NOV 10 1993

Mr. Dwight E. Shelor, Associate Director
for Systems and Compliance
Office of Civilian Radioactive Waste Management
U. S. Department of Energy
1000 Independence Avenue, SW
Washington, DC 20585

Dear Mr. Shelor:

SUBJECT: SUMMARY OF THE OCTOBER 13, 1993, TECHNICAL EXCHANGE ON RADIONUCLIDE MIGRATION, OCTOBER 14, 1993, TECHNICAL EXCHANGE ON NEAR-FIELD RADIONUCLIDE RELEASES FROM THE ENGINEERED BARRIER SYSTEM, AND OCTOBER 15, 1993 SITE VISIT TO LOS ALAMOS NATIONAL LABORATORY

The purpose of this letter is to transmit the summaries for the subject U.S. Nuclear Regulatory Commission/U.S. Department of Energy technical exchanges of October 13, 1993 (Enclosure 1), and 14, 1993 (Enclosure 2), and the October 15, 1993, site visit (Enclosure 3). The three interactions were also attended by representatives of the State of Nevada, Nye County, Nevada, and Inyo County, California. The purpose of the October 13 technical exchange was to hold discussions on recent experimental and theoretical studies pertaining to the migration of radionuclides at Yucca Mountain; the purpose of the October 14 technical exchange was to discuss previous and on-going experiments and computer simulations of near-field phenomena for the Yucca Mountain candidate repository; and the purpose of the October 15 site visit was to provide participants with an opportunity to observe and discuss activities being conducted in support of site characterization of Yucca Mountain.

Should you have any questions related to the summaries or this letter, please contact Ms. Charlotte Abrams of my staff at (301) 504-3403.

Sincerely,

/S/

C. William Reamer, Acting Director
Repository Licensing and Quality Assurance
Project Directorate
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosures: As stated on the shelf

cc: See next page

OFC	HLPD	E	HLPD	C				
NAME	CAbrams		CWReamer					
DATE	11/11/93		11/10/93					

C = COVER E = COVER & ENCLOSURE N = NO COPY

g:oct13min

OFFICIAL RECORD COPY

160001

PART 1

102.2
WM-11
NH16

cc: R. Loux, State of Nevada
T. J. Hickey, Nevada Legislative Committee
J. Meder, Nevada Legislative Counsel Bureau
C. Gertz, DOE/NV
M. Murphy, Nye County, NV
M. Baughman, Lincoln County, NV
D. Bechtel, Clark County, NV
D. Weigel, GAO
P. Niedzielski-Eichner, Nye County, NV
B. Mettam, Inyo County, CA
V. Poe, Mineral County, NV
F. Sperry, White Pine County, NV
R. Williams, Lander County, NV
L. Fiorenzi, Eureka County, NV
J. Hoffman, Esmeralda County, NV
C. Schank, Churchill County, NV
L. Bradshaw, Nye County, NV

DISTRIBUTION

CNWRA
LPDR
BJYoungblood, HLWM
JHolonich, HLPD

NMSS R/F
ACNW
JLinehan, HLWM
On-Site Reps

HLPD R/F
PDR
RBallard, HLGE
KHooks, HLPD

LSS
CENTRAL FILE
MFederline, HLHP
WBelke, HLPD

SUMMARY OF U.S. NUCLEAR REGULATORY COMMISSION AND U.S. DEPARTMENT OF ENERGY TECHNICAL EXCHANGE ON RADIONUCLIDE MIGRATION

October 13, 1993, Los Alamos, NM

On October 13, 1993, representatives of the Nuclear Regulatory Commission, U.S. Department of Energy (DOE), State of Nevada Nuclear Waste Project Office, Nye County, Nevada, and Inyo County, California, participated in a technical exchange on radionuclide migration. The purpose of the technical exchange was to hold discussions on recent experimental and theoretical studies pertaining to the migration of radionuclides at Yucca Mountain. The technical exchange agenda is included as Attachment 1 and the list of attendees is Attachment 2 to this summary. Copies of presenters' handouts are included in Attachment 3.

The exchange included presentations by DOE representatives from the Yucca Mountain Project Office (YMP), Los Alamos National Laboratory, and Lawrence Berkeley Laboratory. Topics discussed included the status and results to-date of solubility, sorption, and matrix diffusion studies, groundwater chemistry modeling, and retardation sensitivity analysis. NRC and Center for Nuclear Waste Regulatory Analyses staff presented discussions of NRC modeling studies.

All participants and attendees were provided opportunities for questions and discussion during the technical exchange. Ms. Ardyth Simmons (DOE YMP) provided a brief synopsis of how the activities discussed at the technical exchange were being integrated with DOE's Total System Performance Assessment (TSPA) and the status of DOE activities to address unresolved NRC Site Characterization Analysis concerns related to radionuclide migration.

In the closing remarks, the State of Nevada representative observed that the meeting agenda had been overly ambitious with too many scheduled presentations resulting in a lack of time for meaningful discussion. All parties agreed that future agendas should allow more time for discussion even if it is necessary to extend the number of days required for a DOE/NRC interaction. Future agenda setting conferences will take this concern into consideration. The State representative noted that the U.S. Geological Survey is developing a three-dimensional stratigraphic model of which the DOE presenter seemed to be unaware; however, in the following discussion, it was clarified that the speaker was aware of and had seen the model.

Although supportive of TSPA efforts, the Nye County, Nevada representative stated concerns related to TSPA development, because of the uncertainty of many parameters due to impacts of thermal loading. The representative of Inyo County, California, was concerned that the lack of an overall repository or waste package design may affect work related to postclosure conditions and

ENCLOSURE 1

performance assessment predictions. He also stated that more emphasis is needed on studies of fracture properties and that the model presented for a high thermally loaded repository may not be the appropriate model. All parties agreed that the information presented at the technical exchange was beneficial.

11/9/93

Charlotte Abrams, Sr. Project Manager
Repository Licensing and Quality
Assurance Directorate
Division of High-Level Waste Management
Office of Nuclear Material Safety and
Safeguards
U.S. Nuclear Regulatory Commission

11/9/93

Christian Einberg, General Engineer
Regulatory Integration Branch
Office of Civilian Radioactive Waste
Management
U.S. Department of Energy

Attachment 1

AGENDA
DOE-NRC TECHNICAL EXCHANGE ON RADIONUCLIDE MIGRATION

October 13, 1993 at Los Alamos, NM

8:00	Welcome/Protocol/Opening Remarks	DOE, NRC, State, Counties
8:10	Overview of radionuclide migration • Philosophy of program • Status of studies - update of activities since 1990 TE • Participants • Purpose/scope of interaction	DOE (Simmons)

Processes / conditions affecting radionuclide migration

8:40	Advances in experimental studies of radionuclide migration	DOE (Triay)
9:10	Recent solubility results	DOE (Roberts)
9:30	Recent sorption results	DOE (Triay)
9:50	Organic Sorption	DOE (Kung)
10:05	Matrix diffusion affecting mobility in fracture flow conditions (Triay)	
10:30	BREAK	

Advances in theoretical studies of radionuclide migration

10:40	Groundwater chemistry modeling	DOE (Ebinger)
11:00	Speciation models - NEA thermochemical data base	DOE (Morris)
11:30	AFM studies to elucidate sorption	DOE (Rogers)
12:00	Surface complexation model	DOE (Leckie)
12:25	LUNCH	
1:40	Retardation sensitivity analysis	DOE (Zyvoloski)
2:10	International Program	DOE (Rundberg, Curtis)
2:40	Modeling studies • Sorption modeling • Geochemistry modeling • KD modeling for Iterative Performance Assessment	NRC
4:10	BREAK	
4:25	Integration with TSPA	DOE (Simmons)
4:45	SCA Open Items	DOE (Simmons)
5:15	Closing Comments	DOE, NRC, State, Counties
5:45	Adjourn	

NOTE: Each topic on the agenda includes time allotted for discussion.

Attachment 2

	NAME (PLEA PRINT)	COMPANY	TITLE
1	Steven E. Le Roy	M&O/Duke	Senior Scientist
2	Homi Minwalla	WESTON	Task Leader, Nuclear Licensing
3	Raymond H. Wallace, Jr	USGS/HQ	Hydrologist/Liaison Officer
4	Chris Einberg	DOE/HQ	General Engineer
5	Charlotte Abrams	NRC	Sr Proj Mgr
6	Deirdre M. Beach	LANL	Engineer
7	Malcolm Siegel	SNL	SMTS
8	Robert W Luce	NWTRB	Sr. Prof. Staff
9	Rich Van Konynenburg	LLNL	Engineer
10	NICK STELLAVATO	NYE County	On-Site Representative
11	David L. Clark	LANL	Staff Member
12	Ardyth M. Simmons	DOE	Physical Scientist
13	John W Bradbury	NRC	Geochemist
14	Ginny Colten-Bradley	NRC	Geochemist
15	AREND MEIJER	Jacobs	Geochemist
16	Charles Cotter	LANL	Research Tech
17	Robert Lopez	LANL	Research Tech
18	MARVA Johnson	State of NV	Tech Coordinator
19	R. William Nelson	INTERA/M&O	Senior Staff Consultant
20	CARL JOHNSON	STATE OF NEVADA	TECH. MGR
21	BILL GLASSLEY	LLNL	GEOCHEM. TASK LEADER
22	ANDERS WISTROM	LANL	RESEARCH POST DOC
23	K. STEPHEN KUNG	LANL	STAFF MEMBER
24	Darryl Leonard	LANL	GRAD Student

DOE-NRC Technical Exchange Oct 13, 1993
Radionuclide migration

	NAME (PLEASE PRINT)	COMPANY	TITLE
25	David Stahl	M&O/BWFC	Mgr, WP Matls & Perf. analysis
26	Steve Saterlie	M&O/TRW	Thermal Loading Study Mgr
27	R Daniel Dresser	Weston	Taskhead Regulatory Compliance
28	DAVID SASSANI	M&O/INTERA	SENIOR STAFF CONSULTANT
29	Bill HALSEY	LLNL	TECH. AREA LEADER - P.A.
30	MAURY MORGENSTEIN	NYE CO STATENV	GAAZ Inc. [illegible] PRESident
31	George Birchard	NRC/RES	Geochemist
32	David Turner	CNWRA	Sr. Res. Scientist
33	[illegible]	ACNW	Sr Staff Scientist
34	William Murphy	CNWRA	Principal Scientist
35	Frank Perry	LANL	PI Volcanism
36	Don Shettel	GMII	Chief Geochemist
37	Ed Taylor	TRW/M&O	Senior Scientist
38	R. Daniel McCright	LLL	Technical Area Leader
39	Ronald C. Livingston	TRAC	Geoscientist
40	Randall D. Manteufel	CNWRA	Research Engineer
41	Don Langmuir	NWTRB	Member
42	Steve Nelson	M&O/WCFS	Geoscientist
43	Alan Mitchell	LANL	TCO
44	Tom Buscheck	LLNL	Hydrologist
45	Marilyn Hawley	LANL	Material Scientist
46	Barbara Carlos	LANL	PI Fracture Mineralogy
47	Bruce Robinson	LANL	PI Reactive Tracer Testing
48	A GREENBERG	M&O	Senior Staff

	NAME (PLEASE PRINT)	COMPANY	TITLE
49	Holly A. Dockery	SNL	Manager, Dept. 6312
50	James O. Leckie	STANFORD	Professor
51	Deward W. Efurd	LANL	STAFF Member
52	W. GEORGE PERKINS	SNL	TSPA, DEPT 6312
53	David Janiman	LANL	Tech. Coord./Mtn. Pet.
54	Paul Bertetti	CNWRA	Research Scientist
55	Peter Lichtner	CNWRA	Principal Scientist
56	KEVIN ROBERTS	LBL	RESEARCH ASSOC.
57	BRIAN VIANI	LLNL	Chemist
58	David Curtis	LANL	[illegible] Staff
59	Robert [illegible]	LANL	Common STAFF MEMBER
60	Richard Codell	NRC	Sr Systems Analyst
61	Everett P. Springer	LANL	Technical Staff Member
62	LARRY E. HERSMAN	LANL	TECH Staff Mem.
63			
64			
65			
66			
67			
68			
69			
70			
71			
72			

U.S. DEPARTMENT OF ENERGY

OCRWM

YUCCA MOUNTAIN

YUCCA MOUNTAIN
SITE CHARACTERIZATION
PROJECT

OVERVIEW OF RADIONUCLIDE MIGRATION PROGRAM

PRESENTED TO

DOE/NRC TECHNICAL EXCHANGE

PRESENTED BY

ARDYTH SIMMONS

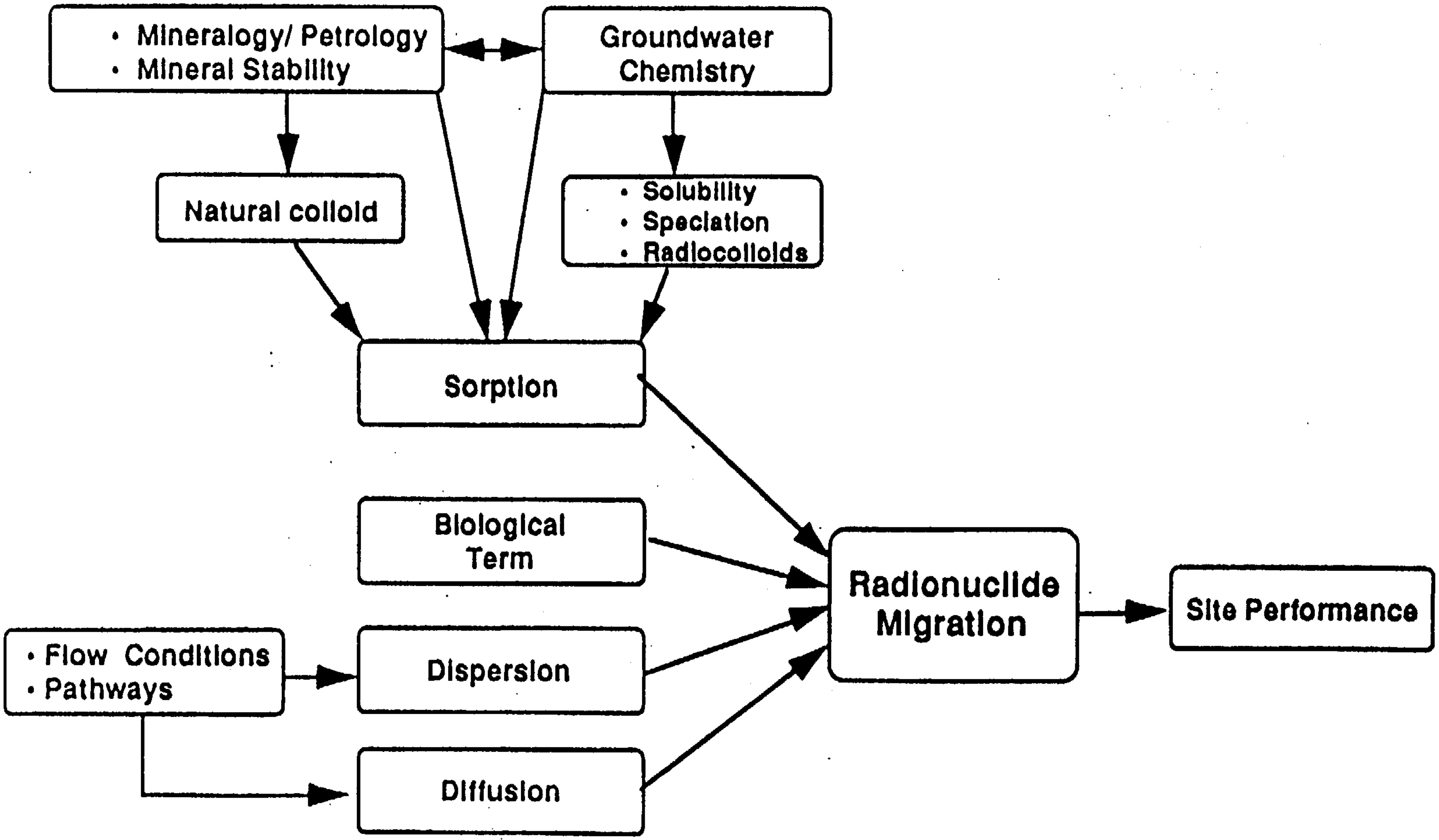
102.8

OCTOBER 13, 1993

OVERVIEW OF RADIONUCLIDE MIGRATION

- Philosophy of program
- Update of activities 1990-1993
- Participants
- Purpose and scope of interaction

LOS ALAMOS
RADIONUCLIDE MIGRATION PROGRAM



- Mineralogy/ Petrology
- Mineral Stability

Groundwater Chemistry

Natural colloid

- Solubility
- Speciation
- Radiocolloids

Sorption

Biological Term

- Flow Conditions
- Pathways

Dispersion

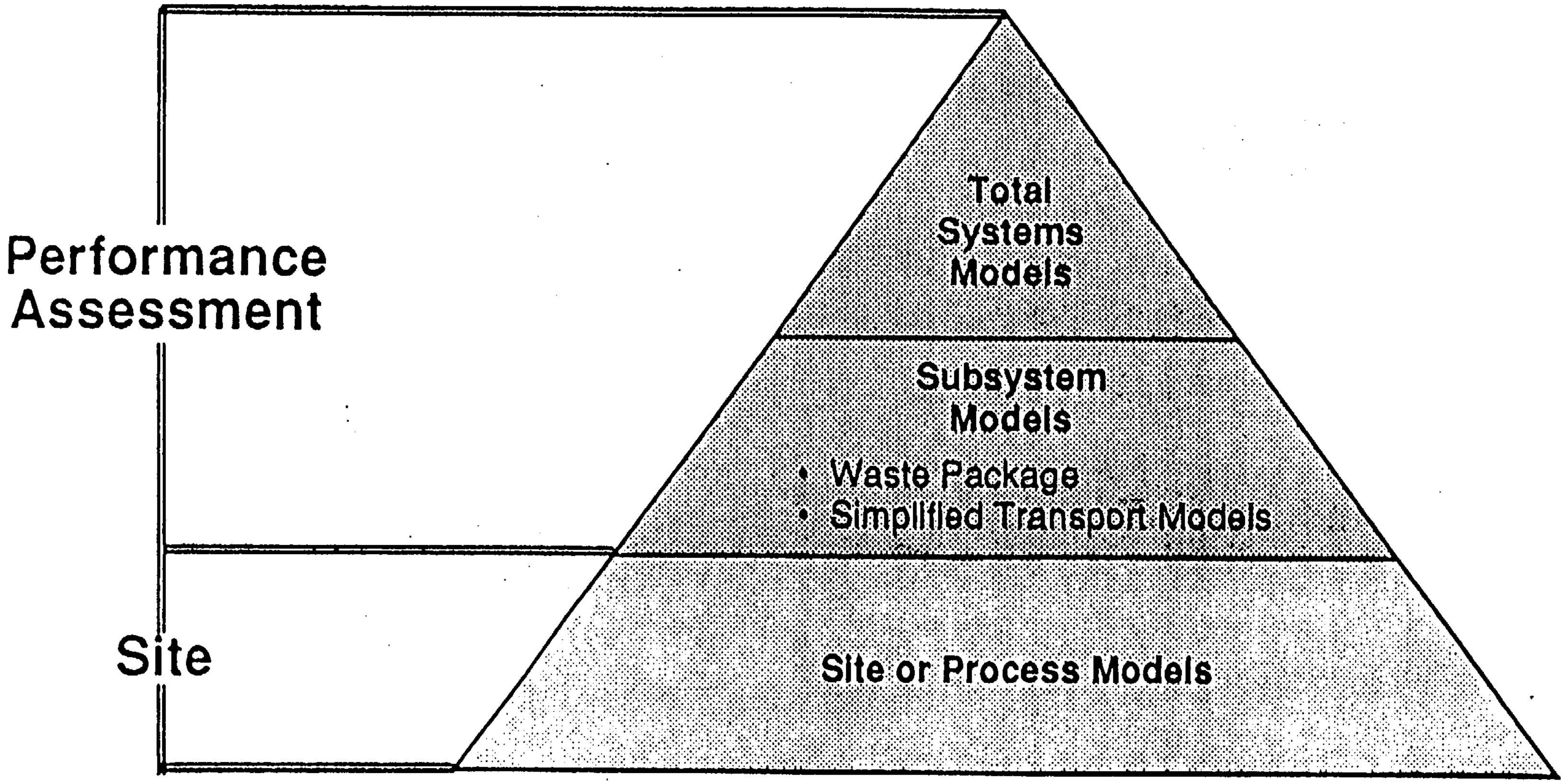
Diffusion

Radionuclide Migration

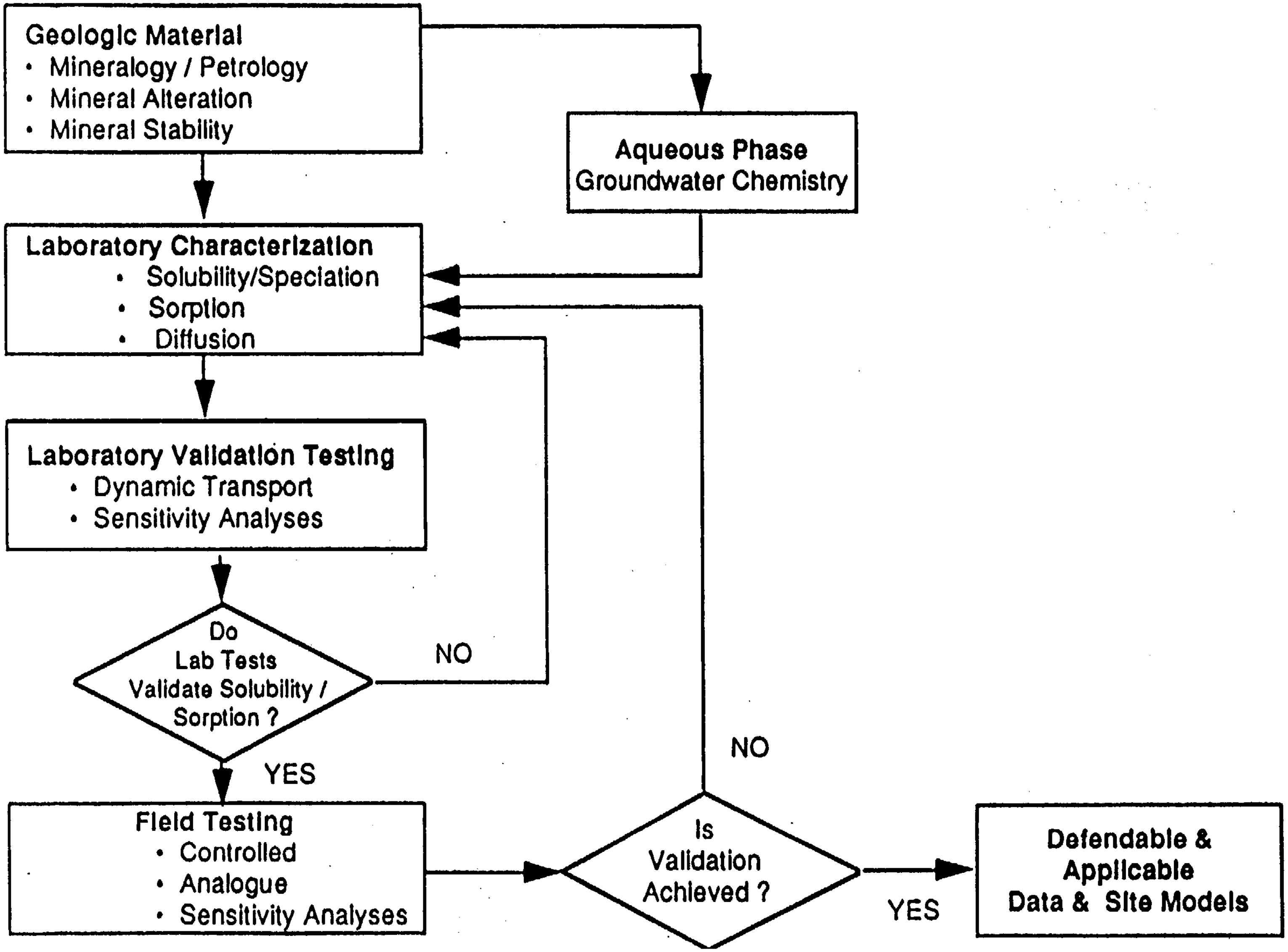
Site Performance

INTPALA4.125/10-12-93

PERFORMANCE ASSESSMENT STRATEGY



LOS ALAMOS STRATEGY FOR RADIONUCLIDE MIGRATION CHARACTERIZATION AND TESTING



Geologic Material
- Mineralogy / Petrology
- Mineral Alteration
- Mineral Stability

Aqueous Phase
Groundwater Chemistry

Laboratory Characterization
- Solubility/Speciation
- Sorption
- Diffusion

Laboratory Validation Testing
- Dynamic Transport
- Sensitivity Analyses

Do Lab Tests Validate Solubility / Sorption ?

NO

YES

Field Testing
- Controlled
- Analogue
- Sensitivity Analyses

Is Validation Achieved ?

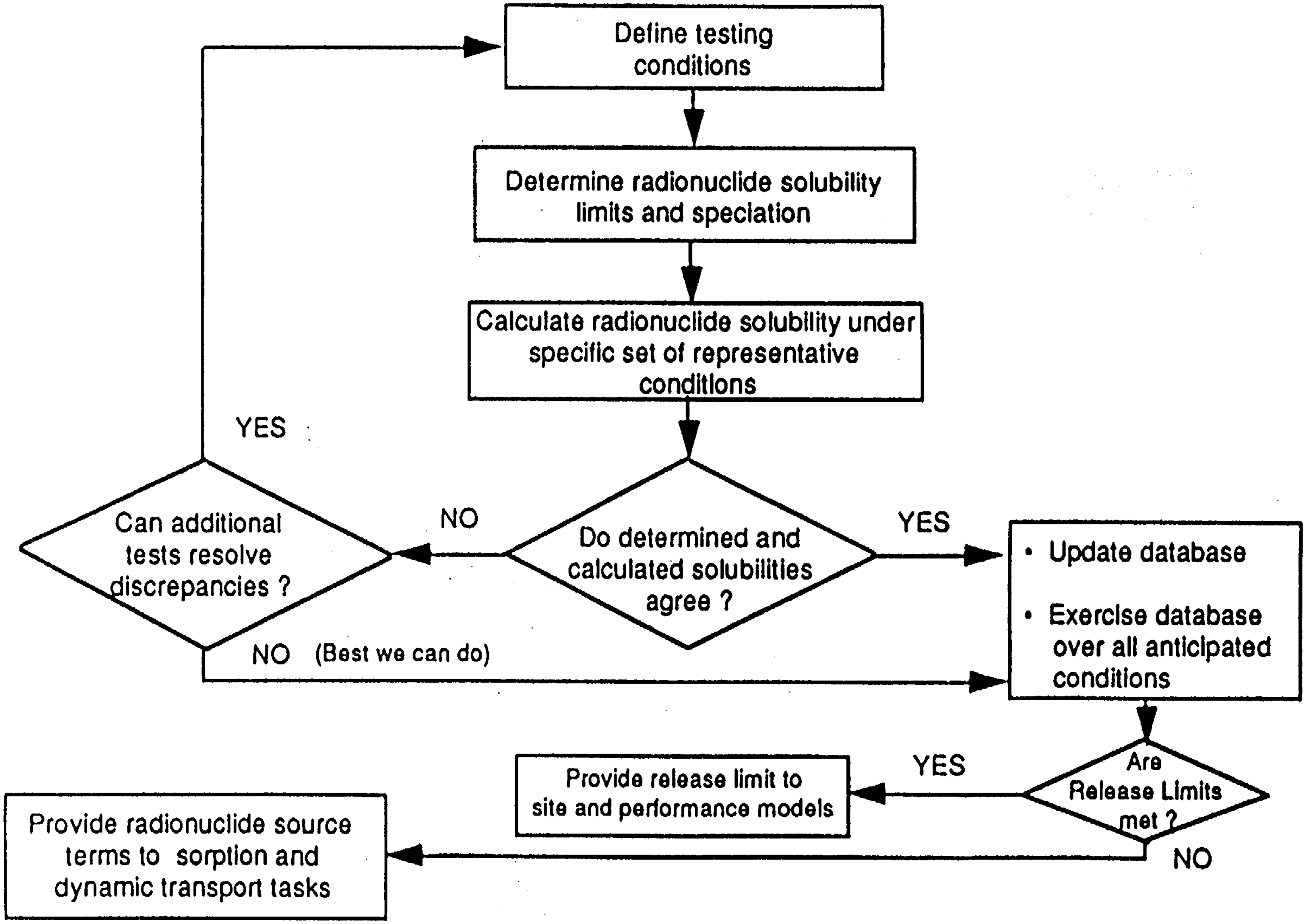
NO

YES

Defendable & Applicable Data & Site Models

INTPALA6.125/10-12-93

STRATEGY FOR DISSOLVED SPECIES CONCENTRATION LIMIT STUDIES



Define testing conditions

Determine radionuclide solubility limits and speciation

Calculate radionuclide solubility under specific set of representative conditions

Do determined and calculated solubilities agree ?

