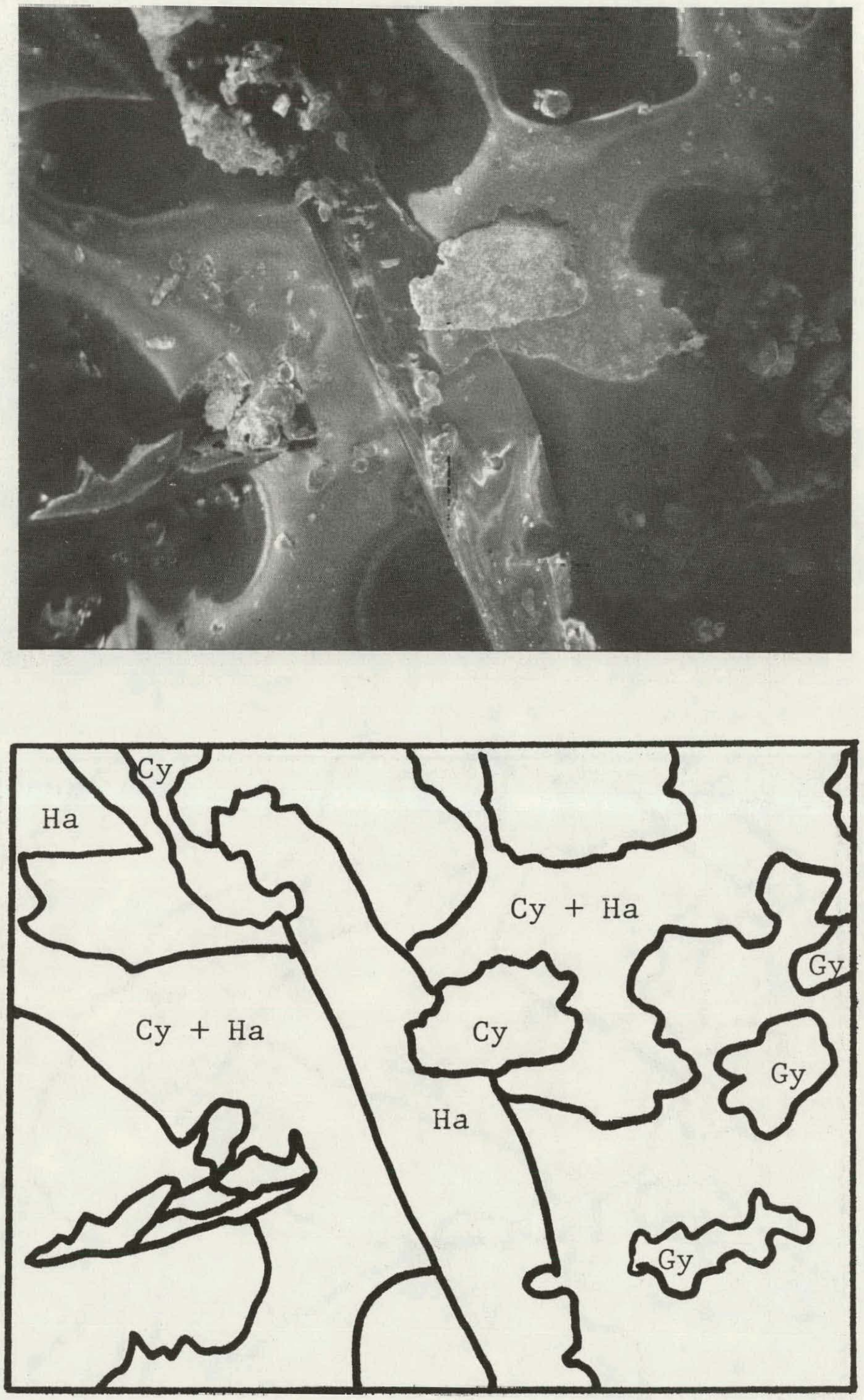
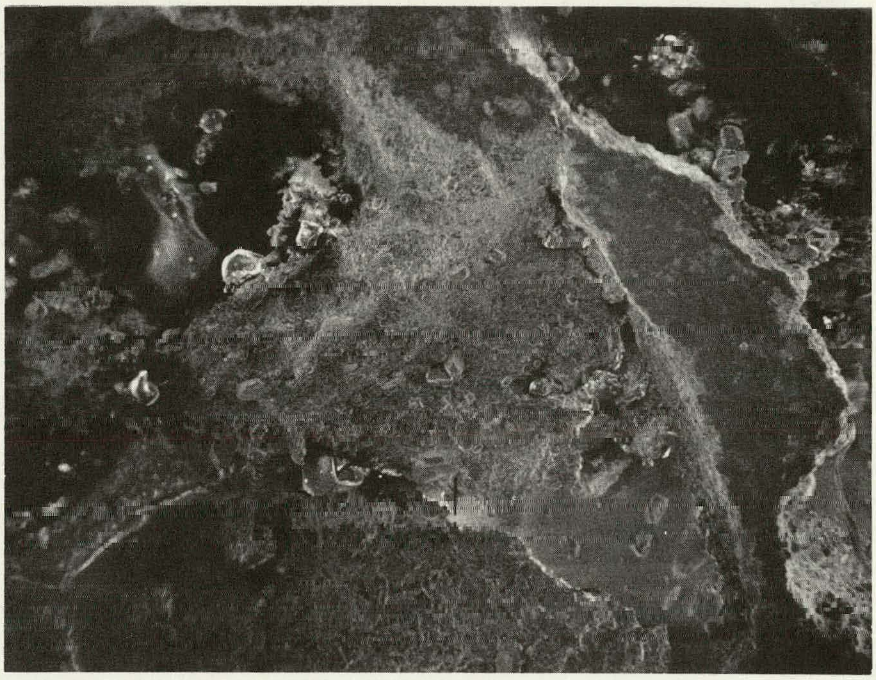


FIGURE 17

IDENTITY OF MINERAL PHASES IN SALT,
AREA A, 100X



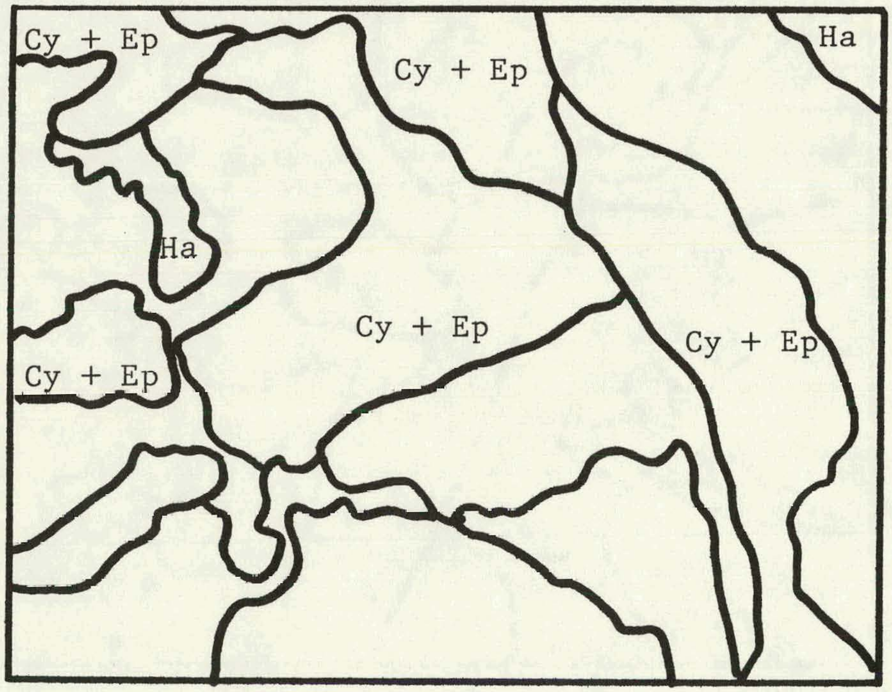


FIGURE 18

IDENTITY OF MINERAL PHASES IN SALT, AREA C, 100X

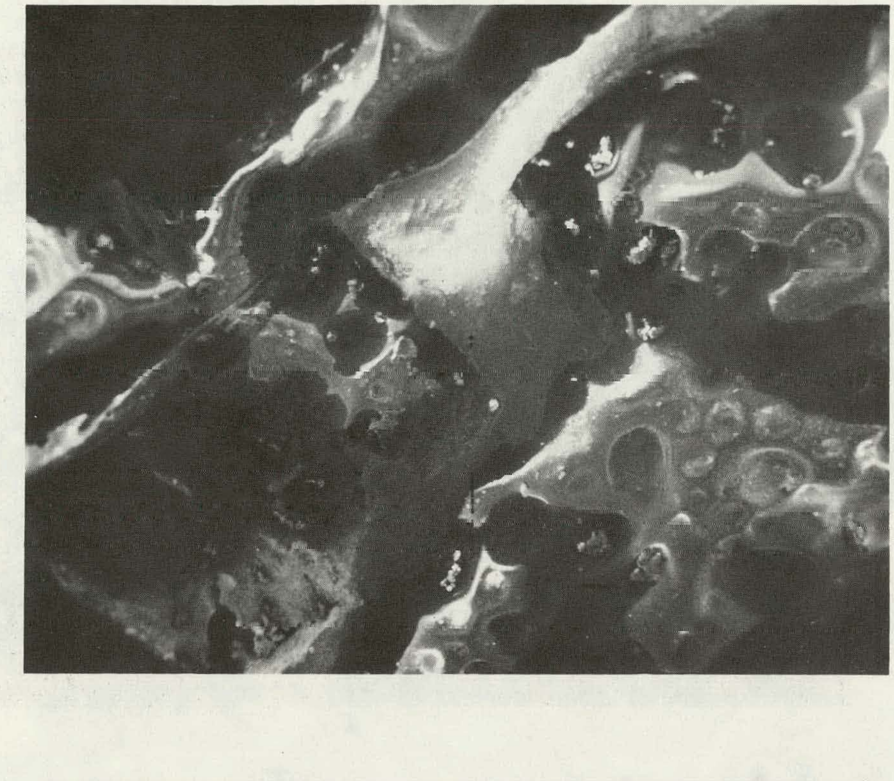


FIGURE 19

IDENTITY OF MINERAL PHASES IN SALT,
AREA D, 30X

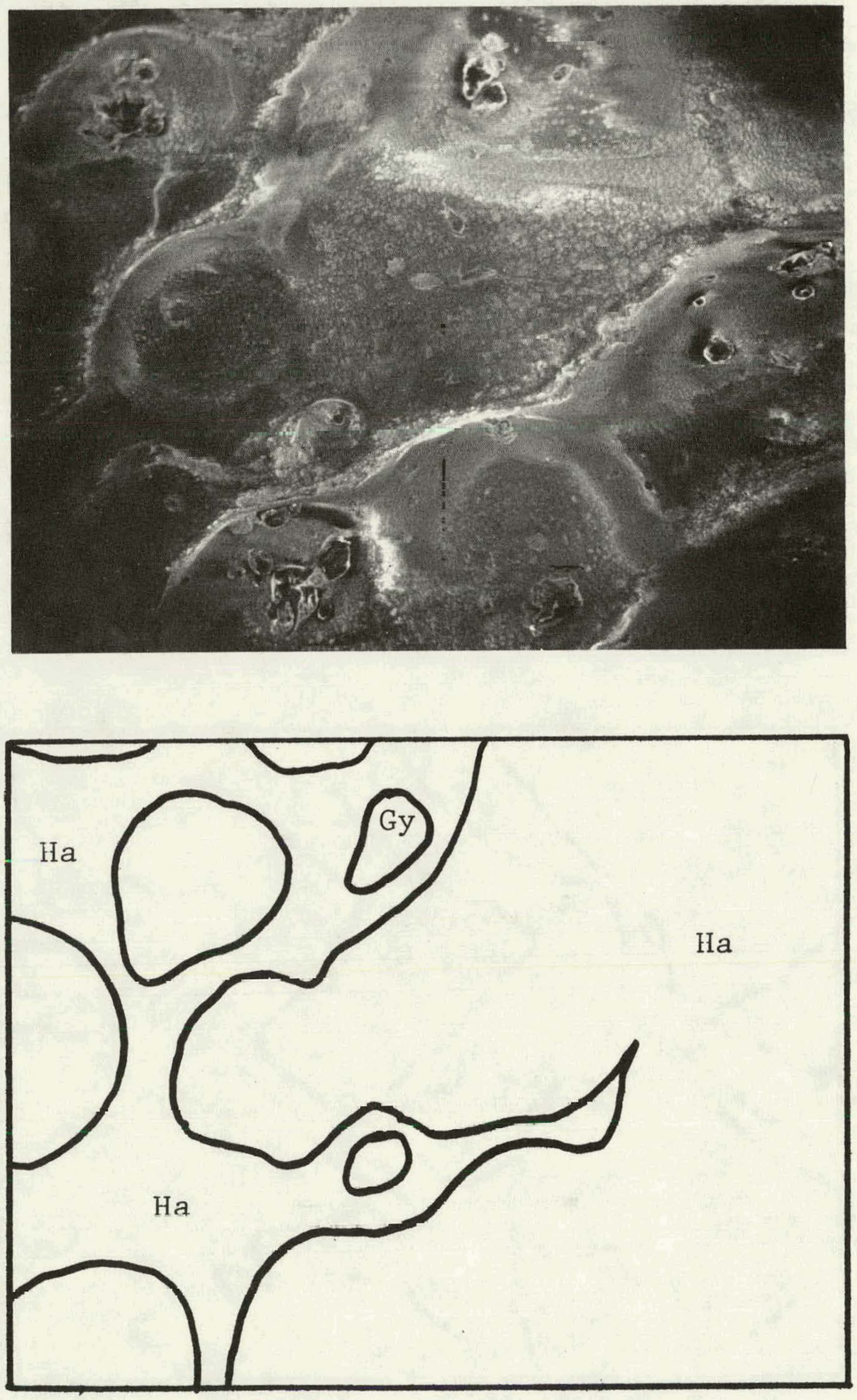


FIGURE 20

IDENTITY OF MINERAL PHASES IN SALT,
AREA E, 100X

DISCUSSION--G. SCOTT BARNEY

Source of Rock Samples (Table I)

Q. Do you know the depth of the sample from the climax stock?

A. No, but we could find out.

Mineral Phases in Basalt, Area A (Figure 2)

Q. Are the bubbles in the rock sample seen with sufficient frequency that they could be interconnected?

A. We made some surface-area measurements in the basalt, and have found the surface area to be somewhat larger than expected. This could reflect a relatively high porosity.

Q. What is the porosity of basalt?

A. We did not measure the porosity of this particular sample. The sample was taken from Sentinal Gap, at approximately the level of the Columbia River. I'm not sure from which portion of the rock the sample was taken; it could have been from the top area, which had a fair amount of vesicular bubbles. The proposed repository site, however, is located underground, where the basalt is dense and has very low permeability. This could be a case, then, where a sample of a rock outcropping is not sufficient to determine the key characteristics of the rock at the underground site.

Surface Areas of Crushed Rock (Table VIII)

Q. Are they all crushed to approximately the same degree?

A. Yes.

Q. Do you have a particle size range?

A. We have not done a particle size analysis.

Q. Are these BET measurements?

A. Yes.

Q. Are BET surface measurements appropriate for an aqueous system? These measurements provide an external particle surface area, whereas the water sees a total of the internal plus external surface area.

A. We'll have to look into that. We used the BET method because it was available to us, and is one way of relating surface area to K_d.

Minerals Identified by the Sem-Microprobe (Table VI)

Q. You have $FeSiO_4$, listed as a mineral found in basalt. That is an unusual mineral to be occurring naturally; are you sure that it wasn't olivine?

A. All I know is that it was an iron silicate. We did not find it throughout the basalt sample, however.

Q. Why did you choose not to use thin sections and a petrographic microscope to examine the samples. Experienced petrologists can determine the composition of small samples very accurately.

A. We had no one to do it at the time. We do have some work along that line planned. However, as a chemist, I feel more confident in identifying phases by their chemical composition.

Q. Are you using the SEM method?

A. Yes, we are.

Q. Doesn't that have rather low precision compared to petrographic methods?

A. Yes, it does.

Q. Basalts generally have a good deal of opaline silica, so there are probably high silica levels in the waters that are in contact with them. In some basalt samples from Australia, for example, the uptake, fixation, and irreversible adsorption of trace elements such as Co are markedly promoted in the presence of elevated concentrations of silica. Consequently, I think it is important to know the dissolved silica content in basalt and argillite.

(No answer given.)

pH Values of Equilibrated Solutions (Table VIII)

Q. Was the final spiked solution equilibrated with rock?

A. We preequilibrated the rock with the groundwater, to prevent changes in the concentration of the groundwater when we added the spiked groundwater.

Q. The other participants at this meeting equilibrated water with ground-up sample and then added a spike to that water. Isn't it easier to equilibrate water with a solid than vice versa?

A. That's one way to do it; I don't know which way is the best.

Q. How do you test for equilibration during the preliminary steps?

A. We have not yet measured concentration as a function of time in the solution; this is part of the kinetics work that we will be doing next year.

Q. What was the form of the Ru?

A. I believe it is Ru(II). We let the Eh, pH, and chemical species come to whatever values were dictated by the groundwater.

Q. Do you know the oxidation state distribution of the Pu?

A. No, I don't.

Q. Were the solutions aerated?

A. The experiment was done in sealed centrifuge tubes, although the water had air in it. With the basalt samples, I assume that, since they are reducing, the concentration of oxygen may change as a function of time.

Summary of Kd Values (Table IX)

Q. In determining the K_d for salt, don't you have to take the effects of temperature into account? With salt, in particular, very tiny changes in temperature could have the effect of skimming off the Pu or other radionuclide on the surface--or depositing additional quantities. For a substance that is as soluble as salt, I would think that extremely rigorous temperature control would be necessary, so that the temperature could be maintained constant within one-tenth of a degree--otherwise, the K_d would be a meaningless number.

A. Determining K_d values in salt is very difficult. You cannot start out with a solution that is 100% saturated with salt, because of temperature variations: a temperature drop of a few tenths of a degree will cause the salt to coat on top of the Pu. Consequently, I am not sure whether our K_d measurements for salt are valid or not--particularly in view of the surprisingly high K_d values for both Pu and Am. On the other hand, the fact that this was not pure salt but rather salt mixed with clay could be a factor.

Summary of K_d Values (Table X)

Q. How do you measure surface area?

A. An inert gas--nitrogen, I think--is passed through the sample at a temperature low enough to maintain the gas in liquid form. Then the sample is heated and the amount of gas given off is measured. A monolayer of gas is assumed to be present on the sample surface.

Q. Why are the K_d values of the granite samples higher than those of the other rock types?

A. For Cs the explanation could be that the granite has a fairly high biotite content, so that irreversible sorption may be taking place. For Pu and Am, I don't know the reason.

Q. Were all five experiments done in the same piece of granite simultaneously?

A. No, they were done on crushed sub-samples.

Q. Then you assume that Sample A of granite is equivalent to Sample B?

A. We hope so. That's why we're taking 5 g of the sample and crushing it into fairly fine particles.

Q. How much of the sample did you start with? It's been my experience that you need to take a large aliquot, grind it, mix it, and sample that.

A. We started with about 10 lb.

Artificial Weathering of Rocks (Leaching Experiments)

Q. Do you continually cycle the same fluid past the rock?

A. No, we leach with hot distilled water.

Q. And you change the solution periodically?

A. Yes, we do.

Q. Have you found the Al content to remain constant during the weathering process?

A. We haven't measured any of the chemical content, either in the boiling flask or in the sample.

Q. Then you are not concerned with mass balance?

A. We are primarily concerned with the chemical changes that take place on the surface of the crushed rock, and how these changes affect K_d.

Q. In the artificial weathering of basalt, it is important to keep in mind that the surface may be grossly different under aerobic and anaerobic conditions. In the presence of oxygen, iron oxides are being formed; in its absence, ferrous iron would remain soluble rather than being precipitated.

A. I agree. We are not simulating precisely the conditions that will occur in the basalt repository. This is just a first attempt; our methods will become more refined later on.

"MICROSTRUCTURAL INTERACTIONS OF GEOLOGIC MEDIA WITH WASTE RADIONUCLIDES"

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SAND78-0108

Microstructural Interactions of Geologic Media with Waste Radionuclides

Thomas E. Hinkebein
Paul F. Hlava

Sandia Laboratories

ABSTRACT

A preliminary investigation of the microstructure of four geologic media was undertaken to examine the interaction of Cs, Sr, Gd and U with those media. Since K_D measurements often vary by more than an order of magnitude on rocks of the same strata separated by several feet, it was probable that minor rock components play an important role in radionuclide sorption. A qualitative analysis of the rock surfaces after equilibration with solutions of Cs^+, Sr^{++}, Gd^{+++} and UO_2^{++} revealed that clay minerals are responsible for all important sorption that takes place on the rocks studied (Magenta dolomite, Bell Canyon silt stone, Eleana shale and clay bearing halite). Thus it is concluded that a relatively small portion of these rocks is actively responsible for sorption characteristics. Gd was bound on all samples, probably as Fe bearing chlorites. Cs was strongly held on the Eleana shale, probably by an illite. Although uranium was associated with an unidentified clay in the halite sample, uranium sorption probably occurred as UO_2CO_3, which would not significantly retard uranium movement at trace concentrations. Similarly Sr was retained only as $SrSO_4$ on Magenta and this mechanism is not significant at trace levels. These analyses were performed by correlating electron microprobe elemental distribution photomicrographs with x-ray analyses of the four rocks.

Introduction

A feasibility study was undertaken to verify the utility of a microstructural analysis of selected rocks to yield relevant information on the mechanism of radionuclide sorption on common rock minerals. It is commonly accepted that ion-exchange is the predominant mechanism of radionuclide sorption. However, the major constituents of common rock such as carbonates, silicates and quartz are generally not recognized as good ion-exchangers. It is thus expected that minor rock components would play the predominant role in retarding radionuclide movement in geologic media. Clay minerals are commonly assumed to be responsible for the bulk of ionic sorption on rocks although this fact has not been verified before now. This study has sought correlations between concentrations of test ions on the surface of rocks and the underlying mineralogy in elemental distribution photomicrographs obtained with the automated electron microprobe.

Our main concern in this study is to verify that the electron microprobe analysis is capable of yielding information on the association of test ions with individual minerals. If clays are responsible for the bulk of sorption which takes place in rock assemblages, it is not at all clear at the outset whether the microprobe has the resolution to identify individual clay particles. For this purpose it is felt that relatively concentrated test solutions should be used. At a later time it is felt that concentrations of the test ions may be reduced by using autoradiography in conjunction with microprobe analyses of the test rocks. The use of concentrated solutions would insure that the microprobe could detect the test ion on the surface and would eliminate the need for the time consuming mapping of the surface required when two techniques are used in conjunction.

Experimental

Four rock samples were chosen for this initial study: a sample of Eleana shale taken from the Nevada Test Site at a core depth of 1805 ft., and three core samples from AEC #8 in the Los Medanos area of southeast New Mexico. The New Mexico samples are a Bell Canyon sandstone from a core depth of 4823.4 ft., Magenta dolomite from the Rustler formation at 749.5 ft., and a very dirty salt sample from the Salado at 2186.0 ft. X-ray analyses of these rocks reveal that the Eleana shale is composed primarily of quartz, siderite, and chamosite with minor phases of chlorite, illite, microcline, oligoclase, pyrophyllite, talc, calcite, and traces of pyrite, marcosite, and ferroan dolomite.(1) The Bell Canyon sandstone was composed of quartz, calcite, kaolinite, chlorite, a small amount of feldspar and possibly some dolomite. Magenta is primarily dolomite with quartz and gypsum present as minor phases. The dirty salt is primarily halite with 7.8% by weight clay inclusions consisting of montmorillonite, chlorite, kaolinite, illite, mixed layer montmorillonite-chlorite, magnesite and talc.