YES

- Update database
- Exercise database over all anticipated conditions

NO

Can additional tests resolve discrepancies ?

YES

NO (Best we can do)

Are Release Limits met ?

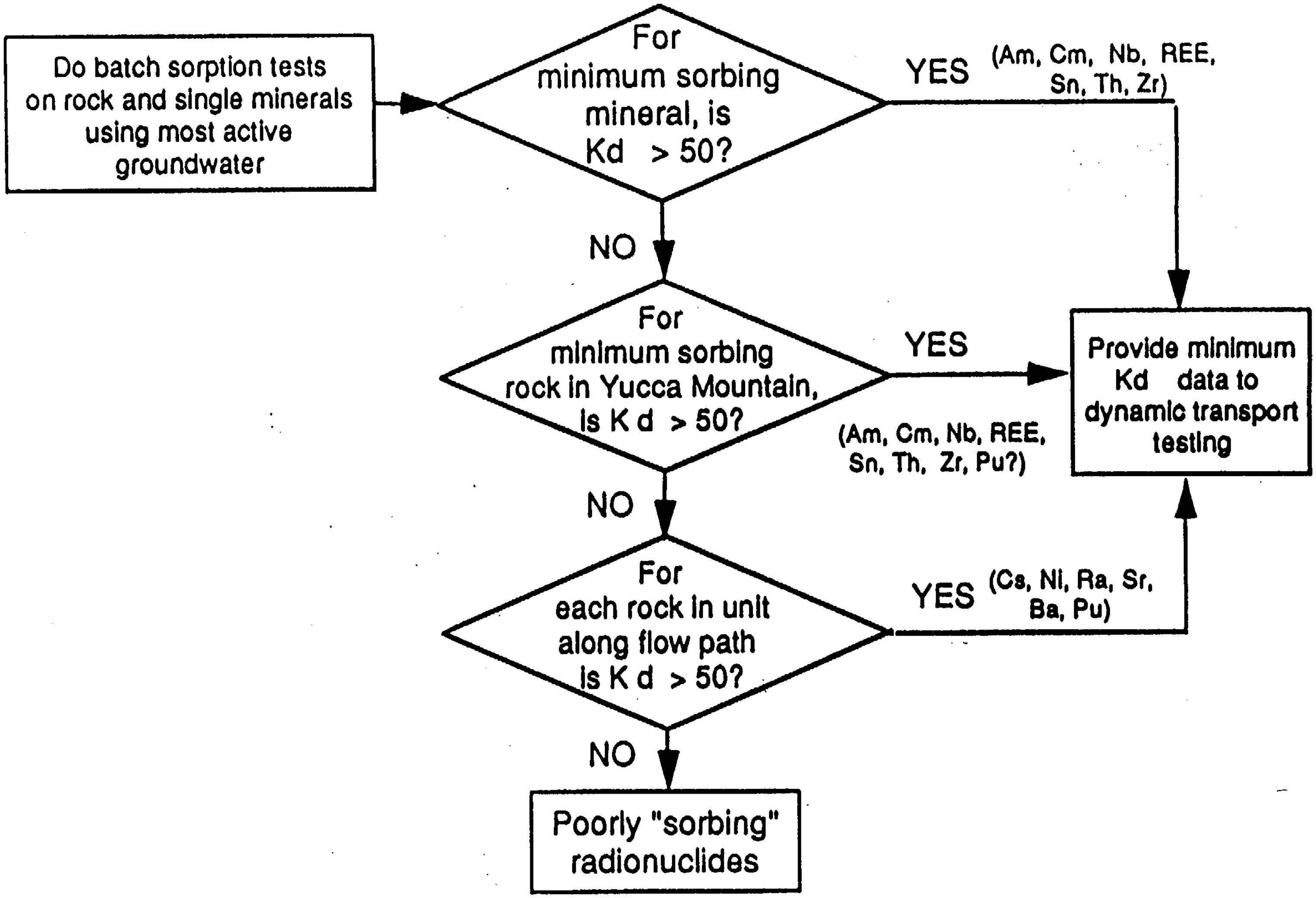
YES

Provide release limit to site and performance models

NO

Provide radionuclide source terms to sorption and dynamic transport tasks

STRATEGY FOR STRONGLY SORBING RADIONUCLIDES (MINIMUM Kd)



Do batch sorption tests on rock and single minerals using most active groundwater

For minimum sorbing mineral, is Kd > 50?

YES (Am, Cm, Nb, REE, Sn, Th, Zr)

NO

For minimum sorbing rock in Yucca Mountain, is Kd > 50?

YES (Am, Cm, Nb, REE, Sn, Th, Zr, Pu?)

NO

For each rock in unit along flow path is Kd > 50?

YES (Cs, Ni, Ra, Sr, Ba, Pu)

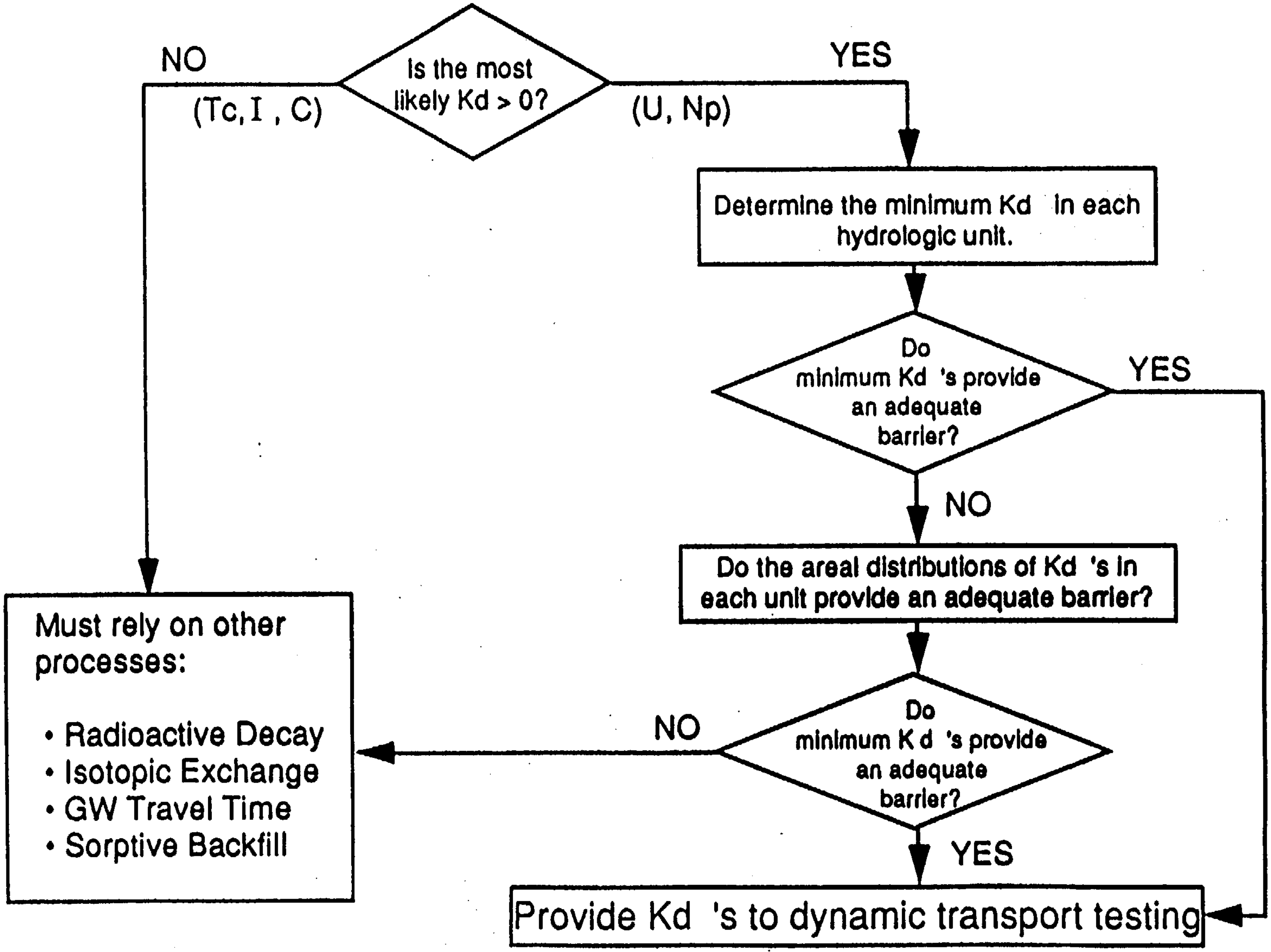
NO

Provide minimum Kd data to dynamic transport testing

Poorly "sorbing" radionuclides

(Kd in ml/g)

STRATEGY FOR "POORLY" SORBING RADIONUCLIDES (U, NP, TC, I, C)



Is the most likely Kd > 0?

NO (Tc, I , C)

YES (U, Np)

Determine the minimum Kd in each hydrologic unit.

Do minimum Kd 's provide an adequate barrier?

YES

NO

Do the areal distributions of Kd 's in each unit provide an adequate barrier?

Do minimum K d 's provide an adequate barrier?

NO

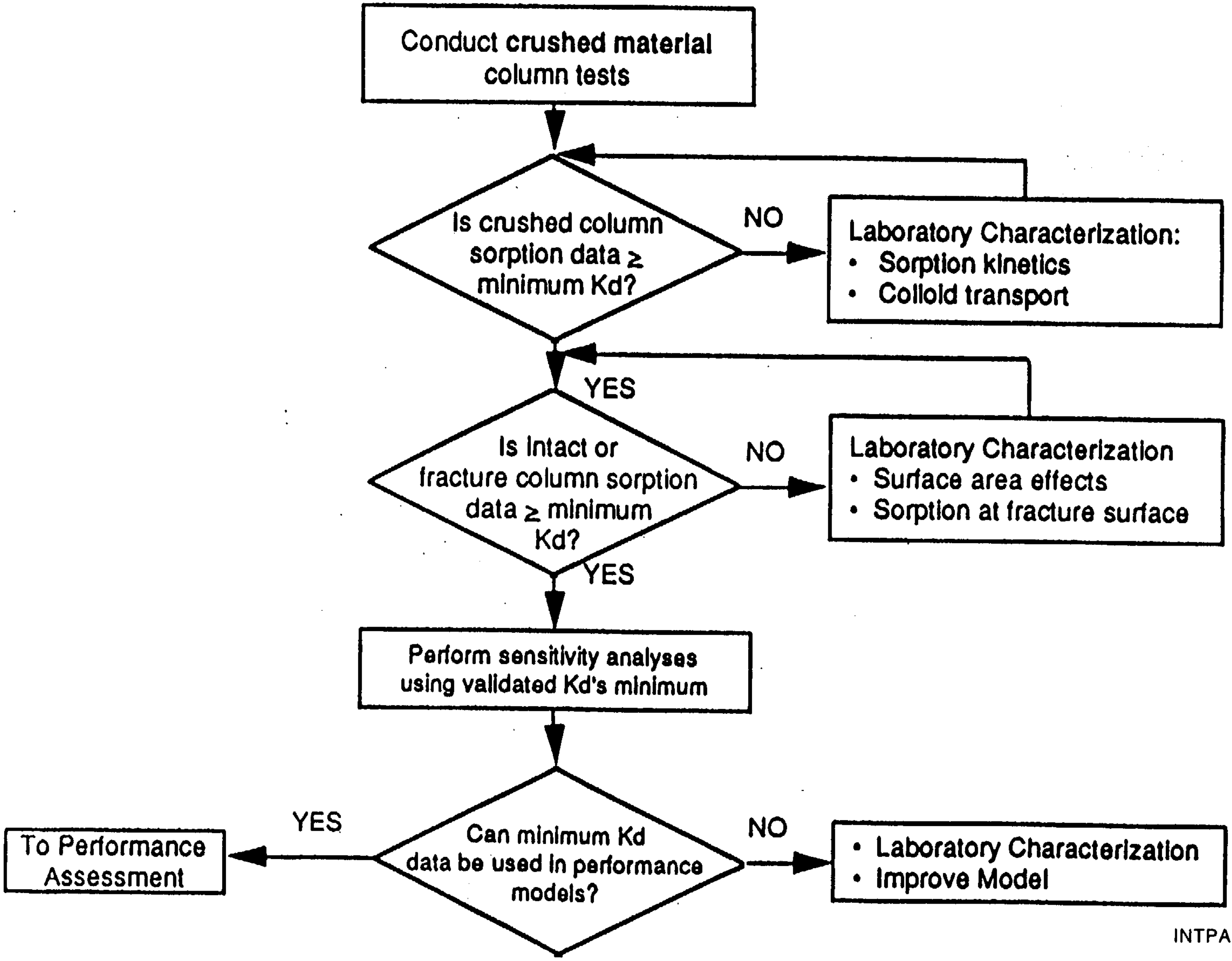
YES

Must rely on other processes:

- Radioactive Decay
- Isotopic Exchange
- GW Travel Time
- Sorptive Backfill

Provide Kd 's to dynamic transport testing

STRATEGY FOR LABORATORY VALIDATION TESTING (DYNAMIC TRANSPORT)



Conduct crushed material column tests

Is crushed column sorption data ≥ minimum Kd?

NO

Laboratory Characterization:
- Sorption kinetics
- Colloid transport

YES

Is intact or fracture column sorption data ≥ minimum Kd?

NO

Laboratory Characterization
- Surface area effects
- Sorption at fracture surface

YES

Perform sensitivity analyses using validated Kd's minimum

Can minimum Kd data be used in performance models?

YES

To Performance Assessment

NO

- Laboratory Characterization
- Improve Model

HIGHLIGHTS OF RECENT WORK

- Modeled speciation of Np in natural groundwaters
- Solubility of Np, Am, and Pu in J-13 and UE25-p#1
- Speciation of actinides using PAS and NMR
- Sorption
  - Effects of grinding, organic coatings
  - Iron oxide minerals - AFM, surface complexation
- Np transport through tuff
- Colloid-facilitated transport
- Intermediate-scale caisson test

OUTCOME OF SORPTION WORKSHOP

- Abandonment of near-field/far-field distinction
- Geochemistry Integration Team since September 1991
- Technical meetings to address significant issues
  - Integration with TSPA
  - Significance of fast-pathway transport
  - Coupled processes characterization in thermal field
  - Model validation and choice of codes (planned)
  - Colloid transport
  - Field and experimental studies

PURPOSE AND SCOPE OF INTERACTION

- Recent advances in experimental and modeling studies pertaining to radionuclide migration
- Adequacy of minimum Kd strategy and alternatives considered
- Iterative approach using defensible strategies
- Integration of Rn migration program, near- and far-field
- Discuss SCA open comments

DOE/NRC TECHNICAL EXCHANGE ON RADIONUCLIDE MIGRATION

OCTOBER 13, 1993

- Welcome
- Overview of program
- Processes and conditions affecting radionuclide migration
  - Advances in experimental studies
  - Advances in theoretical studies
- International program
- NRC modeling studies
- Integration with Total System Performance Assessment
- SCA open comments

SCA OPEN COMMENTS

- **Comment 96**
  - Investigations to characterize radionuclide retardation are focused on the determination of a Kd. It has not been demonstrated that use of these equations to model the complex heterogeneous medium of Yucca Mountain is valid for all expected states of the natural flow system
- **DOE Response**
  - Agrees; recognize need to test assumptions made by retardation model and by performance assessment. Study plans will provide additional detail
- **NRC evaluation**
  - Open. Need to review study plans
- **DOE Response**
  - Credit is taken for retardation by precipitation processes, but only for dissolved species. Empirical solubility determinations are being conducted for key radionuclides and water compositions. Will provide upper limits to solubility. Also conducting speciation studies for thermodynamic data. Strategy provides experimental flexibility.

SCA OPEN COMMENTS

(CONTINUED)

- **Comment 31**
  - The determination of some parameters and conditions such as speciation, kinetics, and matrix diffusion under fracture-flow conditions are not planned
- **DOE Response**
  - Study 8.3.1.3.6.1 will use fracture-flow experiments to validate models describing transport in fractures. Will be following other tests on speciation, kinetics, and diffusion. Will be iterative.
- **NRC evaluation**
  - Open. Still unclear which parameters will actually be measured in fracture experiments
- **DOE Response**
  - Study 8.3.1.3.6.1 is in review cycle

2 -1

DOE-NRC Technical Exchange
Radionuclide Migration

Advances in experimental studies of radionuclide migration

Inés R. Triay, LANL

DOE-NRC Technical Exchange
Radionuclide Migration

Advances in Radionuclide Migration

Part I. Overview of Strategy, J. Canepa

Part II. Overview of Work (1990 - 1993), I. Triay

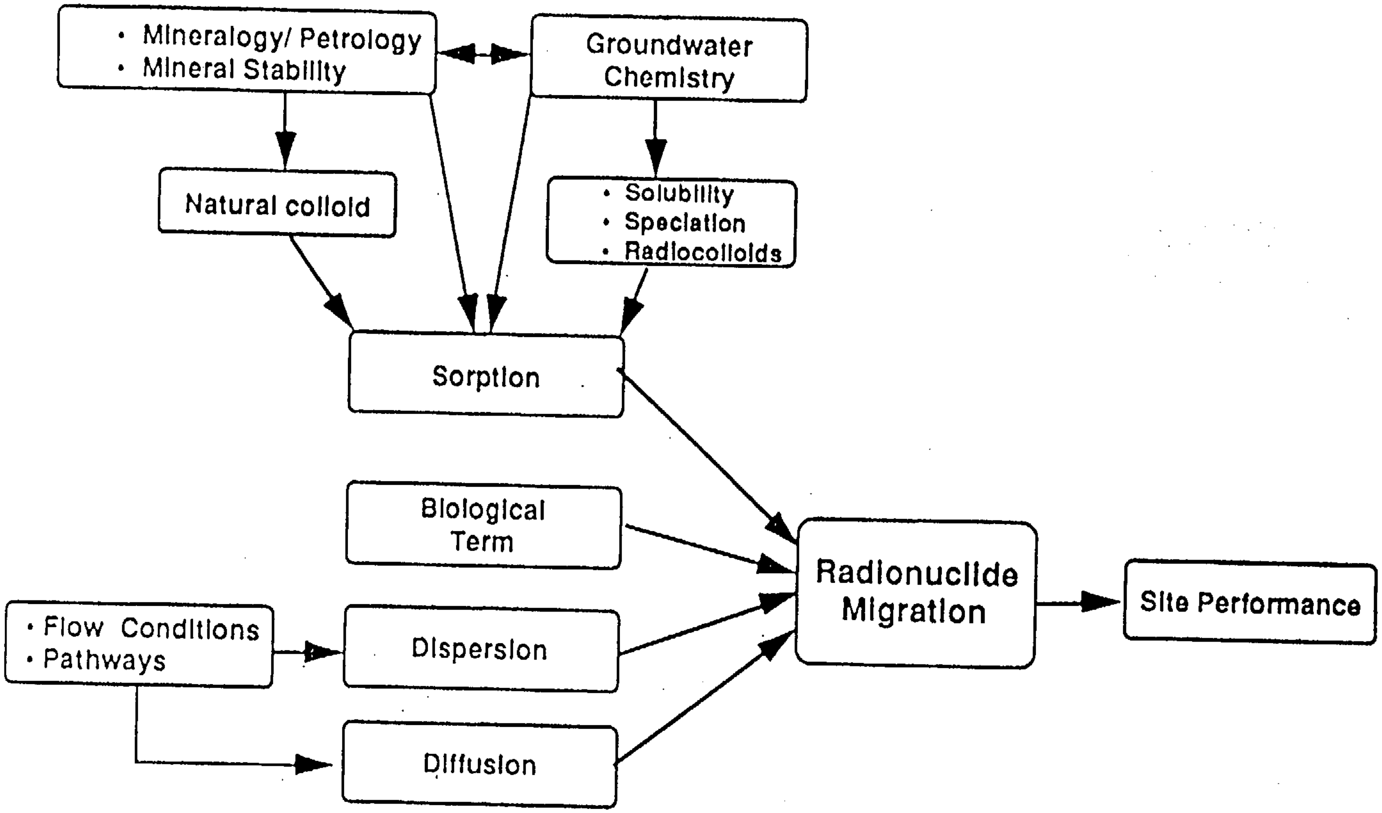
Part III. Colloid-Facilitated Radionuclide Transport, I. Triay

Part IV. Microbial Effects on Actinide Transport, L. Hersman

Part V. Analogs
  Natural, D. Curtis
  Anthropogenic, I. Triay

Part I. Overview of Strategy

Los Alamos
Radionuclide Migration Program



- Mineralogy/ Petrology
- Mineral Stability

Groundwater Chemistry

Natural colloid

- Solubility
- Speciation
- Radiocolloids

Sorption

Biological Term

- Flow Conditions
- Pathways

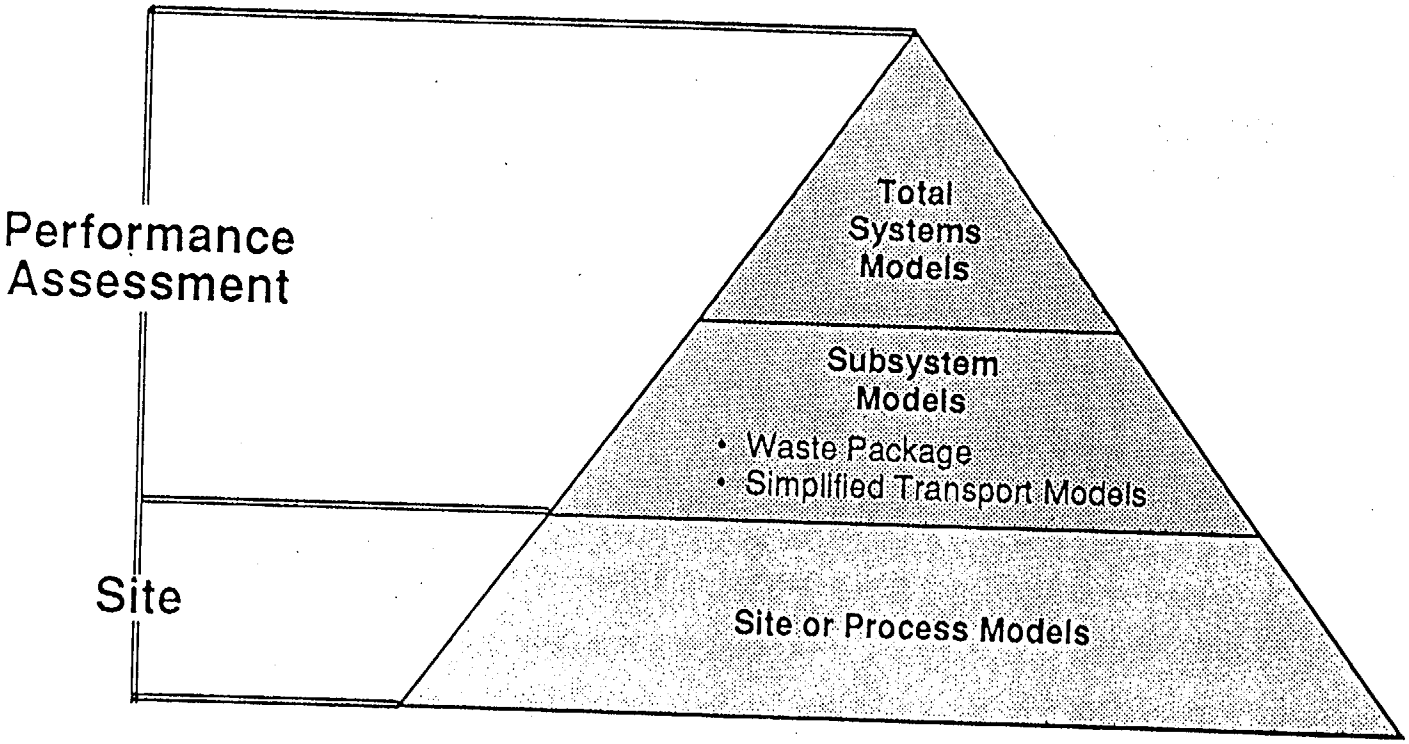
Dispersion

Diffusion

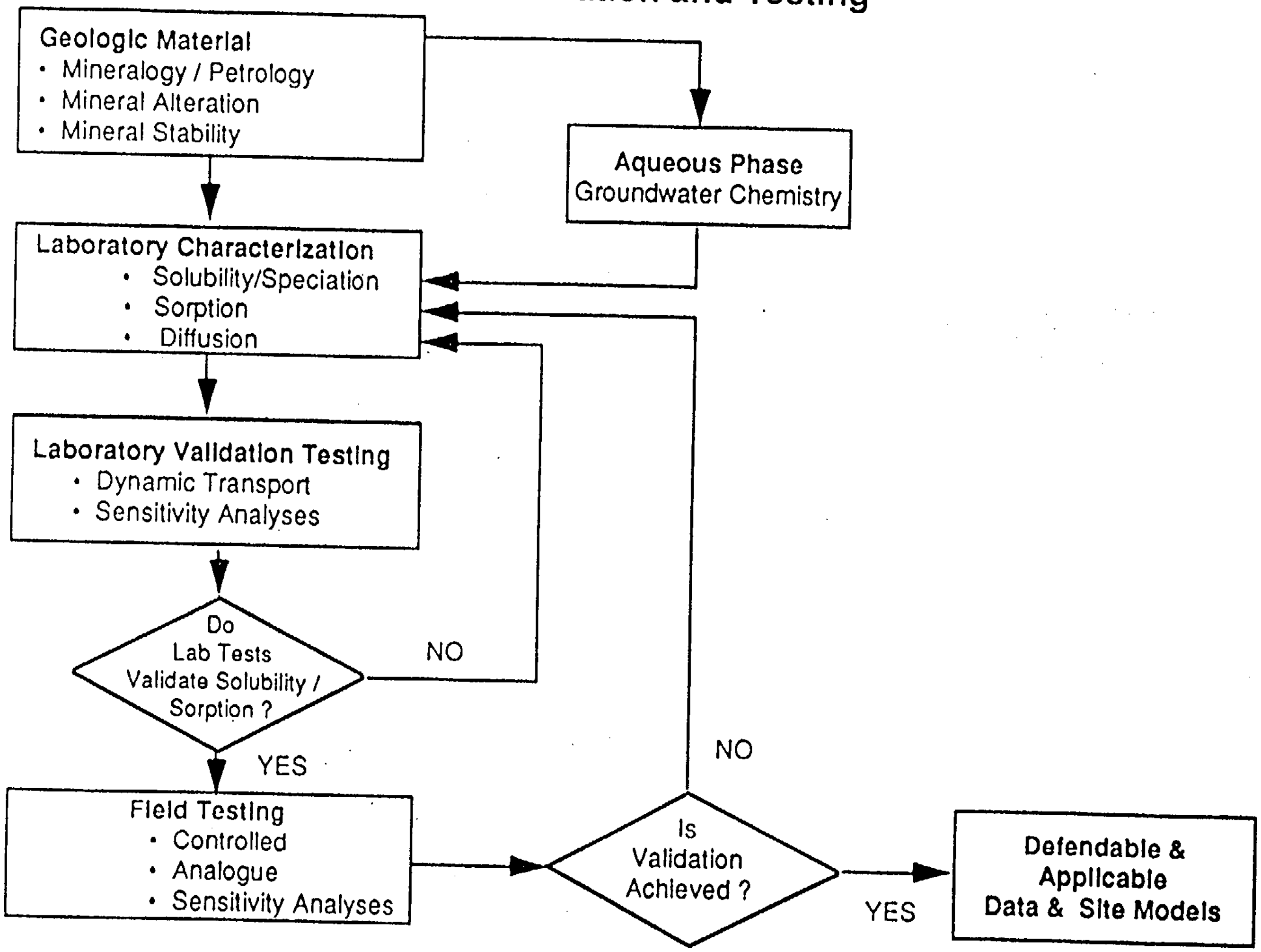
Radionuclide Migration

Site Performance

Performance Assessment Strategy



Los Alamos Strategy for Radionuclide Migration Characterization and Testing



Geologic Material
- Mineralogy / Petrology
- Mineral Alteration
- Mineral Stability

Aqueous Phase
Groundwater Chemistry

Laboratory Characterization
- Solubility/Speciation
- Sorption
- Diffusion

Laboratory Validation Testing
- Dynamic Transport
- Sensitivity Analyses

Do Lab Tests Validate Solubility / Sorption ?

NO

YES

Field Testing
- Controlled
- Analogue
- Sensitivity Analyses

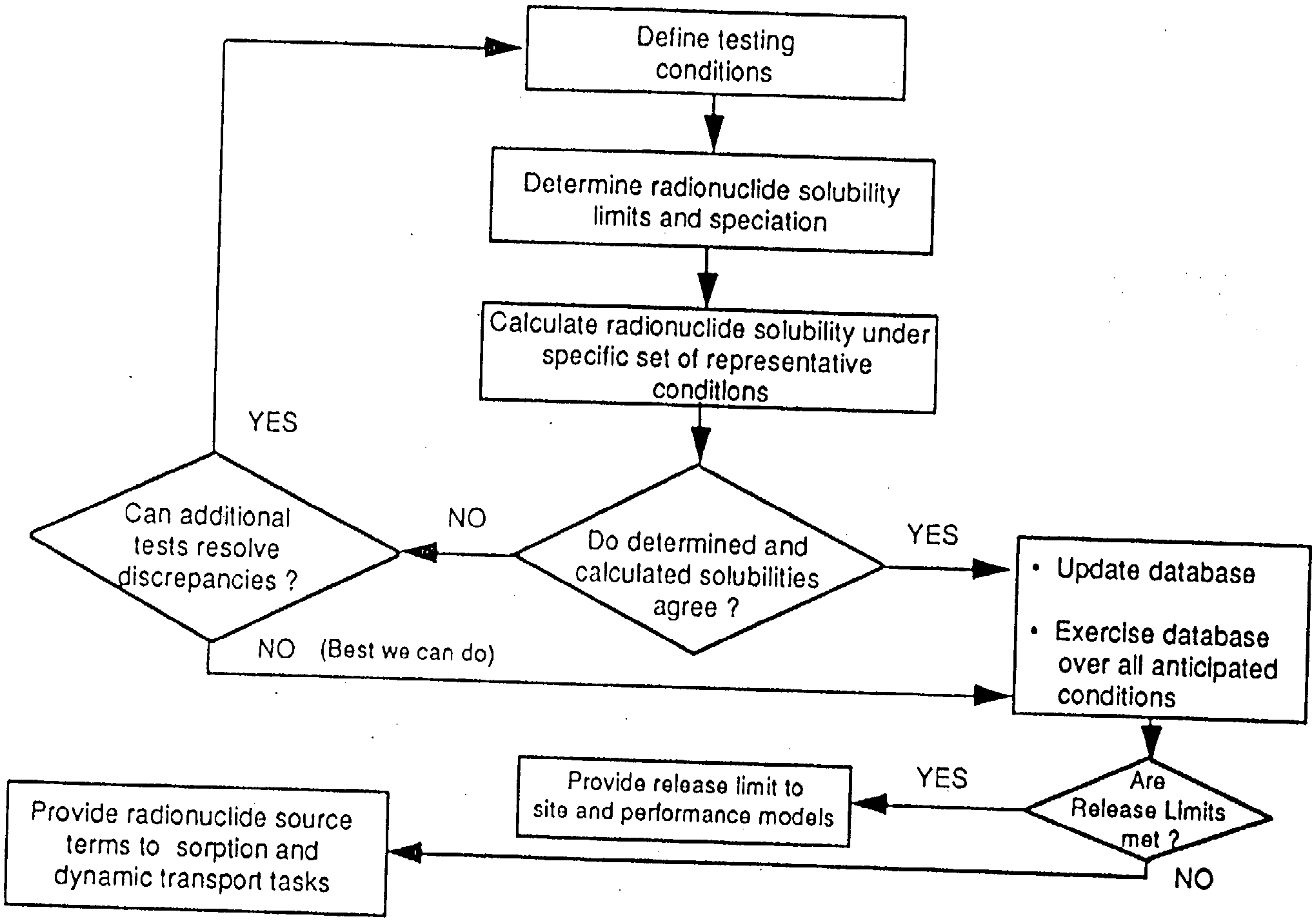
Is Validation Achieved ?

NO

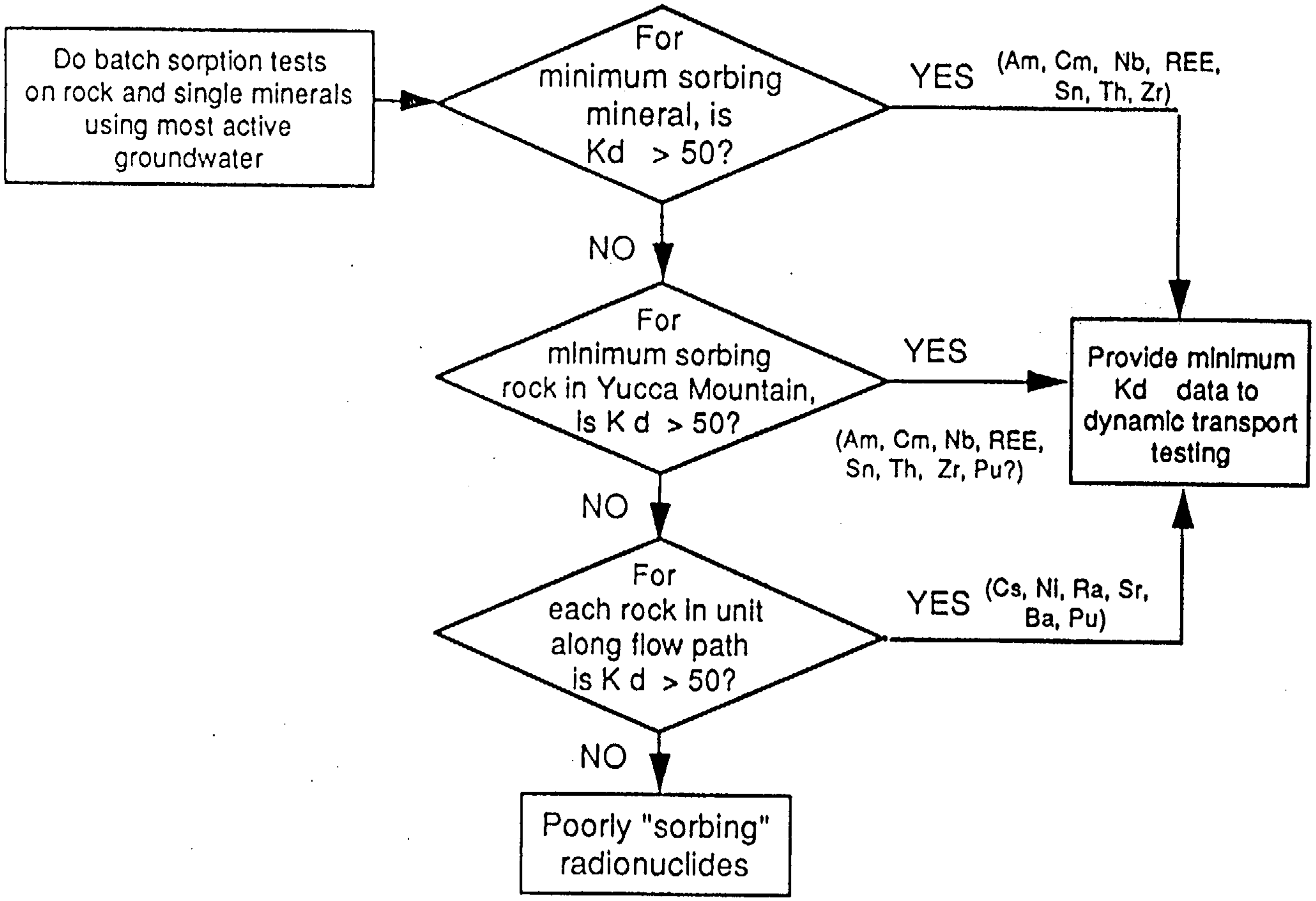
YES

Defendable & Applicable Data & Site Models

Strategy for Dissolved Species Concentration Limit Studies

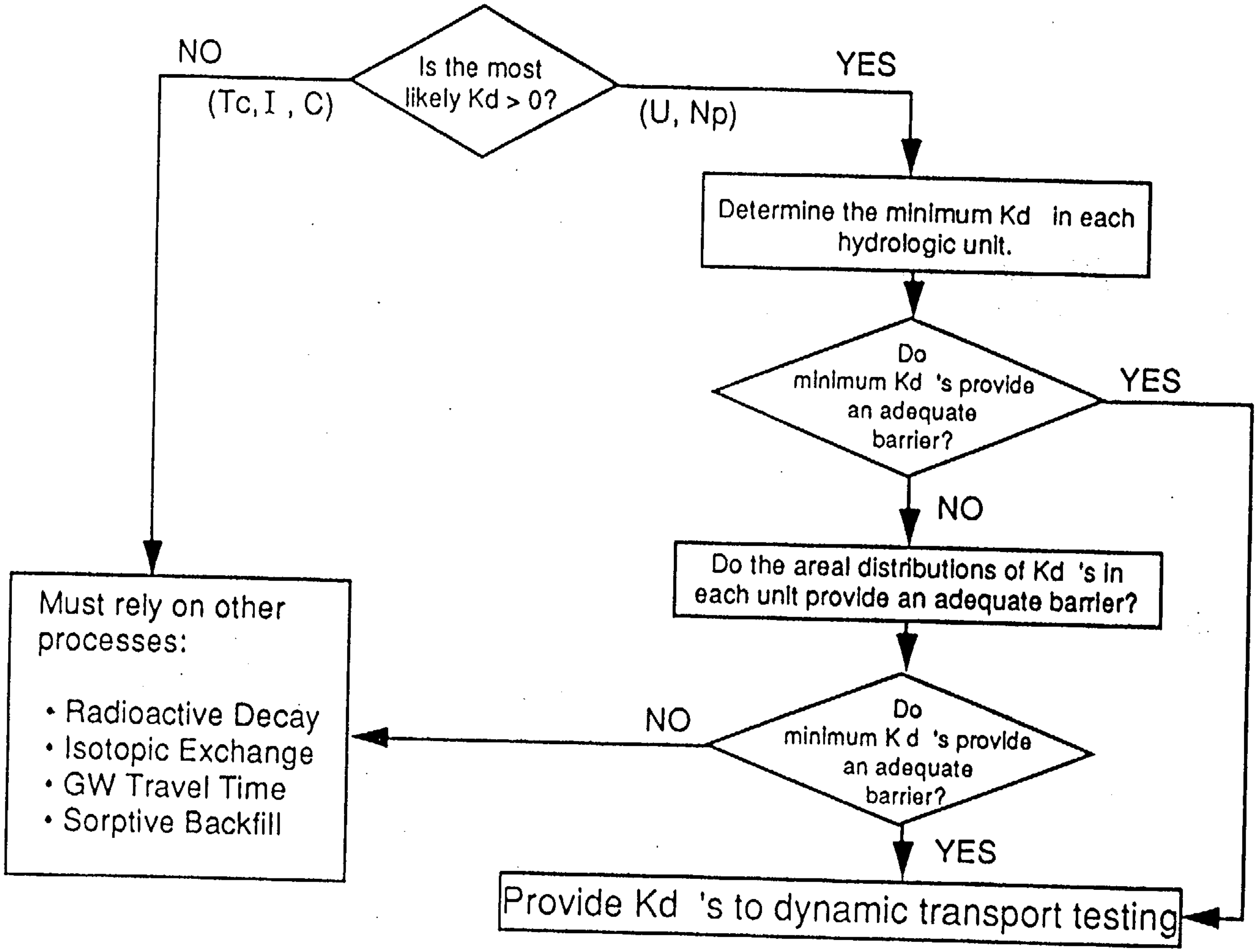


Strategy for Strongly Sorbing Radionuclides (Minimum Kd)

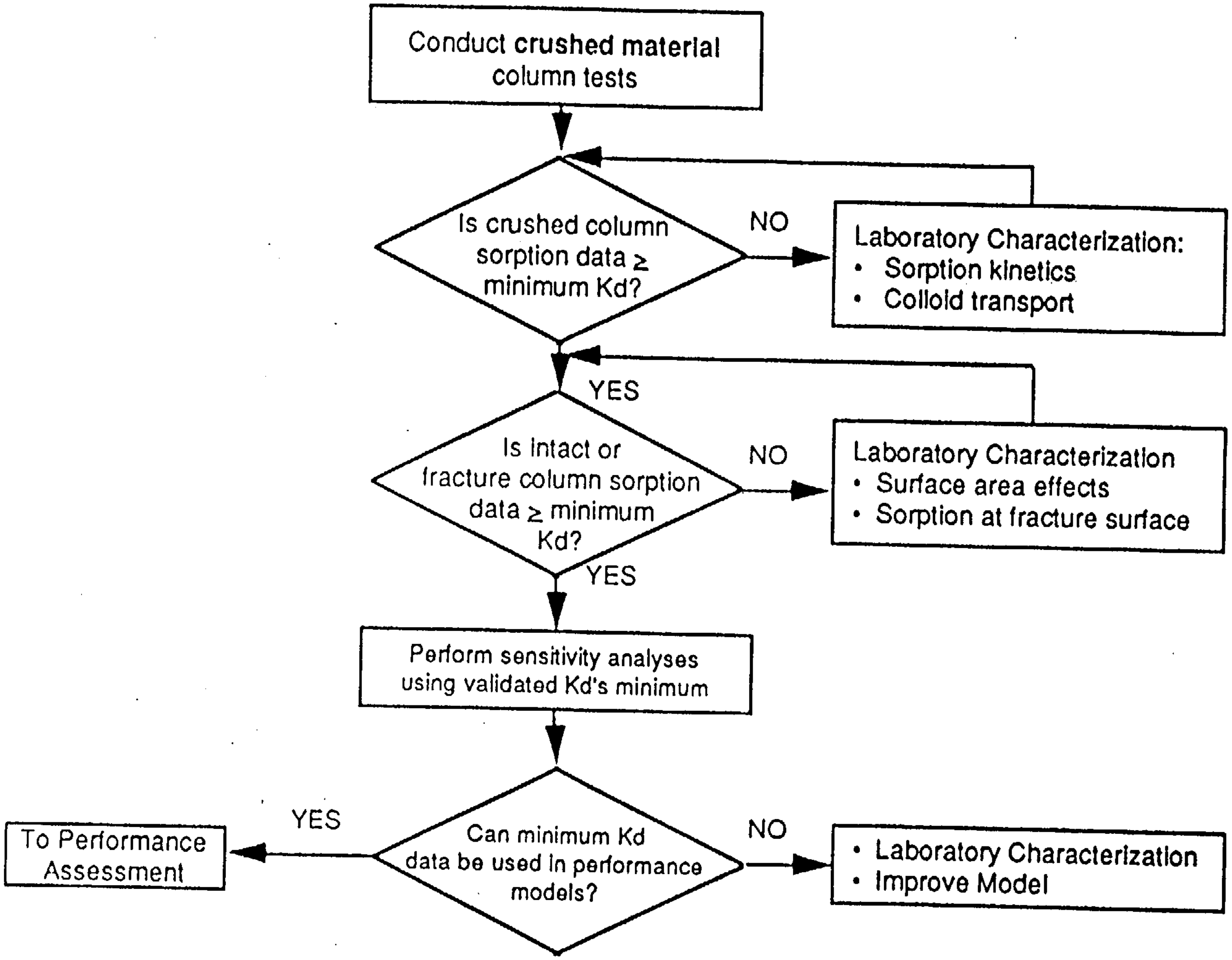


(Kd in ml/g)

Strategy for "Poorly" Sorbing Radionuclide (U, Np, Tc, I , C)



Strategy for Laboratory Validation Testing (Dynamic Transport)



Conduct crushed material column tests

Is crushed column sorption data ≥ minimum Kd?

NO

Laboratory Characterization:
- Sorption kinetics
- Colloid transport

YES

Is intact or fracture column sorption data ≥ minimum Kd?

NO

Laboratory Characterization
- Surface area effects
- Sorption at fracture surface

YES

Perform sensitivity analyses using validated Kd's minimum

Can minimum Kd data be used in performance models?

YES

To Performance Assessment

NO

- Laboratory Characterization
- Improve Model

Part II. Overview o Work (1990 - 1993)

- **Colloid-Facilitated Radionuclide Transport**

- **Microbial Effects on Actinide Transport**
  - Microbial Enhancement of Mineral Dissolution
  - Effect on Transport

- **Groundwater Chemistry Studies**
  - Speciation of Np in Natural Groundwaters

- **Solubility of Np, Am, Pu in J-13 and UE25-p#1**

- **Speciation of Actinides using PAS and NMR**

- **Sorption Studies**
  - Effect of Grinding on Sorption Measurements
  - Np Transport through Tuff
  - Np Sorption onto Iron Oxide Minerals
  - AFM Studies on Iron Oxide Mineral Surfaces
  - Surface Complexation Studies
  - Effect of Organic Coatings on Sorption

Part II. Overview of Wor (1990 - 1993) (continued)

- **Diffusion Studies**

- **Retardation Sensitivity Analyses**

- **Intermediate-Scale Transport Studies**
  - -Caissons

- **Field Studies**
  - - Natural Analogs
  - - Anthropogenic Analog

Part III. Colloid-Facilitated Radionuclide Transport

Colloid Nomenclature

- **Groundwater Colloids**

  naturally occurring in aquatic systems and consist of inorganic and/or organic molecular constituents or microorganisms

- **Anthropogenic Colloids**

  produced by physical, chemical, or biological processes acting on human-introduced materials

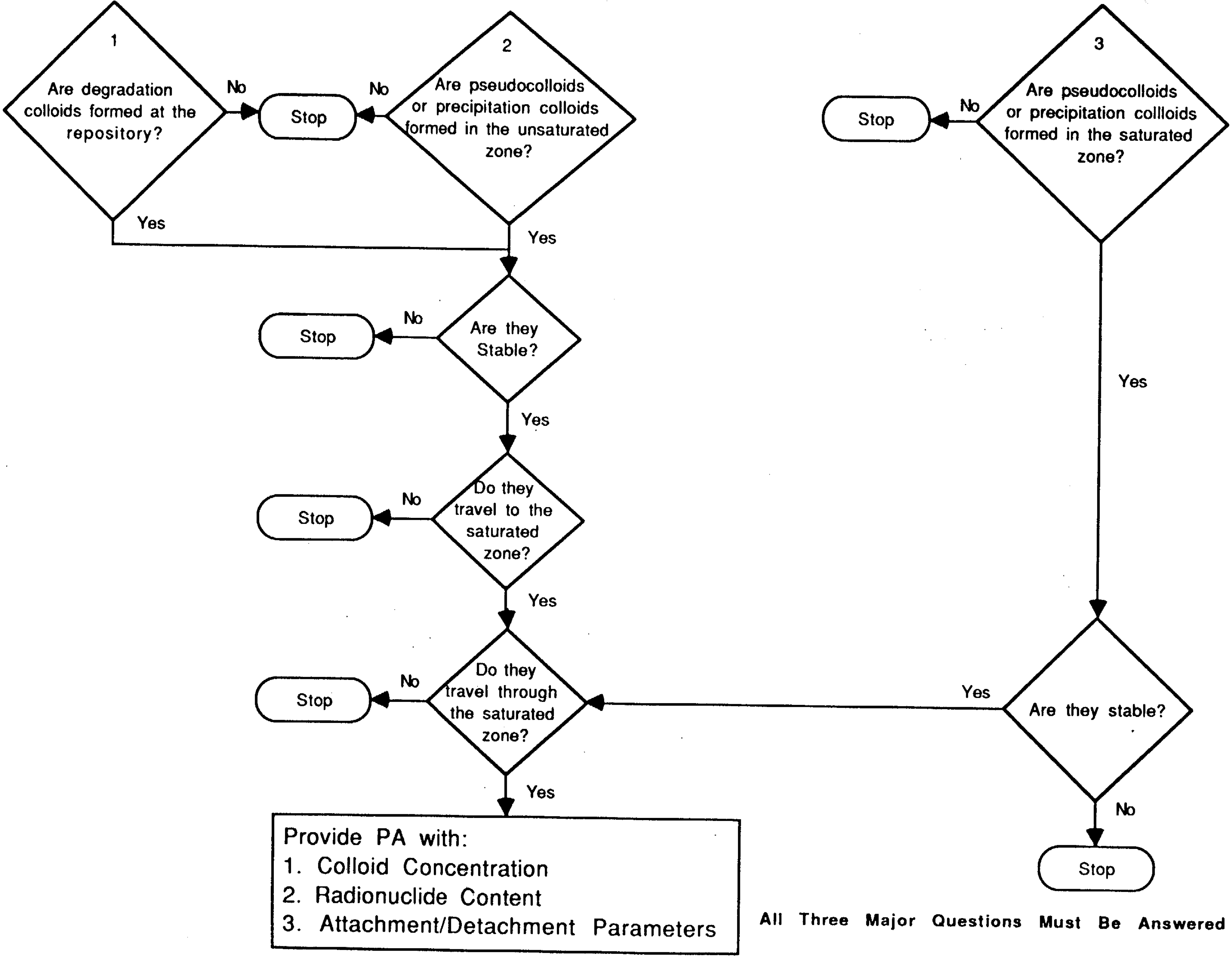
  Radioactive waste-derived colloids

  degradation colloids - generated by disaggregation or spalling of actinide solid phases directly from the waste form

  precipitation colloids - generated from solutions that are supersaturated with respect to actinide solid phases (include real actinide colloids produced by the agglomeration of hydrolyzed actinide ions which are traditionally referred to as radiocolloids)

  pseudocolloids - generated by the attachment of radionuclides (in soluble or colloidal form) to other colloids (such as groundwater colloids)

YMP Colloid Strategy



What colloids are present?

- sample to measure concentrations and perform characterization of inorganic colloids, organics, and microorganisms in waters from the saturated zone
- perform laboratory experiments to address formation and properties of degradation colloids, radiocolloids, and pseudocolloids
- perform natural analog studies at Yucca Mountain to address the formation of colloids by natural glass alteration in a repository hydrothermal environment

Life History of Colloids Under Hydrothermal Conditions

- Generation
- Transport
- Deposition
- Crystallization

Pseudocolloid Formation

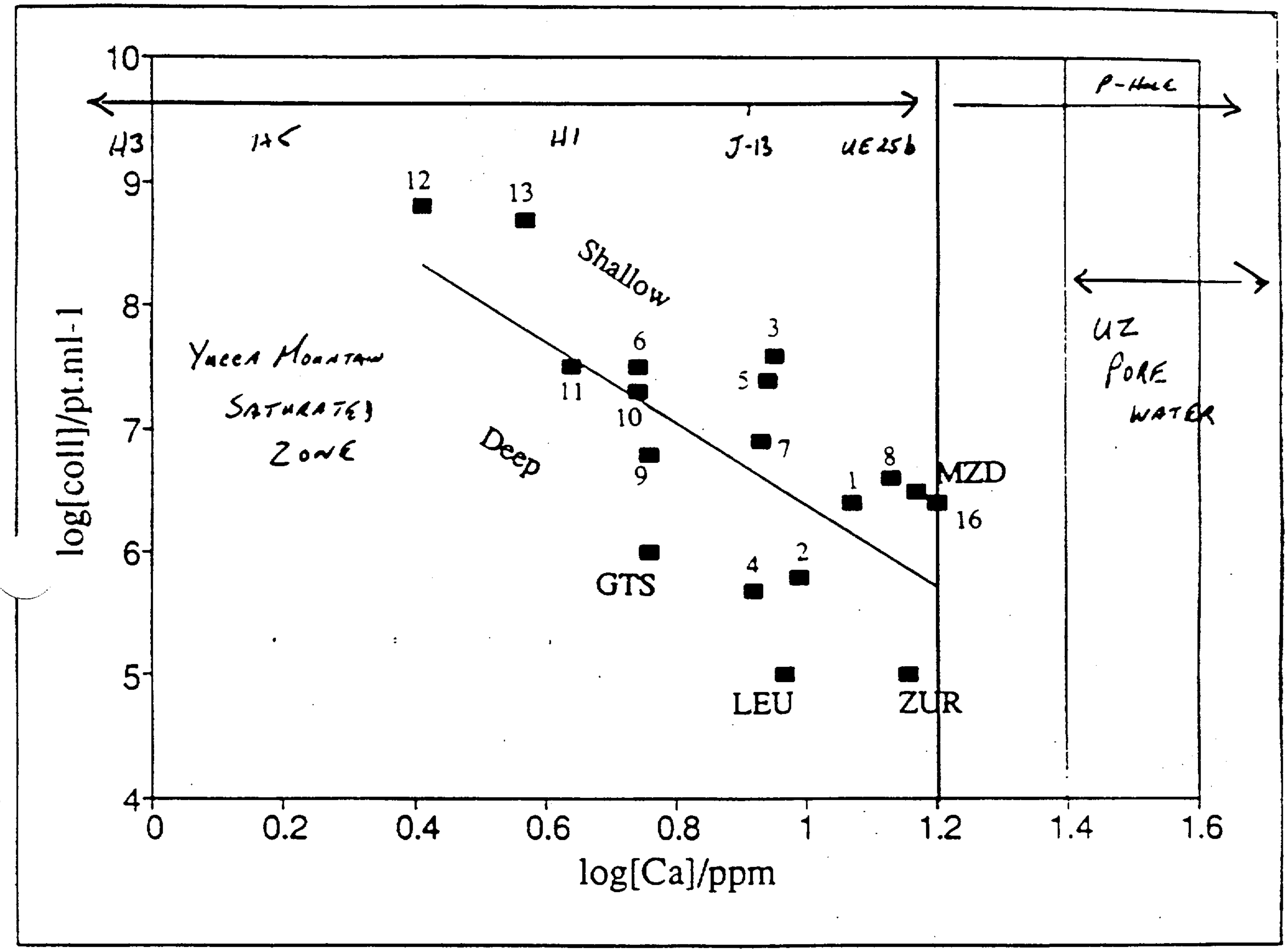
- determine radionuclide distributions between the colloids and the groundwaters and assess the reversibility of the sorption mechanism of radionuclides onto colloids

- use spectroscopy studies to identify the chemical reactions between the radionuclides and the colloids

Colloid Stability

- determine stability of colloids as a function of T and water chemistry

PSI/WASTE MANAGEMENT PROGRAM/COLLOID SUBPROGRAM



Correlation between colloid and Ca concentration in granitic groundwaters.

Conditions: [coll] for size > 100 nm, sites:

Transitgas tunnel (N^0 label), Menzenschwand (MZD)

Grimsel Test Site (GTS), Zurzach (ZUR), Leugern (LEU).

Colloid Stability in a Nuclear Waste Repository

by

Anders O. Wistrom[1] and Inés R. Triay[2]

Introduction

Addressing the question of whether colloids will significantly increase radionuclide releases from a potential high-level nuclear waste repository at Yucca Mountain to the accessible environment requires the study of: colloid generation, colloid stability, and colloid transport along potential flowpaths. The objective of this research is to ascertain under what conditions radioactive-waste derived colloids will remain in suspension. A series of laboratory aggregation experiments are underway to determine the stability of colloids in synthetic and natural groundwaters as a function of groundwater chemistry, temperature, and particle mineralogy and surface coatings. Based on the results of these experiments, particle aggregation rate constants are calculated and the stability of colloids is established for assessment of radionuclide releases as a result of colloids in a nuclear waste repository.

Description of Actual Work

The particle aggregation rate constant for the early stages of the aggregation process is estimated using a light scattering technique, autocorrelation photoacoustic spectroscopy [1,2,3]. The autocorrelation function allows measurement of the translational diffusion of particles in suspension. Particle size is inversely proportional to the translational diffusion coefficient. Therefore, the degree of particle size heterogeneity can be estimated by measuring the change in particle size caused by the formation of doublets in an aggregating monodisperse suspension.

---

[1] EES-13, MS H824, Los Alamos National Laboratory, Los Alamos, NM 87545

[2] INC-9, MS J514, Los Alamos National Laboratory, Los Alamos, NM 87545

For a discrete particle size distribution, the generation of doublets by collisions of primary particles is represented by a second-order rate law [4].

$$\frac{\partial n_1}{\partial t} = - k_{11} n_1^2 \tag{1}$$

In Equation (1), k_{11} is the rate constant for doublet formation and n_1 is the number concentration of primary particles. By measuring the rate of change of the autocorrelation function, one can determine the rate of formation of doublets, k_{11}, which is given by Equation (2), where Φ is an optical factor, $n_{1\,(t=0)}$ is the initial number concentration of primary particles, d_{mean} is the measured mean diameter of particles in suspension, and t is time.

$$d_{mean}\, k_{11} = \frac{1}{\Phi\, n_0} \cdot \frac{\partial(d_{mean})}{\partial t} \tag{2}$$

Autocorrelation photoacoustic spectroscopy measurements are made with a Malvern Zetasizer III Photon Correlation Spectrometer. Experimental run times for three replicate size determinations at each sampling time are typically 30, 60, and 90 seconds. Sampling times are dependent on particle concentration and ionic strength of the medium. Measurements are made at a scattering angle of 90° using a 5 mW He-Ne laser at a 633 nm wavelength.