Samples of these rocks were equilibrated with solutions of Cs, Sr, Gd and U to form an array of 16 rock-ion pairs. Chips of these rocks were allowed to equilibrate for three days at ambient conditions and then rinsed with solutions free of Cs, Sr, Gd or U for one day to remove loosely-bound or soluble ions from the rock surfaces.

Solutions used in these equilibrations were prepared by equilibrating deionized water with powdered samples of the rocks for four days. The rock

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(1) All x-ray analyses were performed by G. T. Gay.

solids were filtered off, and the pH and Eh of the resultant solution are given in Table I. Since no attempt was made to preclude air from these solutions, the oxidation potential, measured with a bright platinum electrode, reflects the "irreversible oxygen potential."(2) This oxidation potential will assure that uranium remains in the +6 oxidation state, as UO_2^{++}. The other ions in this study have only one oxidation state.

Before beginning a detailed study of all 16 rock-ion pairs, it was felt that an initial screening of the rock-ion pairs could be used to eliminate from the matrix those pairs which have little mutual affinity. This initial screening analysis consisted of contacting the rocks with very concentrated test ion solutions (1.0 M in the case of Cs, Sr and Gd, and 0.1 M in the case of U) and then examining each rock for test ion accumulations on the surface. If no accumulation was observed with the automated electron microprobe, operated in the wave length dispersive mode, it was felt that this rock-ion pair could be safely deleted from the matrix. In this manner six rock-ion pairs were eliminated from the matrix as shown in Table II.

Of these rock-ion pairs for which test ions were observed on the surface, the salt sample was found to pick up test ions only in areas of high silicon, representative of clay minerals. Cs was retained on the Eleana shale while Sr was retained as either a relatively insoluble carbonate or sulfate on the Magenta, Bell Canyon sandstone and the dirty salt. Gd was retained on every sample while uranium was retained on both the Magenta as UO_2CO_3 and the clay in the salt sample.

In the case of $SrSO_4$, $SrCO_3$ and UO_2CO_3 formation on the above rocks, these ions were so strongly sorbed that their presence completely masked

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(2) Merkle, F. G., "Oxidation-reduction processes in Soil," in Chemistry of the Soil, F. G. Bear (ed) (ACA Monograph 126). New York, Reinhold 1955, pp. 200-218.

TABLE I

pH and Eh of Solutions Equilibrated with Indicated Rocks

	Magenta	Bell Canyon Silt Stone	Eleana Shale	Dirty Salt
pH	6.96	7.69	7.77	6.98
Eh (volts)	0.58	0.53	0.52	0.53

TABLE II

Detection of Test Ions with Automated Electron Microprobe

	Magenta	Bell Canyon Silt Stone	Eleana Shale	Dirty Salt
Cs	-	-	+	-
Sr	+	+	-	+
Gd	+	+	+	+
U	+	-	-	+

\+ Indicates the presence of the ion on the rock

\- Indicates that ion was undetected. Approximate detection limit for each ion is given in parentheses: Cs (0.05%), Sr (0.03%), Gd (0.13%), U (0.1%).

other active species on the rocks. Since the solubility products of these compounds are too large to make them effective as binding agents for the very dilute solutions expected in situ, the concentration of Sr was reduced to 50 ppm in the more detailed study presented below while U was reduced to 1000 ppm. Calculations using solubility products and the bicarbonate equilibrium indicate that for Sr concentrations less than 10 ppm, no precipitate formation is expected, while for uranium, this limit is 1 ppm.

In our more detailed study, solution concentrations were set at 2.5×10^4 ppm Cs, 50 ppm Sr, 1.0×10^4 ppm Gd and 1000 ppm uranium. Solutions were prepared, as before, by being equilibrated with the rocks prior to addition of the test ion. The rock samples were ground to flatness with No. 600 carborundum paper. Chips of the rocks were then equilibrated in solutions to form the ten rock-ion pairs which had positive responses in the screening analysis. These rocks were rinsed as before and examined with the microprobe. On all elemental distribution photomicrographs (EDPM) light areas indicate the presence of the selected element. These EDPM's are 200X so that the distance between grid lines is approximately 36μ. Since exposure times vary from one EDPM to the next, all results are interpreted only in a qualitative manner. Similarly the identification of minerals must be considered tentative at this time.

At the reduced concentration levels, Sr was found only as $SrSO_4$ on the Magenta sample as shown in Figure 1. Strontium was not detectable on either the Bell Canyon sandstone or the dirty salt. Hence, none of the rocks demonstrated any significant affinity for strontium. In the case of uranium sorption on Magenta, most of the surface Mg and Ca were replaced by uranium, probably as UO_2CO_3 as shown in Figure 2. A normal dolomite distribution for Ca and Mg would almost completely cover the photomicrograph. Although U is also positively correlated with K, Al, Si and Mg as shown in Figure 3, a positive statement that U is sorbed by a clay mineral would be difficult to make on the basis of this series because the uranyl carbonate is so prevalent. On the other hand, uranium is not associated with quartz at coordinates (3,1) or a mineral resembling illite at (-1,-1). In the case of the clay inclusions in the dirty salt, U is associated with the clay rich areas as shown in Figure 4 and 5. Here, U is strongly correlated with Mg, Al, Fe and Si. This behavior may be indicative of saponite-chlorite in view of the negative correlation with K;(3) however, it is likely that uranium has entered a simple exchange reaction with Magnesite to form UO_2CO_3. Ca is present as gypsum and demonstrates no affinity for U. Similarily, pyrite, FeS_2, retains no U. A clay, likely kaolinite, which has Na substituted for K, demonstrates no affinity for U at (-2,1). An illite at (4,-1) shows no affinity for U.

The only sample showing any Cs sorption was the Eleana Shale as shown in Figure 6 and 7. Cs was strongly correlated with K, Al, Si, Mg and Fe. This clay is likely illite-vermiculite which is renown for its affinity to cesium. Areas showing no cesium takeup are ferroan dolomite at (-3,4), quartz (+3,-2) and siderite (-3,0).

Gadolinium was sorbed on all four rock samples. The EDPM (elemental distribution photomicrographs) for the Eleana shale are shown in Figure 8. The light streak running at 45° above horizontal in the top right quadrant reveals the negative correlation of Gd for K. A positive correlation is obtained for Mg, Al, Si and Fe, possibly chamosite or chlorite. In the Bell Canyon sandstone shown in Figures 9 and 10, once again there is a strong preference of Gd for Fe, Mg, Al and Si indicative of chlorite.

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(3) Bodine, M. C. Jr., "Geochemistry and mineralogy of silicate assemblages associated with Permian Basin evaporites," New Mexico Bureau of Mines and Mineral Resources Circular 159 (1977).

An area of dolomite at (3,1) shows no Gd affinity. The dirty salt sample is shown in Figures 11 and 12 reveals that Gd is taken up in a clay pocket which is positively correlated with Fe, Mg, Al and Si, possibly a chlorite. When K is associated with Al and Si, possibly illite, as at (-2,-1), Gd is not retained. Anhydrite (-3,1) is not associated with Gd. Lastly, Figure 13 shows the interaction of gadolinium with Magenta. Here it is seen that Gd is sorbed in several areas, such as (4,2), which are high in K, Al, Si, Mg and Fe (not shown) as well as having a more dispersed pattern which generally correlated with dolomite. This last effect is more than likely caused by displacing the carbonate-bicarbonate equilibrium to form a hydroxide which is relatively insoluble. Hydroxide formation should not occur at Gd concentrations below 10^3 ppm.

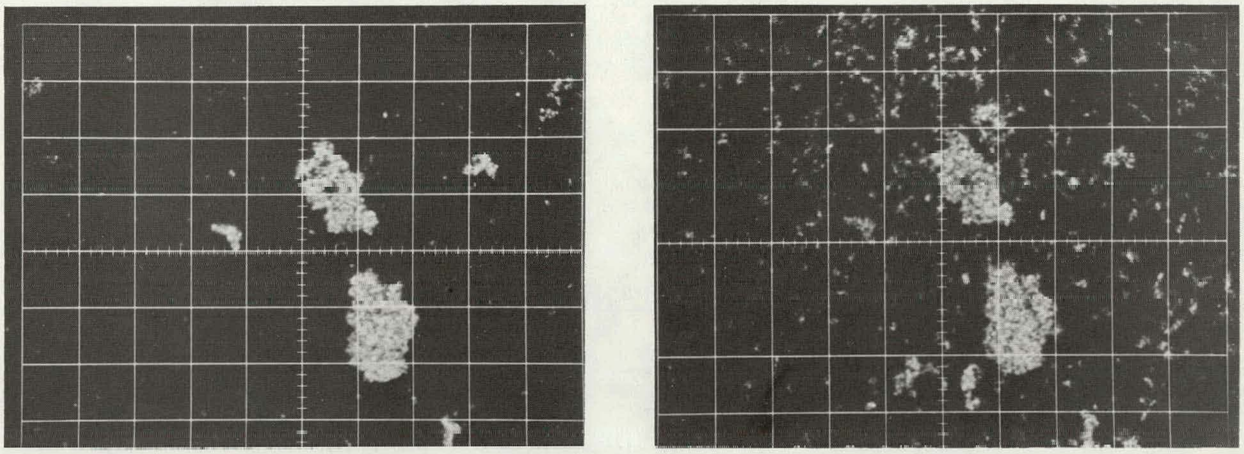
An attempt was made to come up with a better characterization of the mineral phases which are associated with Cs and Gd. For this characterization, geologic thin sections were prepared without cover slides so that the section could be examined both with the petrographic microscope and the electron microprobe. In the case of the Bell Canyon sandstone, this effort was somewhat successful as we were able to obtain a semi-quantitative analysis of the mineral which retained gadolinium. This mineral is chlorite. For the other specimens, the results are at present inconclusive.

Conclusions

Although the results of this study are not to be construed as anything but preliminary, we may make several conclusions. Firstly, at the high concentrations considered in this study, clay minerals appear to be responsible for all of the important sorption which takes place between Cs^+, Gd^{+++} and UO_2^{++} and Eleana Shale, Magenta dolomite, Bell Canyon sandstone and clay bearing halite. It may then be concluded that a relatively small portion of these rocks are actively responsible for sorption characteristics. Gadolinium was bound in all samples, probably as iron bearing clay, with a probable active mineral being chlorite. Cesium was retained by the Eleana Shale, in which illite is the probable active mineral. Although illite was also present in the clay bearing halite, no cesium retention was observed in this case. A possible explanation for Cs not being observed in the halite sample is that the illite may be too finely dispersed to build up Cs concentration above the microprobe detection limits. Strontium was not significantly retained on any samples as $SrSO_4$ is not formed at trace concentrations.

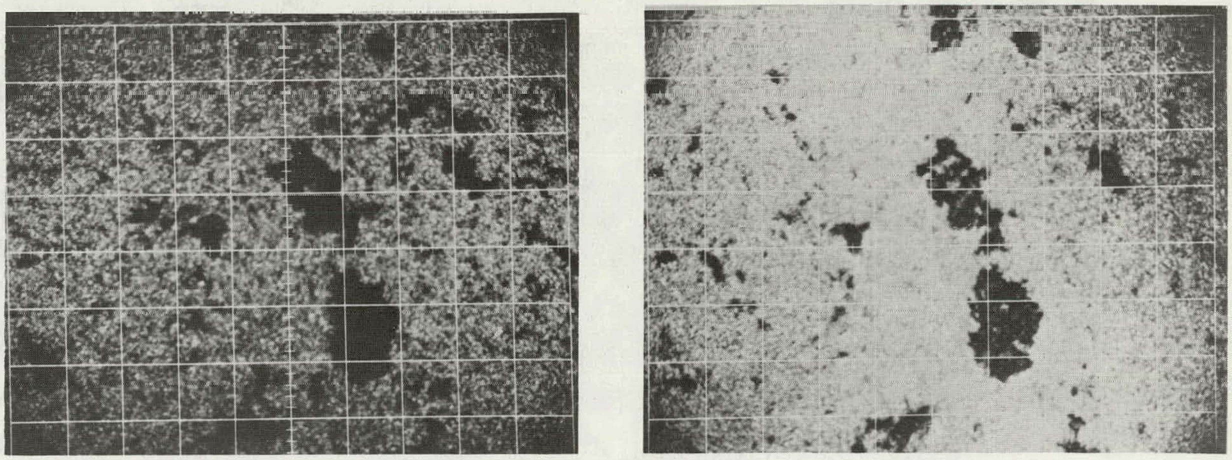
Although the clays observed in this study were in some cases finely divided, as in the case of the illite clay in the halite sample, frequently clays of a given type formed easily recognized patterns or were present in detrital grains large enough to be observed directly. This fact allowed tentative identification of the minerals as well as allowing identification of associations between the test ions and the individual minerals by electron microprobe techniques.

MAGENTA - STRONTIUM



Strontium Distribution

Sulfur Distribution

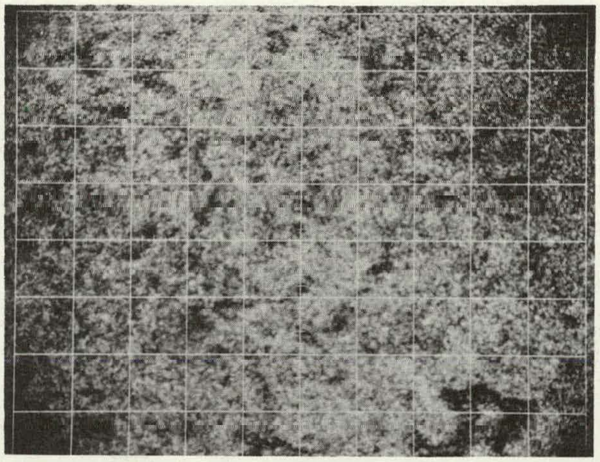


Magnesium Distribution

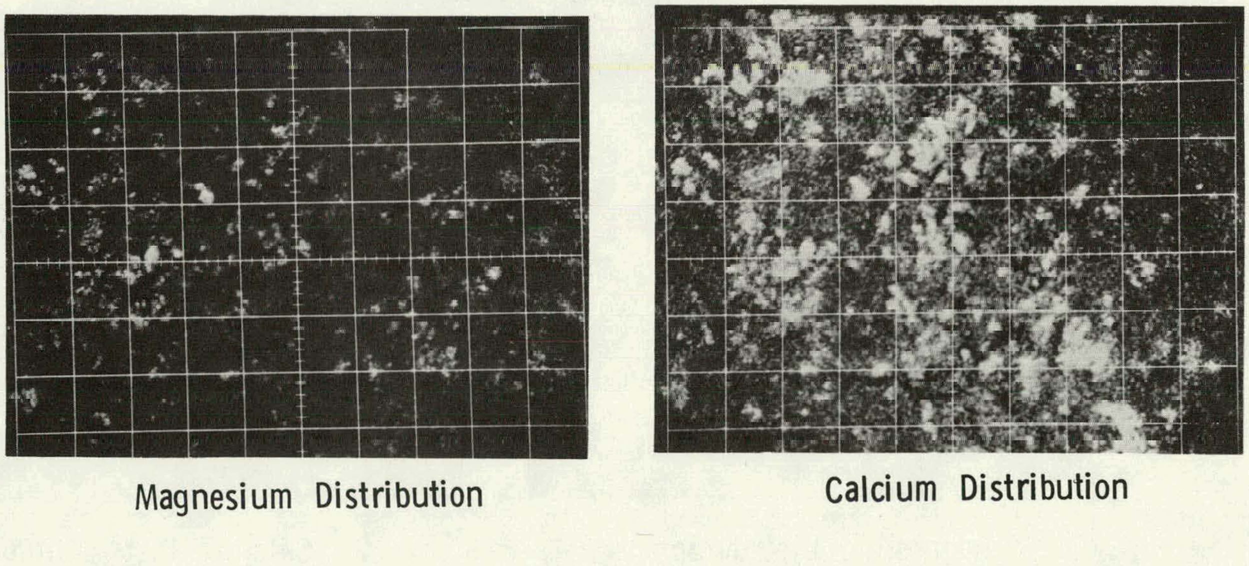
Calcium Distribution

Figure 1. Elemental distribution photomicrographs (EDPM) of Sr contaminated Magenta. The predominant Sr phase is $SrSO_4$ where Sr replaces Ca in gypsum. (200X)

MAGENTA - URANIUM



Uranium Distribution

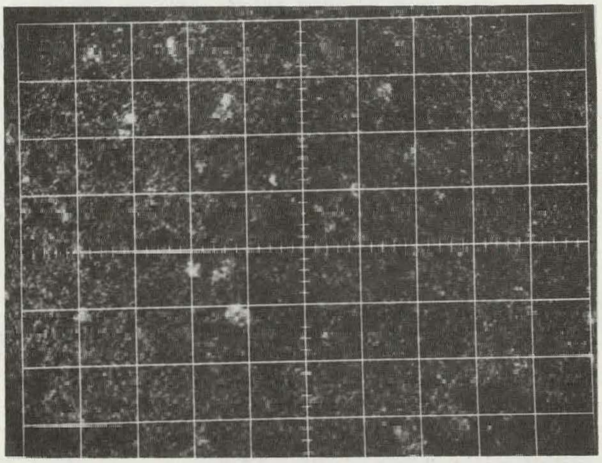


Magnesium Distribution

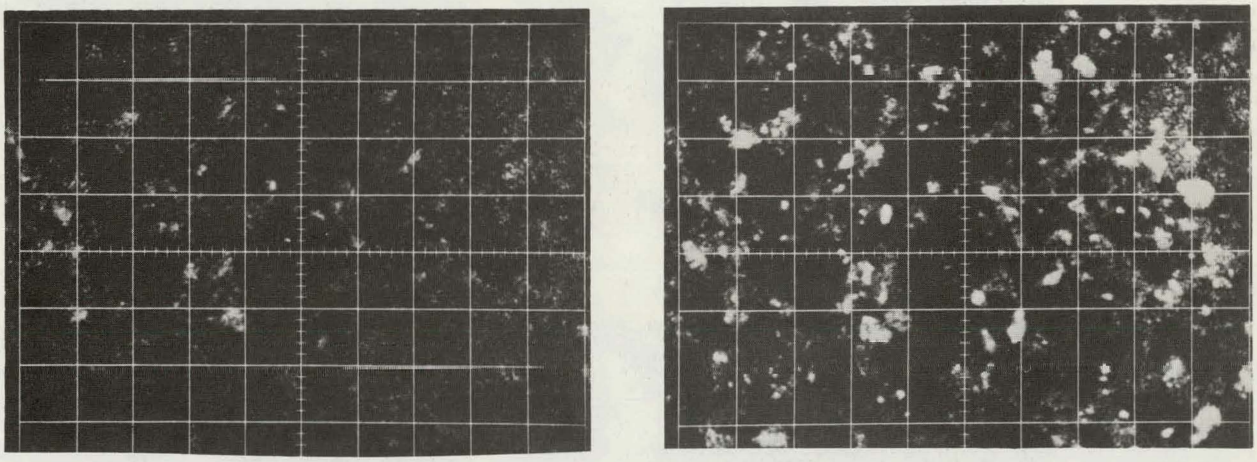
Calcium Distribution

Figure 2. EDPM of uranium contaminated Magenta. The predominant U phase appears to be UO_2CO_3 as Mg and Ca are dramatically reduced from a normal dolomite distribution as shown in Fig. 1. (200X)

MAGENTA - URANIUM



Potassium Distribution

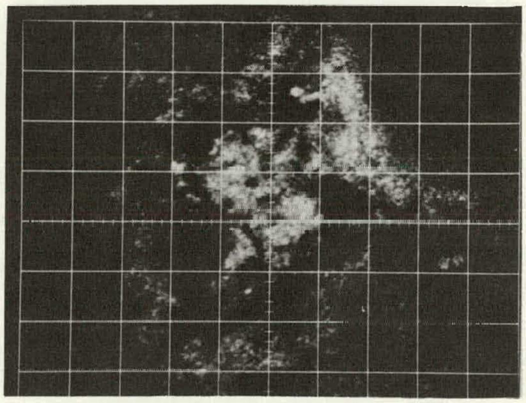


Aluminum Distribution

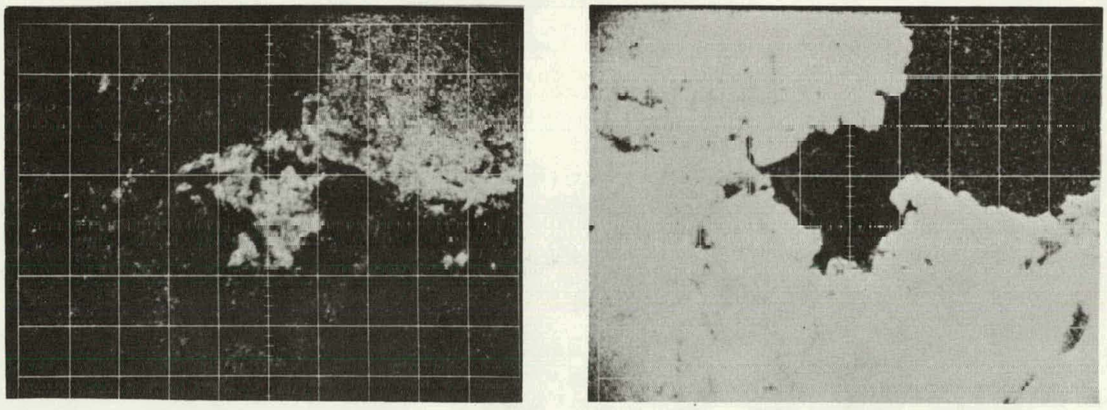
Silicon Distribution

Figure 3. EDPM of uranium contaminated Magenta. Attempts to correlate U with K, Al and Si are difficult because of the strong masking by the predominant UO_2CO_3. (200X)

DIRTY SALT - URANIUM

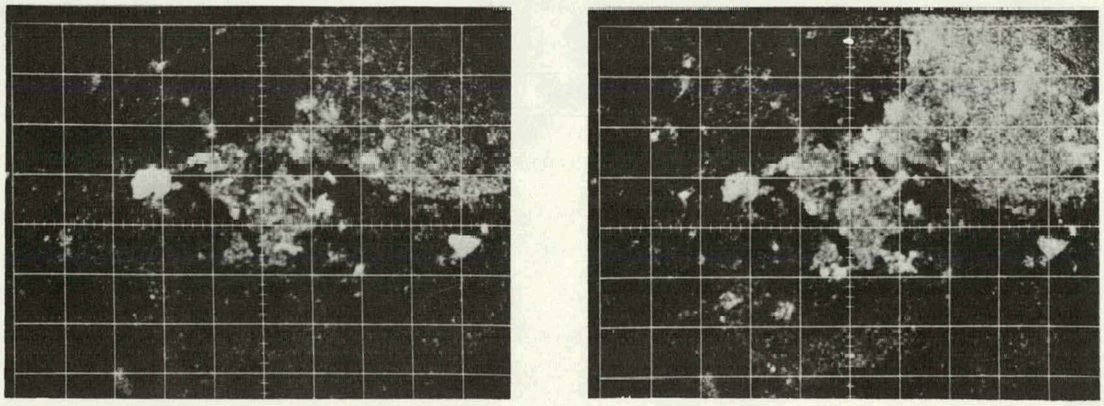


Uranium Distribution



Magnesium Distribution

Chlorine Distribution

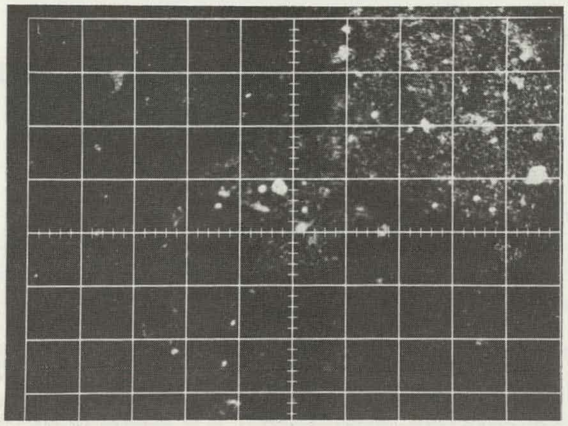


Aluminum Distribution

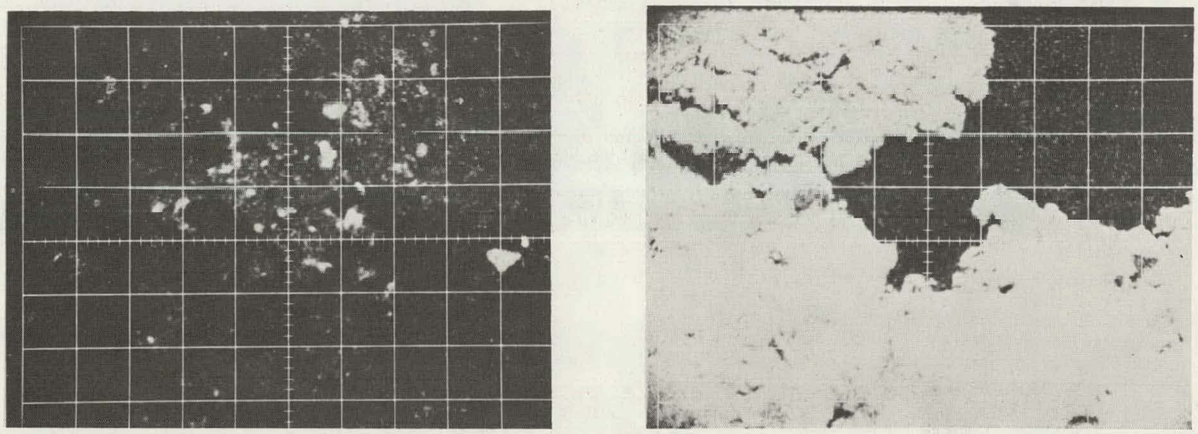
Silicon Distribution

Figure 4. EDPM of uranium contaminated dirty salt. Uranium is associated with clay rich areas and not NaCl. Upper right portion of uranium EDPM is missing because of a topographical effect. The predominant U phase is likely UO_2CO_3, from reaction with Magnesite. (200X)