To fulfill the objectives of this research, the chemical composition of the aqueous medium was designed to mimic prevalent and future groundwater compositions at Yucca Mountain [5]. Particles chosen for this research are smectite clay and amorphous silica. The choice of particles is based on their prevalence in the natural environment, their previous use in aggregation studies, and the requirement that particulate suspensions can be made in a consistent and reproducible manner. All experiments are performed at 20, 40 and 60° C. Observed differences in particle aggregation behavior can therefore be ascribed to differences in solution chemistry (i.e., ionic strength and pH), particle composition and temperature.

Results

The sensitivity to detect differences in the mean diameter, d_{mean}, by autocorrelation photoacoustic spectroscopy is illustrated in Figure 1. In this set of preliminary experiments very small amounts of latex particles with a diameter of 298 nm were added to a suspension of monodisperse latex particles with an average diameter of 105 nm.

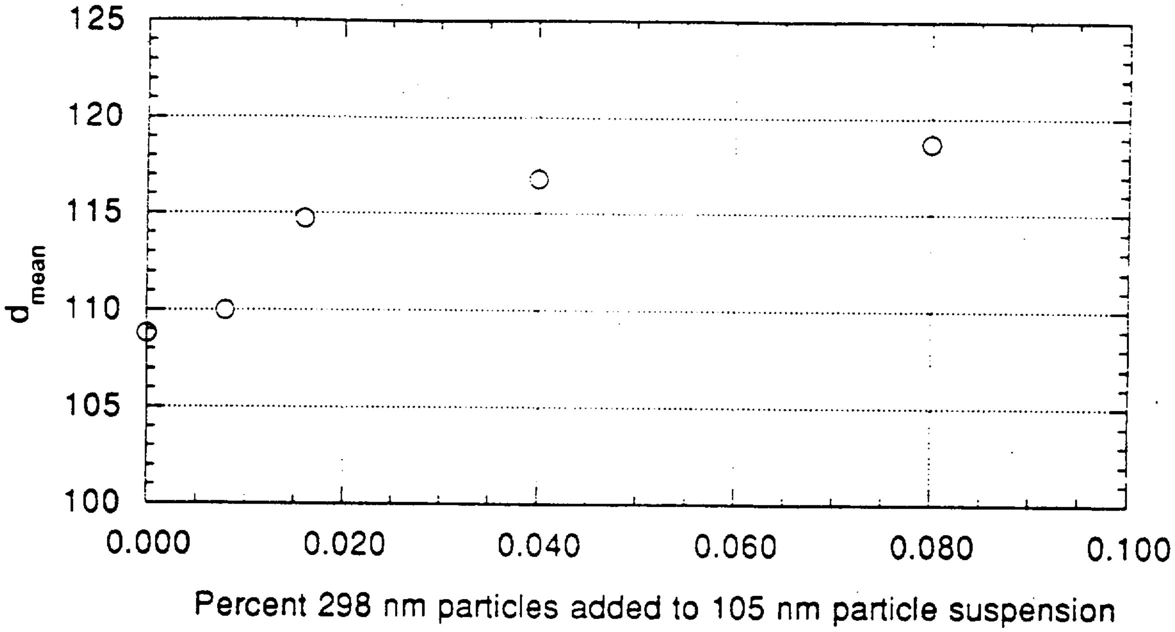


Figure 1. Detection of very small numbers of 298 nm particles added to a 105 nm particle suspension.

It has also been established by others [6] that autocorrelation photon spectroscopy measurements are sensitive to very small changes of the measured mean diameter and can therefore detect the formation of doublets in an aggregating monodisperse suspensions. Consequently, the methodology utilized in this work is capable of accurately determining aggregation rate constants for colloidal suspensions.

The results of aggregation experiments utilizing latex particles and amorphous colloidal silica as a function of ionic strength in synthetic and natural groundwaters from Yucca Mountain will be presented. Aggregation experiments as a function of temperature will also be presented. These results will include the relationship between aggregation rate constants, chemical composition of the medium (e.g., ionic strength and pH) and temperature to allow determination of the highest concentration of a particular chemical species and highest temperature before aggregation takes place. Once the colloidal suspension is destabilized, aggregation results in the formation of large particles that settle out of suspension. Therefore, the experimentally determined particle aggregation constants may be used in predictive transport models to assess the mobility of subsurface colloids along given flowpaths.

Conclusions

In this work, the kinetics of growth of selected particulates in a range of different chemical environments are determined by autocorrelation photon spectroscopy. Comparisons with theoretically derived values will enhance our understanding of the factors dominating colloidal stability. The measured data and the theoretical developments resulting from this work will enhance our predictive capabilities to assess the importance of colloids in facilitating radionuclide transport from a nuclear waste repository to the accessible environment.

References

(1) Virden, J.W. and Berg, J.C., "The Use of Photon Correlation Spectroscopy for Estimating the Rate Constant for Doublet Formation in an Aggregating Colloidal Suspension", J. Colloid and Interface Science, **149**, 2, 528, (1992).

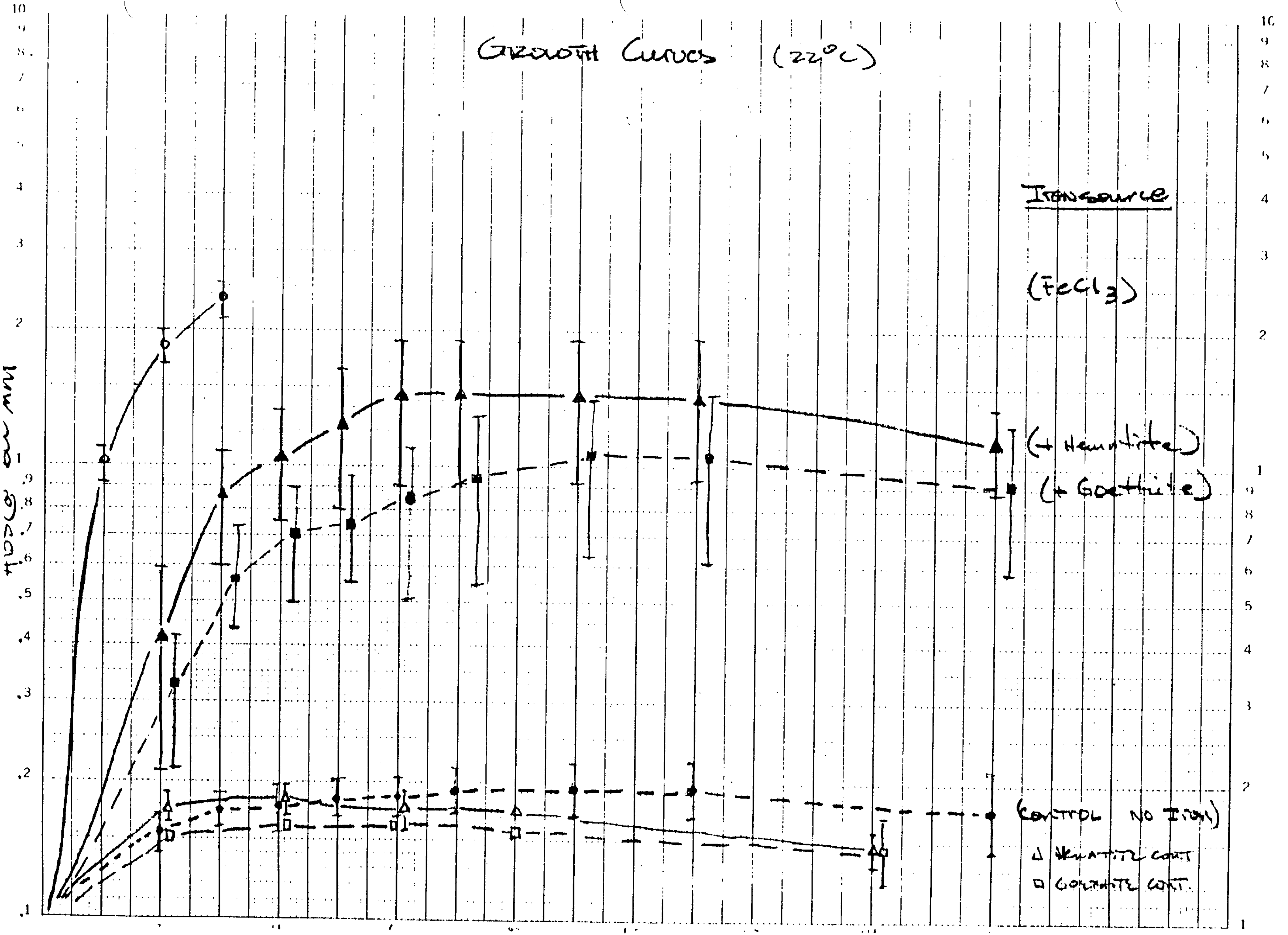
(2) Ostrowsky, N., "Particle Characterization by Photon Correlation Spectroscopy", Proceedings of the 6th Particle Size Analysis Conference, April 19-20, 1988, University of Surrey, Guildford, U.K.

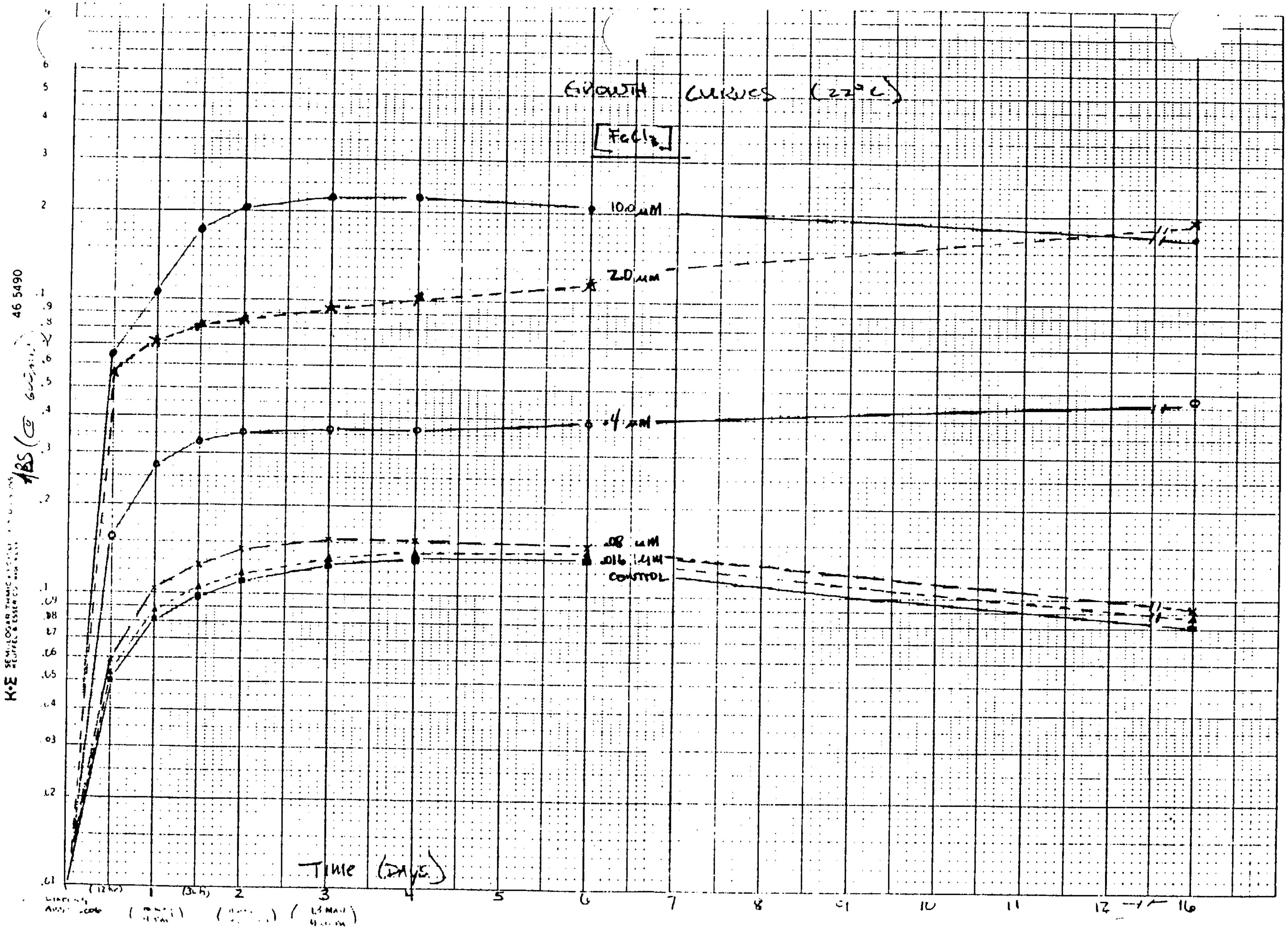
(3) Brown, J.C. and Pusey, P.N., "Photon Correlation Study of Polydisperse Samples of Polystyrene in Cyclohexane", J. Chemical Physics, **62**, 3, 1136, (1975).

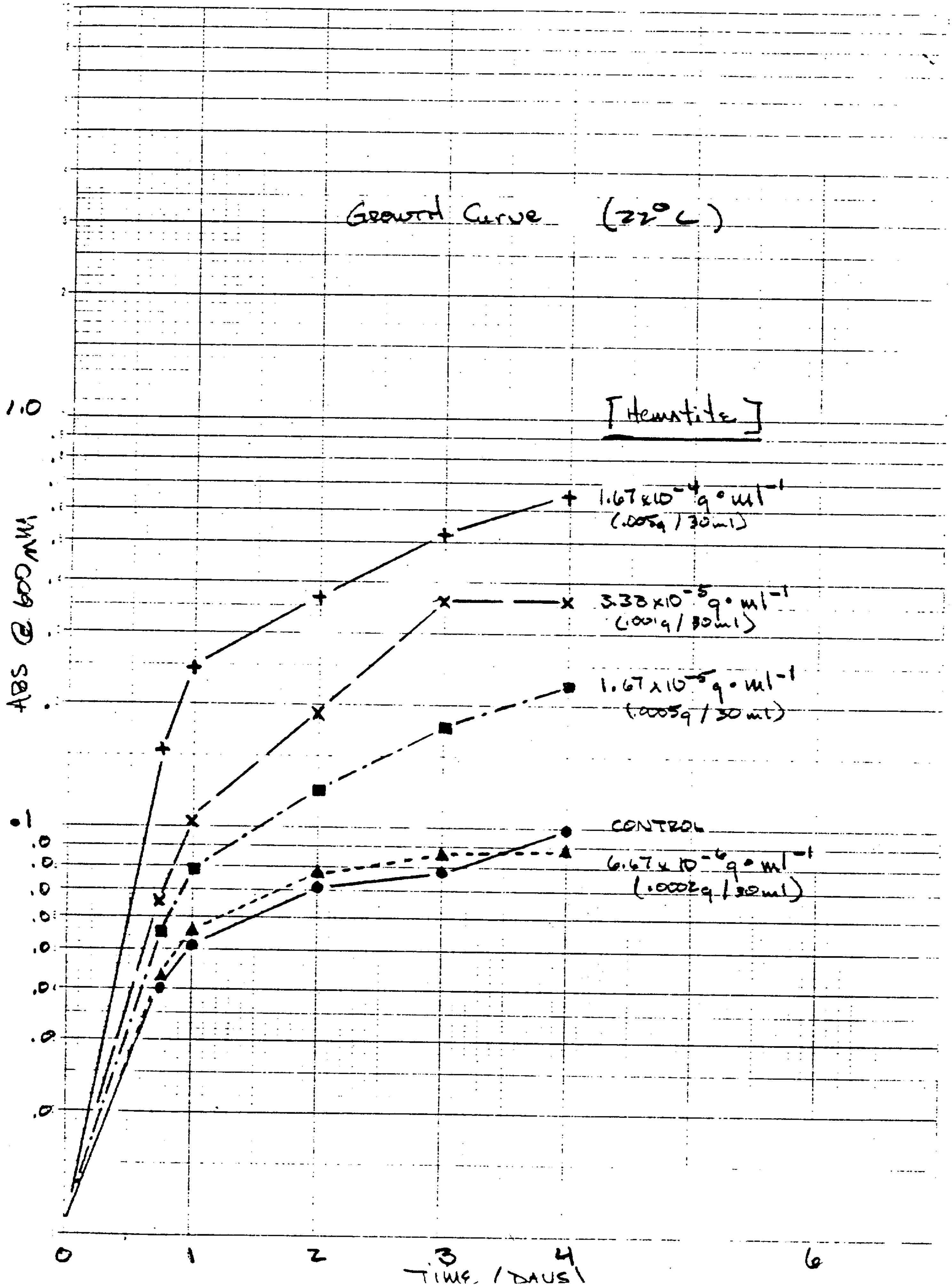
Part IV. Microbial Effects on Actinide Transport

	Cell Culture Abs @ 535nm	Cell Culture + Fe III + BATH ABS - Cell Culture ABS
Control (3 day)	.055	.263
Hematite (3 day)	.125	.646
$FeCl_3$ (6 h)	.097	.943

TABLE 1. REDUCTASE ACTIVITY AS DETERMINED BY Fe(III) REDUCTION.


GROWTH CURVES (22°C)
IRON SOURCE
(FeCl3)
(+ Hematite)
(+ Goethite)
(CONTROL NO IRON)
△ HEMATITE CONT
□ GOETHITE CONT.
+OD@ on MM
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1


K+E SEMI-LOGARITHMIC
KEUFFEL & ESSER CO.
46 5490
GROWTH CURVES (22°C)
[FeCl3]
10.0 µM
2.0 µM
.4 µM
.08 µM
.016 µM
CONTROL
ABS (@
TIME (DAYS)
.01
.02
.03
.04
.05
.06
.07
.08
.09
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
(12 hr)
1
(36 h)
2
3
4
5
6
7
8
9
10
11
12
16

Growth Curve (22°C)
[Hematite]
1.67x10^-4 g • ml^-1
(.005g / 30ml)
3.33x10^-5 g • ml^-1
(.001g / 30ml)
1.67x10^-5 g • ml^-1
(.0005g / 30ml)
CONTROL
6.67x10^-6 g • ml^-1
(.0002g / 30ml)
ABS @ 600 mμ
1.0
.1
0
1
2
3
4
6
TIME (DAYS)

Part V. Analogs

Los Alamos
NATIONAL LABORATORY

ENVIRONMENTAL RESTORATION PROGRAM

Fact Sheet for Operable Unit 1144 Resource Conservation and Recovery Act Facility Investigation Work Plan

January 1993

Acronyms

DOE	Department of Energy
MDA	Materials disposal area
OU	Operable unit
PRS	Potential release site
RCRA	Resource Conservation and Recovery Act
RFI	RCRA facility investigation
TA	Technical area

This fact sheet provides information specific to OU 1144. General information on the environmental setting of the Laboratory, past cleanup efforts, and ER Program requirements is provided in a separate fact sheet.

The Resource Conservation and Recovery Act (RCRA) facility investigation (RFI) work plan is a document that addresses the site characterization activities for all potential release sites (PRSs) at Operable Unit (OU) 1144. This document was submitted to the Environmental Protection Agency in May 1992. The primary purpose of this work plan is to describe the site characterization activities and verification sampling that address potential contaminant releases from OU 1144. The work plan for OU 1144 is available for public review at the environmental restoration reading room located at 2101 Trinity Drive in Los Alamos and at the information repositories in Los Alamos, Española, and Santa Fe.

Background

OU 1144 consists of Technical Area (TA) 49 and is bounded by Bandelier National Monument to the south and west and by other Laboratory areas on the north and east. This operable unit is an aggregate of 20 PRSs. All of TA-49 is located on land owned by the Department of Energy (DOE).

From late 1959 to mid-1961, TA-49 was the site of underground experiments related to the safety of nuclear weapons. Experiments were carried out in approximately 60 shafts located in the experimental areas shown in Figure 1. In addition to the shafts, a number of support facilities were used, such as radiochemical facilities (for analyses), sumps, and a landfill at which decontaminated building debris was disposed. Experiments at TA-49 ceased in 1961. After 1961, the site was used periodically for a variety of purposes that did not cause any significant additional contamination. Currently, because of its remote location, parts of the site are used on a limited basis by the Laboratory's high-power microwave group, the hazardous devices team, and other Laboratory groups.

The PRS types at TA-49 include underground experimental shafts, landfills, units that contain soil contamination, septic systems, and a chemical leach field.

Past Cleanup Activities

Surface contamination consisting of small quantities of plutonium and uranium has been stabilized with asphalt, concrete, and natural vegetative covers. The largest known accidental contaminant release, which occurred in 1960, involved a release of plutonium and uranium during a drilling operation in a test shaft at Area 2. Contaminated materials were returned to the shaft, and the area over and around the shaft was capped with clean soil and an asphalt cover. Since then, this area has been monitored as part of the Laboratory's Environmental Surveillance Program. Other shafts have been sealed with concrete plugs and natural vegetative covers.

After experiments had been completed in 1961, some surface equipment and structures were removed and decontaminated as necessary. Contaminated debris was disposed at the waste disposal site at TA-54. A second cleanup was completed in 1971 as part of a general Laboratory-wide cleanup program. A forest fire in 1978 destroyed most of the wooden structures remaining at the site. Additional uncontaminated building debris was removed in 1984 before the construction of new structures. A landfill in the northwest portion of TA-49 was used for disposing of nonhazardous debris during all cleanups.

Current and future sampling includes soil sampling in areas of surface contamination, drilling and core sampling in underground experimental areas, radiological screening of the surface, and sampling existing monitoring holes.

Contaminants and Pathways of Concern

The experimental shafts that are part of Materials Disposal Area (MDA) AB contain various buried radionuclides, lead, and beryllium from underground experiments related to nuclear safety, which were conducted from 1959 to 1961. Because TA-49 was used primarily for experiments involving materials that needed careful tracking, the identity and quantity of the wastes at TA-49 are known with an unusual degree of confidence. Waste buried in the shafts of MDA AB at depths from 31 to 108 feet contains plutonium, uranium, beryllium, lead, and nonhazardous wastes (such as steel and cables). The work plan for OU 1144 therefore emphasizes MDA AB.

Known or suspected soil contamination at the remaining PRSs at OU 1144 consists of traces of heavy metals, radionuclides, organics, and other chemicals produced at the facilities that supported the underground experiments.

Groundwater, surface water, and soil samples have been monitored frequently since 1960 as part of the Environmental Surveillance Program. No evidence of any migration of contaminants from these potential sources has been found beyond the boundaries of TA-49 or in the main aquifer, which is 1,200 feet below the operable unit. Prior hydrologic studies of the site indicate that no perched water zones exist at TA-49.

The most likely human populations exposed to contaminants originating at TA-49 are onsite workers. In the case of contaminated surface soils, inhalation, dermal contact, and incidental ingestion are identified as the most likely human exposure scenarios that need to be considered. Workers in adjacent technical areas, visitors to Bandelier National Monument, State Road 4 travelers, and area residents are much less likely to be exposed to contaminants than are onsite workers. Plants and animals that inhabit or traverse TA-49 can be exposed to contaminated soils. No significant direct human exposure routes (other than those created by deliberate excavation) in the foreseeable future have been identified for deeply buried contaminants at TA-49. Over longer periods, surface infiltration to groundwater and intrusive scenarios must be considered because of the magnitude of the original sources.

Site-Specific Approach to Characterization

Samples taken at OU 1144 will be analyzed for the following constituents:

- various radionuclides,
- semivolatile and volatile organic compounds, and
- metals specified by RCRA.

Site characterization activities at OU 1144 involve further assessment of the extent of contamination and the selection of possible cleanup actions. It is expected that the first phase of sampling will take 3 years; however, if results of this sampling indicate that further investigation is necessary, a second phase will occur. A second phase of investigation will probably be necessary at MDA AB. Cleanup alternatives as currently identified range from capping (accompanied by long-term monitoring, maintenance, and access restrictions) to excavation and disposal of contaminated soils.

Schedule

Sampling at OU 1144 will begin in February 1993 and is expected to require about 5 years to complete, contingent on the availability of funding.

Additional information on OU 1144 and on the entire ER Program may be obtained from

Patricia Trujillo-Oviedo
Community Relations Project Leader
Environmental Restoration Program
Los Alamos National Laboratory
Box 1663, Mail Stop P355
Los Alamos, NM 87545
(505) 665-2127 or (505) 665-5000

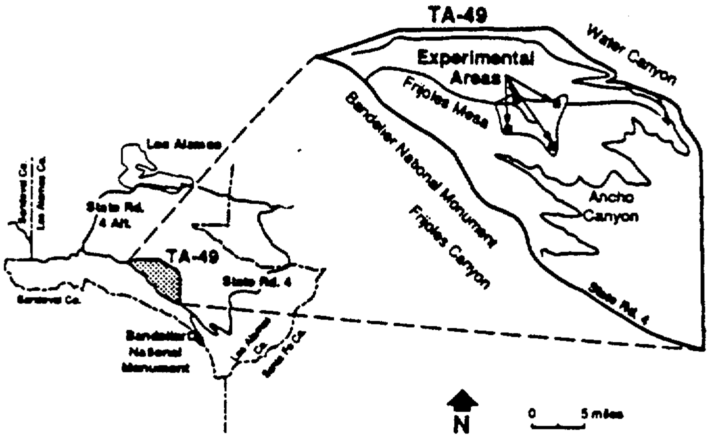


Figure 1. Location of Operable Unit 1144.

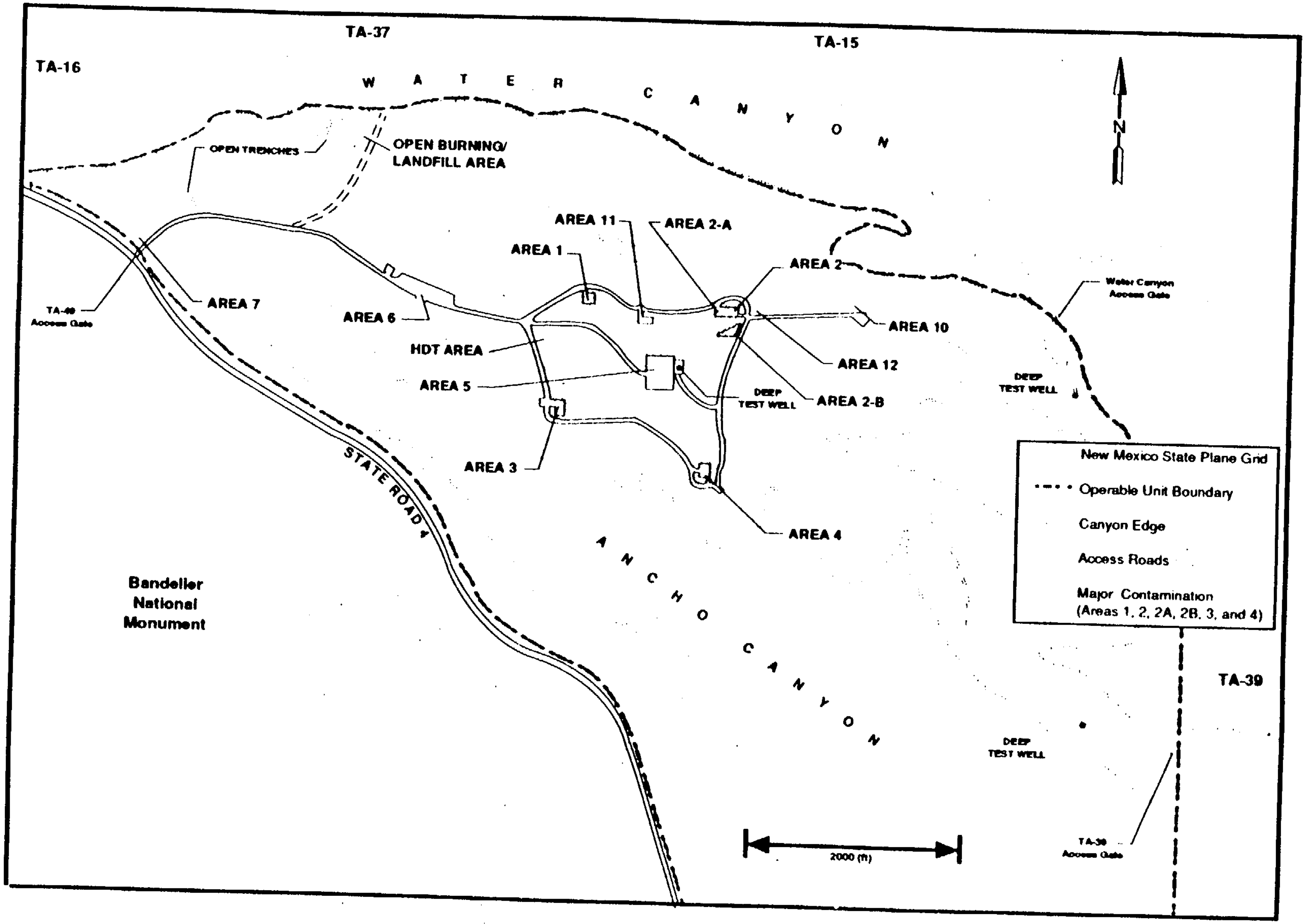
Operable Unit 1144/ Technical Area-49

Los Alamos National Laboratory

Project Leader: Ines Triay
Assistant Project Leader: Greg Bayhurst

Los Alamos
NATIONAL LABORATORY

TA-49 Areas of Contamination



History of TA-49

1959-1961: Nuclear Weapons Safety Experiments
Performed in Underground Shafts

The Lab's objectives were:

- Ensure that no accident involving a nuclear weapon would result in an appreciable nuclear yield
- Develop test containment techniques for NTS

1961-1991: Experimental Activities

- Involved little or no hazardous or radioactive materials

Present Use:

High power microwave experimentation
Hazardous Device Team training area
Buffer zone between high explosives test
areas and National Park Service lands

Los Alamos

Geological and Hydrological Setting of TA-49

Area was selected for tests on basis of USGS study.

Findings:

- Experimental area 1200 feet above main aquifer
- Tests not likely to result in sub-surface water contamination
- 840-870 feet of welded tuffs and pumice
- 500-600 feet of conglomerates, basalts, and dacites

Environmental Status of TA-49

- About 60 underground shafts exist in four experimental areas
- Backfilled shafts are 31 to 130 feet deep
- Shafts contain:

  40 kilograms (88 lbs.) Plutonium
  260 kilograms (572 lbs.) Uranium
  11 kilograms (24 lbs.) Beryllium
  90,000 kilograms (99 tons) Lead

Environmental monitoring has been carried out regularly since the experiments were conducted.

Contamination at TA-49

Area	Pu (kg)	U-235 (kg)	U-238 (kg)
Area 1	1.06	0.00	62.3
Area 2	12.62	47.4	52.5
Area 2A	3.75	9.8	10.6
Area 2B	5.67	6.4	14.7
Area 3	0.00	0.005	0.030
Area 4	17.04	29.4	29.0
TOTAL	40.14	93.0	169.1

Results of Environmental Sampling at TA-49

Since 1959:

- Small quantities of water found in a bore hole in one experimental area
- Minor surface contamination dating from the time of the experiments detected near the experimental areas
- No measurable contamination detected at Laboratory boundaries or nearby public lands (State Road 4 and Bandelier National Monument)

ER Activities at TA-49

Objectives:

- Confirm existing contamination
- Verify the origin of water found in bore hole in experimental area.
- Stabilization and long-term maintenance/monitoring
- Determine if contaminants have moved away from shafts

Activities for 1993

- Collect soil and water samples
- Drill and collect core samples
- Analyze samples for Plutonium, Uranium, Americium, Beryllium, and Lead

DOE-NRC Technical Exchange Radionuclide Migration

Recent solubility results

Kevin Roberts, LBL

50
Los Alamos
NATIONAL LABORATORY
1943 - 1993

DOE-NRC TECHNICAL EXCHANGE
Recent Solubility Results

Kevin E. Roberts, Heino Nitsche, Traudel Prussin,
Anne Müller, Dawn Keeney, Scott A. Carpenter,
Kevin Becraft, and Raymond C. Gatti

Lawrence Berkeley Laboratory
University of California

9/15/93

Acknowledgment

This work was supported by the Yucca Mountain Project Office as part of the Civilian Radioactive Waste Management Program through the Los Alamos National Laboratory (LANL). This project is managed by the U.S. Department of Energy, Nevada Operations Office.

Rationale for Solubility Studies

- Worst case scenario
  - intrusion of water into the repository
- Provide maximum possible concentrations if no retardation would occur
- Identify classes of radionuclides
  - highly soluble
  - insoluble
- Solubility
  - formation of solubility controlling solids
  - formation of soluble species
- Complex Formation
  - oxidation state/speciation/charge

Application of Solubility Information

- Solubility Studies
  - obtain good estimates on the upper limits of radionuclide concentrations in groundwaters from the Yucca Mountain Region
- Predictive Transport Model Validation
  - experimental results verify the chemical component of the transport model
- Data Base Validation
  - validation of existing data in EQ3/6
- Sorption Studies
  - solubility data provide the starting concentration or source terms
    - only soluble species can be transported and absorbed

Experimental Details for the Solubility Measurements

- Used filtered groundwaters from the Yucca Mountain Region
  - J-13 and UE-25p #1
  - different in carbonate concentration and ionic strength
- Supersaturated solubility conditions (Np, Pu, Am)
- pH Values 6, 7, and 8.5
- Temperatures of 25° and 60°C
- Total dissolved carbonate concentration held constant
  - groundwaters saturated with Ar-CO_2 mixture of defined contents for each pH and temperature

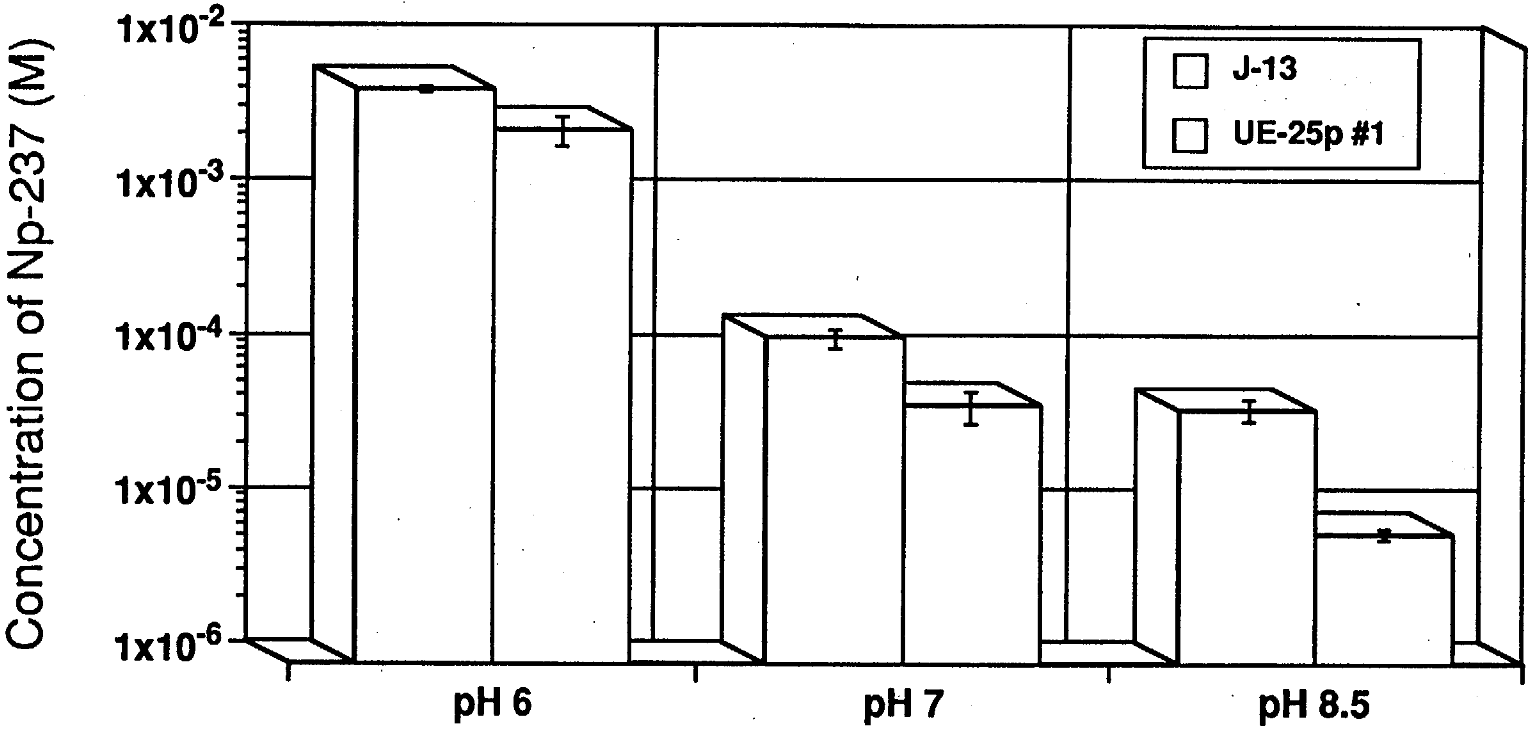
J-13 and UE-25p #1 Groundwater Compositions

Species	Well J-13	Well UE-25p #1
Na^+ (mM)	1.96	7.43
K^+ (mM)	0.14	0.34
Ca^{2+} (mM)	0.29	2.19
Mg^{2+} (mM)	0.07	1.31
$SiO_{2\,(aq)}$ (mM)	1.07	0.62
Cl^- (mM)	0.18	1.04
SO_4^{2-} (mM)	0.19	1.34
F^- (mM)	0.11	0.18
Total Carbonate (mM)	2.81	15.31
Ionic Strength (mM)	~3	~20
pH	7.0	6.7
Total Alkalinity	2.34 meq/L	11.44 meq/L
Eh	700 mV	360 mV

Experimental Details for the Solubility Measurements

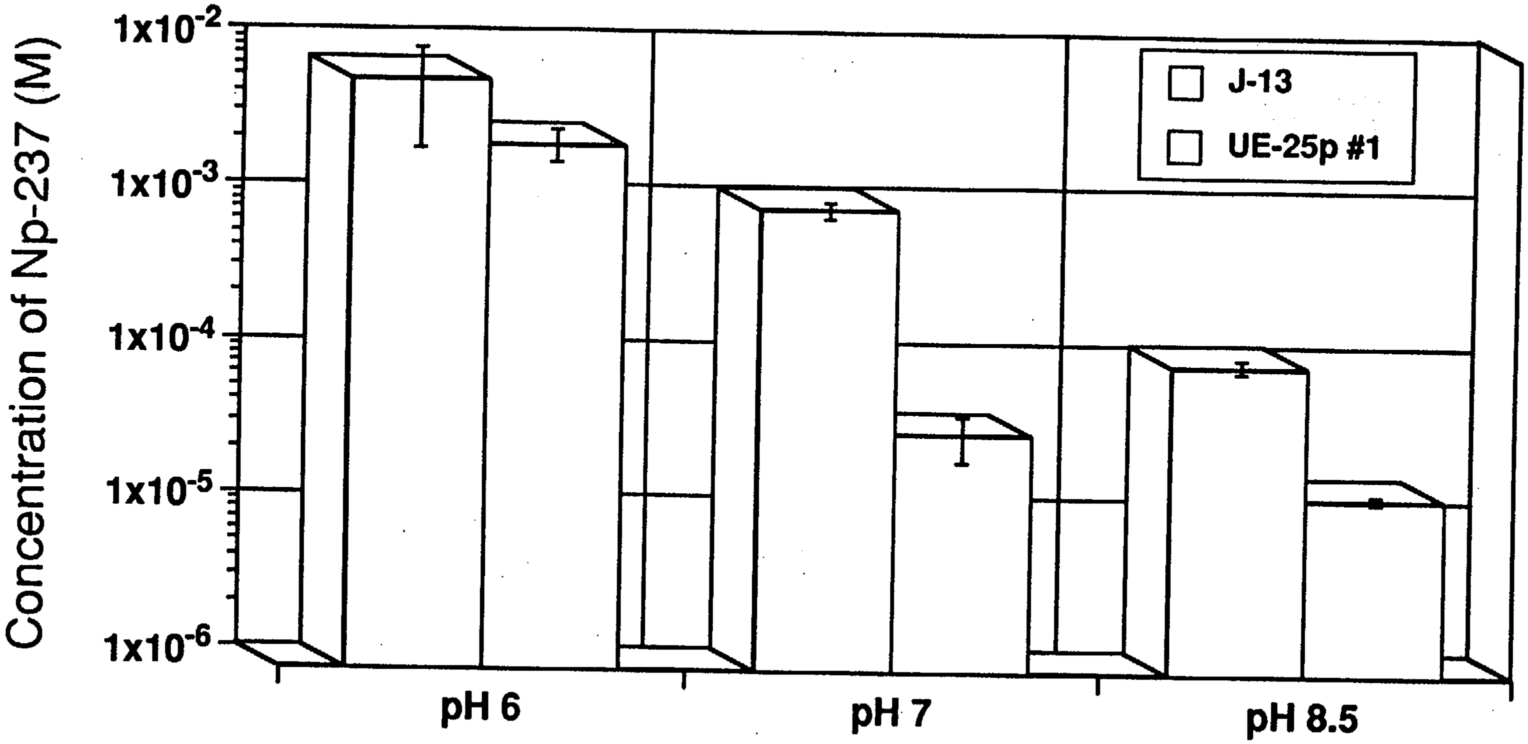
- Used filtered groundwaters from the Yucca Mountain Region
  - J-13 and UE-25p #1
  - different in carbonate concentration and ionic strength
- Supersaturated solubility conditions (Np, Pu, Am)
- pH Values 6, 7, and 8.5
- Temperatures of 25° and 60°C
- Total dissolved carbonate concentration held constant
  - groundwaters saturated with Ar-CO_2 mixture of defined contents for each pH and temperature

Neptunium(V) Solubility in J-13 and UE-25p #1 Groundwaters at 25°C



PRELIMINARY DRAFT
9/15/93

Neptunium(V) Solubility in J-13 and UE-25p #1 Groundwaters at 60°C

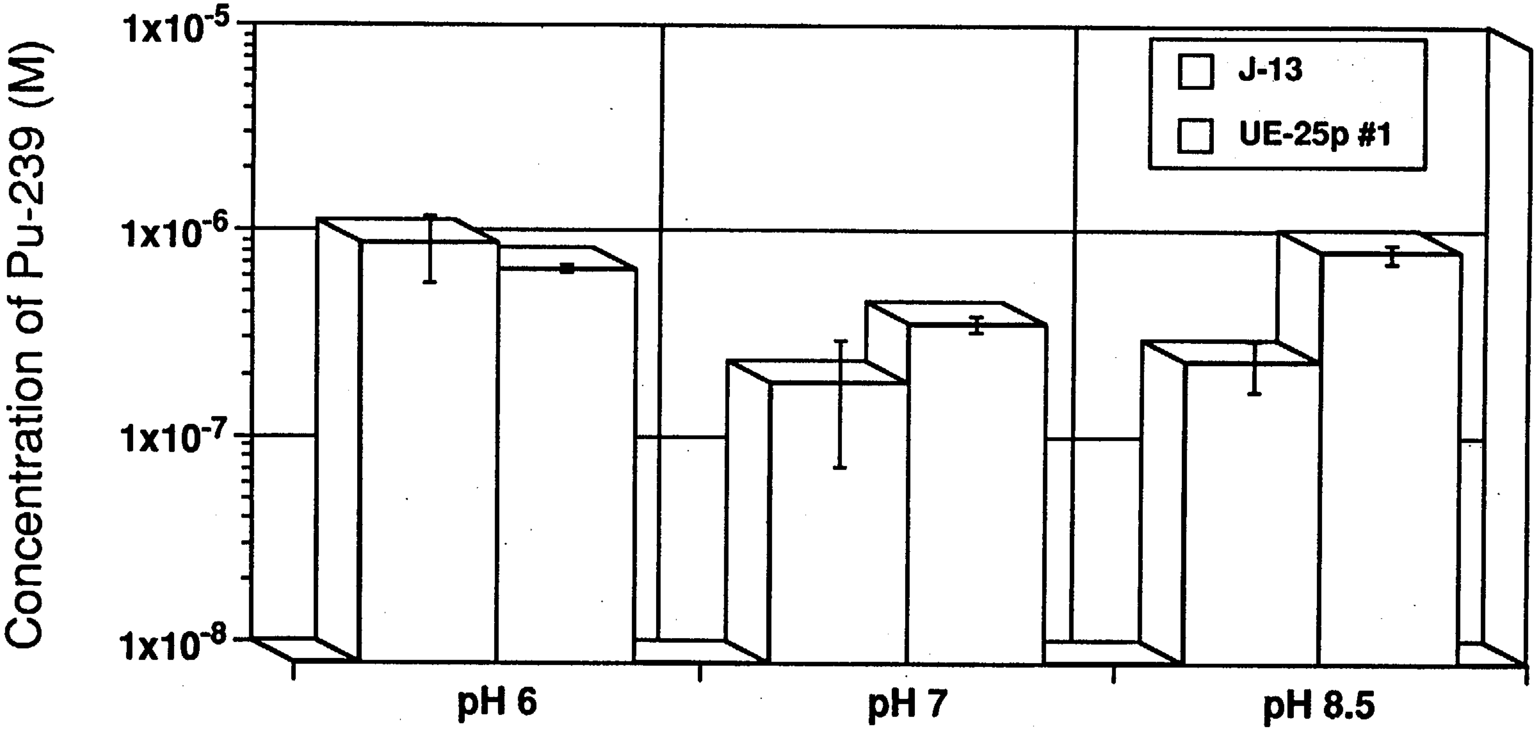


PRELIMINARY DRAFT
9/15/93

Summary of Results for Neptunium

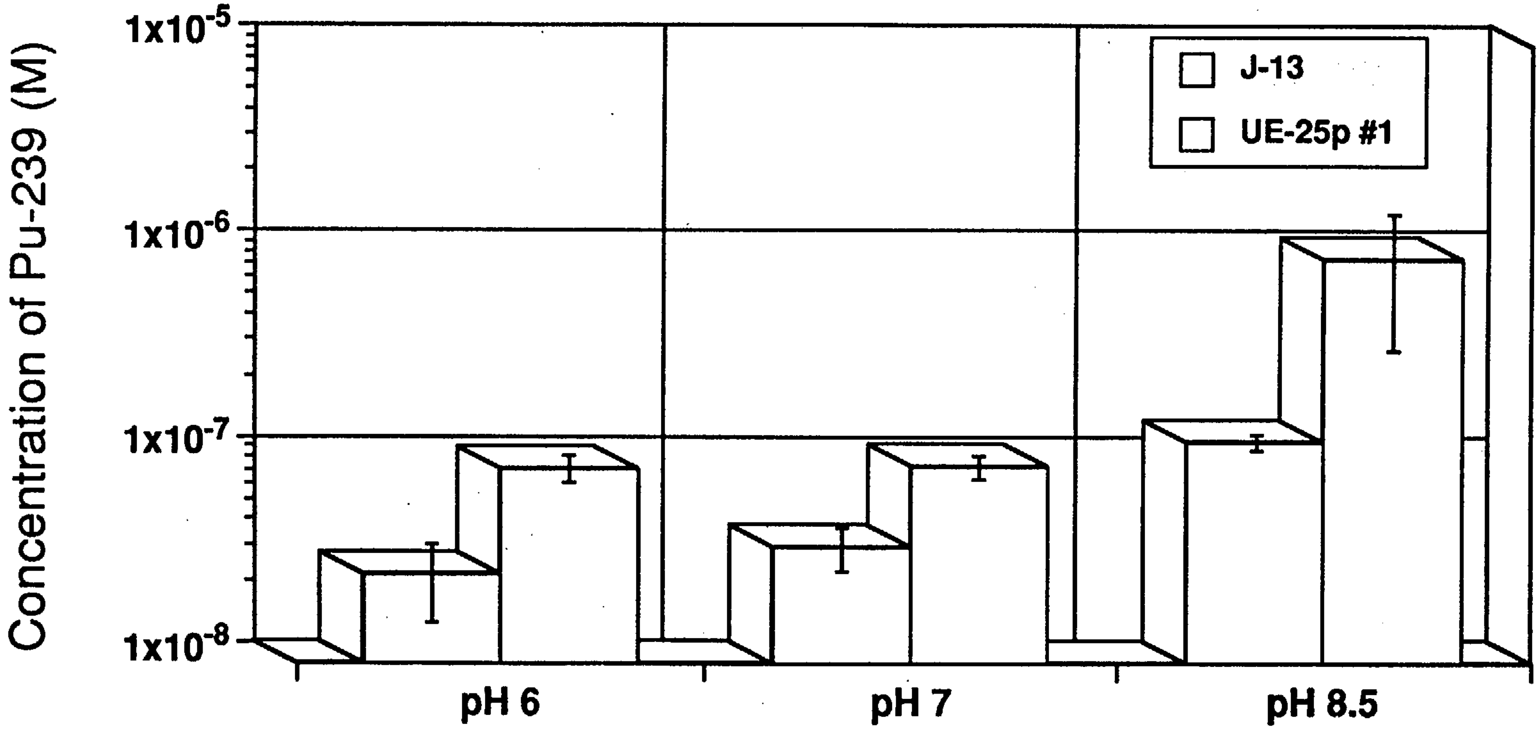
- High solubilities for Np(V) between 10^{-3} and 10^{-5} M
  - – Np(V) solubility decreases with increasing pH
  - – solubility behavior varies slightly as a function of groundwater
    - between 2 to 6 times lower in UE-25p #1
- Solid phases are ternary sodium neptunium carbonates
  - – $NaNpO_2CO_3 \cdot n\,H_2O$
  - – not NpO_2OH as previously assumed by others
- Speciation
  - – Np(V) did not change its oxidation state
  - – increased carbonate complexation with increasing pH
  - – higher neptunium carbonate complexation in UE-25p #1

Plutonium(IV) Solubility in J-13 and UE-25p #1 Groundwaters at 25°C



PRELIMINARY DRAFT
9/15/93

Plutonium(IV) Solubility in J-13 and UE-25p #1 Groundwaters at 60°C



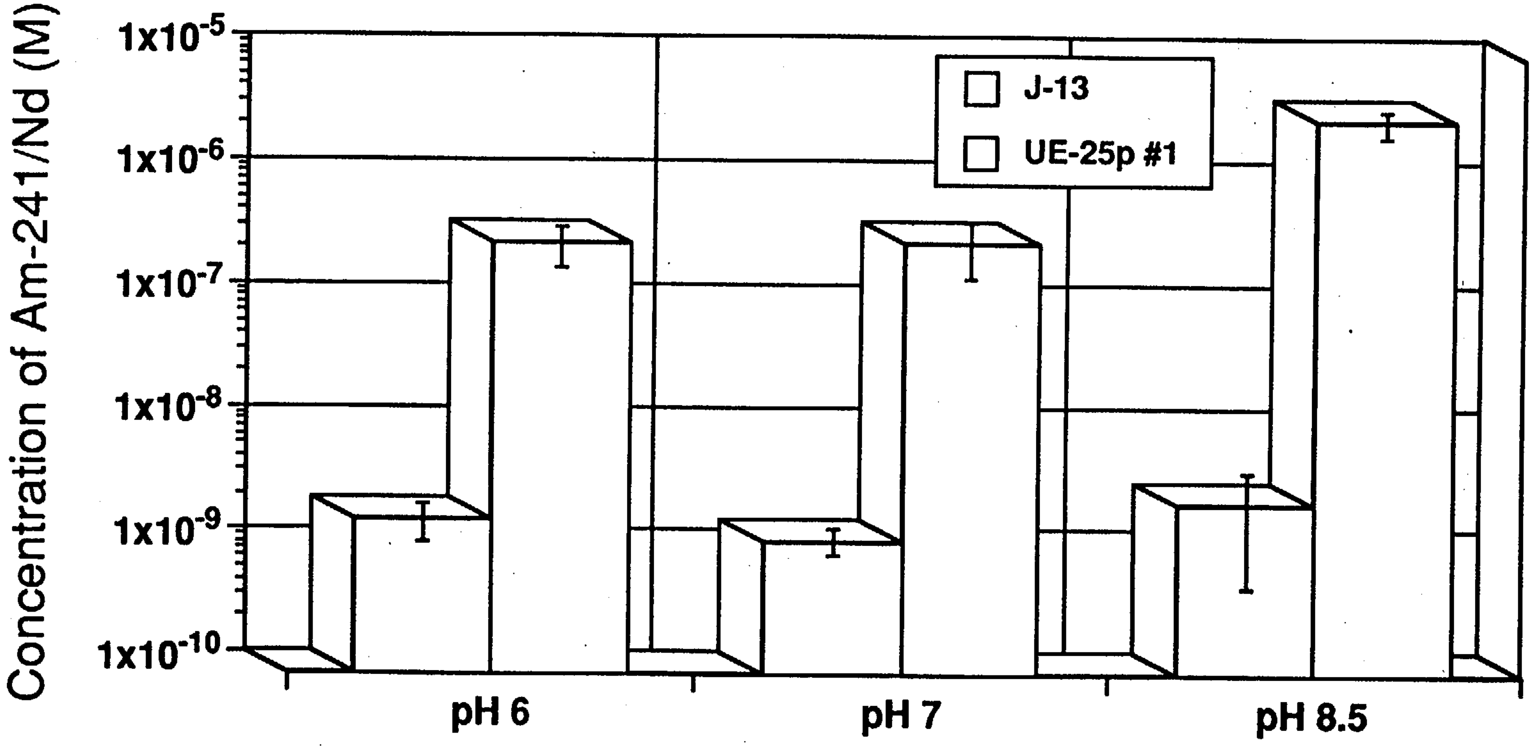
PRELIMINARY DRAFT

9/15/93

Summary of Results for Plutonium

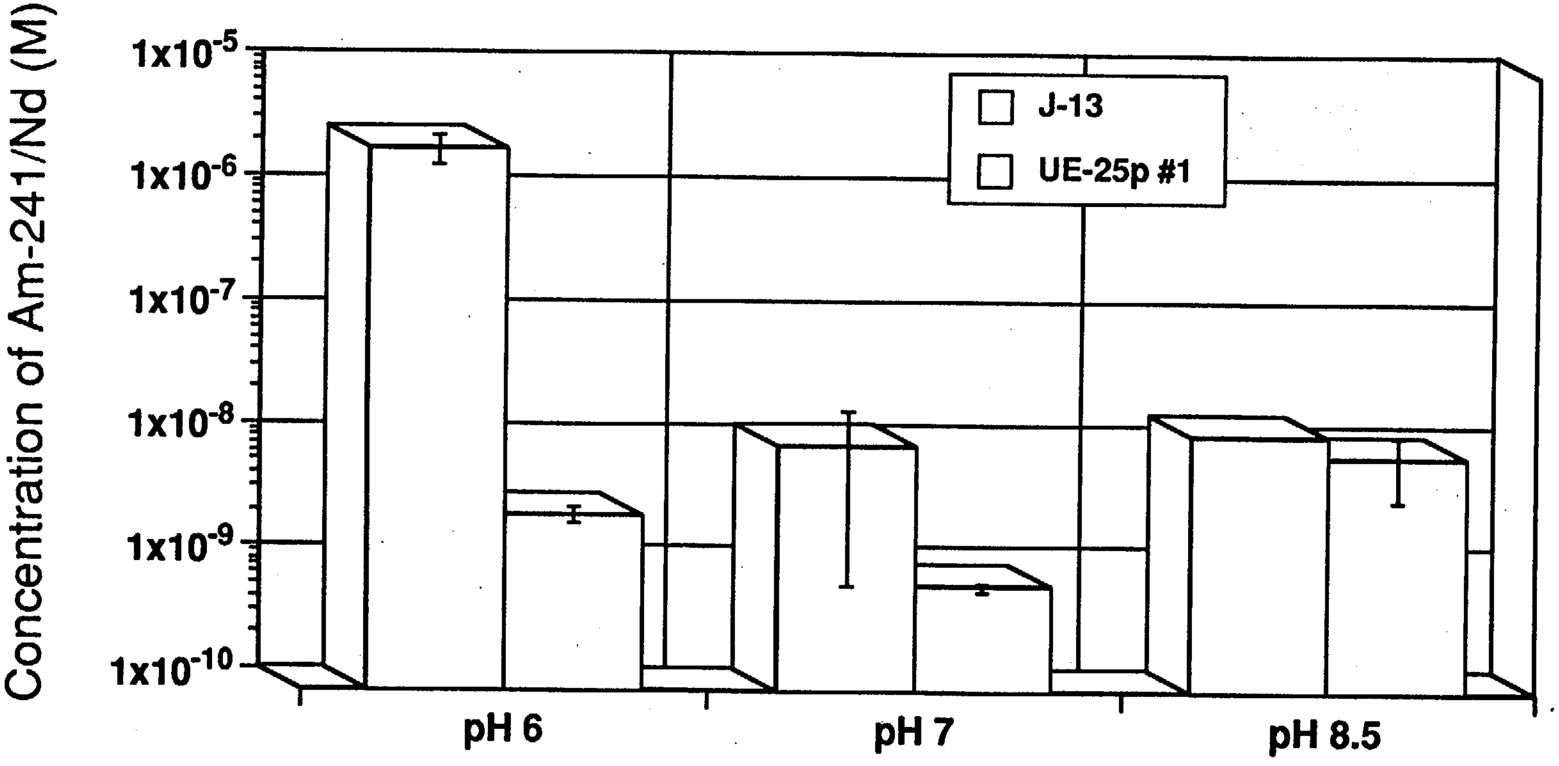
- Plutonium solubilities between 10^{-6} and 10^{-7} M
  - solubility behavior of Pu does not significantly vary as a function of groundwater (J-13, UE-25p #1)
- Solid phases are Pu(IV)-polymers that contain carbonate
  - not PuO_2 as previously assumed by others
- Plutonium speciation
  - indirect method of oxidation state determinations using solvent extractions and a coprecipitation technique
  - Pu(V) is dominant specie in solution in both groundwaters
    - although it was initially Pu(IV)

Americium(III) Solubility in J-13 and UE-25p #1 Groundwaters at 25°C



PRELIMINARY DRAFT
9/15/93

Americium(III) Solubility in J-13 and UE-25p #1 Groundwaters at 60°C



PRELIMINARY DRAFT

9/15/93

Summary of Results for Americium

- Solubility differed significantly for the two waters
  - at 25°C, Am solubilities were two to three orders of magnitude lower in J-13
  - at 60°C, Am solubilities were lower in UE-25p #1
- Solids phases are hydroxycarbonates, $AmOHCO_3$
  - not $Am(OH)_3$ as previously assumed by others
  - hexagonal at pH 6
  - orthorhombic at pH 7 and 8.5 in J-13
- Speciation
  - Am(III) did not change its oxidation state

Conclusion

Solubility and Speciation Studies are Very Important and Useful in Understanding Radionuclide Transport Through the Geosphere

DOE-NRC Technical Exchange Radionuclide Migration

Recent Sorption Results

Inés R. Triay, LANL

50
Los Alamos
NATIONAL LABORATORY
1943 - 1993

Effect of Grinding on Sorption Measurements

PURPOSE

- To determine dependence of measured batch sorption Rd's on <u>sample grinding</u>

- To address concerns raised in an NRC Technical Position Paper

PROBLEM

- Experiments must be performed on actual Yucca Mountain samples

  How does sample grinding interact with the intrinsic porosity, connectivity, and grain size of the sample?