DIRTY SALT - URANIUM

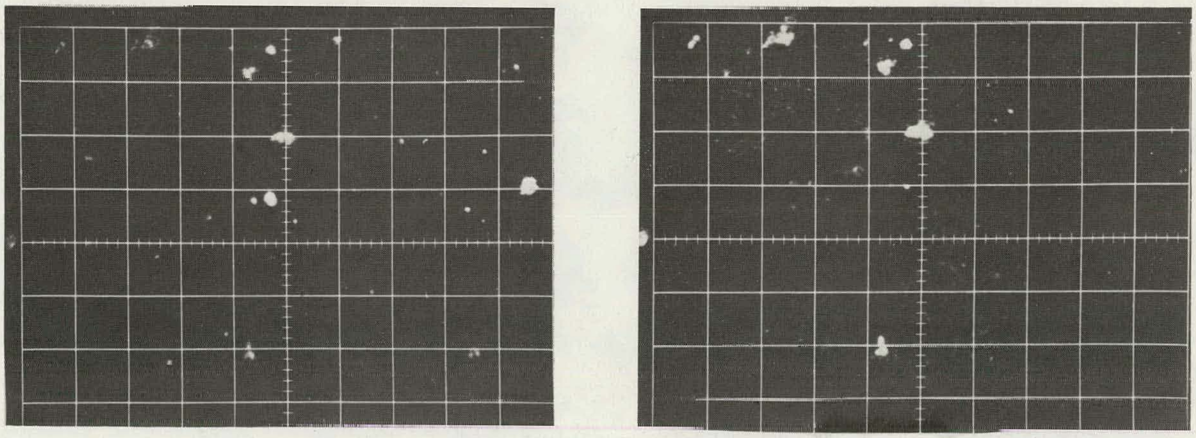


Iron Distribution



Potassium Distribution

Sodium Distribution



Sulfur Distribution

Calcium Distribution

Figure 5. EDPM of U contaminated dirty salt. When Fe is associated with clay, Fe is correlated with U while K, Na, S and Ca are not correlated. However, the positive correlation with iron bearing clay is not definitive in view of the reaction of U with Magnesite. (200X)

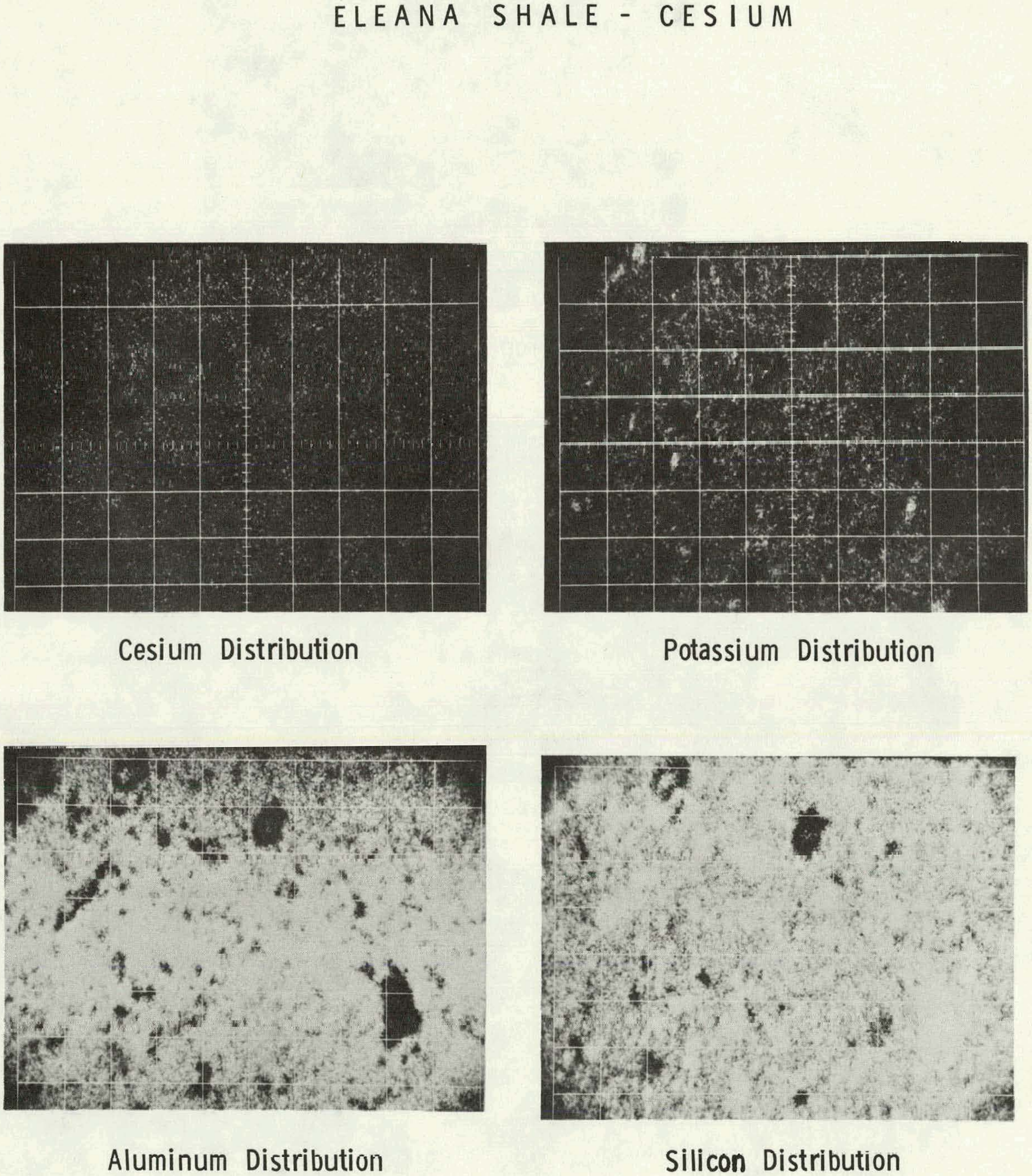
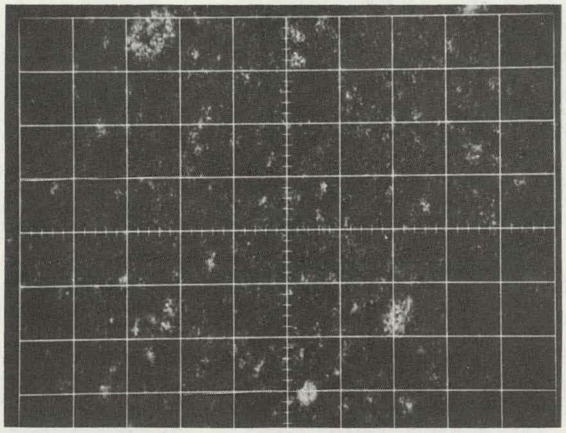
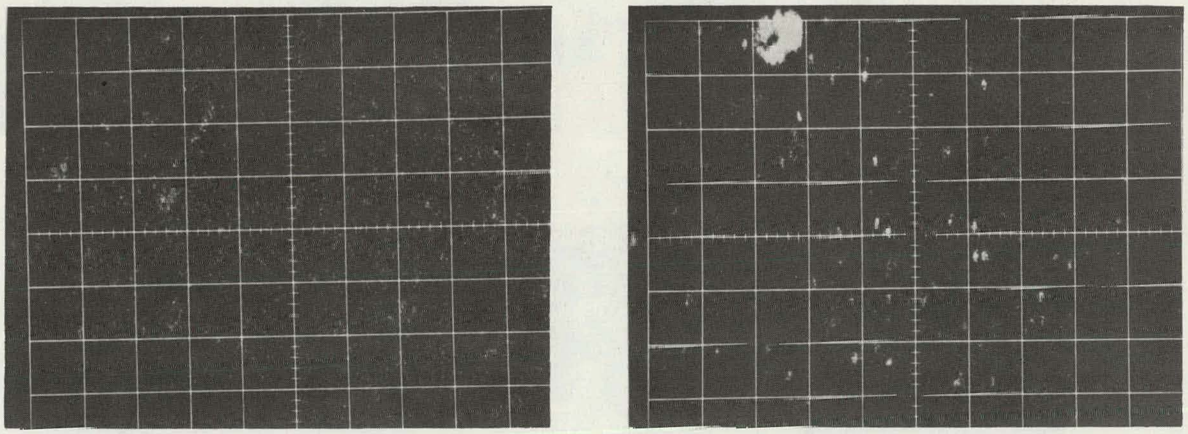


Figure 6. EDPM of cesium contaminated Eleana Shale. Cs is associated with K, Al and Si indicative of illite-vermiculite. (200X)

ELEANA SHALE - CESIUM



Iron Distribution

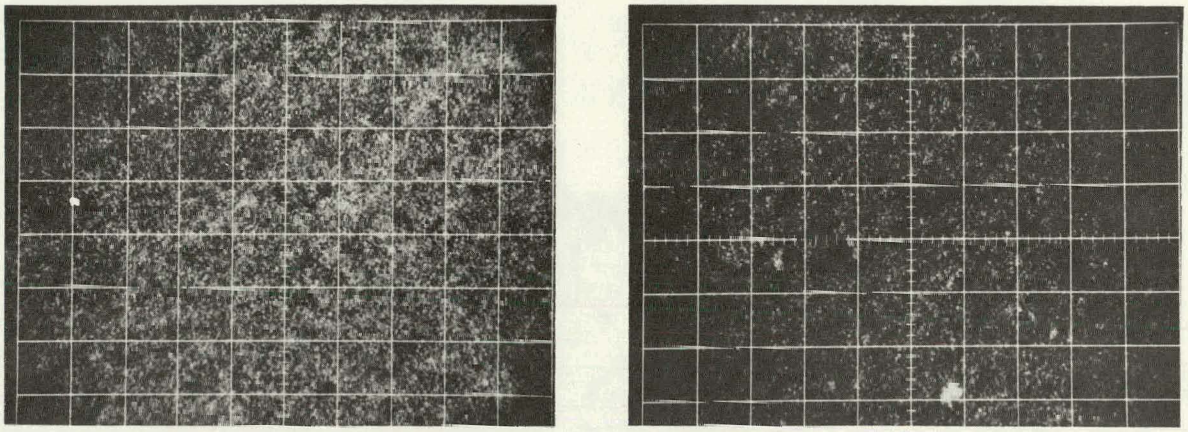


Magnesium Distribution

Calcium Distribution

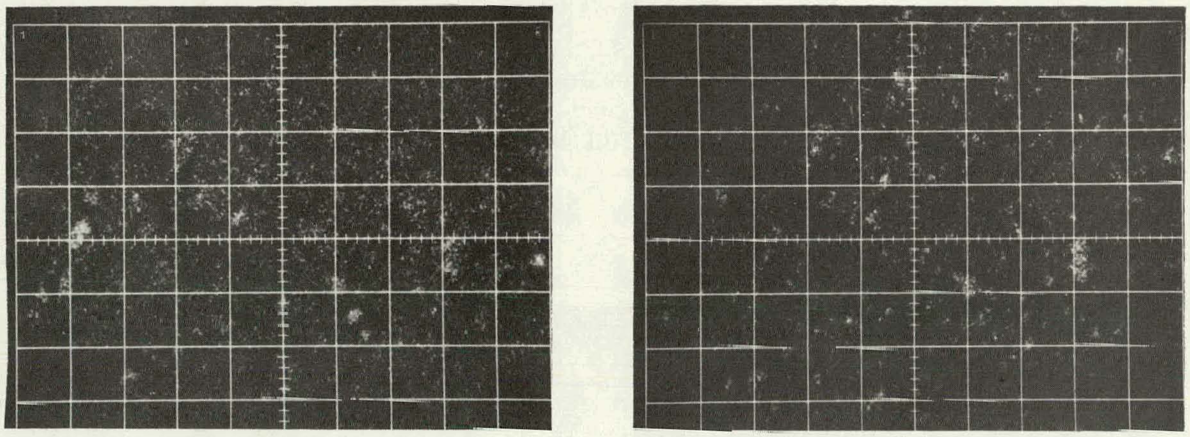
Figure 7. EDPM of Cs contaminated Eleana Shale. Cs is associated with Fe except for the ferroan dolomite at (-3,4). Cs is also correlated with Mg. (200X)

ELEANA SHALE - GADOLINIUM



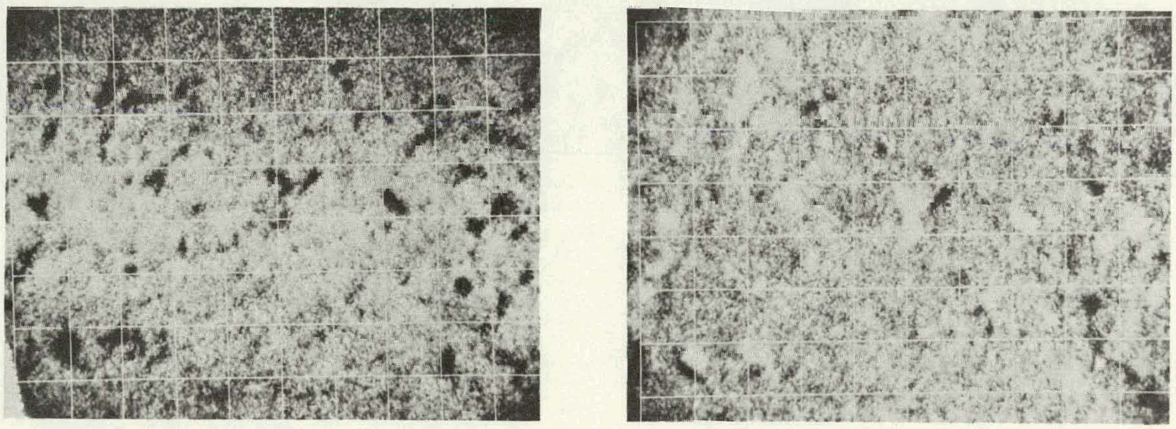
Gadolinium Distribution

Potassium Distribution



Magnesium Distribution

Iron Distribution

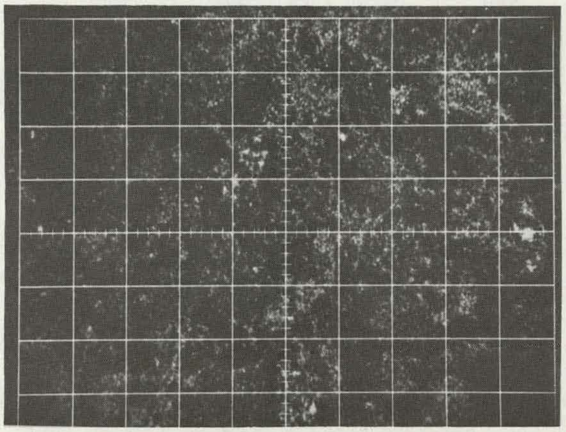


Aluminum Distribution

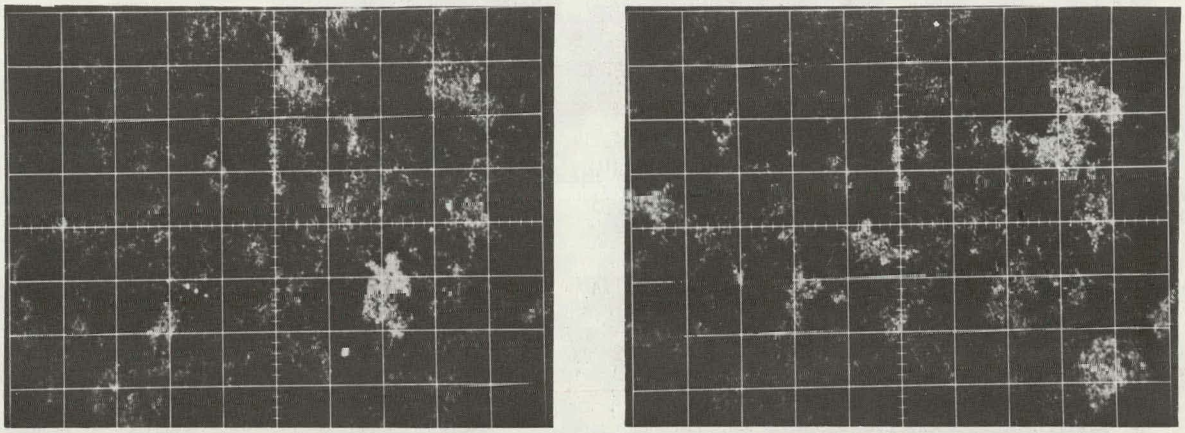
Silicon Distribution

Figure 8. EDPM of gadolinium contaminated Eleana Shale. A light streak of Gd running from the origin into the top right quadrant reveals a negative correlation for K and positive association with Fe, Mg, Al, Si, indicative of chamosite or chlorite. (200X)

BELL CANYON - GADOLINIUM

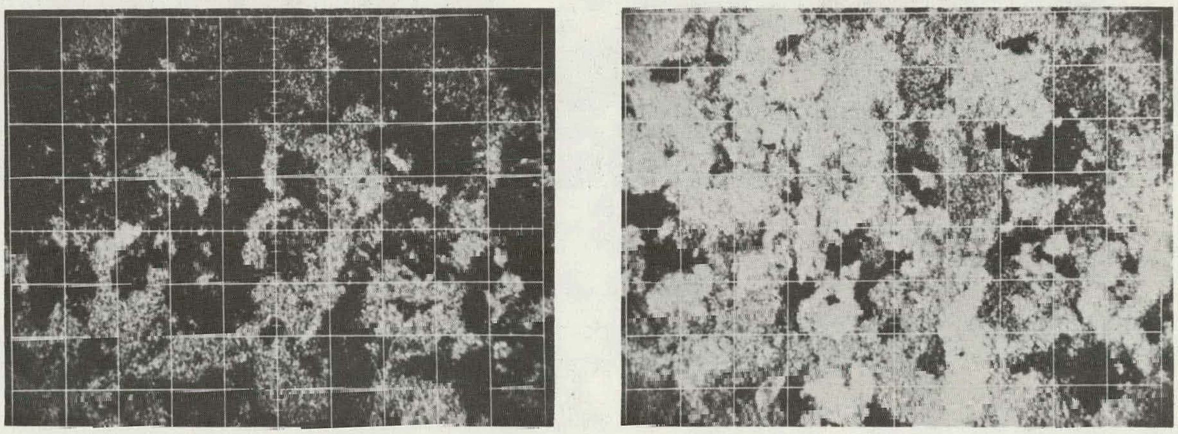


Gadolinium Distribution



Iron Distribution

Magnesium Distribution

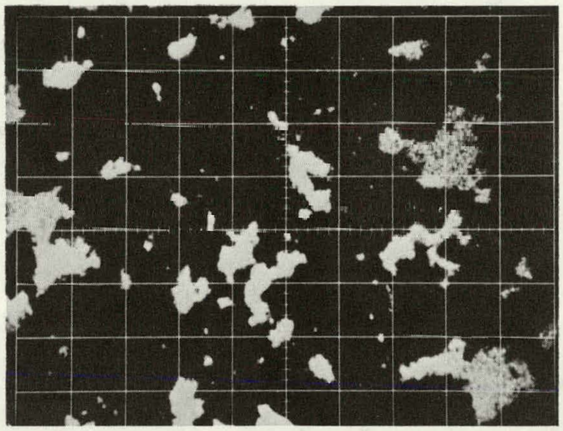


Aluminum Distribution

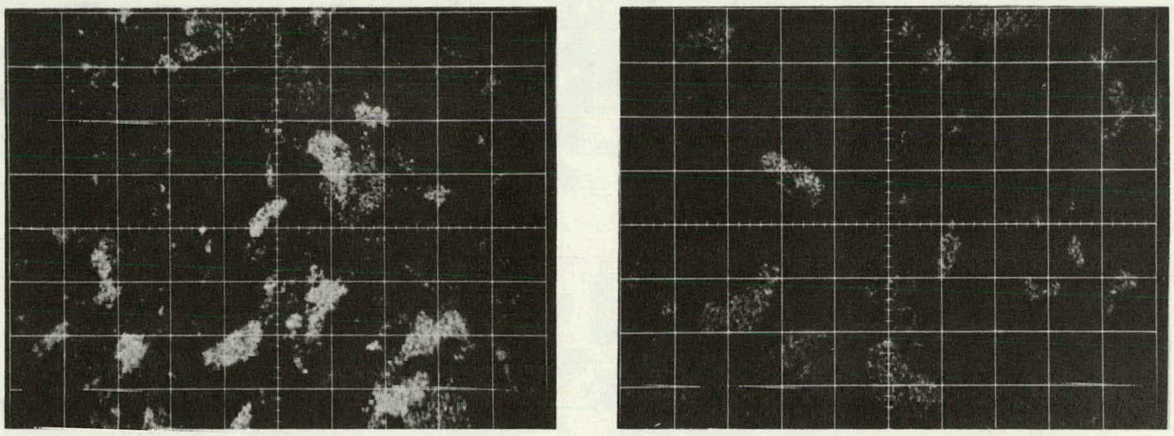
Silicon Distribution

Figure 9. EDPM of gadolinium contaminated Bell Canyon sandstone. Gd is associated with Fe, Mg, Al and Si, indicative of chlorite. (200X)

BELL CANYON - GADOLINIUM



Calcium Distribution

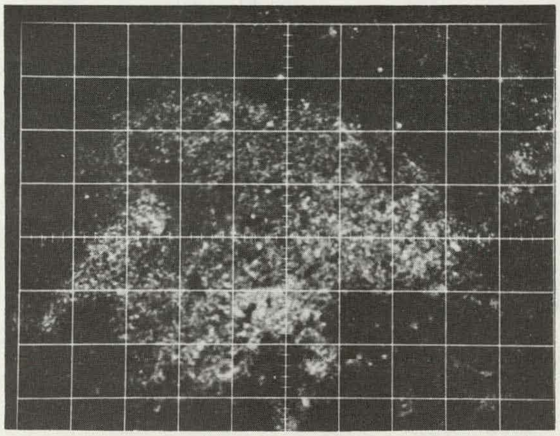


Potassium Distribution

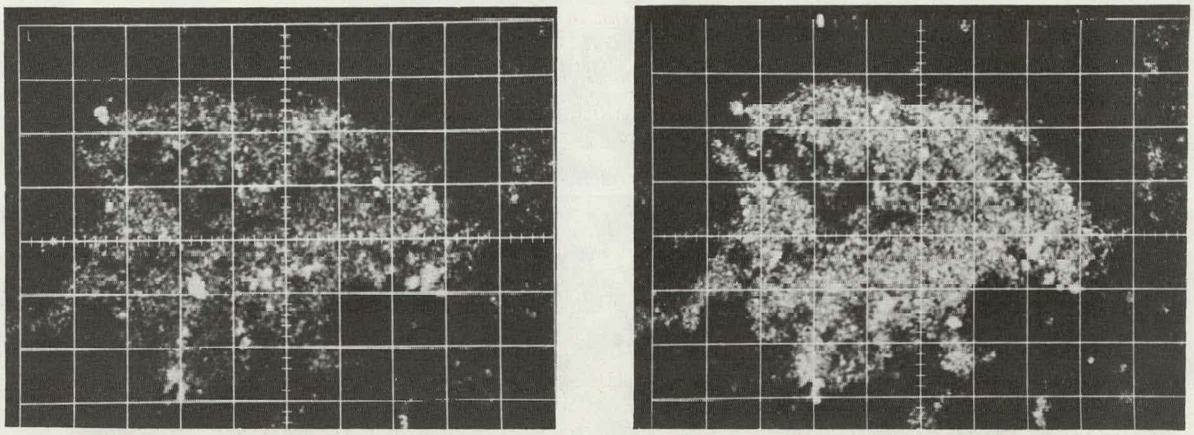
Sodium Distribution

Figure 10. EDPM of gadolinium contaminated Bell Canyon sandstone. The sorptive mineral contains some K but no Ca or Na. Dolomite at (3,1) is not retaining Gd. (200X)

DIRTY SALT - GADOLINIUM

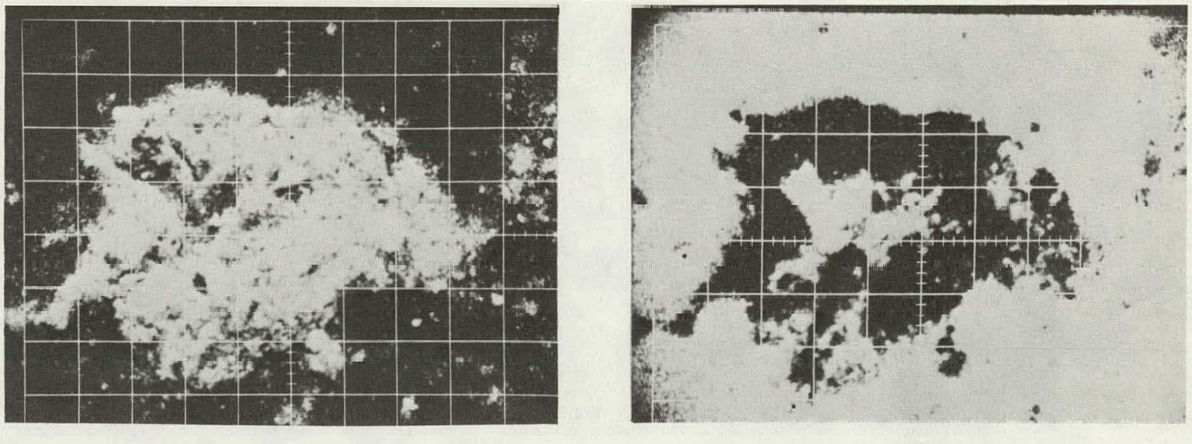


Gadolinium Distribution



Aluminum Distribution

Silicon Distribution

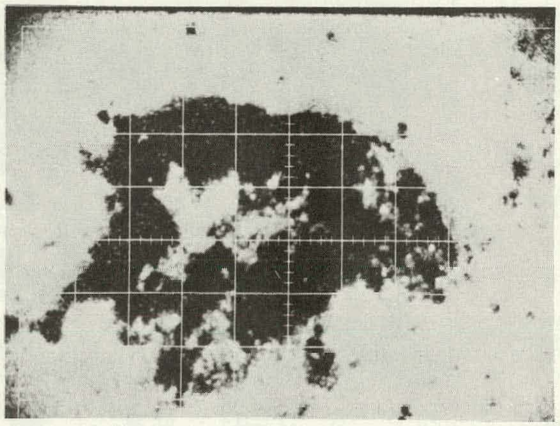


Magnesium Distribution

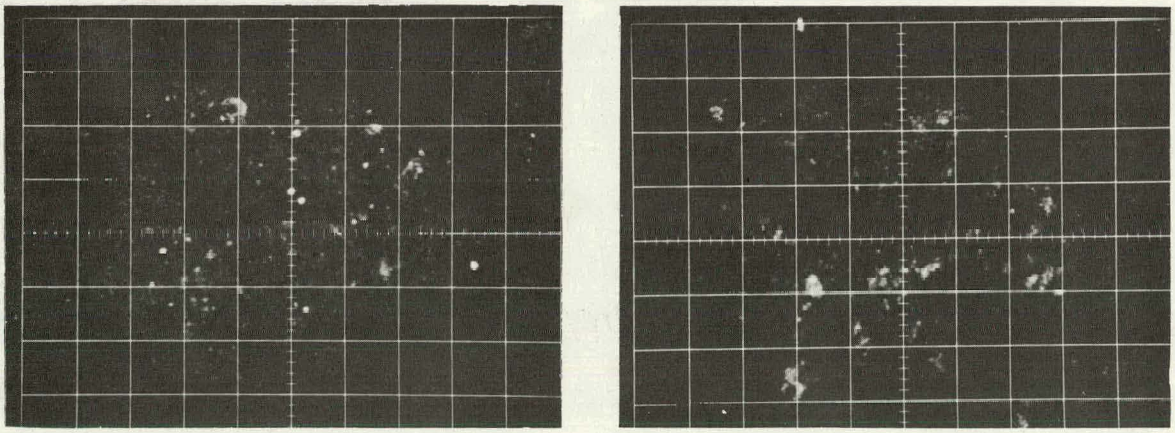
Chlorine Distribution

Figure 11. EDPM of gadolinium contaminated dirty salt. Gd is concentrated in clay pocket, possibly as a chlorite. (200X)

DIRTY SALT GADOLINIUM

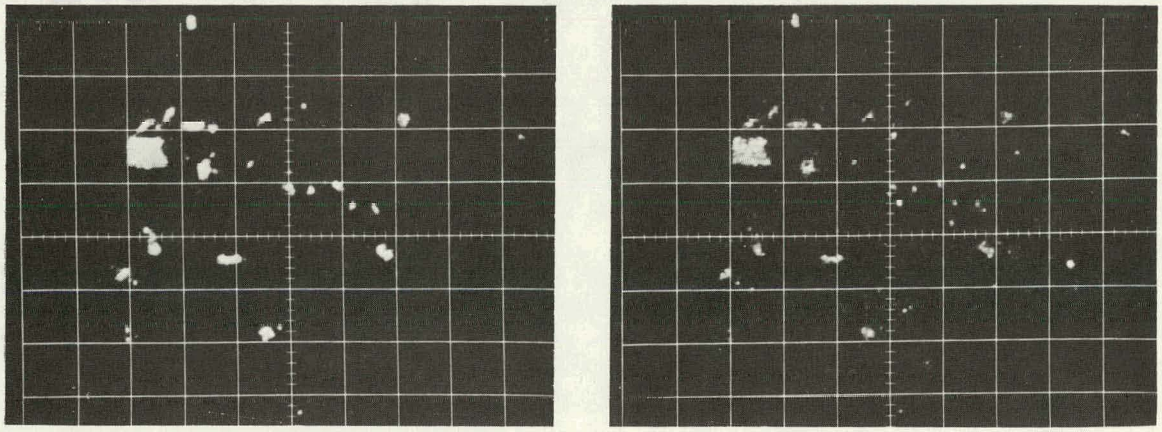


Sodium Distribution



Iron Distribution

Potassium Distribution

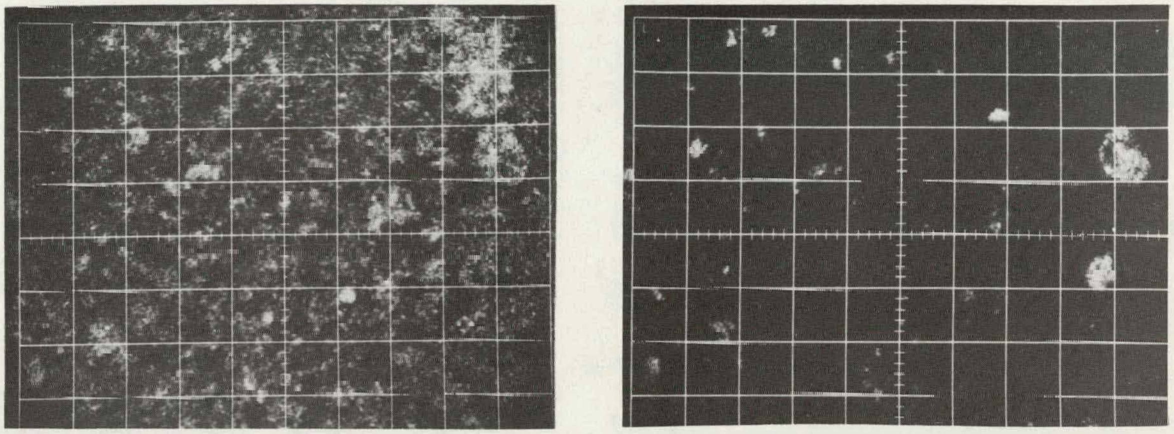


Calcium Distribution

Sulfur Distribution

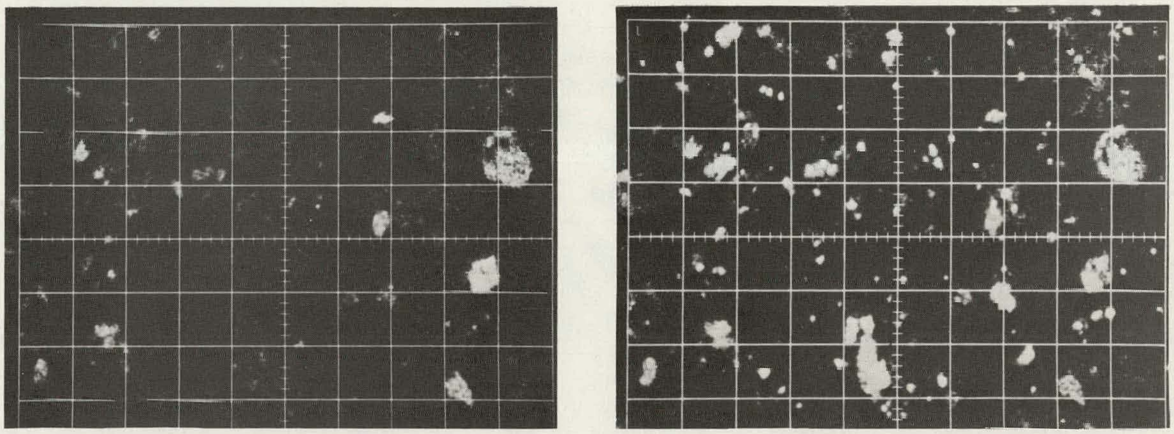
Figure 12. EDPM of gadolinium contaminated dirty salt. Gd is not associated with pyrite, anhydrite or illite. (200X)

MAGENTA - GADOLINIUM



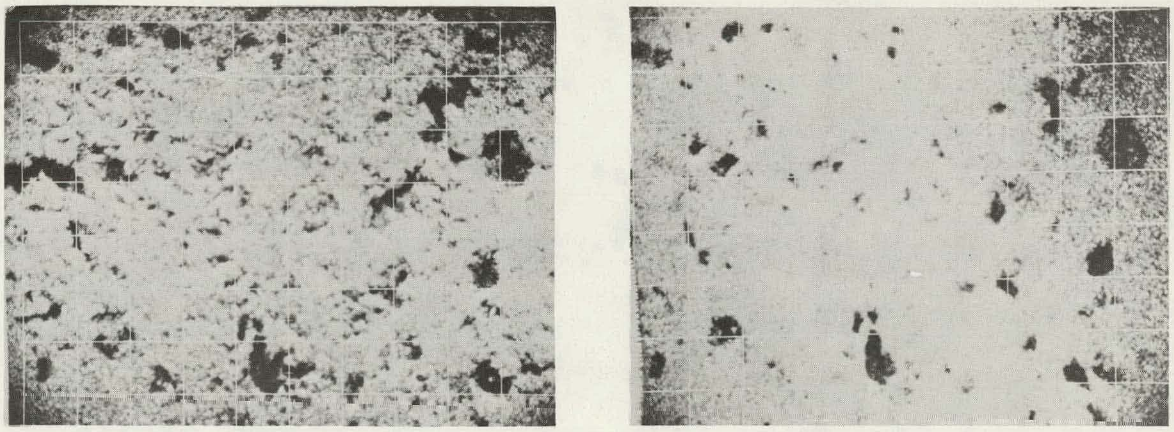
Gadolinium Distribution

Potassium Distribution



Aluminum Distribution

Silicon Distribution



Magnesium Distribution

Calcium Distribution

Figure 13. EDPM of gadolinium contaminated Magenta. Gd is associated with clay at (4,2) which is high in K, Al, Si and Mg, possibly chlorite. Also there is a diffuse Gd pattern associated generally with dolomite which is likely a concentration effect. (200X)

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DISCUSSION--THOMAS E. HINKEBEIN

Contact Circumstances and Valences Related to Test Results (Table 2).

Q. Are your test limits partly the result of the circumstance of contact or the valence indigenous to your materials?

A. No. The detection limits are what you see no matter what the source. We removed surface materials in order to look at those that were retained in a very "real" way. We allowed three days of contact in a doped rock-eqilibriated solution with AL_2O_3. Before any dopement was added all are very close to ph7. All had irreversible oxygen potential and only one valence state.

Description and Identification of Figures

Q. What is the composition of dirty salt?

A. Primarily halite with 7-8% dissolved minerals.

Q. Is that calcium sulfate?

A. No. Gypsum crystal.

Q. Exactly what are your pictures?

A The pictures are all 250 X so the distance between the grid lines is roughly 40 μ. The pictures are not comparable, however, because the times vary. The samples were ground flat, #600 carborundum paper.

Q. Why not use a beam to probe the upper right area of the Mg distribution in Figure 9?

A. We could have, but didn't.

Specific Questions on Test Results

Q. Have you verified that there is no $SrSO_4$ in the magenta dolomite?

A. Yes. There is none.

Q. How do you know it's not $CaUO_3$ in the magenta dolomite instead of UO_2CO_3?

A. Ca has been replaced on the surface. In addition the solubility of $CaUO_3$ is very high, thus no precipitate should form.

Q. How did you know it was the illite that took up the Cs in the eleana shale?

A. It was an educated guess, primarily based on the positive association with K; in looking through the "shopping list" of minerals strongly associated with the shale, illiite is one.

"LABORATORY MEASUREMENTS OF RADIONUCLIDE DISTRIBUTION BETWEEN SELECTED GROUND WATER AND GEOLOGIC MEDIA"

Bruce R. Erdal
K. Wolfsberg, R. Vidale, C. Duffy, and D. C. Hoffman

Los Alamas Scientific Laboratories
CNC-11, MS-514
Los Alamos, New Mexico 87545

LABORATORY MEASUREMENTS OF RADIONUCLIDE DISTRIBUTION BETWEEN SELECTED GROUNDWATER AND GEOLOGIC MEDIA

Bruce R. Erdal
K. Wolfsberg, R. Vidale, C. Duffy, and D. C. Hoffman
Los Alamos Scientific Laboratories

I. K_d Values for Alluvium and Bentonite.

Ratios for the distribution of a number of nuclides have been measured between ground water and bentonite and Nevada alluvium. These studies are pertinent to the NV Radionuclide Migration Project at the Nevada Test Site as well as relevant to the generic studies of nuclide migration being conducted by Task 5. The equilibrium distribution coefficient, K_d, for the distribution of activity is conventionally defined as:

$$K_d = \frac{\text{activity in solid phase/mass of solid}}{\text{activity in solution/volume of solution}}$$

In most of these experiments the activity was counted only in the solutions in order to retain identical counting geometry and, consequently, measure the fraction of the activity in the liquid phase, f. The equation for the distribution coefficient can then be expressed:

$$K_d = \left(\frac{1 - f}{f}\right)\left(\frac{\text{ml of solution}}{\text{g of solid}}\right).$$

It must be noted that, under many conditions, we know that equilibrium is not achieved, or we are not certain if it is. However, we still measure the distribution of activities between phases as defined above and we call the resulting value the distribution ratio, R_d, which is identical to K_d, but does not imply equilibrium.

The alluvium samples are from the Nevada Test Site. Most experiments were conducted with material from hole U5e[1] (RNM-1) in Frenchman Flat from vertical depth of 256 m, and some from 331 m. Material for some other experiments came from a preshot sample taken at a depth of 238 m from hole U3bv in Yucca Flat. All samples were taken below the water table. A geologic description of the unsorted material from the Frenchman Flat samples follows:

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[1] D. C. Hoffman, R. Stone, and W. W. Dudley, Jr. "Radioactivity in the Underground Environment of the Cambric Nuclear Explosion at the Nevada Test Site, Los Alamos Scientific Laboratory Report LA-6877-MS (1977).

Petrographic description:

Alluvium consists of mineral and tuff fragments in an iron-oxide rich, fine grained matrix, not strongly consolidated.

Major constituents large enough to be identified optically are quartz, plagioclase, alkali feldspar, calcite, glass shards, and opaques.

Minor constituents large enough to be identified optically are amphibole, biotite, orthopyroxene, clinopyroxene.

X-ray data:

Glass (broad hump), plagioclase, alkali feldspar, minor quartz

Microprobe data:

Fresh glass, also fine-grained devitrification products (probable zeolites)	$Na_{.76\pm.11}K_{.61\pm.07}Fe_{.05\pm.02}Mg_{.02\pm.02}Al_{1.43\pm.05}Si_{7.52\pm.06}O_{18}$
Plagioclase phenocrysts	$Na_{.55\pm.02}Ca_{.46\pm.04}K_{.03\pm.01}Al_{1.47\pm.03}Si_{2.96\pm.02}O_8$
Alkali feldspar	$Na_{.43\pm.03}Ca_{.02\pm.01}K_{.58\pm.03}Al_{1.04\pm.02}O_8$
Calcite (one analysis)	$Ca_{.99}Mg_{.01}CO_3$
Clinopyroxene (one analysis)	$Ca_{.85}Mg_{.77}Fe_{.32}Si_{2.0}O_6$
Orthopyroxene (two analyses)	$Ca_{.04}Mg_{1.30}Fe_{.72}Si_{1.95}O_6$

Portions of the dried samples were graded by sieving. A small amount was also ground and graded. Bentonite is the material sometimes used in drilling mud at NTS. It was used without grading. Since we are interested in the behavior of the samples in their natural state, no attempt was made to purify the materials or change the ions already on the sorption sites. Cation exchange capacity was determined by shaking separate 100-mg portions of the solids with 20 ml of 0.5 M CsCl (pH = 8.2) or 0.5 M $SrAc_2$ (pH = 8.5), spiked with ^{137}Cs or ^{85}Sr, respectively, for 3 to 5 days. The pH of these solutions was not adjusted because it was sufficiently close to that of the ground waters. After washing of the solids with water, they were gamma counted to determine the amount of Sr or Cs that exchanged. Portions of the samples were also sent to LLL for determination of surface area by nitrogen absorption (which we recognize may not be applicable) and sieve analysis. The results of these characterizations are given in Table I. It appears that neither the cation exchange capacity nor the gas-absorption surface area vary more than about a factor of two with the sieve size or source of the alluvium. However,

TABLE I. CATION EXCHANGE CAPACITY, SURFACE AREA, AND SIEVE ANALYSIS

		Cation Exchange Capacity (meq/100 g)		Surface Area[a]	Sieve Analysis[a,b] (μm)		
Material	Mesh Size	Sr	Cs	(m^2/g)	10%	50%	90%
Alluvium[c]							
U5e, 256m	100 - 200	14	10	14.9	70	105	155
U53, 256m	100 - 200[d]	16	13	12.4	29	90	175
U5e, 256m	200 - 400		17	20.2	26	50	71
U5e, 256m	+ 100	10		6.11	200	780	4000
U5e, 331 m	ungraded	16					
U3bv, 238m	100 - 200	16	12	11.7	61	95	122
U3bv, 238m	+ 100	16					
U3bv, 238m	ungraded	22		9.2	87	270	2000
Bentonite	ungraded	56	72	33.8	21	35	85

[a] Surface area and sieve analyses arranged for by D. G. Coles (LLL) and performed by A. H. Bierman (LLL).

[b] Particle size diameters corresponding to 10, 50, and 90 percentiles of the cumulative distribution.

[c] The material is labelled by hole designation and depth.

[d] Ground material. All others are sievings of natural sizes.

the relationship between the surface area and cation exchange capacity is also no better than a factor of 2. The diameters of the particles as calculated from the gas-absorption measurements are in the 0.2- to 0.4-μm range, much smaller than the sieve sizes. These data, together with the cation exchange capacity measurements, indicate that internal surface area must play a major role in sorption for alluvium. The ungraded bentonite has a somewhat greater cation exchange capacity and surface area.

Ground water used in the sorption experiments came from a depth of 341 m in well RNM-2S which is near U5e. Analysis of the water was arranged for by W. W. Dudley, Jr. and performed at the USGS Laboratory in Denver. The following are concentrations in mg/l: Ca^{+2}, 18; Mg^{+2}, 5.5; K^+, 10; Na^+, 66; Li^+, 0.030; HCO_3^-, 170; CO_3^{-2}, 0; Cl^-, 23; F^-, 0.6; SiO_2(diss.), 62; SO_4^{-2}, 41. In addition, total anions, 4.32 meq/l; total cations; 4.48 meq/l; evaporated residue at 180°, 314 mg/l (calculated, 310 mg/l); pH, 8.5. Our deionized water has a Na^+ concentration of < 1 ppb and a resistance of > 18 MΩ-cm. The pH is 5.9 to 6.6.

Three types of tagged solutions were prepared for the sorption studies. The first was prepared by evaporating a mixture of the following commercially available "carrier-free" nuclides to dryness in a polyethelyene tube: ^{144}Ce, ^{152}Eu, ^{133}Ba, ^{85}Sr, ^{95}Zr-^{95}Nb, ^{137}Cs, ^{85}Sr, ^{60}Co, and ^{124}Sb. Concentrated HCl was added, and the mixture was taken dry again to convert the salts to chlorides. Then ground water was added and, after stirring, the mixture was centrifuged for 1 hour at 16000 rpm. The supernate was centrifuged a second and a third time in fresh tubes and was then diluted with more ground water and stored in polyethylene. The ^{95}Zr was not soluble in the ground water. The pH of the spiked ground water remained at 8.5, and no activity was deposited on the polyethelene bottle or on the polyethyene tubes in which the experiments were performed. Similar spiked solutions of ^{88}Y and ^{237}U in both ground water and deionized water were prepared. The uranium was in the form of uranyl ion. A last type of radioactive solution was prepared by leaching a tuff sample containing volatile fission products from an underground nuclear explosion. The ground-water leach contained mostly ^{131}I, and also measurable quantities of ^{99}Mo, ^{103}Ru, and $^{124,126,127}Sb$. Ascending paper chromatography revealed at least three iodine species having the following R_f values and percent of total of iodine: 0.02, 10%; 0.25, 40%; 0.68, 50%. These species are probably IO_4^-, IO_3^-, and I^-, respectively.