- Impossible to completely separate the major variables:

  Mineral composition (major and trace)
  Sample Surface Area
  Particle Grinding Size

Approach

- Grind samples
- Dry sieve through a stack of graded size sieves
- Check for mineral fractionation

- Regroup -

- Regrind resistant fraction, sieve it, check mineral composition
- Recombine fractions to match original, bulk mineralogy
- Reanalyze and reassess

MINERAL FRACTIONATION DURING GRINDING
ZEOLITIZED SAMPLE

Sample	Clinop.	Mordenite	Quartz	Feld.	Opal-CT	Smectite
Early, Easily Crushed						
250um	29	18	10	15	26	-
106um	34	16	7	17	25	2
75um	37	19	5	11	27	2
Last Crushed						
250um	6	8	24	40	23	-
106um	15	11	20	34	22	-
75um	19	11	15	30	26	-
Combined Early and Last Crushed						
250um-Washed	29	16	13	19	21	-
106um-Washed	27	19	11	16	25	-
75um-Washed	29	18	11	19	24	-
Unwashed						
Original Large Piece	30	15	9	19	28	1

Mineral abundances as obtained through Quantitative X-ray Diffraction

Size Fraction	Smectite	Quartz	Tridymite	Cristobalite	Feldspar	Mica	Hematite	Total
Original Bulk?	1±1	14±1	3±1	19±1	66±9	Trace	Trace	103±9
Devitrified Tuff Size Fractions Pretreated with J-13 Water								
4000-2000μm	Trace	16±1	3±1	18±1	60±8	Trace	Trace	97±8
2000-1000μm	1±1	15±1	3±1	18±1	63±8	Trace	Trace	100±8
1000-500μm	1±1	16±1	3±1	18±1	62±8	Trace	Trace	100±8
500-250μm	Trace	15±1	3±1	19±1	64±9	Trace	Trace	101±9
250-106μm	1±1	15±1	3±1	17±1	63±8	Trace	Trace	99±8
106-75μm	1±1	17±1	4±1	17±1	63±9	Trace	Trace	102±8
75-63μm	Trace	16±1	2±1	18±1	66±8	---	---	102±8
63-38μm	1±1	16±1	3±1	17±1	63±8	Trace	Trace	100±8
<38μm Washed	1±1	16±1	4±1	18±1	62±9	Trace	Trace	101±9
<38 Dry Sieved	1±1	18±1	5±1	17±1	62±9	---	Trace	103±9

Mineral abundances as obtained through Quantitative X-ray Diffraction

Size Fraction	Smectite	Clinoptilo.	Mordenite	Quartz	Opal-CT	Feldspar	Mica	Total
Original Bulk	1±1	30±5	15±4	9±1	28±8	19±4	2±1	104±11
	Zeolitized Tuff Fractions Pretreated with J-13 Water							
4000-2000μm	Trace	26±4	15±4	11±1	30±9	19±4	2±1	103±11
2000-1000μm	Trace	31±5	16±4	11±1	25±7	17±4	2±1	102±10
1000-500μm	1±1	26±4	16±4	16±1	24±7	19±4	1±1	103±10
500-250μm	Trace	29±5	16±4	13±1	21±6	19±4	3±1	101±10
250-106μm	Trace	27±5	19±4	11±1	25±7	16±4	7±2	105±11
106-75μm	Trace	29±5	18±4	11±1	24±7	19±5	4±1	105±11
75-63μm	Trace	36±6	18±4	9±1	23±6	13±3	5±2	104±10
63-38μm	Trace	35±6	18±4	9±1	25±7	12±3	5±2	104±11
<38 Washed	Trace	37±7	19±5	5±1	30±8	11±3	2±1	104±12

Sorption Measurements

- Chose two rock types of very different mineralogy/sorption properties
- Performed batch sorption measurements using ^{137}Cs, ^{85}Sr, ^{237}Np radioactive sorbates
- Solid and solution fractions were separated by brief centrifugation
- Solution fraction was then filtered through a ~.002 μm pore size ultrafilter
- Both solid and solution fractions were gamma counted to eliminate error in Rd due to lack of mass balance

Pre-Conditioning Samples

- Samples were allowed to react with excess J-13 water for a minimum of 3 weeks

<u>Purpose:</u> To allow new surfaces produced by crushing to react with the ambient groundwater

- A second suite of samples was reacted with a synthetic, Paleozoic-type groundwater

<u>Purpose:</u> To mimic the effects of J-13 water contacting deeper layers of tuff previously saturated with Paleozoic-type water

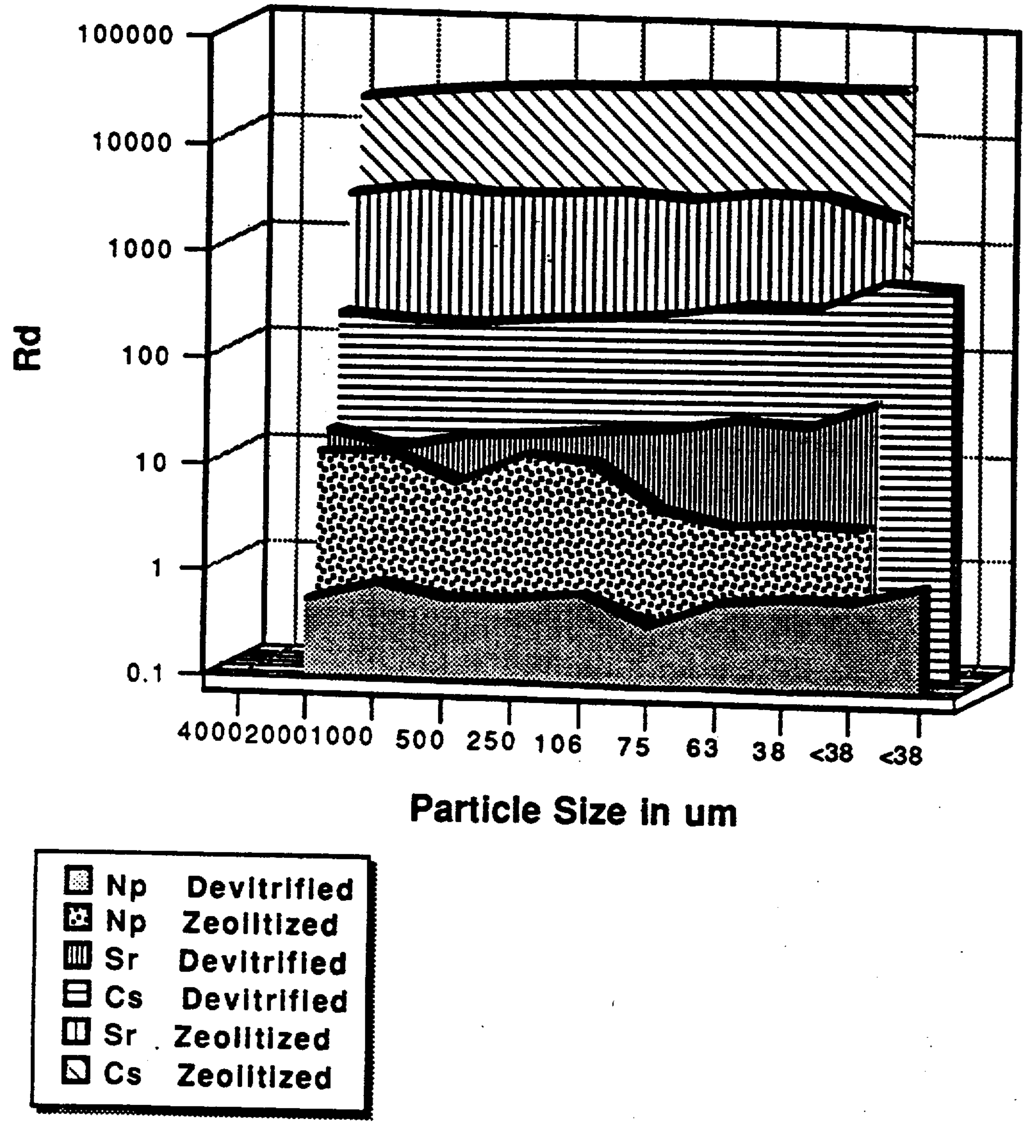
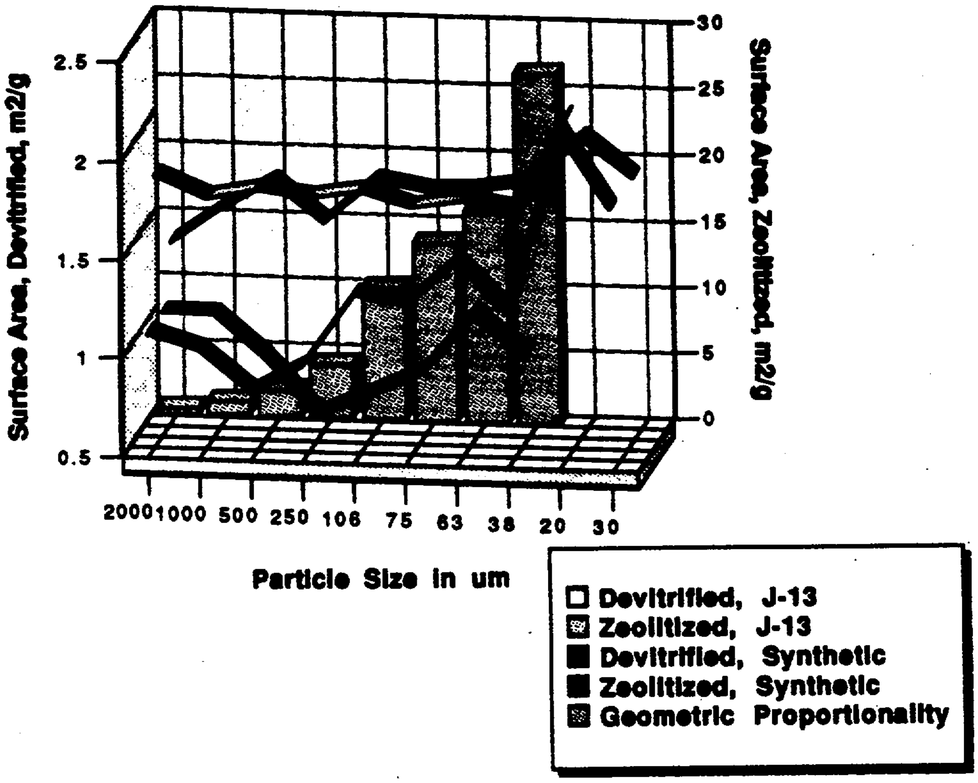


Figure 1 - General Dependence of Sorption Coefficients on Particle Grinding

Dependence of Surface Area on Particle Size



CONCLUSIONS:

- Parameters other than particle grinding size determine the surface area available for sorption for both rock types tested.

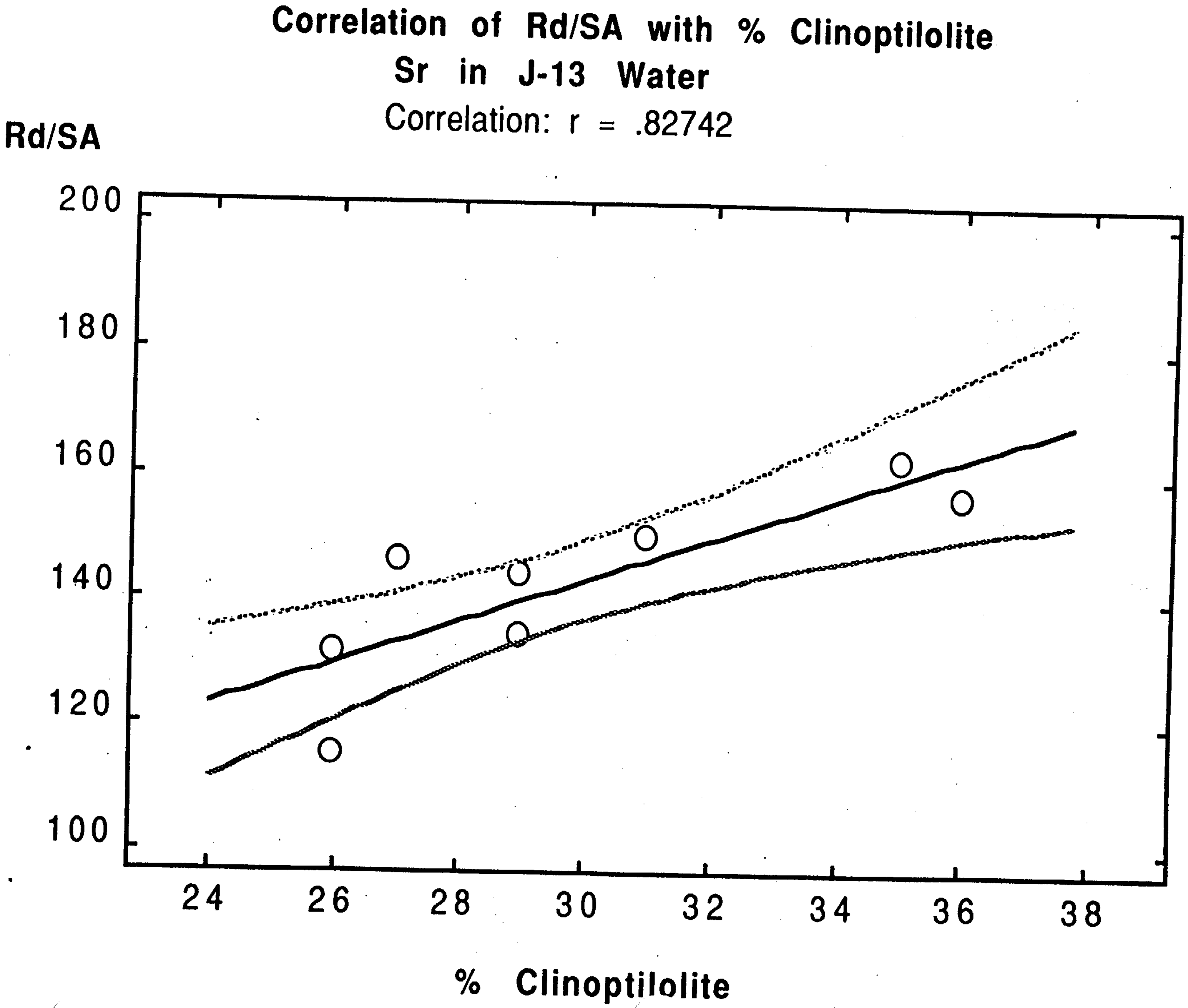
- The "effective" grain size of the tuff samples is under 38 μm.

- The "effective" grain size is defined as the average grain size exposed to the solution, as determined by open mineral boundaries, microfractures, or porosity.

IMPLICATIONS:

- Any differences in retention found between solid and coarsely crushed samples (comparing batch sorption with transport measurements on solid disks or columns) should be due to flow or diffusion processes, not to differences in surface area or to changes in the type or activity of the exposed surfaces.

- This conclusion holds provided that the batch experiments were performed with well-washed samples.

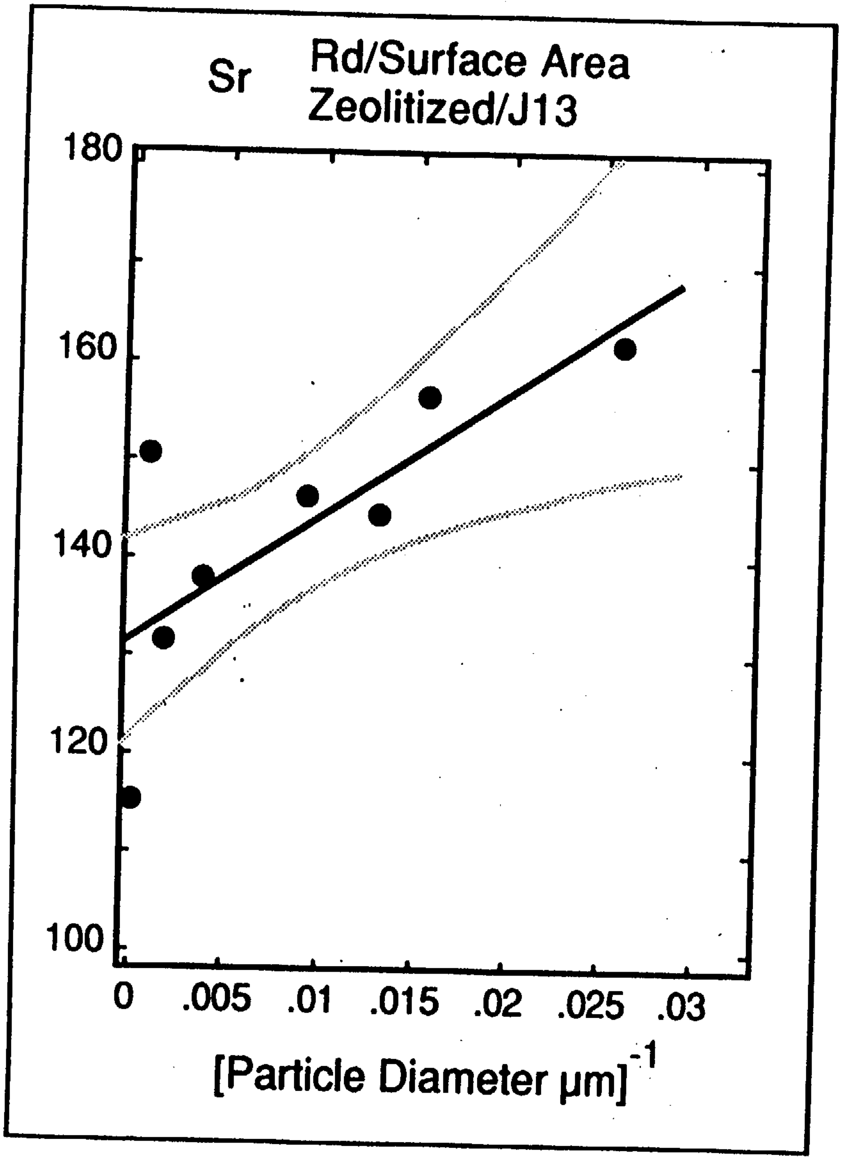


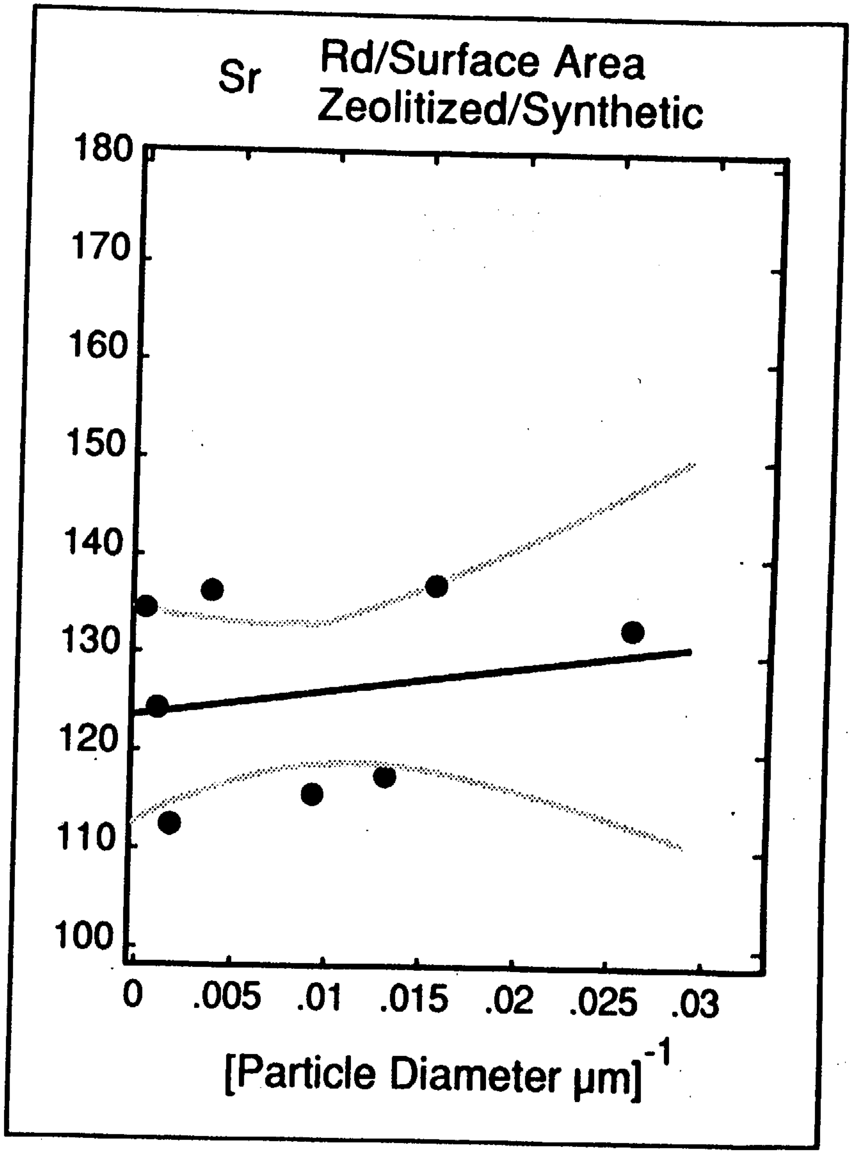
Correlation of Rd/SA with % Clinoptilolite

Sr in J-13 Water

Correlation: r = .82742

Linear fits of Rd/SA *vs* the inverse of the particle size

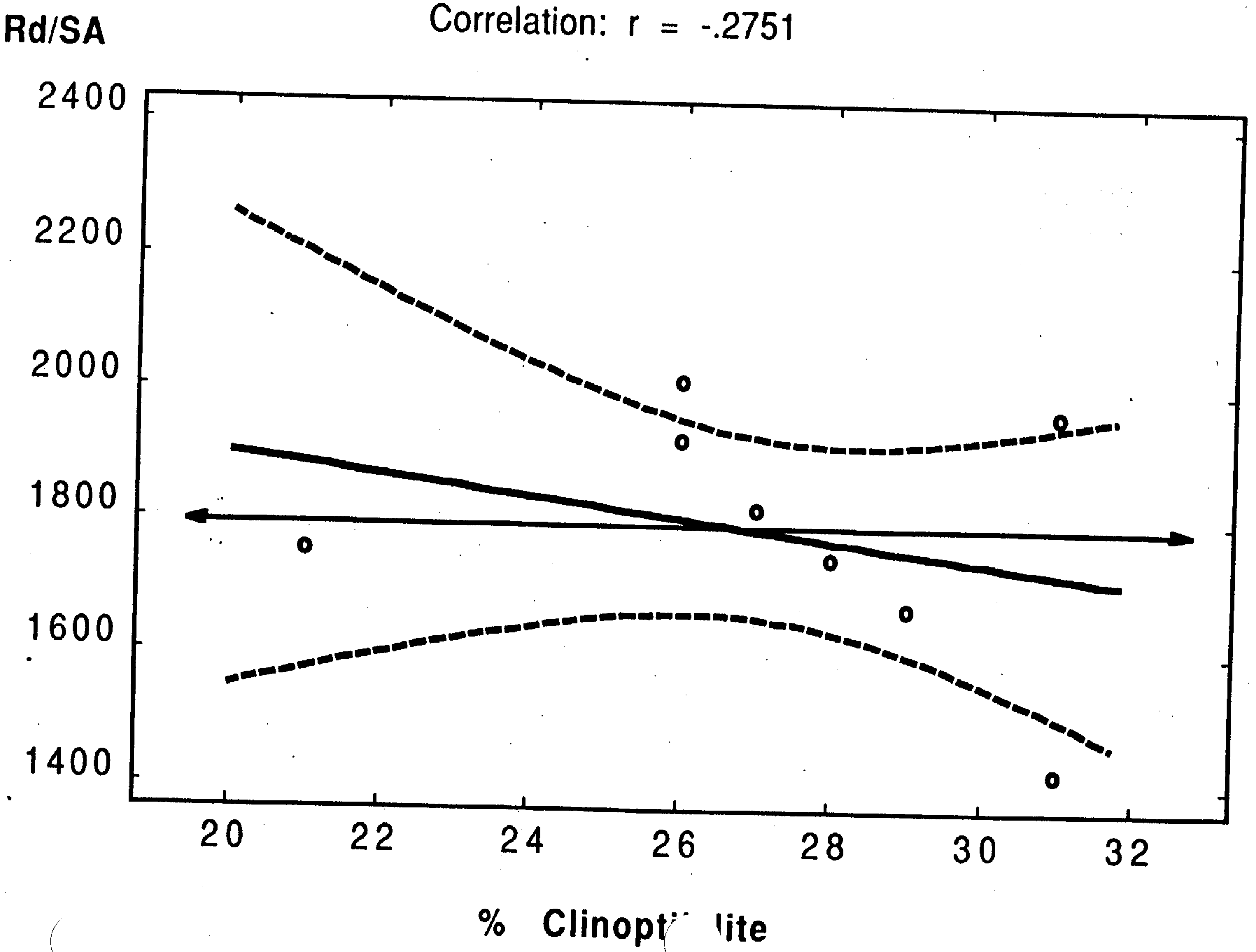




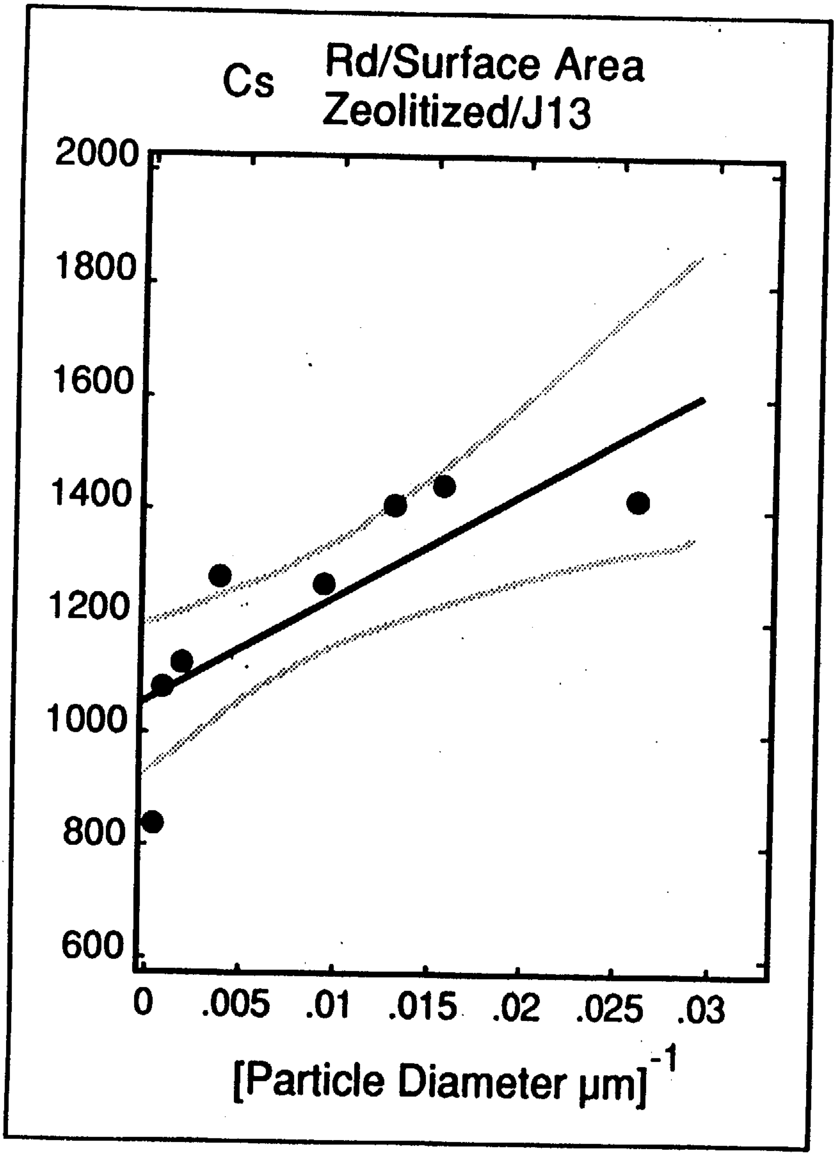
Correlation of Rd/SA with % Clinoptilolite