Batch sorption and desorption experiments were performed by shaking weighed quantities of a specified solid, which had been pre-equilibrated with ground water, with 20 ml of tagged water for a given time in stoppered polyethylene centrifuge tubes at room temperature or in sealed polyethylene bottles at 70°C. At the end of the shaking period, the liquid phase was separated from solids by three centrifugings, each in a new polyethylene centrifuge tube, for 1 hour at 16000 rpm. A 9- or 10-ml aliquot of the solution was acidified and counted on a calibrated, 95 cm^3, coaxial Ge(Li) detector. An aliquot of the original solution was also counted in the same geometry so that the fraction in solution could be determined. Intensities of individual peaks in the spectra were resolved and atoms of each nuclide at zero time were determined with the GAMANAL code.[2]

The pH of the water was measured after many of the experiments. There was very little change in pH after alluvial ground water (initial pH 8.5) was contacted with alluvium or bentonite; final pH values ranged randomly between 8.3 and 8.7. The pH of the deionized water (initial pH ≈ 6) increased to values of 8 to 8.6 after contact with alluvium and to ≈ 9 with bentonite. The potential of the platinum half-cell immersed in our solution was measured relative to a calomel half-cell (244 mV). All the ground waters measured in the laboratory gave values of 400 to 435 millivolts. According to Garrels and Christ[3], the dissolved oxygen from air provides a mild oxidizing effect and Eh values between 300 and 350 mV at a pH of 8. We also attempted to measure the potential of water fresh from the RNM-2S well, before the water equilibrated with air, and obtained a value of 330 mV for the platinum half-cell indicating, still, a mild oxidizing effect. The pH of the water at that time was 8.0. We are aware of the difficulties in making good Eh measurements and of the problems with electrode measurements, and, consequently, do not attempt to interpret these measurements further.

The R_d values obtained from each experiment with alluvium are tabulated in Tables II and III; those for bentonite in Tables IV and V. The values are arranged first according to sorption or desorption values, and then according to shaking time. The reader should carefully note the type of alluvium, temperature, and other conditions explained in the footnotes.

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[2] R. Gunnink and J. B. Niday, "Computerized Quantitative Analysis by Gamma-ray Spectrometry", UCRL-51061 (1972); extensively modified for use at the LASL Central Computer Facility by B. R. Erdal, CNC-11.

[3] P. M. Garrels and C. L. Christ, Solutions Minerals, and Equilibria (Freeman, Cooper and Company, San Francisco, 1965), p. 136.

TABLE II. DISTRIBUTION RATIOS FOR ALLUVIUM

Experiment[a,g]	Mesh Size	Shaking Time (days)	Distribution Ratio, R_d Sr	Ba	Cs	Co	Y	Eu(III)	Ce(III)
4870 (70°C)	100-200[d]	2.7	416	5620	5840	17500		28800	>28000
4870	100-200[d]	2.7	284	2910	3810	9710		>20000	>24000
4090	100-200	2.8	219	1680	3600	3440		>4800	>300
4100	100-200	11.6	272	3360	8090	7800		>5270	>720
4800 (70°C)	100-200[d]	23.7	629	9100	6520	16800		22000	>20000
4860 (70°C)	200-400	23.7	48	973	2670	9560		>59000	>13000
4850[b] (70°C)	Ungraded	23.7	68	1100	7420	11200		7950	>13000
4810	200-400	23.7	433	7990	9140	14300		48500	>24000
4820	+100	23.7	569	8690	7880	21100		14100	>23000
4830[c]	Ungraded	23.7	151	4080	6510	14000		42000	>20000
4840[b]	Ungraded	23.7	109	2010	8100	44900		7640	>20000
4890 (70°C)	100-200[d]	23.9	563	8417	5730	19600		22000	>23000
4800	100-200[d]	23.9	266	4740	6300	14300		>90000	>20000
4110	100-200	27.6	205	4150	9150	12100			>500
4170[h]	100-200	27.8					13700		
4130[e,h]	100-200	27.8					24600		
4120	100-200	41.8	186	6160	10400	13400		>640	>1090
4140[e,h]	100-200	42.9					36100		
4131[e,f,h]	100-200	34.7					117000		
4093[f]	100-200	39.0	182	5420	10600	25000		>27000	>9100
4181[f,h]	100-200	49.0					17700		
4172[f,h]	100-200	53.8					12900		
4103[f]	100-200	144.1	165	3380	7310	21900		>39000	>2000
4112[f]	100-200	144.6	177	3570	6230	37700		12400	>2400

[a] Unless otherwise specified samples from U5e, 256 m; weight of alluvium was approximately 1g. Ground water from RNM-2S was used. Experiment involved sorption from solution.

[b] From U3bv, 238 m.

[c] From U5e, 331m.

[d] Different sieving from rest of 100-200 mesh from same source.

[e] Deionized water was used.

[f] Experiment involved desorption from solid.

[g] Unless otherwise indicated, experiment conducted at room temperature (20 ± 5°C).

[h] 0.5 g of alluvium.

TABLE III. DISTRIBUTION RATIOS FOR ALLUVIUM

Experiment[a,g]	Mesh Size	Shaking Time (days)	Distribution Ratio, R_d Sb	U(VI)	I	Mo	Nb	Ru
4870 (70°C)	100-200[d]	2.7	8.63					
4780	100-200[d]	2.7	3.90					
4430[i]	100-200	2.7	25.3		16.6	15.8		
4090	100-200	2.8	5.33				529	
4100	100-200	11.6	6.35				1520	
4440[h]	100-200	11.7	33.7		25.0	23.4		976
4450[i]	100-200	18.7	29.4		23.7	23.4		1020
4880 (70°C)	100-200	23.7	12.5					
4860 (70°C)	200-400	23.7	4.67					
4850[b] (70°C)	Ungraded	23.7	2.43					
4810	200-400	23.7	6.26					
4820	+100	23.7	16.3					
4830[c]	Ungraded	23.7	5.40					
4840[b]	Ungraded	23.7	1.84					
4890 (70°C)	100-200[d]	23.9	12.5					
4800	100-200[d]	23.9	8.43					
4110	100-200	27.6	6.35				2800	
4170[h]	100-200	27.8		7.45				
4130[e,h]	100-200	27.8		55.9				
4120	100-200	41.8	6.32				2720	
4180	100-200	42.9		5.75				
4140[e,h]	100-200	42.9		65.3				
4460[i]	100-200	60.7	36.4		24.7			1120
4431[f,h,i]	100-200	24.8	19.5		421			1630
4171[f]	100-200	34.8		8.9				
4093[f]	100-200	39.0	116				5100	
4441[f,i]	100-200	48.8	235		858			3390
4103[f]	100-200	144.1	71				2630	
4112[f]	100-200	144.6	58				2640	

[a-h] See footnotes in Table II.

[i] Tagged solution from leaching of material from an underground nuclear test was used.

TABLE IV. DISTRIBUTION RATIOS FOR BENTONITE

Experiment	(g) Weight	Shaking Time (days)	Distribution Ratio, R_d[c] Sr	Ba	Cs	Co	Y	Eu(III)	Ce(III)
4010	2	2.8	1380	1790	1580	637		>280	>190
4050	1	2.8	2640	2800	1780	1610		>5400	>360
4029	2	11.6	904	1660	1420	428		>1490	>330
4060	1	11.6	1130	1560	1570	504		1430	>540
4030	2	27.6	1110	2590	1480	460		1450	>280
4070[a]	1	27.6	2040	3340	2080	990			>510
4230	0.5	27.9					3890		
4120[a]	0.5	27.9					5830		
4040	2	41.8	2490	14800	1890	2080		>4500	>300
4080	1	41.8	1140	6880	1940	2260			>660
4240	0.5	42.9					1580		
4220[a]	0.5	42.9					3840		
4231[b]	0.5	34.8					3880		
4211[a,b]	0.5	34.8					3490		
4013[b]	2	39.0	2510	7350	2190	1510		>5900	>740
4053[b]	1	39.0	2370	6920	2040	4800		>14000	>1520
4212[a,b]	0.5	53.8					44600		
4241[b]	0.5	65.7					5610		
4221[a,b]	0.5	65.7					16500		
4023[b]	2	141.1	2900	5380	1960	2600		>5740	>1060
4063[b]	1	141.1	2310	4730	2280	7610			>2200
4032[b]	2	144.6	2680	6100	1800	2950		>14000	>1470
4072[b]	1	144.6	2690	5450	2150	9410		24100	>2400

[a] Deionized water was used.

[b] Experiments involved desorption from solids.

[c] All experiments conducted at room temperature.

TABLE V. DISTRIBUTION RATIOS FOR BENTONITE

			Distribution Ratio, R_d^c		
Experiment	weight (g)	Shaking Time (days)	Sb	U(VI)	Nb
4010	2	2.8	5.80		184
4050	1	2.8	6.90		940
4029	2	11.6	5.20		511
4060	1	11.6	8.51		505
4030	2	27.6	5.35		465
4070	1	27.6	6.57		843
4230	0.5	27.9		77.8	
4210[a]	0.5	27.9		334	
4040	2	41.8	4.97		465
4080	1	41.8	6.51		1690
4240	0.5	42.9		73.1	
4220[a]				214	
4231[b]	0.5	34.8		271	
4211[a,b]	0.5	34.8		168	
4013[b]	2	39.0	22.8		1490
4053[b]	1	39.0	58.7		2901
4023[b]	2	141.1	10.9		1490
4063[b]	1	141.1	53.6		
4032[b]	2	144.6	18.3		1400
4072[b]	1	144.6	44.1		

[a,b,c] See footnotes of Table IV.

In examining Tables II - V one can make some general observations as well as obtaining K_d's which are R_d's at equilibrium or steady state. The scatter in the apparent equilibrium values is larger than the experimental uncertainties, which are usually smaller than 10%. Consequently, we feel that we are not sampling strictly identical samples or conditions, and when giving errors on averages we give the standard deviation of the population as a more realistic error rather than the standard deviation of the average. Species with low K_d values attain equilibrium by sorption in times of less than one week whereas those with large K_d values require three to four weeks.

In some cases apparent equilibrium values reached by desorption are different from those reached by sorption. We speculate that these observations may be a consequence of the following phenomena. The solution from which sorption takes place may contain different species of the same element (for example, ions of different oxidation states, differently complexed ions, and various degrees of hydration or polymerization). If the exchange between such species is very slow and they exhibit different sorption characteristics, only one species may sorb strongly while the other remains in solution. The soluble species is then absent in the desorption experiment.

The sorption properties for some ions are more sensitive to the type of alluvium, degree of grading, and temperature than those for other ions. This may be due to various types of minerals or grains playing different roles in the sorption of different ions. We hope to study this possible effect.

Such uncertainties lead to larger errors in K_d, sometimes factors of 2 or more, than we like. However, we hope that the values will still be useful since some of the other parameters in modeling the transport of nuclides are only known with much larger uncertainties. Some of our conclusions for the alluvium studies are outlined in the following paragraphs;

Strontium: Equilibrium appears to be attained by sorption in less than 3 days. However, the K_d appears to be quite dependent on temperature, and particle size. For the sorption experiments with the 100-200 mesh size, we obtain values of K_d of 239 ± 40 ml/g at room temperature and 536 ± 109 ml/g at 70°C. For desorption at room temperature and the same mesh size, we obtain a somewhat smaller value, 175 ± 9 ml/g. The change may be due in part to changes in the solid during the sorption and desorption runs (perhaps dissolution of carbonates). We would recommend using 217 ± 45 ml/g for the equilibrium value for sorption-desorption for 100-200 mesh alluvium at room temperature. The behavior of Sr as a function of alluvium source and particle size should be studied further.

Barium: It appears that the time for equilibrium is 12 to 24 days at room temperature and more than 3 days at 70°C. As with Sr, the K_d is dependent on the source of the alluvium. If we take all values for the 100-200 mesh material after 12 days for both sorption and desorption, we obtain a K_d value of 4400 ± 1100 ml/gm at room temperature and 8750 ± 500 ml/gm at 70°C. For all U5e samples at room temperature after 12 days, we get 5200 ± 2000 ml/gm. For Sr and Ba a rather constant ratio of K_d's (Sr/Ba), 0.056 ± 0.014, is obtained for all experiments in spite of the large variations in the individual K_d's.

Cesium: Equilibrium appears to be established after ≈ 12 days at room temperature and ≈ 3 days at 70°C. For the 100 to 200 mesh alluvium, the K_d is 8300 ± 1800 ml/g at room temperature and 6000 ± 400 ml/g at 70°C. The difference between these values is not as great as those for Sr and Ba. Further, the values for other particles and sources are similar to these numbers. We recommend using an overall average of 7700 ± 1600 ml/gm.

Cobalt: Equilibrium for sorption seems to be attained after about 2 weeks for room temperature and 70°C. For sorption, the apparent K_d's are 13300 ± 1200 ml/g and 18000 ± 1500 ml/g for room temperature and 70°C. For desorption, the apparent K_d is significantly higher at room temperature, 28000 ± 9000 ml/gm. The difference may be due to the preparation of the tracer from an evaporated chloride residue. There may be some small competition between ion exchange and chloride complex formation in the sorption experiments.

Yttrium, Cerium, Europium: In macro quantities the trivalent ions of these elements form quite insoluble hydroxides at pH 8 to 8.5. The measured K_d's are quite large. Any small values are probably due to incomplete centrifugation or the presence of colloids. We believe that all the K_d's are greater than 20,000 ml/gm.

Antimony: The complex chemistry of antimony, particularly in basic solution, is reflected in the spread of distribution ratios with different experimental conditions. Sorption experiments using the commercial tracer dried to the chloride, and then hydrated, gave K_d's of 6.0 ± 1.5 ml/g and 12 ± 2 ml/g at room temperature and 70°, respectively, in periods of greater than 3 days. The K_d for desorption is much greater than for sorption, ≈ 65 ml/gm, assuming equilibrium was attained in 140 days. This difference may be due to chloride complex formation, or to almost irreversible changes on sorption. Also noteworthy is the fact that the alluvium from U3bv has a significantly lower K_d for Sb than the material from U5e. The Sb obtained from leaching of shot debris where no extra chlorides are involved gave a still different K_d's: 32 ± 5 ml/g for sorption, and ≈ 200 ml/g for desorption.

Uranium (uranyl): The contact times for experiments with ^{237}U were limited by its 7-day half life. The K_d's for sorption and desorption from ground water are ≈ 7 and ≈ 9, respectively. From deionized water, the K_d for sorption is ≈ 60. The difference may be due to higher carbonate concentration in the ground water leading to competition between carbonate complexing and sorption of the uranyl ion.

Iodine: The three iodine species in the leach water have been mentioned above. For sorption, we get a relatively small K_d, 24.5 ± 0.7 ml/g; however, the K_d for desorption is 400 - 900 ml/g. Perhaps only one species absorbs strongly.

Molybdenum: The 66-hour half life of ^{99}Mo severely limited its usefulness. The K_d appears to be ≈ 23 ml/g.

Niobium: Equilibrium seems to be established in 3 weeks for sorption and somewhat longer periods for desorption. The K_d is 2700 ± 100.

Ruthenium: For sorption, the K_d appears to be 1040 ± 80 ml/g, and is attained in 2 weeks. As with I the K_d is much larger for desorption.

We are not interpreting the bentonite studies extensively in this report, since they are probably of limited interest to task 5. The mixing for the 2-gram samples may have been poor and the overall scatter of ratios is worse than for alluvium. The K_d's for Sr and Ba do not differ as much as for alluvium.

II. Selection of Materials

A field trip was conducted to NTS during the week of 12-16 September to gain first hand knowledge of the test-site geology with special reference to problems of radionuclide migration. In particular, we wished to examine and collect appropriate samples of genetic rock types upon which sorption experiments might be conducted. We feel the trip was fruitful both in giving us an overview of the structure of the test site and in providing us with the samples we sought.

Surface exposures of basalts, tuffs, and limestones appear fresh and quite suitable for our needs. Surface alluvium samples were collected from Jackass Flats, but the degree to which these samples are representative is difficult to assess. Drill core samples of alluvium may be needed. Material was also collected from the Climax stock (granite) and the Eleana formation (shale). Surface material from the Climax stock proved unrepresentative of the stock as a whole due to weathering. Therefore samples from the subsurface were also obtained. Surface samples from the Eleana formation are also unrepresentative, since only the silicified portions of the formation form outcrops. It will therefore be necessary to obtain drill core samples of the Eleana formation.

DISCUSSIONS--BRUCE R. ERDAL

Leachability and Sorption

Q. When you use waters obtained from leaching contaminated tuff are the retention factors really more related to leachability not really K_d?

A. Yes, its leachability and sorption, so you have two mechanisms at that point.

Q. Did you contact the same rock samples used in the adsorption experiments with "clean" groundwater to obtain the description values that you report?

A. Yes.

GUEST SPEAKERS

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"IMPLICATIONS OF OKLO TO WASTE STORAGE"

Guest Lecture by
Kenneth E. Apt
Los Alamos Scientific Laboratories
P.O. Box 1663
Los Alamos, New Mexico 87545

Dr. Apt presented information obtained over the last two years under the OWI-funded "Investigations of the Natural Fission reactor Program." The reader is referred to two progress reports:

1. "Investigations of the Natural Fission Reactor Program, October, 1976 - September, 1977," edited by K. E. Apt, LA-7032-PR, November, 1977.
2. "Investigations of the OKLO Natural Fission Reactor, July, 1976.

for more details on this program.

Other pertinent papers funded under this program include:

3. "Migration Paths for OKLO Reactor Products and Applications to the Problem of Geologic Storage of Nuclear Wastes," G. A. Cowan, LA-UR 77-2787 and IAEA-TC-119/31.
4. "Applications of Eh-pH Diagrams to Problems and Retention and/or Migration of Fissiongenic Elements at OKLO," D. G. Brookins, Department of Geology, University of New Mexico, IAEA-TC-119/33.
5. "Search for Other Natural Fission Reactors," K. E. Apt, J. P. Balagna, E. A. Bryant, G. A. Cowan, W. R. Daniels, R. J. Vidale, and D. G. Brookins, LA-UR-77-2796 and IAEA-TC-119/37.

All three of these papers were presented at the Technical Committee Meeting (Experts Group) on Natural Fission Reactors, International Atomic Energy Agency; December 19-21, 1977; Paris, France.

For more information on this program consult OWI Monthly Progress Reports Y/OWI/IN-3/1 to Y/OWI/INF-3/12, and Y/OWI/TM-43/1 to Current, or contact Ken Apt or George Cowan directly, FTS 843-4457 or commercial (505) 667-4457.

DISCUSSION -- K. E. APT

U Crystalization (Slides 1, 2, 3)

Q. Do you mean recrystalization or do you mean infiltration of new uranium into the field?

A. No new uranium has accreted on the old crystals. Similarly we know that the old crystals have not dissolved and then been recrystallized because we see this retention of the configuration on a centimeter scale and we see it also on a micron scale, so it has stuck together for 1800 million years.

Depth is Oxygen Buffer

Q. Would you say the depth was a natural buffer in oxygen fugacity?

A. Yes, the depth provided this buffer so that there was essentially no free oxygen and hence the U remained insoluble. Even if you keep U in solution that long, apparently there is no regrowth of crystallization on the surface of the old veins.

Four Reactors at Oklo

Q. Are you saying there were four separate reactor volumes at Oklo?

A. At least four; they originally thought there were six but, as they investigated, two grew together. They are 10-20 m in area and one m in thickness. All are of a comparable age, within a million years or so.

Reactor Uplift

Q. If the reactor occurred at a depth of three to four kilometers how long has it been up near the surface?

A. The uplift occurred within the last couple of million years. It's a fairly recent event. It seems that the only ore deposits being discovered are those that are being uplifted. Otherwise they would still be down there and we would not be able to find them.

Xe Loss

Q. Can you comment about the Xe isotopes in the Oklo grains? Is the loss more than you would predict from the fission recoil?

A. Yes. I think the simple interpretation is that Xe is not retained in the crystalline lattice of the UO_2. It can migrate out; its ionic potential considerably differs from that of Pu or U. It can diffuse out at a more rapid rate.

Circulating Groundwater

Q. Is it the circulating groundwater that made the ore fissionable in the first place?

A. We know that water must have been there at the time. Certainly water was the vehicle for the precipitation of primary and secondary ore. It was also, probably, a heat dissipating medium. Convection currents no doubt occurred around the reactors, again something like 25 kilowatts of power were produced there. Fluid inclusion indicates temperatures between 300° and 400° C. Since the critical point is 374° and 218 atmospheres we could have been very near the critical point of water. That would have meant that above that point it was a two-phase system, the solid ore then the fluid. The circulating fluid then would not only have moderated the reactor but cooled and controlled it, modifying expansion. If you were below that critical point you could have had bubble formation. The bubble formation would have been a more rapid control mechanism to slow the criticality of multiplication down. You would still have had circulation.

Situation Unique?

Q. Isn't this disposal quite unique since it would be so difficult to create such a low oxygen fugacity? Most rock types are nowhere near 10^{-69} atm. in oxygen. I'm thinking of any rock system which have Fe_2O_3. You require the presence of organic carbon in your systems to stabilize it. At these low values that requires an active carbon as well, so these are very special geological circumstances.

A. I don't think it's that hard to create a low oxygen fugacity. I think that's what's in existence at a km or two in most rock types. When rock deposits are two and four km deep do you still find higher oxygen fugacity?

French Provide Samples

Q. Do you take these samples yourself?

A. No, that's been one of the problems. We deal through the French Atomic Energy Commission. They're very helpful but nevertheless there's an ocean between us, a language, and a lot of other things too.

Russians Share Information

Q. Do they give these answers to the Russians, and so forth, too?

A. Yes, they've been quite cooperative in giving them to the Russians. The Russians haven't done much work on them however.

Criticality

Q. I see this; there are two aspects to Oklo. The geological historian is looking for precedence, at least hoping for verification that the concept is workable. However, the other side of the question is that the repository represents a great number of critical masses and under the right circumstance to go critical with the infiltration of water. There are rumors that such an explosion occurred in Russia.

A. I think the hypothesis has been suggested for that cryptic explosion that occurred in the Soviet Union some years back. Waste did accrete and form a critical mass. I don't believe that myself, though.

Poison Release Period Undetermined

Q. Did you infer from the problems of reactor poisons whether some of the fission products are removed during the time of the reactor or whether they are removed afterward? Is there anything you can infer about the exact timing of fission product mobilization.

A. I don't think so. There are so many parameters that could turn a reactor off--decreasing the water content, the decrease in ^{235}U content, and the buildup of reactor products, which are poisons. There could be the accretion of other poisons. If you had a perfect system that you could control and watch, then yes, but we are looking at the difference between big numbers and I don't think you could infer that it was the buildup of fission product poisons which stopped the reactor.

Reactor Cycles

Q. You don't mean to imply that one particular reactor source operated for awhile and then another one. The implication is that each is fluctuating, is it not?

A. The French have speculated that the reactors propagated themselves somewhat like "brushfires" once you got the critical mass going, as in the one distribution when the neutron flux went out quite a bit further than that region which was actually critical. Well the neutron flux would tend to burn out those poisons that might exist there, more so than it would burn ^{235}U, hence it would propogate itself off into larger regions. But yes, the zones probably did occur somewhat continuously--simultaneously--for 600,000 years. I think that's the implication.

Q. I wanted to make sure that the process was intermittent, randomly intermittent over half a million years, which complicates trying to deduce any fine structure in the movement of some of the fission products.

A. The simplist interpretation was that it was constant, and we're almost certain that this wasn't the case. There was no doubt cycling depending on water content and so on.

Reactor Temperatures

Q. Are there other indications of the temperatures attained other than fluid inclusions, say for example the mineral assembladge? I have done a lot of rock melting and that evidence is pretty shaky.

A. That criticism is valid. There are new techniques and mineral assembladge is one of them.

Q. What was the mobility of Pb?

A. Interestingly enough more than two-thirds of the Pb has escaped from the reactor system. It seems to be in the adjacent neighborhood outside but it did escape from the uranite grains and formed the sulfides found outside.

Q. Sorry, I guess I don't understand the mechanisms you envision for these things getting out. You said that 10% of the added fission products might have escaped by recoil and that the only other mechanisms, since the grains never recrystallized, are solid diffusion at 10^{-14} cm^2 per year. So how are you getting these fission products out of grains by which they are escaping from the pile?

A. Well, it appears that certain fission products and reactor products--the lanthanides and actinides primarily--were retained at those rates and were retained by their very low diffusion rates in the uraninite. This is aside from the mechanism of recoil when they were produced. Elements like iodine and Xe were not retained in the crystalline structure and came out much faster. We see that Cs for instance came out within its half life of 30 years and it migrated away from the very rich uraninite source.

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"TRACE ELEMENT SORPTIONS BY SEDIMENTS AND SOILS -- SITES AND PROCESSES"

Guest Lecture by

Dr. Everett Jenne
United States Geologic Survey
Water Resources Division
345 Middlefield Road, MS-21
Menlo Park, California 94205

Dr. Jenne presented a paper based on his publication "Trace Element Sorption by Sediments and Soils--Sites and Processes," published as Chapter 5 of a book Symposium on Molybdenum in the Environment: Vol. 2, edited by W. Chappel and K. Petersen. The publisher is Marcel Dekker, Inc. (New York, 1977, pages 425-553).

In this article Dr. Jenne presents a hypothesis that the most significant role of clay-size minerals in trace element sorption by soils and sediments and during trace element transport by fluvial systems is as a mechanical substrate for the precipitation and flocculation of organics and secondary minerals. A corollary is that the clays themselves are a relatively unimportant trace element sink. A rationale is presented for the occurrence of the various sinks on clay-mineral surfaces.

The second proposition is that any one of the number of trace element sinks may be a quantitatively important repository for certain elements or groups of elements in a given sediment, depending on the relative abundance and reactivity of the various sinks, distribution coefficients, and the depositional environment. Evidence is summarized that the important sinks are oxides of iron and manganese, organic matter, sulfides, and carbonates. Of lesser importance are the phosphates, iron salts, and the clay size aluminosilicate minerals themselves. The reactivities of the various sinks are interpreted in terms of their structural and surface properties. Various sinks are evaluated as to their nature and properties, as well as to their distribution in soils and sediments.

The moderators felt that these views would broaden the horizons of nuclear waste scientists who, in general, have been considering ion exchange as the most important sorption mechanism.

For further information the reader is encouraged to consult the complete paper or correspond directly with Dr. Jenne, (415) 323-8111, ext. 2143.

DISCUSSION--E.A. JENNE

Relevance of Near Surface Data

Q. I hope that in the discussions sometime during this week we will have the opportunity to discuss how relevant these phenomena, in soils and near surface waters and the like, are to those to be anticipated in the vicinity of the depository. I know that they are relevant at certain low level storage facilities on the surface and in SURF considerations and other things of that sort, but I'm wondering how far they can be extended into the regime with which we should be specifically concerned.

A. That's a very good point, and part of the reason that I prefaced my talk by saying that unfortunately I'm not accustomed to working at 4 km depth because you're not likely to have large quantities of the amorphic Fe oxides or the amorphic Mg oxides presumably at 4 km.

Implications For Burial of Waste

Q. Is there much known about the kinds of phenomena that you illustrated; about how that material decomposes with burial?

A. There is at least a small group of people who are very actively involved in that, and they write reaction sequences. I'd say relatively little is known of the rates of these things.

Q. I want to mention that, if we're looking at its potential hazards to man, eventually radionuclides will reach the surface and of course we really would have a hazard. Therefore, some of the near surface mechanisms that you discussed will be relevant in the final analysis.

A. Yes, as the radionuclides approach the biosphere the studies I refer to become quite valuable.

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"^{210}Pb GEOCHEMICAL STUDIES"

Guest Lecture by
Dr. Larry Benninger
Yale University
Deartment of Geology and Geophysics
New Haven, Connecticut 06520

Dr. Benninger presented material describing his studies on the mass balance and natural cycling of lead in the geosphere. Lead inputs from rainfall, natural geologic weathering, and man-caused pollution are compared with lead exports in surface and groundwaters to elucidate the fate of trace constituents in the geosphere such that a better understanding of element cycling may be obtained.

The experience and sampling designs worked out by Dr. Benninger and co-workers can offer insight for proposed nuclide migration field studies.

For further information the reader is encouraged to correspond directly with Dr. Benninger.

DISCUSSION -L. BENNINGER

Problems in Measuring Stable Pb

Q. I don't think it's been done in that Illinois work, but has anyone attempted to relate the stable Pb concentration to groundwater--the variability of stable Pb to ^{210}Pb concentration?

A. Our prejudice is that in most natural waters it is not analytically possible to measure stable Pb. Claire Patterson is the world's expert on attempting that, and it's definitely made his life very difficult. He has never succeeded in measuring what he considers to be an accurate concentration of Pb in seawater, and I think the situation is not much better for fresh water. It is very difficult to collect an uncontaminated sample to test for Pb.

Significant Residence Time For Some ^{210}Pb

Q. Isn't ^{210}Pb just an equilibrium constant from decay--from ^{226}Ra and Rn--and the sorption coefficient of lead onto the material in the groundwater?

A. I think it depends on how you look at equilibrium. If you think you know that there is a finite population of sites which are good sites for the sorption of Pb, then you can say you have an equilibrium situation. However, you never have equilibrium unless you think there is a very specialized site. If you want to make the mean residence time calculation then you get numbers between zero and 17 years. Based on those data and leaving ^{222}Rn out of it, the count probably causes you to overestimate the residence time in some of those cases. Nevertheless, that water has been down there for a long time. When you take a sample and you find soluble ^{210}Pb, it sugggests that there is a significant residence time. And if that concentration is maintained at steady state, then it is capable of moving away. This defies our prejudice with respect to

^{210}Pb, because we suppose that it's going to go out on particles very rapidly, and there is a fraction of it which is not doing that.

Organic Matter Complexes

Q. What about organic matter complexes?

A. I don't know of many strong complexes for lead, whether in groundwater you'd expect that.

Sub-micron-size Particles

Q. Is it possible that those water samples contain sub-micron-size particles which have sorbed the ^{210}Pb?

A. Yes, it is possible, but it has to do with how you define "soluble." If you can pump fine particles out of a well; then they can move through the groundwater regime naturally. From that point of view it doesn't matter.

Silt Factor in River Systems

Q. Don't your results (that all but a miniscule amount of lead is transport on particulate matter) depend to some extent on the fact that both of the river systems you have used have a fairly heavy silt load?

A. That's not true for the Connecticut, which has a very low suspended solid concentration. The Susquehanna is somewhat higher. They're both puny in comparison to rivers like the Mississippi. We don't have anything in a really dilute system, but the average concentration of suspended solids in the Connecticut River is on the order of 20 mg/ℓ.

Q. Doesn't most of the Pb get swept up by whatever silt there is?

A. It gets swept up by something. I'm not convinced that it doesn't have something to do with reactions in the river, because if it was going to be just particles, there shouldn't be any in the groundwater.

Pb More Serious Pollutant than Pu

Q. At one point in the discussion you implied the relative seriousness between deep geologic mobility of Pb and Pu. I guess then in societal terms Pu is immediately looked upon as a terrible problem. But if you look at the history of man, perhaps one of the most harmful elements is Pb consumed in water from Roman viaducts, with lead pipes. So Pb is a serious pollutant. As a relative societal hazard I think Pb has had a far greater effect than Pu.

A. Yes, that's right.

INFORMAL PARTICIPANT PRESENTATIONS

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INTRODUCTION

In addition to Task 4 presentations by subcontractors and guest lecturers, several scientists working on related programs--both under OWI's auspices and independently--were invited to the information meeting. To put the ongoing work into perspective, representatives of the programs were asked to present a short information discussion of the objectives of their work and progress to date which related to nuclide transport data. A brief synopsis of each talk follows:

WIPP (WASTE ISOLATION PILOT PLANT) PROGRAM

Bob Dosch
Sandia National Laboratories

The purpose of the Waste Isolation Pilot Plant (WIPP) is to demonstrate the safety of disposing of radioactive wastes in a bedded salt facility. The demonstration, in part, will be validated experimentally, both in the laboratory and in situ (underground) at the WIPP. The major focus of the pilot plant operation involves ERDA defense-related low- and intermediate-level transuranic (TRU) wastes. However, the scope of the WIPP project also specifically includes experimentation using commercially generated high-level wastes (HLW) and spent unreprocessed fuel elements.

Some WIPP/HLW experiments are currently being conducted, and others are planned in an interrelated laboratory bench-scale and in situ program. Laboratory testing is performed under controlled conditions, within a small physical scale; its useful results can be obtained in a cost-effective manner. In situ testing may be necessary to validate laboratory results where combinations of actual disposal conditions cannot be adequately simulated in the lab. These conditions include large thermal fields, large radiation fluxes from the waste in combination with the lithostatic pressure (180 atm), and a potentially corrosive salt mine environment. In situ testing is necessary to adequately demonstrate, in a specific geologic facility, that HLW can be safely isolated from the biosphere. Bench-scale experiments in large salt blocks will provide a bridge between the laboratory and in situ experimental programs.

Laboratory experiments in progress include radionuclide migration, sorption, and distribution coefficient measurements in brine and rock samples from southeastern New Mexico; leaching tests on candidate HWL waste materials plus their chemical and physical interactions with bedded salt; and rock mechanics measurements on such properties of salt as plastic, thermal, and structural behavior. Current programs also include measurements of radiation-induced stored energy in WIPP salt; effects on the chemistry (oxidation-reduction behavior) of actinides in the interactive radiation-temperature-pressure-brine environment surrounding the wastes; and development of additional (secondary) long-term migration barriers (e.g., getters) for radionuclides. Bench-scale programs in progress include heated salt block measurements of thermal and structural response, brine migration toward a heat source, and corrosion testing of candidate materials for waste canisters, overpacks, and engineering and experimental equipment. The materials and metallurgy programs are of major importance for the spent unreprocessed fuel element part of the experimental program.

For more information the reader is encouraged to correspond with Bob Dosch and Martin Molecke (FTS 475-1565 and FTS-475-8816, respectively). Commercial numbers are (505)264-1565 and (505)264-8816 respectively.

NRC (NUCLEAR REGULATORY COMMISSION) PROGRAM

Dana Isherwood

Lawrence Livermore Laboratory

Dana Isherwood (LLL) presented an outline of a simple prototype one-dimensional model capable of predicting the travel times of radionuclides from a repository to the biosphere assuming a disruptive event has occurred and a given path length to the biosphere. Input data requirements include solid waste form leach rate, hydrologic values, and K_d values. The work is being performed for the Nuclear Regulatory

Commission whose role will be to independently judge the environmental and safety reports which DOE submits for each repository.

The reader is encouraged to correspond directly with Ms. Isherwood for more information.

STUDIES FOR GEOLOGIC STORAGE OF RADIOACTIVE WASTE IN THE SOUTHEAST

I. W. Marine and S. J. Fritz
Savannah River Laboratory

I. W. Marine and S. J. Fritz presented an outline of studies they are performing to evaluate the feasibility of storage of radioactive waste in the southeastern United States. They are concentrating on granites, metamorphic rocks, and argillaceous rocks in the Piedmont and Coastal Plain from Maryland to Mississippi. The studies fall into two categories: (1) those with the aim of ultimately designating a suitable site and host rock for initial-phase operations of a repository, and (2) those concerned with research applicable to storage in the rock types of interest irrespective of the specific location.

The initial studies on site designation are reviews of literature and existing knowledge by subcontractors for five subregions that cover the entire region. The aim of these studies is to designate favorable areas for field studies. Before requests for proposals for these literature studies are issued, the state geologist offices and other interested state offices are being contacted and informed. During April 1977, information meetings were arranged for Maryland, Virginia, North Carolina, South Carolina, and Georgia.

Research applicable to radioactive waste storage in the rock types of interest includes the following studies:

1. A parametric study of geologic and hydrologic performance characteristics required of a subsurface storage facility.
2. A documentation and evaluation of damage to mines, wells, and underground facilities caused by earthquakes.

3. A study of membrane phenomena in the ground.
4. A study of the applicability of methods of measuring in situ stress when a free rock surface is unavailable.
5. A study of fracture closure with depth in crystalline rock.

The reader is encouraged to read OWI monthly reports Y/OWI/INF/3/1 to Y/OWI/INF-12 and Y/OWI/TM-43/1 to Current for summaries of progress and to correspond directly with the speakers.

AN INVESTIGATION OF THE UTILITY OF GULF COAST SALT DOMES FOR THE STORAGE AND/OR DISPOSAL OF RADIOACTIVE WASTES

R. E. Ferrell, Jr.
Louisiana State University

R. E. Ferrell, Jr., outlined the major components and studies of interest to nuclide migration include geochemical and geohydrologic studies of groundwater and strata present in domed salt environs. Salt samples are being analyzed for sodium, potassium, calcium, magnesium, and strontium. Anions will be measured also.

The reader is encouraged to consult the OWI monthly reports cited previously for summaries of progress, and to correspond directly with LSU investigators J. D. Martinez, R. L. Thoms, and R. E. Ferrell, Jr.

GEOCHEMICAL INTERACTIONS AND CHARACTERIZATIONS

D. B. Stewart
U. S. Geological Survey - Reston

D. B. Stewart described the OWI-sponsored technical support study "P-1 Physical Chemistry of Salt and Brine."

The amount and physical properties of brine that can occur in salt repositories at elevated temperatures and pressures adjacent to waste-bearing canisters will have considerable impact on the mechanical strength and stability of the repository. Brine will form readily from water absorbed on surfaces; diffusion along grain boundaries; movement of fluid inclusions; dehydration of hydrous minerals such as gypsum, polyhalite or clays; or even from leakage through failed shaft openings.

The temperature-pressure diagram for NaCl-H_2O describes the limits for coexisting solid-liquid-gas assemblages in salt repositories. Isobaric temperature-composition diagrams show compositional details at pressures below the critical point and above it. Properties of the fluid phases such as volume, density, heat capacity, enthalpy, viscosity, surface tension, osmotic coefficients, etc., can be well described ($>0.1\%$ - $<2\%$) from available data.

Addition of other components causes changes in the solid-liquid-vapor relationships. However, equilibrium is attained rapidly, large freezing point depressions occur, and the boundary of the liquid field shifts markedly. USGS is determining this shift for NaCl-$CaSO_4$-H_2O and for the system NaCl-KCl-$MgCl_2$-$CaSO_4$-H_2O that is in equilibrium with solid NaCl and $CaSO_4$ (or intervening compounds). All of the physical properties of the ensuing bulk brines will be measured, or deduced from a corresponding state argument and properties of the system NaCl-H_2O.

Because aggregates of solids are mechanically weakened by interstitial liquid, determination of mechanical properties of brine-bearing aggregates is needed. A maximum of one-third by weight of brine (not water), and probably much less, will destroy rock strength. Hence, physical chemical data will set limits to permissible water access at specified temperatures, assist in the design of critical measurements of mechanical strength, and will enable the volume and other properties of brines generated by the access of water to be determined.

The reader is encouraged to consult the previously cited OWI monthly reports for summaries of progress and to correspond directly with Dr. Stewart.

SHALLOW LAND BURIAL STUDIES

W. W. Wood

U. S. Geological Survey - Reston

This program, jointly sponsored by EPA, is looking at the migration of nuclides from burial trenches at facilities such as Maxey Flats, Ky., and West Valley, N. Y.

W. Wood described a field study being performed in which USGS is obtaining leachates from commercial shallow-land burial grounds and characterizing the leachate chemistry and migration of nuclides. The importance of thorough characterization and proper sample handling procedures was stressed. For complicated leachates, such as present in shallow-land nuclear burial sites, the use of actual, as opposed to synthetic, leachates is important.

The reader is encouraged to correspond directly with Dr. Wood.

NEAR FIELD WASTE/ROCK INTERACTION

D. M. Roy

Pennsylvania State University

D. M. Roy described several studies being performed for OWI under technical support, including "Chemical Reactions with Repository Rock/Waste" which has the objectives of assessing contact metamorphism of waste with host rock during the thermal period of waste storage.

The high-level wastes (HLW's) to be placed underground in rock formations, will contain significant amounts of radioactive decay heat for the first hundred-or-so years of isolation. Several physical-chemical changes analogous to natural geochemical processes can occur during this "thermal period." The waste canister can act as a heat source and cause changes in the mineralogy and properties of the surrounding rocks. Geochemically, this is "contact metamorphism". In the event that the canister is corroded and breached, chemical reactions can occur between the HLW, the surrounding rock, and possibly the remains of the canister. In a dry repository which has not been backfilled (and thus pressurized), these interactions could be slow at best with rates decreasing rapidly as the HLW cools. However, significant interactions can occur in years, months, or even days under hydrothermal conditions. These conditions could be created by the combination of HLW heat, overburden pressure, and water mobilized from the rocks or derived from groundwater intrusion. At the end of the thermal period these interaction products would constitute the actual HLW form (or "source term") subject to the low temperature leaching and migration processes under investigation in other laboratories. It is quite possible that these interaction product waste forms will have superior properties compared to the original HLW.

Experimental programs initiated at Penn State during the last year aim at determining the nature of any chemical or mineralogical changes in, or interactions between, HLW solids and host rocks under various repository ambients. Studies with basalts as the repository rock are supported by Rockwell Hanford Operations and with shales by the Office of Waste Isolation.

A second study investigates the sorption and fixation of cesium by shale. Large cations such as Cs^+ are preferentially sorbed and partially fixed by fine-grained 2:1-type layer silicates such as micas, vermiculites, smectites, and various mixed-layer minerals. Since these minerals are common constituents of many shale formations, the formations may provide suitable location for the burial of radioactive waste containers. However, the usual investigations of cation sorption and fixation must be extended to the conditions likely to develop in the vicinity of buried radioactive waste.

Prior to possible leakage from buried containers, elevated temperatures around the burial site will develop, leading to hydrothermal modification of the surrounding mineralogy. A range of temperature and of mineralogy must be envisaged. If and when there is leakage, an outward diffusion of radioactive ions will occur by solvation in the fluids in the shale. The ratio of radioactive ions/normal ions will diminish outwards from the source. At near distances from the source, high temperature modifications of the clay minerals and high concentrations of radioactive cations may lead to saturation of the fixation capacity. At greater distances, little or no thermal modification of the clay minerals and lower concentrations of ions will permit maximum sorption and fixation.

The reader is encouraged to consult the previously cited OWI monthly reports for summaries of progress and to correspond directly with Pennsylvania State University personnel Drs. Della Roy, G. W. Brindly, J. V. Biggers, G. J. McCarthy, W. B. White, S. Komarneni, and B. Sheetz, for more information.

ORNL ECOLOGY STUDIES

E. A. Bondietti
Oak Ridge National Laboratory

Dr. Bondietti reported on some of the plutonium-organic complex and plutonium-geologic material sorption studies which show Pu sorption is very sensitive to the valence state present in the system. The work is supported by DOE-Division of Biomedical and Environmental Research.

Speciation of transuranium elements in the environment was discussed with particular emphasis on Pu. The thermodynamic approach to evaluating Pu speciation was reviewed, and examples presented to exemplify the complexities of Pu chemistry in aqueous solutions. An example of the actual evaluation of Pu oxidation states in natural water was presented. The results, which indicated that Pu(III) and/or Pu(IV) dominated the soluble Pu fraction, were compared to a simple model involving the hydrolytic species of Pu(IV). Literature data were also evaluated with respect to the Pu(IV) model. In all cases, the soluble concentrations of Pu in natural waters were in reasonable agreement with the model. Dissolution studies with PuO_2 were reviewed and data presented to demonstrate that oxidized Pu, (Pu(V), and/or Pu(VI) species may be responsible for the relatively high Pu concentrations reported. The mechanism of oxidation appeared to be related to radiolytic effects.

The reactions of Pu with selected organic substances found in the environment were studied to evaluate the valence and metal-complex behavior of Pu. Hexavalent Pu (and, by inference, pentavalent Pu) was unstable in the presence of fulvic acid, polygalacturonic acid, and alginic acid. Citrate-Pu(VI) complexes, however, were relatively more stable. Plutonium (IV) was the most stable valence upon interaction with these organics. Further reduction of PU(IV) to PU(III) occurred by fulvic and humic acids. The reduction, under aerobic conditions, does not appear to occur above pH 3.1 and the mechanism is probably similar to the FE(III) reduction previously documented for phenolic humic substances.

Data were presented that demonstrate that Pu is at least partially associated with humic materials in ORNL soil contaiminated 30 years ago with trace levels of Pu. Desorption studies using solid exchange resins also showed that, while a cation exchange resin did not desorb Pu from soil after 14 weeks equilibration, chelating resin effected Pu desorption. The desorption rate was not constant, suggesting differential Pu forms. While the resin-extractable Pu was believed to originate from solid-phase organic complexes, over 80 percent of the Pu in this soil was not readily resin-desorbable. This indicates that more inert soil-Pu reaction products effectively immobilize soil Pu. Some of these associations also appear to be organic.

Details may be found in the following articles:

1. Bondietti, E. A. 1974. Adsorption of Pu(IV) and Th(IV) by Soil Colloids. Agronomy Abstracts.
2. Bondietti, E. A., S. A. Reynolds, and M. H. Shanks. 1976. Interaction of Plutonium with Complexing Substances in Soils and Natural Waters. IAEA-SM-199/51.
3. Bondietti, E. A. and S. A. Reynolds. 1977. Field and Laboratory Observations on Plutonium Oxidation States. BNWL-2117, pp. 505-533.
4. Bondietti, E. A. and F. J. Sweeton. 1977. Transuranic Speciation in the Environment. In: Proc., Symposium on Transuranics in Terrestrial and Aquatic Environments, M. G. White and P. B. Dunaway; eds., NVO 178.

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WISAP--OPEN FLOOR DISCUSSION

From Thursday afternoon through Friday (September 22-23) participants met in unstructured open discussion. The following is a distillation of the salient points and concerns aired by the attendees, none of whom are directly identified in this summarization. Subject matter has been arbitrarily categorized under the six subtasks that constitute Task 4, Nuclide Transport Data. (See R. J. Serne's overview introducing this report.)

SUBTASK 1: EVALUATION OF EXPERIMENTAL SORPTION/DESORPTION METHODOLOGY

One participant noted a weakness in the collection of experimental data. Typically, nuclide sorption is measured only in the adsorption direction. In leaching experiments, however, he has found that Plutonium resists desorption--Pu is reacting with the minerals and is not exchangeable. Such irreversible sorption should be identified, so that overly-conservative assumptions that sorption is readily reversible may be revised in future safety assessments.

In a discussion of the advantages and disadvantages of batch-versus-column K_d experiments, the time required for measurement was described by one researcher as extremely lengthly. In his case, he reported, three months have been spent on batch experiments that have only "scratched the surface." The process is described as weighing out samples, washing samples with groundwater, adding a hot solution, shaking, centrifuging, taking off the solution and measuring (for pH, Eh), counting it, and putting it back. If a time study is required, this must be repeated two or three times.

When column experimentation was suggested as a speedier alternative to get comparable data, it was countered that column experiments are only fast if distribution coefficients are low and the column can be made to "behave properly." On high-distribution coefficients (10 or beyond), such experimentation becomes tedious since enormous amounts of effluent must be collected before a breakthrough occurs. Sometimes it is preferrable, e.g., with Np and other lower-valence cations, to work on columns, because of difficulties in differentiating blanks from those that have small sorption.

Not infrequently, the sorption tubes are higher than the blanks because of an ion exclusion in some of the minerals. It was generally agreed that on low K_ds, column experiments are best, and batch experiments are preferred where high K_ds exist. In experiments with a "loaded" column (extremely high K_ds), when the tracer is put in and a solution passed through it, results can require long elution times. With a K_d of 10 to 10,000, it is probably desirable to do batch experiments. Between 10,000 and 1,000,000, this becomes difficult.