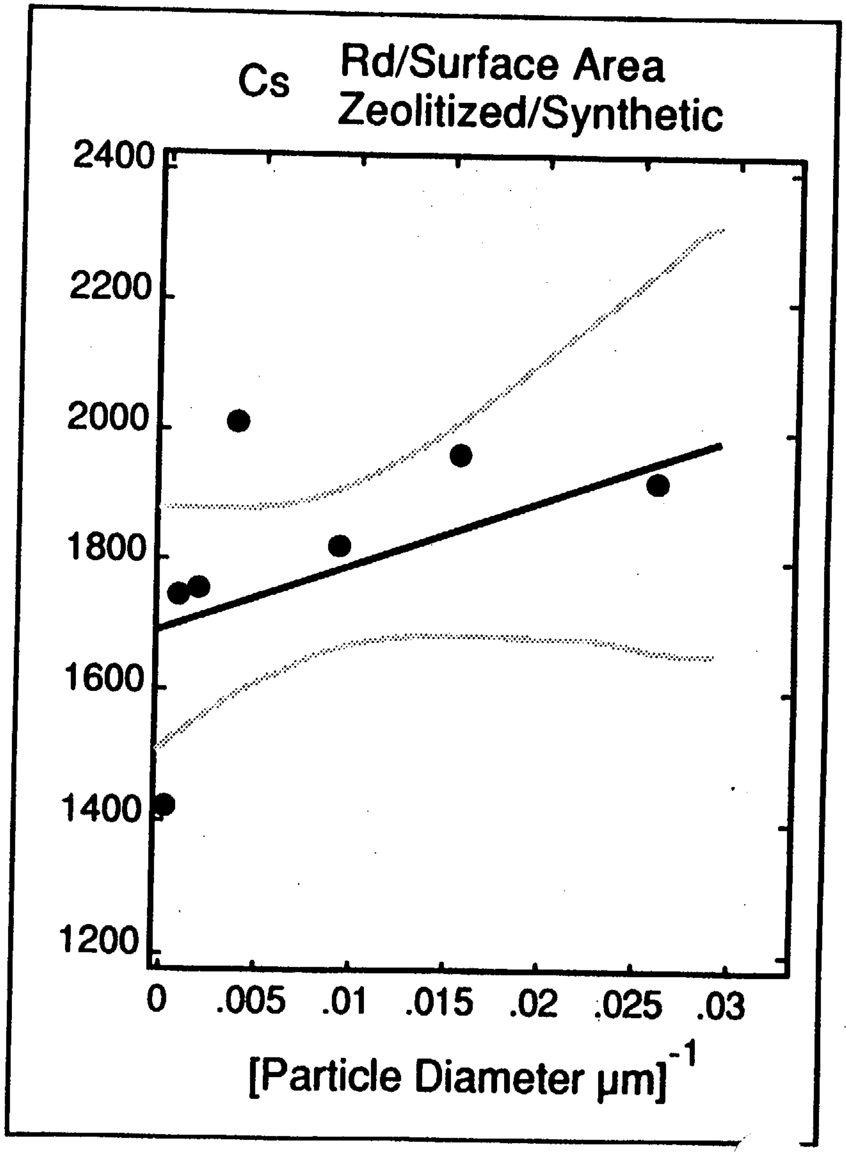
Cs in Synthetic Water

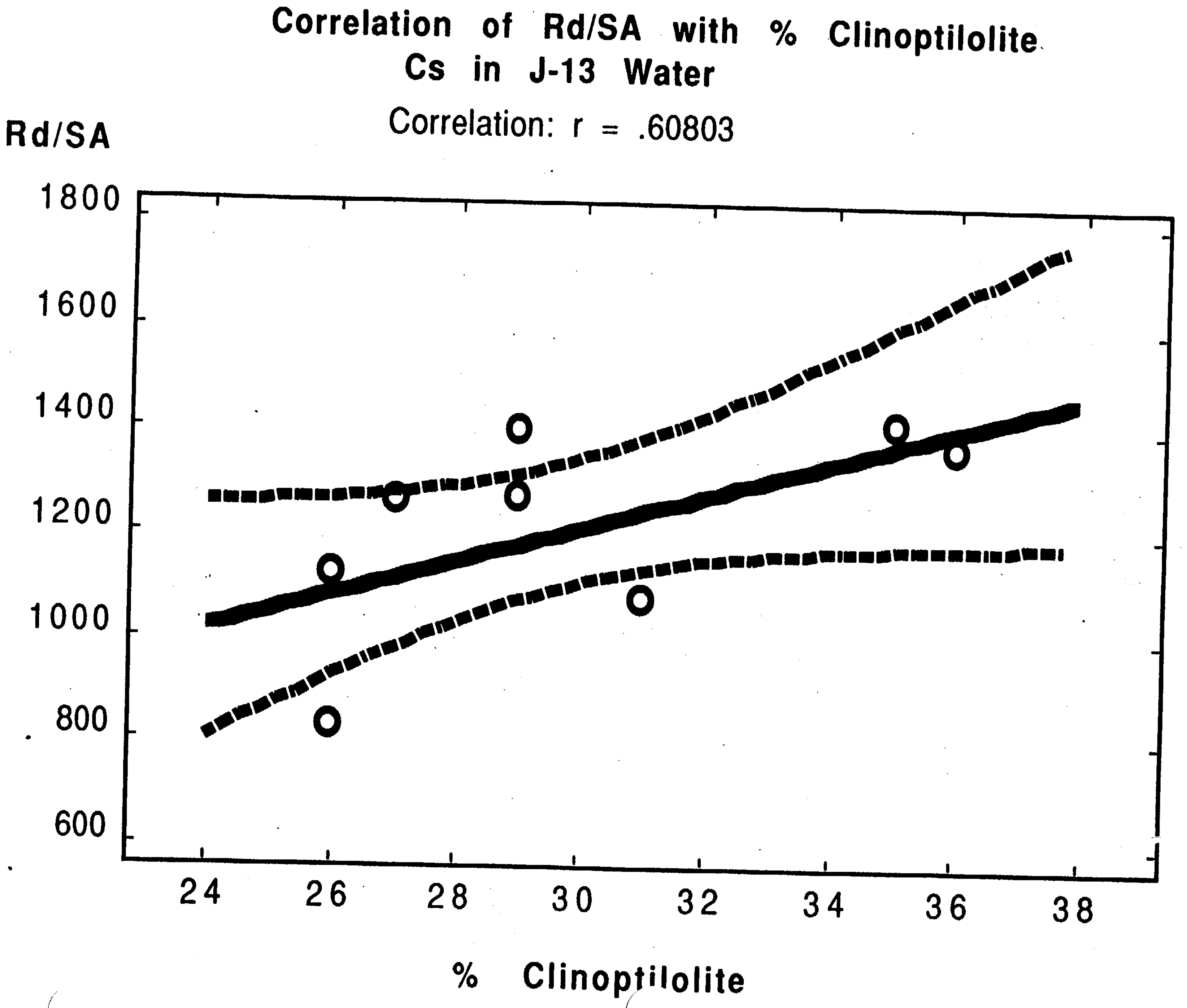
Correlation: r = -.2751



Linear fits of Rd/SA *vs* the inverse of the particle size





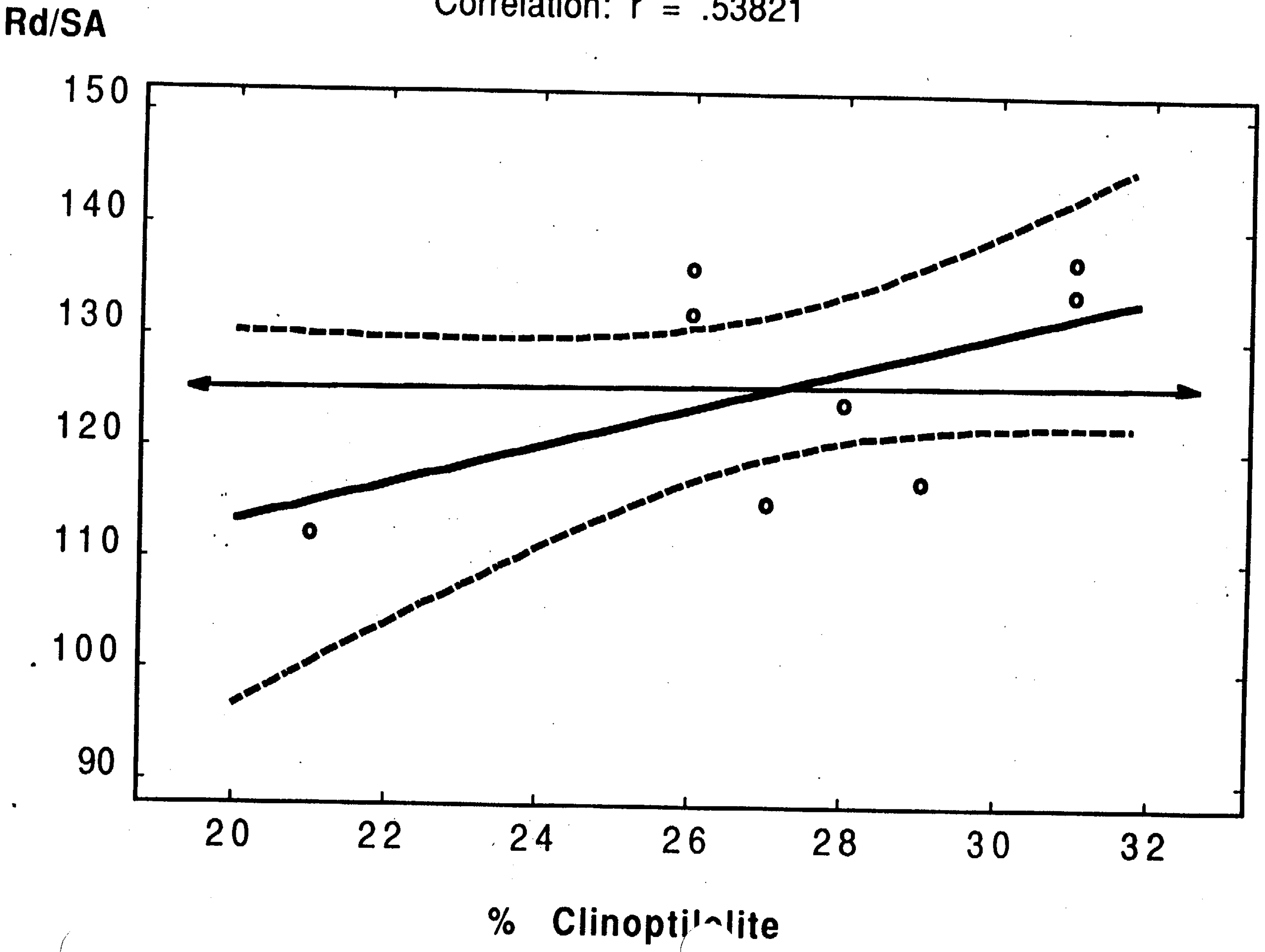


Correlation of Rd/SA with % Clinoptilolite
Cs in J-13 Water

Correlation: r = .60803

Correlation of Rd/SA with % Clinoptilolite
Sr in Synthetic Water

Correlation: r = .53821



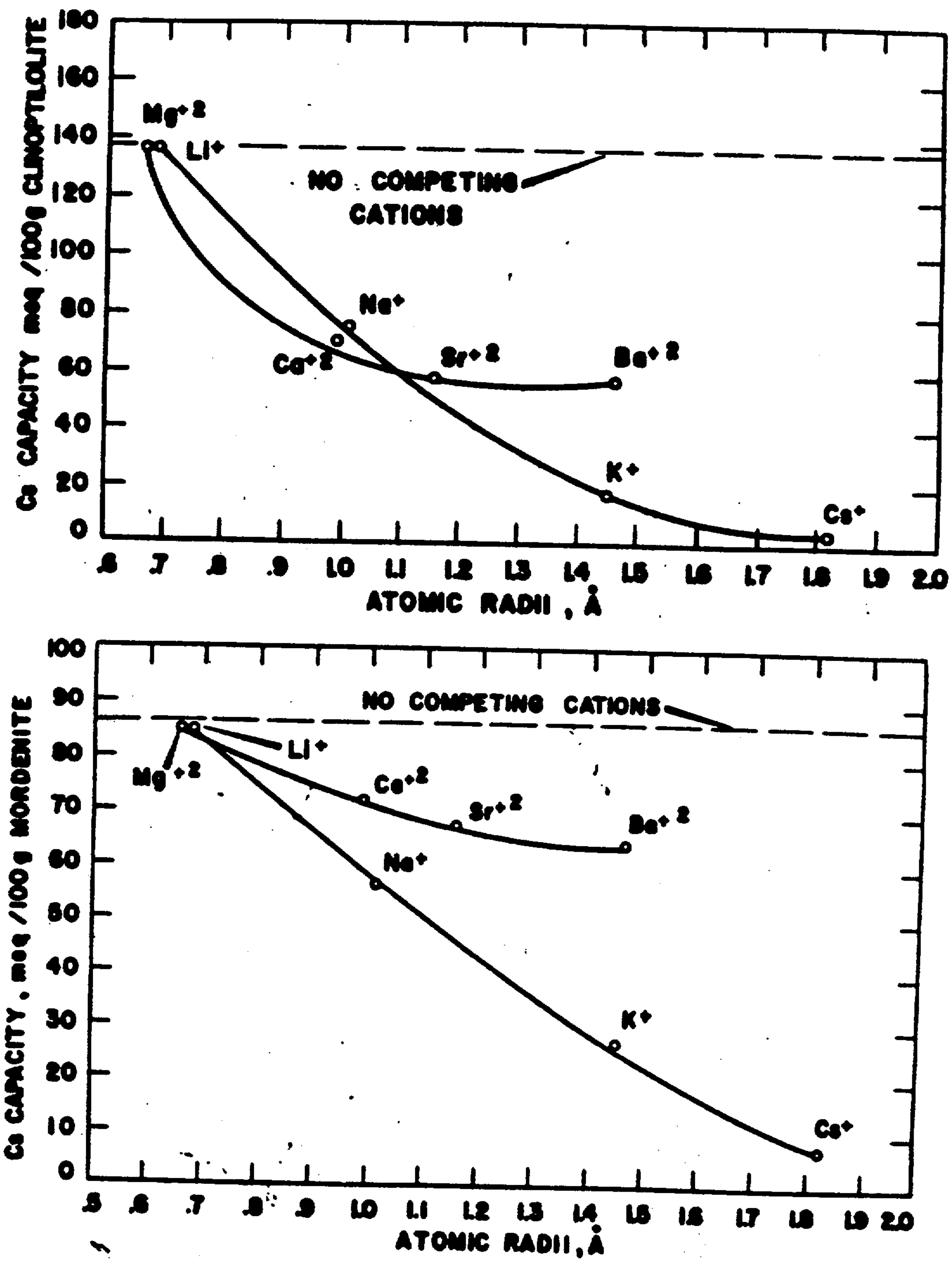
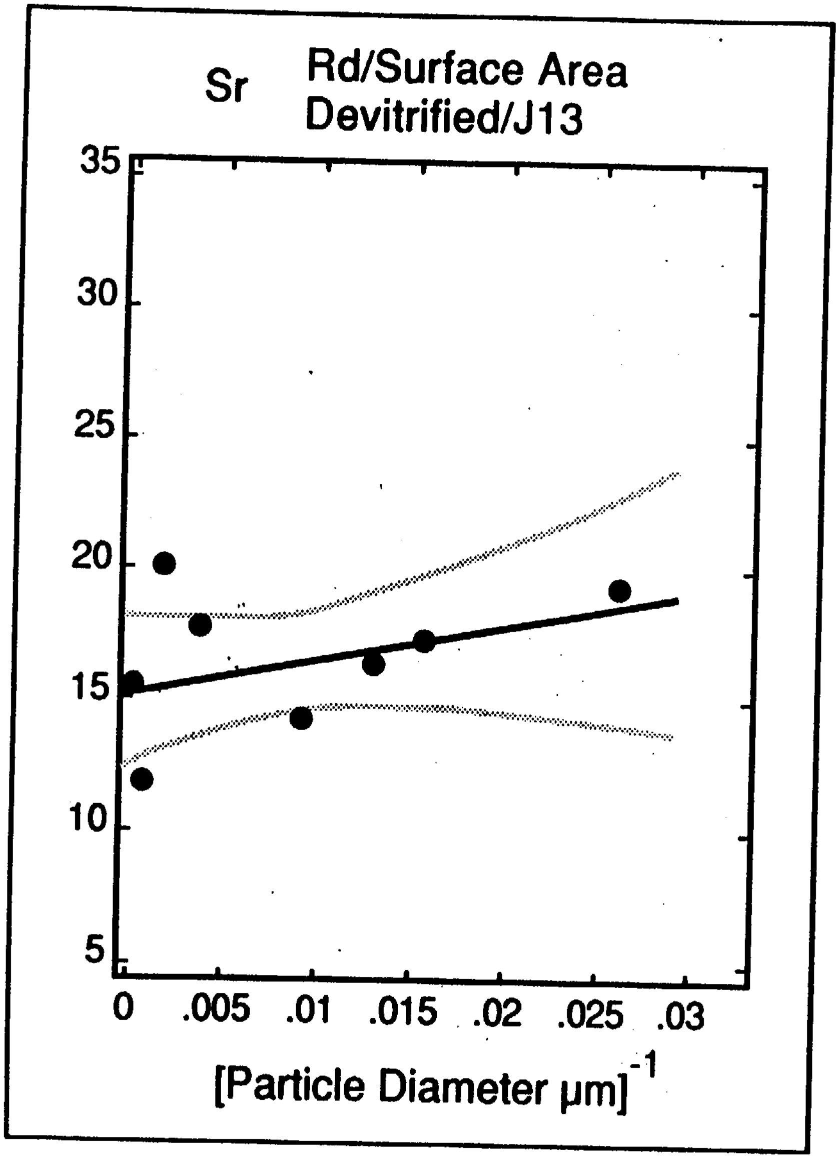
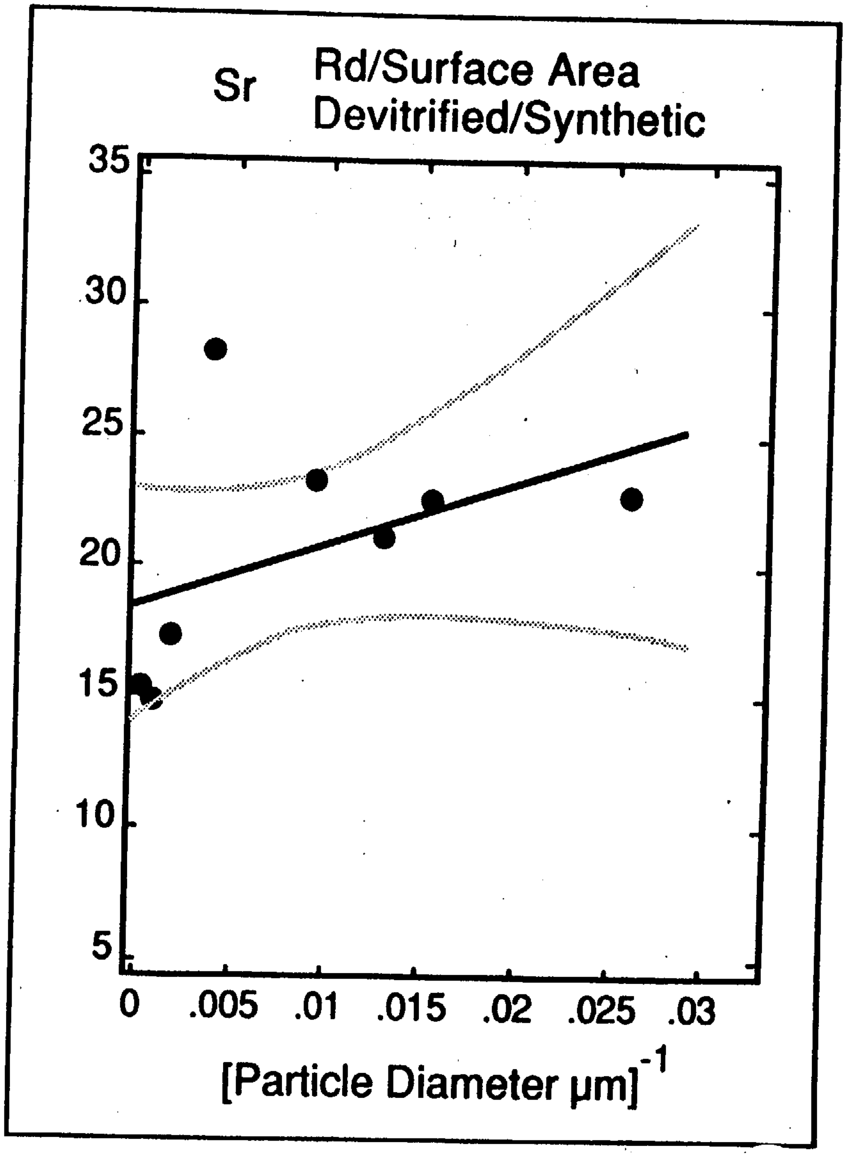


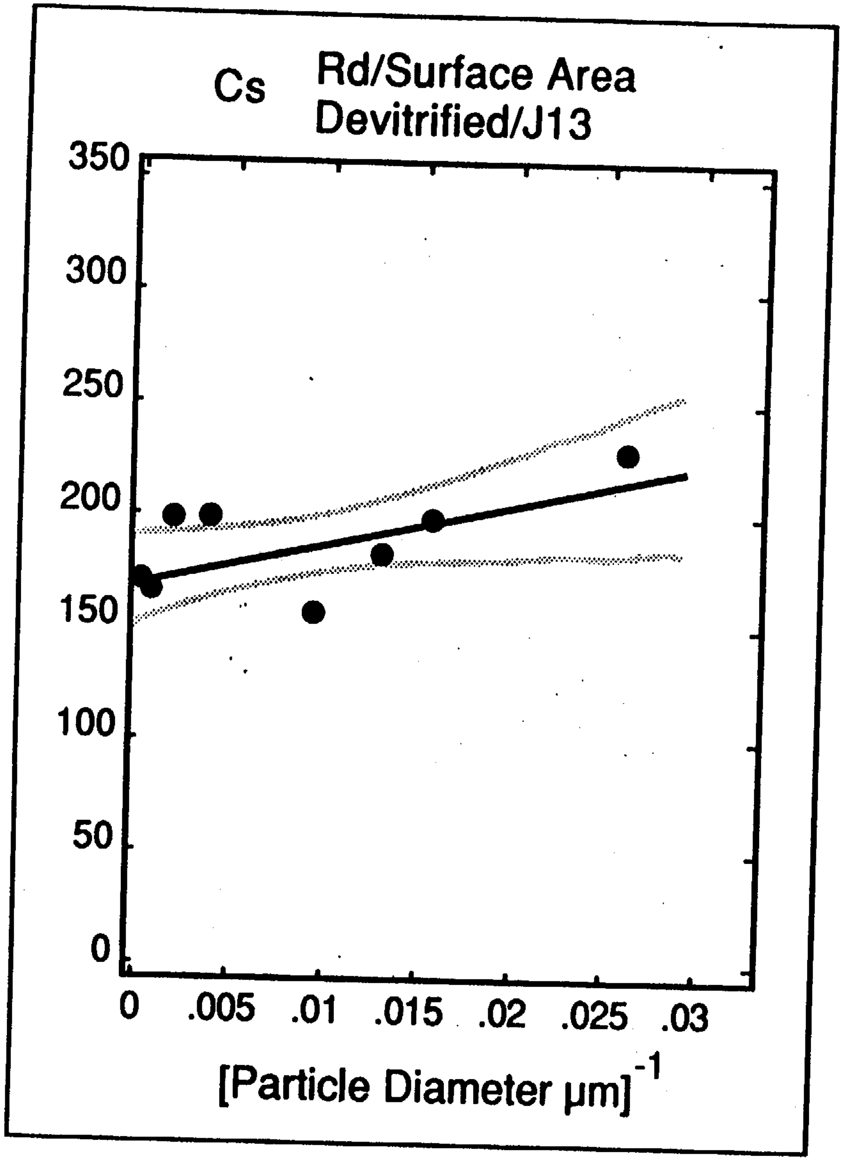
FIG. 4. The effect of competing cations on the cesium capacity
Common influent solution 0 01*N* competing cations as indicated, 0.01*N* Cs^+

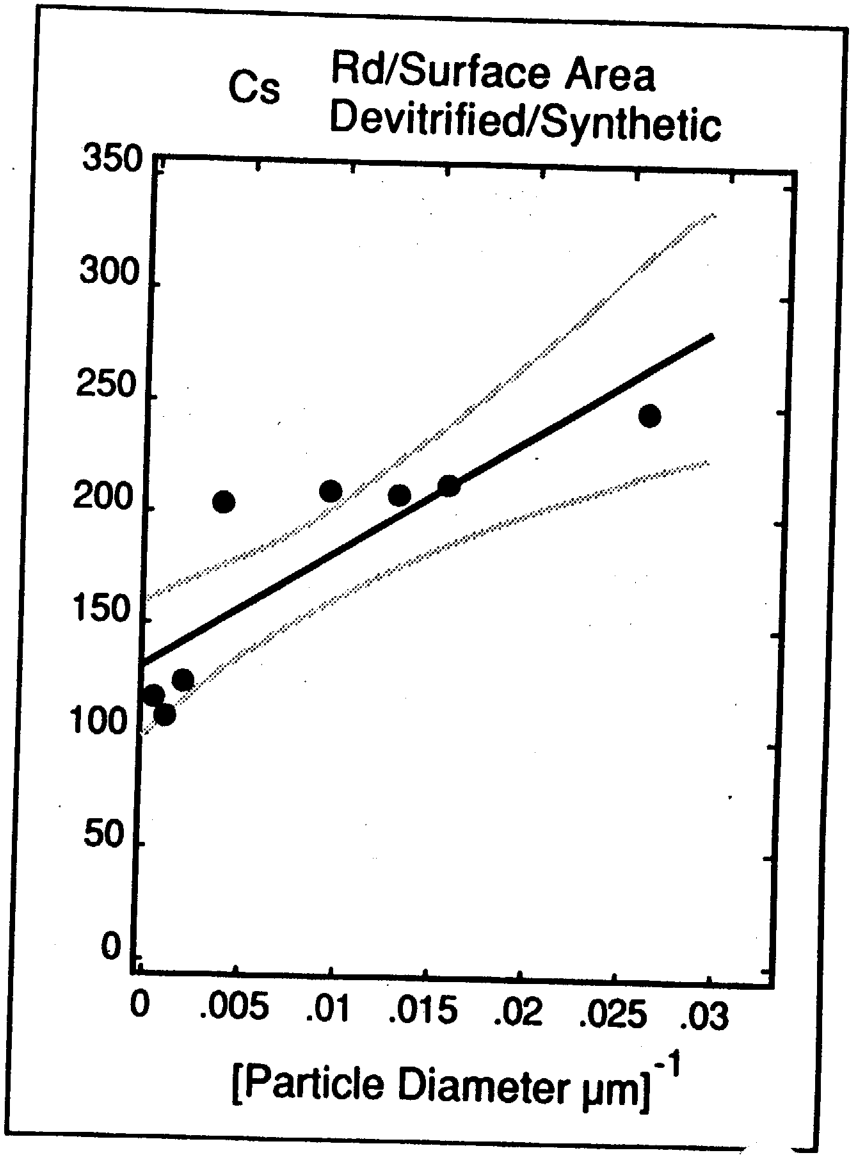
Linear fits of Rd/SA *vs* the inverse of the particle size