An attempt was made to jusge the merits of differing methodologies to eliminate those which were less acceptable, so that the scope of the WISAP experimental program could be narrowed in the hope of better satisfying difficult time constraints. However, a caution was raised on bringing the analysis down to one or two approaches and missing the "wealth of alternatives." OWI, before it was subdivided, used materials from deep geological (fresh) cores under rigidly-controlled conditions. To anyone's present knowledge, no one is doing this today, and it is considered a most unfortunate gap. The cost, however, was enormous; over $1/2 million per site to sample a core. Therefore, at present, none of the experimental methods will be dropped. Hopefully, data gathered in the fiscal year 1978 will allow the most promising methods to be identified, and future efforts will concentrate on these.

It became apparent during discussions that, in fiscal year 1977 methodology evaluations suffered from lack of standardization and inadequate direction on which geologic samples should be used in experimentation. The initial approach was to allow investigators to utilize samples which were convenient to obtain and varied in type, so that the program would show rapid results and provide a more generic data bank. After much discussion, it was concluded that some experimentation must be performed by all investigators using the same rock, to permit analysis of differences resulting from methodology, but that it is also necessary to have a variety of reference samples to broaden the data base of the study. Selection of a "suite" of samples would not prevent any laboratory from working with others, based on time and equipment available.

The questions remain of where suitable samples may be obtained in quantity and the financial outlay involved. Free donations, while helpful, may not provide the desired quality control.

There are now in existence some 25 geochemical standards of one kind or another. It is necessary to check with the USGS and talk with others who have produced standards, since high-quality material is in short supply. Canada probably produces the best available standards and has the most experience, but USGS, along with the French, Japanese, East Germans, and South Africans, are also producers. Commerical products exist which are not necessarily top quality, but have the homogeneity essential to this research.

Standardized solutions are also needed for experimental control. Argonne's technique of contacting rock with rock-equilibrated water is mentioned, but there is some question that a rock-equilibrated solution can be obtained contacting crushed rock and distilled water for a few weeks. Lack of characterization of the solution is also a problem with this method. Some expressed the need for more than a single solution for each rock to obtain distribution coefficients. However, a uniform solution can be modified, keeping other factors constant by varying one constituent up or down. This applies particularly to the case of the sodium ion to obtain data relevant to salt deposits.

A protocol must be developed for creating standard samples. This problem has been approached by every group preparing geochemical standards and it is not an easy exercise to crush a large amount (100 lbs. or more) to the acceptable size. Typically, standards produced are required to pass a 200-mesh seive. There is also the problem of adding a lot of iron into the sample during the grinding process.

Some questioned the need for such a high degree of homogeneity in terms of long-term safety assessment extrapolation. The opinion was expressed that any experiment measuring trace adsorption must have this degree of refinement in order to follow variations in trace element composition. Frequently a minor constituent may be doing most of the sorption.

Standardization is important and it is also essential to separate the natural range of findings from what might be called the "bias" of each experiment to find the true natural variation.

The granitic rocks found at many test sites indicate that early work with NBS Standard and G[1] Westerly Granite would be productive. A great deal of peripheral information already exists about the ranges and properties of these, since they have already been analyzed in laboratories around the world.

At Hanford, where research is underway on the feasibility of locating a repository cavern below the reservation, basalt samples are readily available. It was suggested that a large core sample be split by USGS or another agency for analysis by various labs, along with samples of basalt from the same region which are fairly homogeneous and can be provided in rock or powdered form to specification.

It was suggested that the group initially use relatively inexpensive generic samples and some "simple" system to check out experimental differences; a round-robin approach designed to identify any lab's "inherent bias." Then the analysis would go on to more realistic samples (the best homogenization or mixture obtainable) which would bring back some of the "confusion," yet not mask the point being sought, e.g. natural variation in K_ds, retardation, etc. Individuals could optionally utilize experimental designs on other materials available or convenient to cover as large an array of geologic materials as possible, but with improved characterization over the present system.

The final details of the controlled sample program were left to PNL and OWI to negotiate, based on time, money, and logistical constraints.

SUBTASK 2: DATA BANK GENERATION

The question is being asked, in a generic sense: "What are the risks; what are the retardation factors in a hypothetical environment?"

An essential first step in answering this is the creation of a generic data bank containing the inherent characteristics of selected geologic materials and the solutions with which they come in contact. These, along with their appropriate sorption coefficients (K_ds), tied into a common data base and statistically analyzed, will give modelers the data they need to carry out a risk assessment.

Within the existing two-year time frame there is a pressing need to consolidate isolated studies (the numbers generated) in a meaningful way for statistical interpolation on which to base predictive trends. This can be accomplished by utilizing a common "laundry list" of variables for measurement.

Laundry list characteristics of water composition would include such factors as major cations, anions, pH, Eh, plus, if possible, soluble organic content and some of the minor constituents. For geologic materials, characterization would include surface area and/or cation exchange capacity, the amount of minerals, and the organic content of the material. All are parameters that may have an effect on K_ds.

These parametric characterizations should make it possible to interpolate from one regime to another. While not conclusive, since statistics cannot show cause and effect and variation exists in sorption by the same rock at different sites, the resulting predictions would have more validity than any that can be made to date.

A conceptualization of the Generic Data Bank follows.

Generic Data Bank

Independent Variables

Geologic Material Properties

Mineralogy	Amount
Primary Minerals	%
Secondary Minerals	%
$CaCO_3$	%
Hydrous Oxides	%
Organic Content	%

Cation Exchange Capacity
Anion Exchange Capacity
Surface Area

Hydrologic Properties
  Hydraulic Conductivity
  Permeability
  Porosity
  Water Velocity
  Percentage Saturaton
  Porosity
  Water Velocity
  Percentage Saturation
  Fissure Surface-Area-to-Volume Ratio

Groundwater Properties

pH
Eh
Major Cations
Major Anions
Soluble Organic Composition
Soluble SiO_2
Soluble Minor Species
Temperature

Nuclide Properties

Tracer Concentration
Tracer Valence State Distribution
Equilibration Time

Dependent Variables

K_d Isotopes	Uncertainty Limits
a. Pu	
b. Np	
c. Am	
d. Tc	
e. I	
f. etc.	

It was observed that most of the determinations are routine petrographic descriptions with costs per sample tested in the $100-$150 range; not a great expenditure compared to funds spent on "other projects."

Until a site specific focus is possible, risk analysis must be made using generic tools. At the "bottom line" before construction begins, a great deal of site specific work will be required.

It is difficult to provide a single laundry list for the geologic world and it is acknowledged that, in setting measurement parameters, some effort may be wasted. However, if there is no physical basis for measuring a parameter, the results should not correlate with the trend predicted and, if the parameters are not measured, there is no way to formalize a statistical approach and develop predictive capability from the mass of data.

Many felt it is not essential to concentrate attention on the complete characterization of rocks except with certain types in which fixation and exchange may be important (Cs and Sr) and with Pu, Cm, and Np in their reduced state.

Obtaining samples of groundwaters that do not change before reaching the surface is a major problem, although a few well-characterized samples are available, e.g. WIPP salt brine.

The suggestion that plain distilled water be substituted for uniformity, was discarded because distilled water changes character when it comes in contact with rock. However, well water is valid because--while not in equilibrium--it has been down with the rock for a long time and cations which are easily measured, control the sorption of many of the nuclides being dealt with. In some instances, a minor constituent or anions may have an important effect, e.g. carbonates, but there are few cases in geologic waters where fluoride, etc., is high enough to make this a factor in characterization.

In regard to the composition of solutions, there are many factors not yet understood in experiments at the tracer level of radionuclides, underscoring the importance of the researcher comprehending exactly the project on which he is working. In addition, since the arbitrary variation of a solution constituency changes the character of the rock with which it comes in contact, Argonne's approach (shaking up water with rock to obtain a starting solution) is recommended if complete chemical characterization is performed at the time sorption experiments are performed.

Decisions must be made on how extensively to characterize solutions, whether to the point of determining every constituent or focusing on major constituents only. The consensus was that there will be variation in detail required, based upon individual situations.

While scientists can make up most standard solutions, if the experiment calls for adding radioactive elements such as Pu, the method must be highly refined since speciation is dependent on how this is done. Suggestions will be requested from participants in future correspondence regarding the concentrations of tracers to be used, the history of their purification, and how traces are to be added.

After more heated discussions on the pro's and con's of complete characterization, the moderator issued a decree that assimilation of data for statistical analysis will require a higher degree of characterization for both solids and liquids, in order to compare the K_ds generated by the group so far. The goal is to analyze the effect of a dependent variable (K_d) with many independent variables--the parameters on the "laundry list". It is acknowledged that some time may be wasted on characterizing certain materials, but having the numers is essential to understanding the system. Also, more inventiveness is urged in working out experimental techniques under anoxic conditions.

A protocol will be designed for water sample selection. If the repository of interest is salt dominated, the overlying and underlying geologic materials will be affected by salt brine. The aquifer expected to be present in equilibrium will not contain all the salt, but the disruptive event which moves material from one layer to another must be considered, so a range of possibilities will be covered for each situation.

A final point voiced on rock characterization suggested that rocks in general represent a series of mineral phases and these phases affect K_ds, rather than the overall rock chemistry. From a single chemistry, literally hundreds of rock-mineral compositions are possible, e.g. granite, in which the K_d is dominated by biotite or some other very small mineral, with feldspar and quartz making only minor contributions.

The moderator countered that, besides total chemical analysis, detailed mineralogic studies should be performed to identify minor constituents. As K_d experiments on isolated minerals are carried out, those which have a very high selectivity for nuclides will be identified. Rocks which commonly contain traces of these excellent sorbers will be characterized, specifically to determine the presence or absence of these minerals.

The correct method of measuring surface areas of geologic materials was discussed in detail, during which the adequacy of BET measurement was questioned, and use of glycerol or ethylene glycol was described as "still somewhat inadequate."

Measurement of surface area may be an important link since it may correlate with the distribution coefficient or retardation factor in hydraulic modeling. Of equal interest is sorption capacity (cation exchange capacity) as information relating to distribution coefficients. While agreeing that cation exchange is a principle mechanism in radionuclide sorption, researchers express concern about empiricism involved in "just taking sample rock and seeing how much it adsorbs." (It is pointed out that there is no more empiricism here than in BET measurement.)

Most see a need for further standardization of methodology to permit comparison of results. Soil and rock methodology, some indicate, may not correlate; because a method is used in soil analysis does not automatically make it useful on geologic materials. This is especially true for soils of secondary minerals versus rocks whose primary minerals resist weathering such as basalt and granite. A counter opinion was offered suggesting that the glycerol process is not just for soils but also for clay minerals that have been "cleaned up."

An improved method of utilizing aqueous solutions with their surface tensions and viscosity is needed. Recent studies using humidity (plain water) and other experiments with microporous substances (10/20 angstroms in diameter) have produced results similar to those using ethylene glycol. Problems exist, e.g. reaching the inner layer of montmorillonite with the glycerol technique, and montmorillonite--while not a major constituent--can be found in both "dirty" salts and granites. In summary, participant's experience indicates, despite some problems, the ethylene glycol or a "wet" method is best for characterizing surface area, since BET does not relate physically to anything meaningful in sorption studies using aqueous solutions. Also, since some small particles may dominate in sorption, particle size distributions are important in controlling cation exchange capacity, whether looking at clays or ground-up rock. A standardized mesh range should be used for comparison of surface areas of different materials.

A dilemma exists in finding a new name for what has been called the "K_d." On one hand, extensive use of the term has been made in the literature over the past 30 years. However, there is growing confusion on the part of many scientists who regard the term as a constant instead of the variable it represents (except in certain solvent extraction situations).

Among the alternatives suggested are: "sorption ratio," "selectivity quotient," "sorption quotient," "specific retention," or simply "distribution coefficient."

The opinion is voiced that, while it is doubtful the scientific community will drop the use of K_d after all this time, some alternative should be found. It was decided to seek feedback from the group; then permit the coordinator to arbitrarily impose some "simple designation" that, hopefully, will not duplicate any scientific symbol already in use.

SUBTASK 3: DATA BANK SYNTHESIS

Concern and much discussion centered on the interpretation of breakthrough curves observed in experiments, as opposed to the symmetrical or chomatographic curves predicted by current models.

A 1973 month-long experiment was described by a modeler using two forms of Pu in which one moved slowly and the other much faster (10 to 100 times faster). The investigator has spent the last several years studying the migration of Pu and Am in large blocks of tuff (several cubic feet) with the same effect(s) noted--the bulk of activity at the surface and a small peak at the end of the flow path with both tails varying asmmetrically. The experimenter, who does not believe the results are due to cracks or colloids, indicated he sees the same results for everything with a K_d of 10 or over, but acknowledged this might not be important in terms of migration. Therefore, calculations assuming each element has a velocity or K_d is not valid.

The feeling was expressed that such experiments must extend over a much longer period for anything to come out the bottom of the column and that the slicing technique described was comparatively "rough."

Among other observations, the modeler called special attention to the asymmetric effect of nuclide distribution in columns, illustrated by a slide of strongly bound Cs which did not move but also produced a small percentage of activity through the column. Questioned if this might be due to crude slicing and sluffing off of the material, the speaker pointed out that two techniques were used for chalks and shales and yielded similar results. The modeler feels that current simple chromatographic models don't adequately predict a complex system.

It was countered that what is really being seen is different sites with differing specific adsorption tenacities--the first adsorption at the "best sites" and faster movement when these sites are saturated. The modeler replied, with that kind of site dispersion there will always be self-sharpening fronts that tend to reduce spread because the leading edge of any concentration wave is going to have the lowest concentration and is going to be adsorbed by "best sites." Followed to its logical conclusion, he pointed out, the leading edge (lowest concentration) will be taken up on solid sites with the highest specivity for that ion, and what is observed is self-sharpening on the leading edge and broadening on the trailing edge.

An experimentor described column experiments with Sr and sandy materials (in which the K_d for the Sr was 15), using constant input that showed a tailing effect. When eluting the column, the curve produced was a mirror image of the adsorption curve, indicating that the adsorption isotherm is linear. The effect is physical, rather than a non-linearity in the isotherm, and can be explained on the basis of diffusion and the inaccessability of certain pore spaces. The same results have been observed in a number of fields (a paper published within the past year, based on pesticide data shows exactly the same trend by putting in a first-order reaction term. This does not indicate that the adsorption was a first-order type reaction, but that there is probably some first-order effect--possibly diffusion into inaccessable pores. In the case of a fractured medium it could represent diffusion of the solute into pore spaces within the solid matrix, followed by diffusion back out again and convection through the fracture causing complex velocity patterns or "tailing."

Concerns were also voiced over whether these phenomena are dependent on the direction of flow. From a purely chemical standpoint, whether the flow is vertical or horizontal is not a critical factor. When a column is run and the intermix begins between chemistry and water transport, subtle differences will probably be noted, but hopefully these can be referred to hydrologists or hydrodynamicists for further study.

Some participants questioned the accuracy of the model, and it was explained that the WISAP modeling system treats a chain of radionuclides, allowing each nuclide to have more than one species with its own migration properties. It further allows a chemical reaction of species as they migrate, e.g. starting out with a Pu(IV) and changing to Pu(VI). In this non-equilibrated situation, the thermodynamic force will convert one species to the other. The chemical reaction can be modeled and a curve predicted with one peak coming out of the second curve, possibly showing chemical interchange between the two species. At some point a "smear" will occur. With rate control adsorption it skews in front of the peak and with rate control desorption it skews in back. This model holds true for all of the radionuclides, not just Pu, but the question remains whether the model is adaptable to the concept of the safety assessment program.

A participant asked if, under a given set of circumstances, there would be three K_d values needed to described this effect and was answered in the affirmative. A comment was offered that one number cannot be used to describe a given set of material and solutions, and this might also explain why variations are found between labs since they are working with different forms of radionuclide.

Another participant pointed out that he felt two issues were being confused. If the model proposed is correct, it must be assumed either that there is a non-linearity in the isotherms (so that as it becomes more dilute the adsorability changes) or that it's non-equilibrium. However, he added, if his understanding of chromotography is accurate, when there are a great many sites there will be very different adsorbabilities. Tracer movement at equilibrium with a linear sorption isotherm should result in bell-shaped curves. He asserted that the explanation given cannot be correct without non-linearity of the isotherm or a kinetic problem. (In the latter, he would include channeling through gaps rather than channeling described as "hopping from one particle to another.")

A second comment indicated that, in a complicated system, there might also be certain fine particles moving out of the flow channel (e.g. montmorillonite or another tiny adsorbing particle) without presenting microscopic channeling, leaching, or a break in the column. He added that this has been a long-term problem for chromotographers.

The point was made that the modelers are not in the business of "making perfect columns," but of describing a geologic system and, if the geologic system "is an imperfect column," that is what needs to be described.

While there was general agreement with this point, it was further argued that, in dealing with the kind of idealized model being proposed, there must either be added to it a non-linearity in the isotherm or something else.

In conclusion it was pointed out that the modelers will watch what individual researchers are doing closely in the future in order to make assessments as to whether certain complexities identified by various labs might be important but, because of various constraints (financial, personnel, time, etc.) within the program, a simplified model will continue to be used. There is a kind of "optimazation" that has to be gone through in planning what is to be modeled so--at least in the short run--modelers may produce something that will be less-than-acceptable to everyone involved, and this must be recognized.

A numerical model exists for radionuclide transport (attributed later in the discussion to George Pinder, Princeton) that takes into consideration the kinetic sorption properties of materials in contact with fluids. The model balances the rate of sorption and desorption against the carrier rate or fluid flow so that there are combinations of the two rates that can produce irreversible sorption at one extreme, and virtually reversible at the other.

A strong second was voiced on the importance of kinetics by a participant who believes that, however measurements are done, the point is not the time required to reach equilibrium but the rate at which equilibrium is attained. At a conference several weeks earlier, he pointed out, the primary question was "What is the rate?" Long-term rates are needed, but emphasis should be on the rate of approach. A serious gap is created if this is not part of the data collected.

Discussions turned to the subject of interaction with hydrologists and the coupling of the chemistry to the hydrodynamics of the repository environs. The coordinator observed that the creation of the most probable scenarios and the evaluation of their consequences is the goal of WISAP within the broader scope of the safety assessment program. In discussing preferred sites, short of being site specific, everyone should have a general picture of the kind of repository and the materials likely to be involved with any of them. Among these are the Columbia River basalts, the Climax stick granite and Eleana shale of the Nevada Test Site, bedded salts in several locations, cap rock from salt domes in Louisiana, and possibly some pre-Cambrian material from Minnesota.

The extent of exposure to water is also an important parameter, e.g. whether accident or "earthquake" conditions should be taken into account with the corresponding large amount of water injected rapidly into a repository; as well as the more common situation in which very small quantities of water will be going in at a very slow rate. In establishing priorities for scenarios dealing with the intrusion of water, for whatever reasons, it was agreed that conditions must be precisely defined so that everyone will be working with the same system. At the same time, it was stressed that modeling assumptions must be broad enough in scope to have the potential of covering other similar cases if questions are raised about them.

It was pointed out that there is no intention of putting waste into sites where flowing water at any appreciable velocity or volume is present. Therefore, in dealing with hypothetical situations there will be a residual uncertainty about the direction from which any existing water will come, its velocity, and in what direction it will go. Regardless of how deeply the problem is pursued, it cannot be addressed in a completely scientific manner.

The response was that, by the same token, Task 4 can set limitations when experimentation is underway. The most probable scenario must be examined without absolute understanding of flow rates and compositions in the hope that the findings will be relevant to the total assessment program. Even though everyone may not be completely comfortable with the results, the statistical interpolative approach and sensitivity analysis will be helpful. It would not be productive to group scenarios too closely into a narrow range, but to allow some spread that will provide the basis for interpolation.

In terms of creating a "realistic fluid" flow for a risk prediction scenario, an average taken from the literature shows a range of .016 to 16 km per year according to Meinzer and Wenzel, Hydrology, Dover Publications, 1942. A typical velocity at the WIPP site is .01 feet per day, but this varies with the stratigraphy. Some estimates are as low as a few kms in a million years. NTS reports a 2 to 200 m range per year. (It was pointed out that the primary concern is with flows for accident scenarios, and that the OWI philosophy has been changed in regard to the granites. Because granite is usually associated with water, any repository put in granite will be subject to water seepage and some finite flow would be involved.

A participant suggested that diffusion must be considered to determine whether this is the controlling mechanism in the transport equation where K_ds are used. There has been work reported in which, when diffusion rates were identified for water, it was found that the diffusion rate for the sorbing material essentially is reduced by the same retardation factor used for nuclide advection.

One Ph.D. thesis surveyed diffusion coefficient literature and reports 10^{-11}, 10^{-12} cm^2 per second for elements with K_ds in the order of 10^3 to 10^4. The investigator indicated he could in fact predict the diffusion coefficient better with the K_ds and the water content porosity in this way than by measuring them with experimental procedures.

Some scientists questioned the value of laboratory measurements versus field studies because the real interest in risk assessment lies in dispersivity through fractures rather than through homogeneous materials. While the laboratory numbers are the ones that are used in risk analysis, it won't be known for years if the model developed is really capable of predicting what is going to happen. With a small laboratory column the researcher is looking at intergranular velocity variations. On a larger scale, some degree of heterogeniety is introduced and the heterogeniety "takes over" in the mixing. On going to the field scale, presumably dispersivity is on the order of kms because of the scale of heterogeniety is on the order of kms. There is some question about whether to call it the "scale of heterogeniety" or dispersion.

Another subject for debate was whether to go out into the field to measure dispersivity or to attempt to determine velocity distributions "very carefully." It was generally felt that if velocity distributions are known with extreme accuracy, dispersivities will all be extremely insignificant. Mixing will be accounted for by velocity distribution of the fluid (groundwater).

The opinion was also expressed that understanding dispersivity, does not take care of channeling. Also in cases in which flow is rapid, kinetic effects are very important in predicting nuclide sorption. Where flow goes very slowly through other paths, kinetic effects are not important.

It was argued that, in a heterogenous system which contains, for example, a six-inch layer of gravel intermixed with vast layers of firmer glacial soil, the water will go through the gravel. Therefore, it is not the K_d in the till but the K_d in the gravel that matters, posing a real sampling problem.

A participant asked whether, when a site-specific case is taken, there would be an effort to measure dispersivities of the appropriate formations, because at the present time there are only about three or four values in the literature for dispersivity and they vary by orders of magnitude. Since little is known about dispersivity, he also questions the value of "putting a lot of effort" into K_d determination. The group acknowledge that the problem is a very real one, but that there are other factions working on it.

An opinion advanced was that increased dispersion is not necessarily bad because it has the effect of spreading the activity out over many cubic miles of material and lowering the concentration--a healthy factor. In doing calculations for a recent project, the participant said, about half the reduction in the activity level at the boundary with the biosphere was caused by major disperison, with the other half due to decay. A critical point is whether the spread is faster than the decay which, in turn, depends on path lengths and half lives. (In this situation it helped rather than hindered. In others, potential damage would be great because nuclide spread will be much further.)

In summary, it was agreed that the chemists should continue a close liaison with hydrologists and disruptive-event predictors to ensure that sorption-desorption work is compatible. Essential to the meaningful use of models in the safety assessment, will be the ability to relate a range of measurements to a corresponding set of models covering that range, to check for sensitivity.

SUBTASK 4: VALIDATION STUDIES

Subtask 4 (of Task 4), "Validation Studies," enters the realm of long-term extrapolation, drawing on thermodynamics, knowledge of weathering, natural observation, and historical events (such as Oklo, etc.) in the search for data to verify short-term laboratory measurements.

In recognizing that changes in water composition produce corresponding changes in minerals, one approach is to hypothesize a certain type of water going into a system, run some K_ds through the material, and utilize thermodynamics and mineral stability diagrams to predict whether the rock should weather to another form. The procedure is to identify a final product through contacting a rock with the groundwater. If higher K_ds are found for the weathered materials the situation is relatively stable; if K_ds are lower, there is probably going to be some movement. This is one way of compensating for the long-term change in solid materials.

In response to the issue of whether rock materials would be considered as weathering in the presence or absence of air, the reply was that the scenario would dictate that consideration, but the most likely situation would be in the absence of oxygen. One scenario, however, must certainly involve material that is lifted to the surface or near surface, and some systematic and objective manner of determining what kind of experiments to run for this contingency is required.

It was advanced that weathering (metasomaticism) in rocks is an extremely complex field and somewhat beyond the scope of the immediate study, but the group should look closely at what research has been done in order to make the soundest educated guesses.

Moving from generic to site-specific analysis requires the selection of a basic set of materials that are highly comparable (so the numbers generated will show some agreement) and of immediate significance in respository selection.

For long-term extrapolation of waste isolation risk, it suggested, the flow over thousands of years becomes a decisive factor as, for example, in the infiltration of limestone with magnesium-rich water. The composition of the rock does not remain the same year after year. However, it was countered, with much of the rock under discussion (aquatards), the transport rate is so slow that a predictable weathering sequence will occur.

A question was raised about restoring equilibrium in the case in which Pu is put on a repository in the reduced state Pu(III) or Pu(IV), but mobilizes as a Pu(VI). The equilibrium relationships would create more Pu(VI) to replace that mobilized until eventually all Pu was changed to Pu(VI).

This raised the further question of whether time is being wasted arguing about the stability of Pu(IV) because over geological time it is known that plus six is relatively mobile and, given a chance, it will be removed. The kinetics of Pu(IV) oxidizing to Pu(VI) at environmental pHs and tracer concentrations are not known. Also, as long as the repository remained in a reduced state this trend should be minimized.

Knowledge of the short-range hydrological conditions surrounding a repository site is important, but there is a definite limit to the number of bore holes desirable and this remains a serious constraint on risk assessment field studies.

Since it is not established how sophisticated the group may be in its understanding of geologic time frames and weathering, certain ideas may be introduced in the program geared to locating some authority who is able to "pick up the ball" and produce answers that will prove satisfactory both to the scientific community and the general public. Because of time constraints and the pressing need for long-term solutions, the task at hand might be compared to conducting an "accelerated time test" such as is done to measure durability of certain commercial products. The utilization of crushed rock is akin to running an accelerated time test in certain aspects. Grinding creates much greater surface areas upon which sorption can occur and should speed up the approach to equilibrium.

A question was raised regarding public concern about possible bacterial effects over the long-term in waste repository locations. In a deep sub-surface environment, can bacterial effects occur in an organic complex or is this a problem that may be eliminated from consideration?

WIPP has indicated that you cannot dismiss the problem out of hand and that part of the acceptance program will be to retain biologists delegated to investigate whether bacteria growth is possible at the depths under discussion and in the absence of air (anaerobic bacteria). Since WIPP has different restraints than OWI on acceptance criteria, OWI is at present taking the position of non-acceptance of any organic material to be buried in a repository.

It was pointed out that while there is the possiblity of traces of organic material (shales, etc.) and inorganic chemical decomposition of organic materials to be considered, there is still some question in terms of whether viable organisms can exist in the deep repository environment.

A philosophical point was raised by one geologist who indicated he feels "fairly comfortable" about the ability to predict what is going to happen as far as nature is concerned but "very uncomfortable" predicting what will happen to this system when man interjects one of his facilities (storing wastes, bringing in bacteria, etc.) as operations begin. He feels that man-induced changes, which may be of a much shorter duration than geologic changes, are far less predictable.

There was general agreement on this point but it was also observed that the question being raised is a "near field" problem and responsibilities delegated to this group (WISAP) are "far field" in nature. The opinion was also advanced that if you study the effects on the total path length back to the biosphere the warp caused by the repository is small. At Hanford, for shallow land burial, the approach is to work "backward" beginning with the problem starting at the Columbia River (akin to the biosphere) and working toward the storage tanks that have 11 and 12 molar sodium hydroxide solutions. Research is extended to the saturated aquifer near the river and back through the 200 feet of unsaturated soil closer to the tank. For calculations, the "worst case no-man's land" situation is used, e.g. a segment around the tank prior to dilution with groundwater ID given zero retardation capbilities. Using this assumption, conservative results are obtained which are acceptable under safety assessment standards.

A question was raised about the source of water entering the repository, and whether humic acid or other material of this type coming in with groundwater will effect retardation of nuclides by forming soluble complexes. The response was that if there is cause for concern such as for certain type of rock (e.g., shale) the problem would be looked at more carefully.

A further comment was offered on the "biology problem," pointing out that there are two totally different situations in types of repositories. In high-level wastes made up of glass and capable of heating up to between 300 and 400° C there is not likely to be much biological activity of any type. For low-level waste including organics the situation may be different. NRC may require the destruction of all organics by incineration to obtain an assured product for burial.

In summary, no suggestions of new methods or concepts were forthcoming when compared with activities planned in Subtask 4, to attempt to bridge the gap from short-term laboratory studies to the tens of thousands (or a million) years necessary for a complete safety assessment.

SUBTASK 5: SORPTION-DESORPTION MECHANISM STUDIES

The role of oxidation-reduction in controlling nuclide sorption evoked considerable discussion. One topic was methods of controlling Eh and whether, in fact, one can properly measure it.

In interpretation of reversible potential (Eh electrode measurement) findings may not be too reliable because without a great deal of experience in this area it is difficult to obtain a "good" reversible electrode reading. Ag Chloride and Pt (properly activated with H) offer the best possibilities. Ferrous may also be used under some circumstance but, beyond these few examples, results are difficult to obtain at normal laboratory temperatures.

A second approach by some scientist doing soil extract pH measurement, follows a less complex path. The pH measurements of different experimenters are compared to establish a trend or relative scale. This might also be done with Eh, e.g. a measurement of 400 millivolts would suggest strong reducing conditions in natural water, while a second measurement of +200 would indicate the system is operating in the direction of an oxidizing condition, whatever the "real" values may be.

It was pointed out that if oxygen is bubbled into a solution with almost any metal the potential will rise, so that in a sense the more oxygen present the more likely material present will be oxidized, provided the kinetics are satisfactory. In theory the oxygen content and Eh are related but it is questioned whether this relationship holds in practice, since Eh measurements using pt electrodes often do not stabilize.

One researcher is reported to be using a controlled potential coulometer to make certain the oxidation potential is constant, and by doing so controls the valence of ions in solution. It is possible to poise the system with chemical buffers also, but there is then a further problem of the material used to poise it, which may interfere with the rock composition, sorption, etc. The same researcher reports he has not observed Pu plating on the electrode, but it was questioned if this would hold true over the long run.

Another participant asked if bubbling a gas mixture of known oxygen fugacity would have less impact on the system. However, it was pointed out that, with gases, kinetic problems arise depending on how soluble they are and whether the kinetics or the redox reaction is fast enough to "do what you want to do." A participant suggested redox potential may be controlled in this way if the pH is controlled, but there is a limited range in which to operate and the researchers must be aware again of the kinetics of the reaction in which he is interested.

It was suggested that this has been commonly done for a crude control of redox at Battelle, e.g., +200 vs ± 400 mv. Experiments at L.S.U. on soils and sediments utilized such a system which have controlled potentials to ± 50 mv.

Experimental designs must concentrate on a reducing situation. While it is a bigger problem to have a continous reducing situation going on, this--along with several control experiments carried out at the atmospheric level--permits a check for significant differences.

If these differences are not forthcoming, it is likely that the need for further anoxic experiments with that same nuclide are unnecessary and the research can return to simpler atmospheric conditions.

So far, the group has not addressed the anoxic versus the oxygen situation except for the fact of recognizing the challenge of experiments at the infinitesimally-low fugacity of oxygen required. Even if the investigator feels he is controlling the system in an anoxic condition in the laboratory, without some expensive and very sophisticated atmospheric chamber the results are questionable.

The suggestion was offered that results can be obtained in a "good vacuum" if the researcher is willing to remove oxygenated water by freezing-thawing cycles, then injecting anoxic water into the vacuum. This would be especially workable with static batch experiments, e.g., a series of vacuum tubes with various types of minerals or samples evaluated and allowed to equilibrate.

Another commented that the redox problem was germane to Pu but not for Cs, Sr, etc. The response was that if you consider only the possible valence states of the nuclide itself, this is true. But, in interaction with a heterogenous mixture of minerals--allowing changes to go on in the solid material and the solution--the K_d will be affected by redox-sensitive constituents. While the valence state of the nuclide may not change, there may be some other effect.

An objection was raised concerning the use of powdered rock because of its oxygen content. The general feeling, however, was that the oxidation that takes place when rock is ground and powdered in air is not extensive (e.g., the lunar samples which have been circulated throughout the world and are still useful sample rocks).

In the search for useful figures in the literature of scientists working with actinides regarding redox potentials between the four oxidations states of Pu in solution, the feeling was that there is little known for Pu in either concentrated or neutral solution.

However, it was learned that redox potentials for Pu, Np, and U were calculated some 30 years ago by one of the participants and published. It is believed the numbers still stand or at most "have changed minimally" in the interim.

Known oxidation reduction potentials in (one molar) acid are not especially helpful to the research at hand. Recently, in order to resolve the question of whether ferrous ion will reduce Pu(IV) in neutral solution, an experiment was carried out determining that this action does, in fact, occur.

A typical repository will contain ferrous iron (neutral) and sulfides in some cases. The question of whether a situation might evolve to the point where a small concentration of Pu would require an equal amount of iron to reduce (a one-to-one ratio) was considered, along with whether the iron would need to be in solution or part of the geologic material to have this effect.

Experiments are contemplated using $FeCO_3$ (siderite, a ferrous carbonate) in a hydrogen atmosphere, at 50° C--the approximate temperature for a 1000 m subsurface repository--to provide ratio guidelines, e.g. 10^{-12} molar of ferrous to reduce 10^{-12} molar of Pu. The process involves pumping out gases from water containing 10^{-5} m or $^{-6}$ m Pu by freezing and melting cycles and distilling the water in an extremely high vacuum onto $FeCO_3$ and Pu in a vacuum tube. Variations may include introducing other gases such as N and CO_2.

The problem of detailed analysis of ferrous ion in groundwater in situ was raised. Ferrous iron found in groundwater has a slow rate of oxidation and is acid-dependent; the more acidic the medium, the slower the oxidation. Most mineral iron is ferrous and, instead of being liberated to a free solution, it prefers to oxidize in situ in the lattice.

The comment is made that it is one thing to measure Eh in water after it is drawn to the surface and another to do so in situ. This is an important consideration from the point of view of geothermal wells because of oxidation, scaling, etc. Battelle is currently working on an in situ probe to measure pH and Eh of geothermal wells, with high temperatures one of the major constraints.

Although no clear consensus was reached on whether Eh can be properly measured, it was established that it can be controlled, at least crudely, and experiments need to be performed to better simulate suggested anoxic conditions in repositories. In addition the "Pu situation" for safety assessment might be considerably less complex than had been assumed, since it is highly probable that any Pu found underground may be entirely in the Pu(III) state.

Several other mechanisms were briefly mentioned as needing to be addressed.

- If solution pH's are of importance in nuclide sorption, sorption onto silica gel may provide useful information for modeling purposes. With hydrophobic elements, solution concentrations govern sorption activity and control movement in the system. There is a tendency for these elements to precipitate, and this is an important mechanism for study.
- Since there will be increased emphasis on very high salinities, the matter of complexing when working with chlorides should be considered.
- No one has addressed the basic problem of sorption on rock. Everyone assumes rock is a solid phase, not undergoing any reaction with liquid. This is not the case. If solution in contact with rock is monitored, the concentration, e.g. silica and aluminum, is observed going up. Presumably a steady state will be reached, but most minerals are not at thermodynamic equilibrium and will continue to slowly change.

WISAP--OPEN FLOOR DISCUSSION

SUBTASK 6: TECHNICAL MANAGEMENT

Interplay with Other Organizations

It was suggested by seminar participants that one of the major benefits of the meeting was the opportunity to identify the "many parallels" between WISAP and others working toward the same (or similar) goals. An observer commented that such opportunities frequently have subtle but lasting effects on future work and subsequent interactions between agency representatives, through recognition of the need to articulate problems more carefully and a greater understanding of the problems faced by other agencies. One indicated that some immediate impact would be seen in the modeling variations on which his group is working.

Another asked that his organization have the option of commenting upon developments "before they become absolute." Should they fail to take advantage of that option, he said, the responsibility would fall on them alone.

A third speaker indicated that he felt there appeared to be a great many decisions imposed on WISAP from above (in addition to the time schedule) many of which did not necessarily coincide with "technical realities." He inquired about any established mechanism for feedback. In response it was pointed out that an advisory committee exists, and if the group feels itself in difficulty, help can be enlisted in resolving problems. It was also observed that if experts are frustrated by being denied essential information concerning project constraints, the effort will be seriously compromised. More complete data would help reduce the scope of the study and the amount of programming necessary.

On the same problem, the rhetorical question was raised about what would happen if the time came when the group, or any individuals involved, felt that they could no longer live with the restrictions imposed. While alternative routes exist toward the same goal through other organized efforts, it was felt that, to the extent that individuals remain associated with the program, they should make an effort to accomodate the specified deadlines. The obvious solution, several observed, is not to try to cover every conceivable avenue of investigation, but to define the problem as narrowly as possible so that the work can be done to the extent that is possible. If it cannot be done, as responsible scientists all have a moral obligation to say that, at this time, they are not ready to make that definitive a statement for the specific reasons stated. However, at present, whether or not the goal is patently impossible has not been established. Only when the work is underway with "a sound group of people and a sound technology established," if it is recognized there is not going to be sufficient time, should this be communicated to the proper source.

In regard to the political ramifications of such action, another participant suggested that the sponsoring organization be consulted first. He indicated he could not see that the scientific inquiry had been stifled in any way beyond the possible withholding of predetermined conditions.

Another participant indicated the meeting had been informative with regard to some specific problems, and in showing "where his own work fits into the broader picture." He was, he pointed out, impressed most by the amount of talent and technical knowledge that can be brought to bear on one particular problem in a short period of time.

Still another observed that he thinks there is a regretable tendency for people to get bogged down in small problems, failing to recognize the long-term advantages of this kind of interchange of ideas.

Expressing appreciation for the participation in which "deep commitment could be felt to the solution of this very complex and difficult problem," OWI invited participants, at their option, to follow up the meeting with any impressions not already on record after they have had some time to consider the discussions.

Information Dissemination

To a question about whether the exact parameters to be measured would be distributed (upper and lower limits, ranges of temperatures, ranges of pressures, etc.), the reply was affirmative. Any further constraints, the chairman said, will be a matter for the sponsor to determine, e.g., how much they are willing to finance and which problems within that scope the group can best address constructively.

WISAP will also keep participants informed of developments through an information bulletin or some other type of round-robin letter to solicit further comment and response, and to announce the availability of samples, etc.

PROGRAM REDIRECTION

A need is generally expressed to narrow the range of study in order to speed up the anlysis in line with OWI time constraints. Those beginning with the "building block" approach (simple mineral systems), are encouraged to work toward reality, a heterogeneous mixture of minerals. One suggestion was made that the number of experimental points could be substantially reduced through utilizing the selectivity coefficients (mass action equilibria type) which implicitly treat the problem of variable concentrations of solution composition. The selectivity coefficients may be combined, explicitly treating the problem of variants. It was observed, however, that this technique works well at nuclide concentrations above the tracer range, but little success has been realized at extremely low concentrations. A counter argument was voiced that sorption results at higher-than-normal tracer concentrations in the region where selectivity coefficients can be successfully measured, should give conservative K_d values and thus be useful for safety assessment. This would be true as long as the radionuclide under study did not precipitate or hydrolize at the higher-than-normal concentrations.

It was observed that at this stage in the program the "natural experiment" might supply some convenient constraints. While this may seem confining to the research process, setting limits cannot be avoided if progress is to be realized and competence gained in characterization.

SUMMARY AND CONCLUSIONS

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SUMMARY AND CONCLUSIONS

On the topic of experimental methodology evaluation, the participants felt it was premature to select only a few methods and dismiss other techniques. Eventually decisions must be made on which experimental methods are most accurate, least costly, and least time consuming. Program time and monetary constraints will help ensure that such a method selection occurs. Two aspects must be considered when selecting methods: (1) which laboratory method most accurately predicts the migration rate of nuclides leached from a deep geologic repository, given time and monetary constraints, and (2) from the overall safety assessment what are the accuracy and sensitivity requirements. Since WISAP was still in its infancy these points could not be objectively addressed. Work in FY 78-79 should provide the necessary data.

A consensus was reached that, dependent on the K_d value, certain experimental methods are less useful. For example for nuclides with large K_ds (>1000 ml/g) flow through column experiments require extremely long times to produce quantitative results. It was also emphasized that experiments must be run in both the sorption and desorption directions to explore reversibility. If a nuclide is irreversibly absorbed, its migration potential is greatly diminished.

It became apparent during discussion that progress to date suffered from little standardization or direction on what geologic samples should be utilized in laboratory experimentation. It was concluded that some standard samples should be distributed to each experimenter. These standard rocks would be used with designated groundwaters in a round-robin approach to identify inherent laboratory bias and differences in experimental methods. The rocks would be called "controlled samples," as opposed to standard samples which can note a very well homogenized and characterized sample which has been prepared under rigid protocol. The rock samples will be solicited by PNL from potential repository sites and private vendors with preference placed on cost and rapid availability. The samples will be crushed, homogenized, fully characterized, and distributed by PNL. It was noted that institutions or individuals with samples can obtain some free laboratory work if they donate about one hundred pounds of material.

It was agreed that a variety of controlled samples should be used to broaden the data base and that selection of a "suite" of samples would not prevent any laboratory from working with other samples also.

A generic data bank of K_d values is needed to allow safety assessment calculations based on retardation factors for any environment. Within the next two years there is a pressing need to consolidate isolated studies in a meaningful way to construct a complete data bank. The method proposed is to statistically interpolate between known data points to create a continuous K_d function. In order to perform this statistical interpolation, besides the nuclide K_d, the rock and water used must be thoroughly characterized. A "laundry list" of parameters which should be measured is included in the text. The list includes such factors as major cations, major anions, pH, Eh of the groundwater and surface area, cation-exchange capacity, types and amounts of minerals, and organic content of the rock. These parametric characterizations should make it possible to interpolate from one K_d experiment environment to another. While not conclusive, since statistics cannot show cause and effect and variation exists in sorption by the same rock, the resulting predictions will have more validity than any which can be made to date.

The moderater admonished all experimenters present that proper statistical analysis will require a higher degree of characterization of both rocks and groundwater in the future.

The goal is to analyze the effect of a dependent variable (K_d) with many independent variables--the paraments on the "laundry list". It was acknowledged that some time may be wasted on measuring certain parameters, but having the numbers is essential to performing the statistical interpolations.

The proper way to measure the surface area of crushed rock samples and soils was debated. Currently experimenters are using two methods--an adsorption method (B.E.T.) and a "wet" method (ethylene glycol).

Participants' experience indicates, despite some problems, the ethylene glycol or similar "wet" method is best for characterizing surface area.

A dilemma exists over the use of the term K_d to describe the ratio of the activity of nuclide sorbed on a solid to the activity of the nuclide in the contacting solution. The correct usage of K_d, which originates in ion exchange theory, requires several criteria or conditions which nuclear waste experimentalists have often overlooked. To chemists and strict scientists, usage of the term K_d for much of the empirical data generated by nuclear waste management personnel is improper and leads to incorrect interpretations. The opinion was voiced that, while it is doubtful the nuclear community will drop the use of K_d, some alternative should be found. It was decided to seek feedback from the group; then permit the PNL coordinator to arbitrarily impose a new designation.

Much concern and discussion surfaced on the interpretation of column breakthrough curves observed from experimental data as opposed to symmetrical curves predicted from chromatographic theory. Skewed or tailing curves with a major peak and one or more "mini" peaks are ofter observed. Causes and data reduction techniques were discussed, but no clearly supportable hypothesis or numerical methods, respectively, were identified.

In light of the above complexities, some participants questioned the accuracy and validity of the WISAP (or for that matter any other) transport model being proposed to perform safety assessments. It is pointed out that the modelers will watch what individual researchers are doing closely in the future in order to make assessments as to whether certain complexities identified by various labs might be important and merit inclusion in the safety assessment model, but because of various constraints (financial, personnel, time, etc.) within the program, an idealized chromatographic model will continue to be developed. There will be a kind of "optimization" procedure followed. As more information and data become available, the modelers will determine whether more sophisticated models are warranted.

Subtask 4 of the Nuclide Transport Program will attempt to justify the long-term extrapolation of the short-term laboratory measurements by using thermodynamics, knowledge of weathering, interpretations of field data from OKLO, uranium deposits, existing nuclear waste burial grounds, and future field experiments. Methods discussed for performing these validation studies included the study of adsorption onto existing rocks in the environs of repositories as well as rocks types to which the existing ones might logically weather, and the use of experiments similar to "accelerated time tests" performed to test durability of commercial products. It was also pointed out that the rate of approach to equilibrium, or rate of change in mineralogy, etc., is the key data to determine rather than time to reach equilibrium.

The potential for organic or biological (bacteria) effects over long-term in the repository was discussed. The consensus was that bacteria probably would not exist in a deep repository and, in most rock types, very little organic matter would be present. Shale was one rock type in which organic matter might be present in large enough concentrations to merit study.

The role of oxidation-reduction in controlling nuclide sorption evoked considerable dialogue among the participants. Although there was no consensus on whether Eh could be accurately measured, participants agreed that future experiments must concentrate on anoxic or reducing environments to better simulate assumed deep repository conditions.

Methods of controlling oxidation-reduction potentials identified are: mixtures of gases, chemical buffers, biological buffers and electrical (potential coulometry). The first and last methods appear to offer the most promise for performing nuclide sorption experiments.

Anoxic experiments will be more complex and costly to perform, but if preliminary anoxic sorption experiments show no significant differences from experiments at atmospheric conditions future experiments can return to the more easily-performed atmospheric conditions.

A need was generally expressed to narrow the range of study in order to speed up the analysis in line with OWI time constraints. Those beginning with the "building block" approach (simple mineral systems), are encouraged to work toward reality--a heterogeneous mixture of minerals. One suggestion was made that the number of experimental points could be substantially reduced through utilizing the selectivity coefficients (mass action equilibria type) which implicitly treat the problem of variable concentrations of solution composition. The selectivity coefficients may be combined, explicitly treating the problem of variants. It was observed, however, that this technique works well at nuclide concentrations above the tracer range, but little success has been realized at extremely low concentrations. A counter argument was voiced that sorption results at higher-than-normal tracer concentrations in the region where selectivity coefficients can be successfully measured, should give conservative K_d values and thus be useful for safety assessment. This would be true as long as the radionuclide under study did not precipitate or hydrolize at the higher-than-normal concentrations.

It was observed that at this stage in the program the "natural or most likely conditions" might supply some convenient constraints. Every reasonable limit placed on the program helps narrow the problem into a time frame that may make it possible to meet established deadlines. While this may seem confining to the research process, setting limits cannot be avoided if progress is to be realized and competence gained in characterization.

It was agreed that limits on temperature, pressure, pH, oxidation reduction potential, nuclides of interest, geologies, and groundwaters would be appreciated. No one could agree on definite limits for any of these parameters. For guidance, the coordinator suggested the following limits be imposed, subject to input from the general scientific community:

Arbitary Limits for Experimental Parameters

Temperature	4° to 70°C
Pressure	14.7 to 2000 psi
pH	5 to 9
Eh	-400 to + 400mv
Rocks	All types
Groundwaters	All types with some emphasis on salt brine
Nuclides	First Priority - Tc, Pu, Np, I, U, Cs, Ra, Sr, ^{14}C
	Second Priority - Am, Sn, Ni, Se, Cm
	Lower Priority - Zr, Sm, Mo, Eu, Pd, Th, Pb, Pa, Nb

The reader with comments on these limits is encouraged to correspond with Coordinator R. J. Serne, PNL.

Finally, the PNL-WISAP team was encouraged to set up an independent peer review group to monitor the overall program and individual tasks, such as Nuclide Transport Data. The coordinator requests attendees and others interested to nominate appropriate individuals in separate correspondence.

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