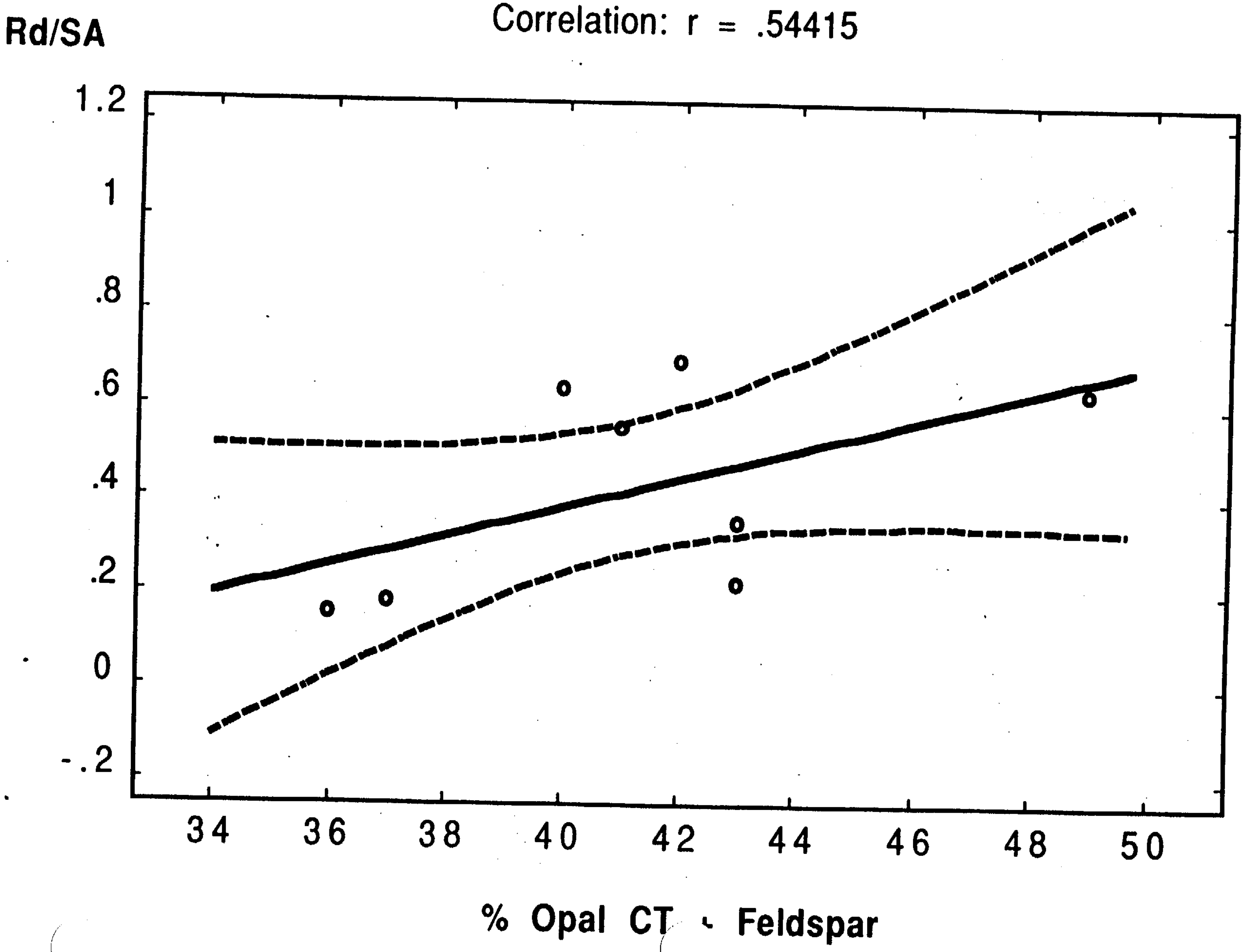
Linear fits of Rd/SA *vs* the inverse of the particle size



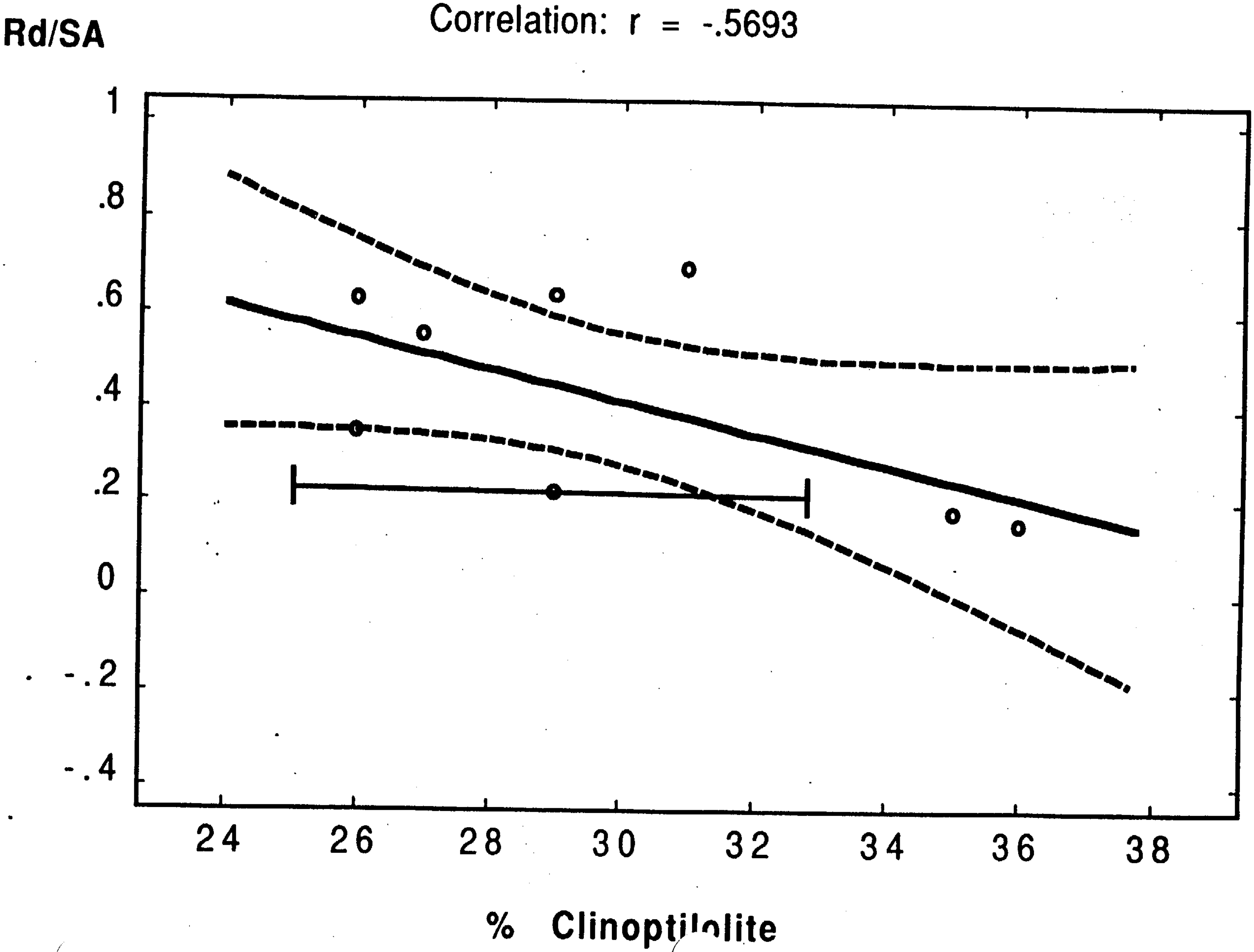


Correlation of Rd/SA with % Opal CT + Feldspar
Np in J-13 Water

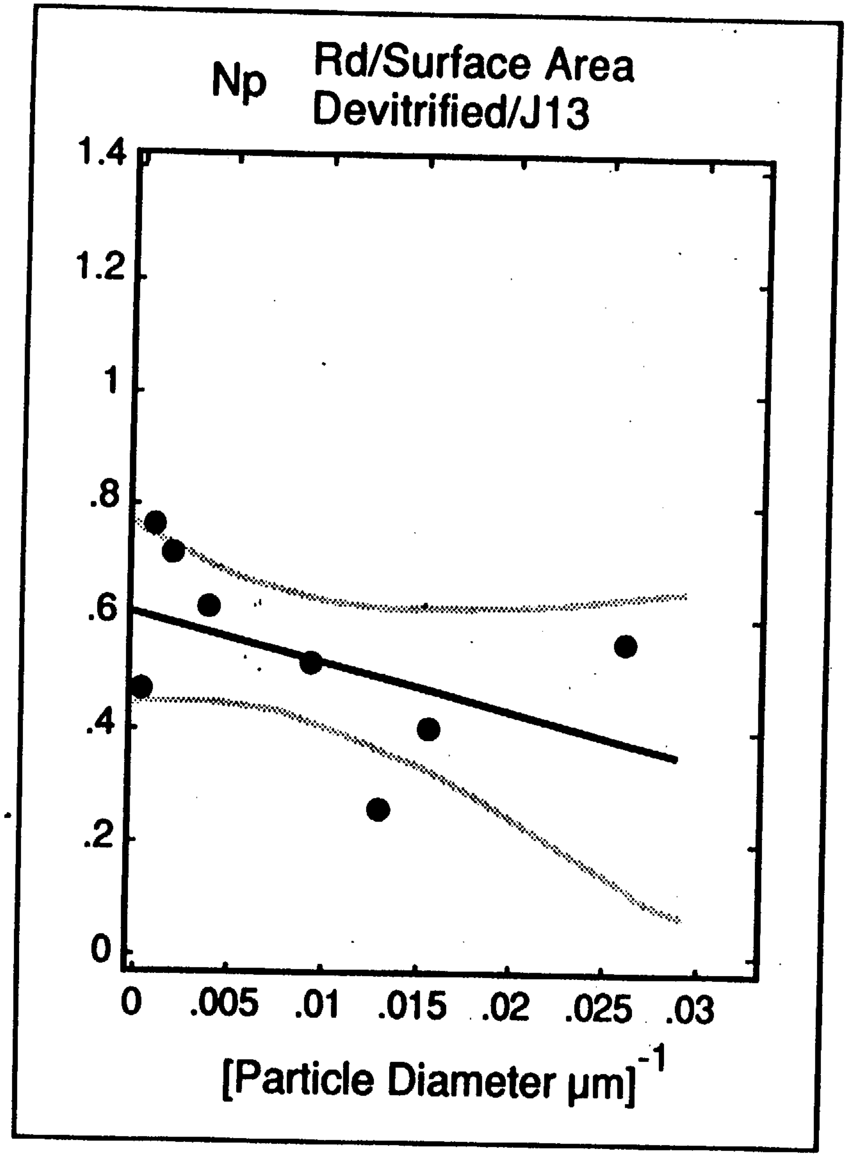
Correlation: r = .54415

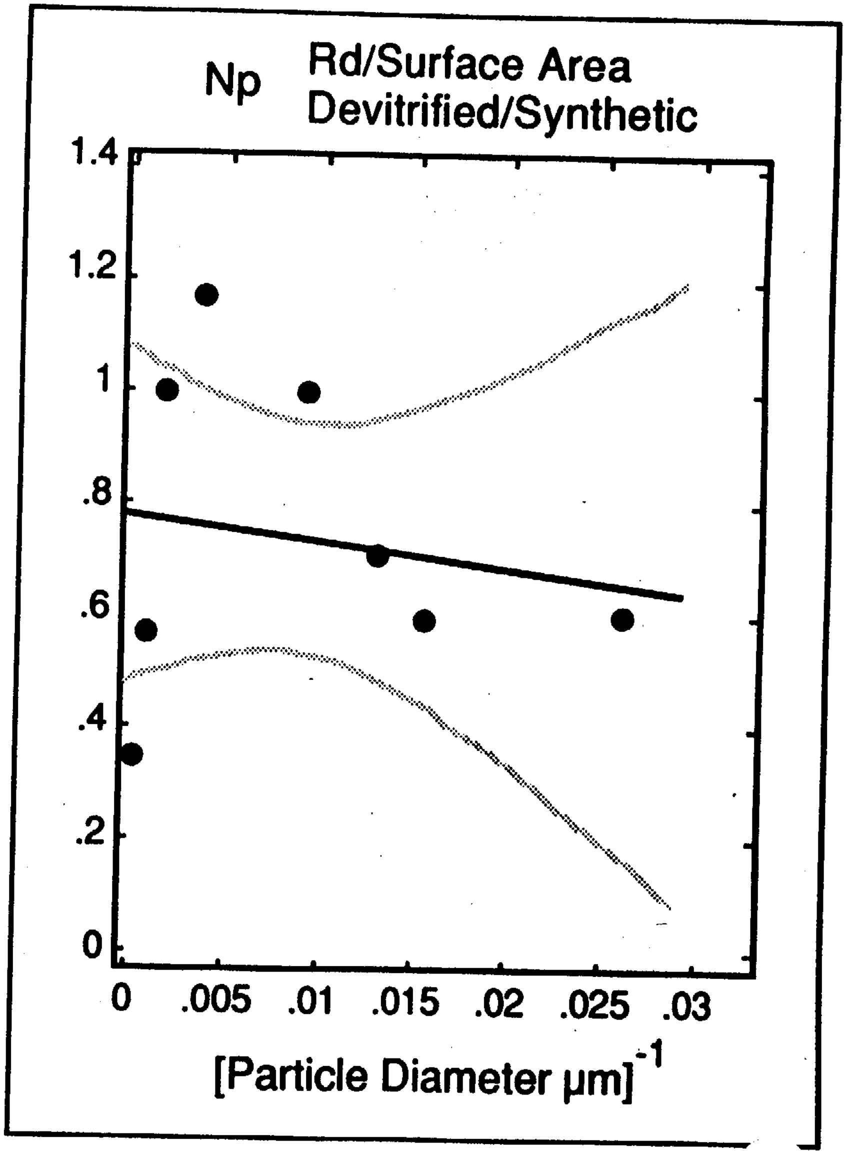


Correlation of Rd/SA with % Clinoptilolite
Np in J_13 Water
Correlation: r = -.5693

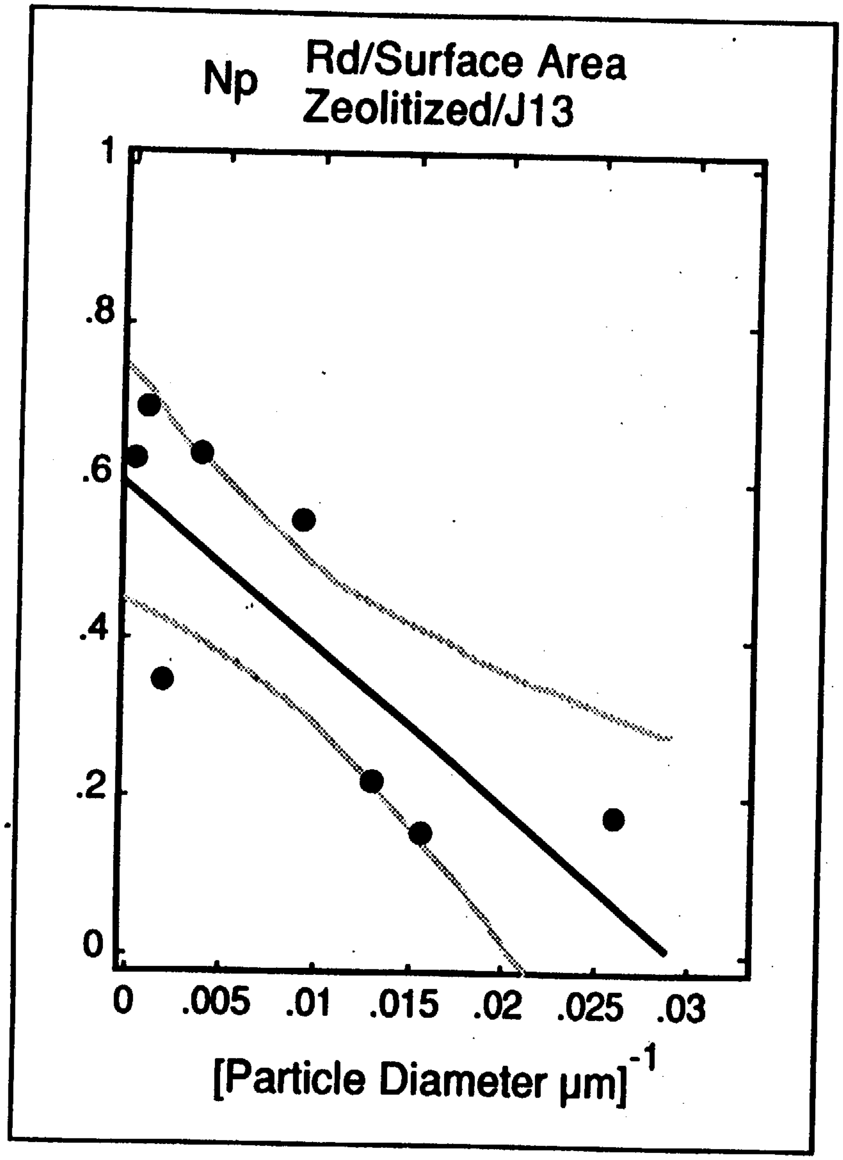


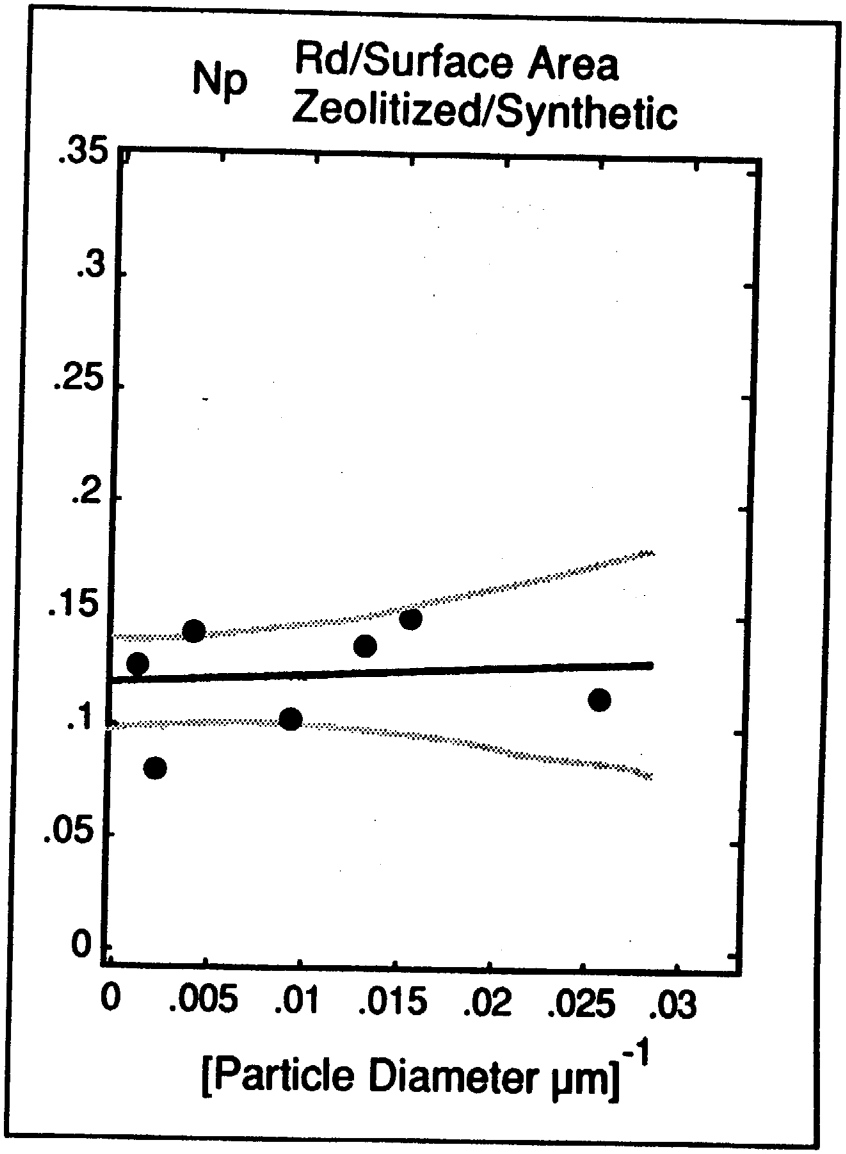
Linear fits of Rd/SA *vs* the inverse of the particle size





Linear fits of Rd/SA *vs* the inverse of the particle size





Conclusions

1. Particle grinding does not influence the sorption behavior of the tuff samples studied here until the particle size becomes smaller than about 38 µm. However, the ground samples must be washed carefully, because any amount of grinding creates very fine particles that do lead to an increase in sample surface area and measured Rd.

2. Previous batch sorption experiments using particle size ranges of 63-500 or 75-500 µm are experimentally ideal. They provide an optimum compromise between possible sampling error due to too large a grain size and creation of active surface area and mineral fractionation through excessive grinding.

3. There should be no experimental artifacts due to sample grinding in previous work as long as the experimental samples were washed after preparation.

Conclusions

4. The BET surface areas of the tuff samples studied here are largely independent of the particle grinding size, indicating that the "effective" grain size of the tuffs is less than about 38 μm.

5. Adsorption Rd's for neptunium are very small, averaging .65+.15 for the devitrified tuff sample. This is consistent with the designation of Np as a "poorly sorbing" radionuclide under the minimum Kd strategy.

6. Further experiments are necessary to determine the parameters important to Np adsorption and to clarify the contribution of hematite in the Yucca Mountain tuffs to Np sorption.

DOE-NRC Technical Exchange Radionuclide Migration

Recent Sorption Results, Part II

Inés R. Triay, LANL

Los Alamos
NATIONAL LABORATORY
1943 - 1993

NEPTUNIUM SORPTION ONTO YUCCA MOUNTAIN TUFFS

Inés Triay
Charles Cotter
Bruce Robinson

Acknowledgment:
Phil Palmer
Dave Bish
Steve Chipera

Goal:

Study the transport of Np in minerals (available in tuff) and in whole rock samples using relevant water compositions

Waters:

J-13,UE-25 p#1, synthetic HCO_3^- / CO_3^{-2} buffers

Minerals:

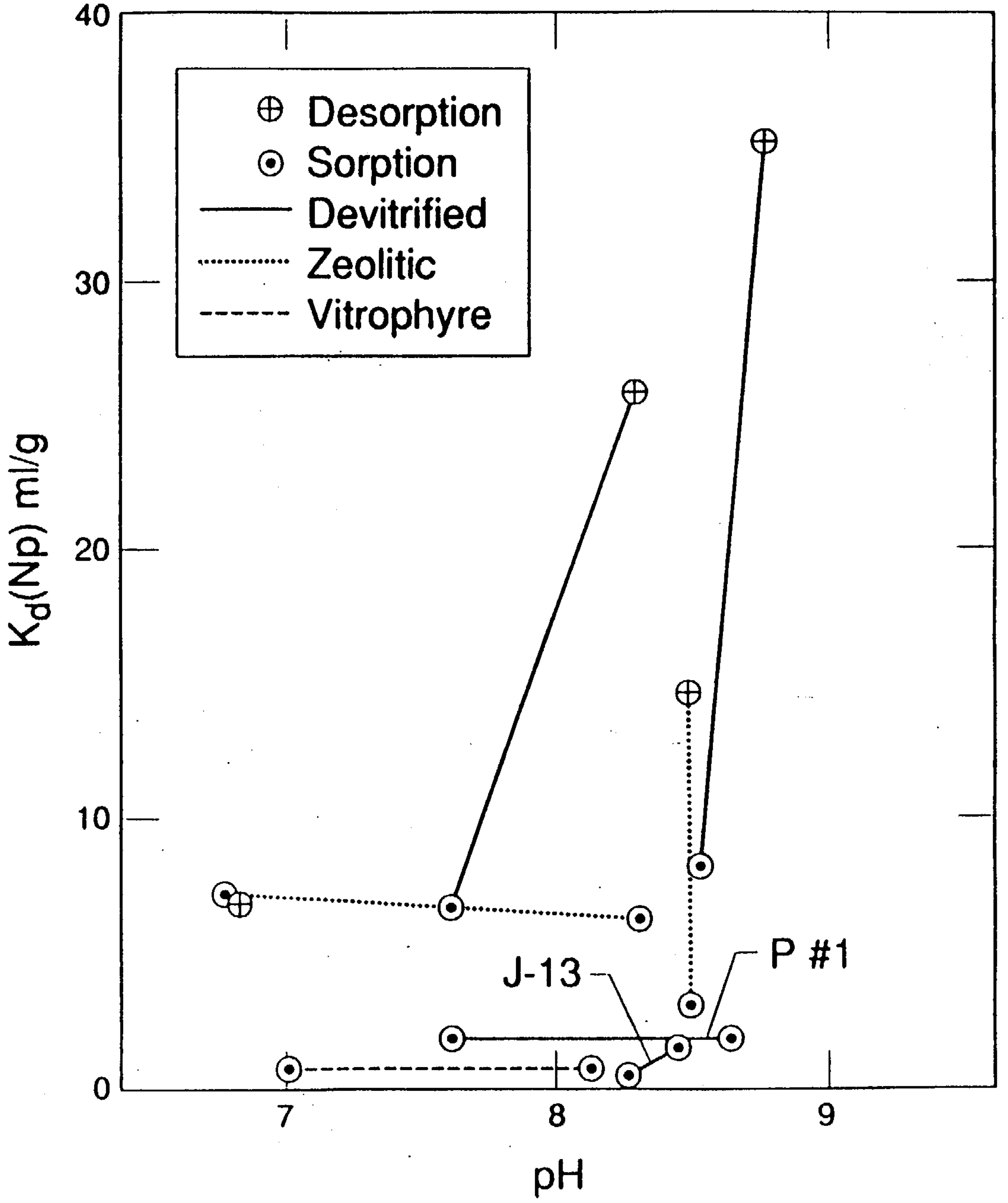
hematite, quartz, clinoptilolite, montmorillonite, albite

Tuffs:

from USW G-1, G2, GU3, and G4

Parameters Varied:

Np concentration, T, and pH



Neptunium on Yucca Mountain Tuffs (J-13)

Composition of Groundwaters

Element	Concentration, $\frac{mg}{l}$ J-13	UE-25 p#1	Anion	Concentration, $\frac{mg}{l}$ J-13	UE-25 p#1
Ca	13.	8.0	F^-	2.2	4.0
Mg	1.6	32.	Cl^-	7.2	25
Na	47.	150	SO_4^{-2}	27.	160
K	5.4	11.	NO_3^-	8.6	0.5
Si	20.	14.	CO_3^{-2}	1.5	31
Li	0.04	0.5	HCO_3^-	120	300

pH at Los Alamos, NM: J-13 is 8.5 and UE-25 p#1 is 9.0

Neptunium Solutions in Groundwater

- **Prepared from well-characterized Np(V)acidic stock**
- **Nitsche reports:**
  - **Np solubility in J-13** @ 25 °C and pH of 8.5 is **4×10^{-5} M**
  - **Np solubility in UE-25 p#1** @ 25 °C and pH of 8.5 is **7×10^{-6} M**

Properties of Minerals and Tuffs

Solid	XRD	Surface Area, m^2/g	Size, µm	% Fe_2O_3	% FeO
calcite, synthetic	no impurities	0.1	39		
calcite	no impurities	0.1	86		
quartz	no impurities	0.2	200	<0.01	0.02
clinoptilolite	no impurities	17.	6.8	0.14	0.16
montmorillonite	over 99% montmorillonite	78.	16.	1.4	<0.01
hematite, synthetic	no impurities	8.9	1.2	99.6	<0.01
G4-270 Topopah Spring	feldspar - 65% tridymite - 25% cristobalite - 7% hematite - 1%	5.1	75-500		
G4-275 Topopah Spring	feldspar - 61% tridymite - 24% cristobalite - 11% hematite - 1%	4.3	75-500	1.2	0.02
G4-1506 Calico Hills	clinoptilolite - 64% opal-CT - 16% mordenite - 7% quartz - 5% feldspar - 4%	26.	75-500		
G4-1530 Calico Hills	clinoptilolite - 55% opal-CT - 16% mordenite - 12% quartz - 7% feldspar - 7%	4.3	75-500	0.53	<0.01

Minerals and tuffs have negative surface charges in J-13 and UE-25 p#1 waters

Batch Sorption Experimental Procedure

Pre-treatment Step

- 1g of mineral equilibrated with 20 ml of groundwater
- Phases separated by centrifugation

Sorption Step

- Pre-treated mineral equilibrated with 20 ml of solution containing radionuclide
- Phases separated by centrifugation
- Amount of radionuclides in liquid phase determined by radioanalytical techniques
- Amount of radionuclide in solid phase calculated by difference

Controls

- Containers without mineral phases utilized to monitor radionuclide precipitation and/or sorption onto walls

Np Sorption onto Tuffs in J-13

Initial Np Concentration - 3.0 x 10^{-5}M

Sorption pH Range 8.5 - 8.6

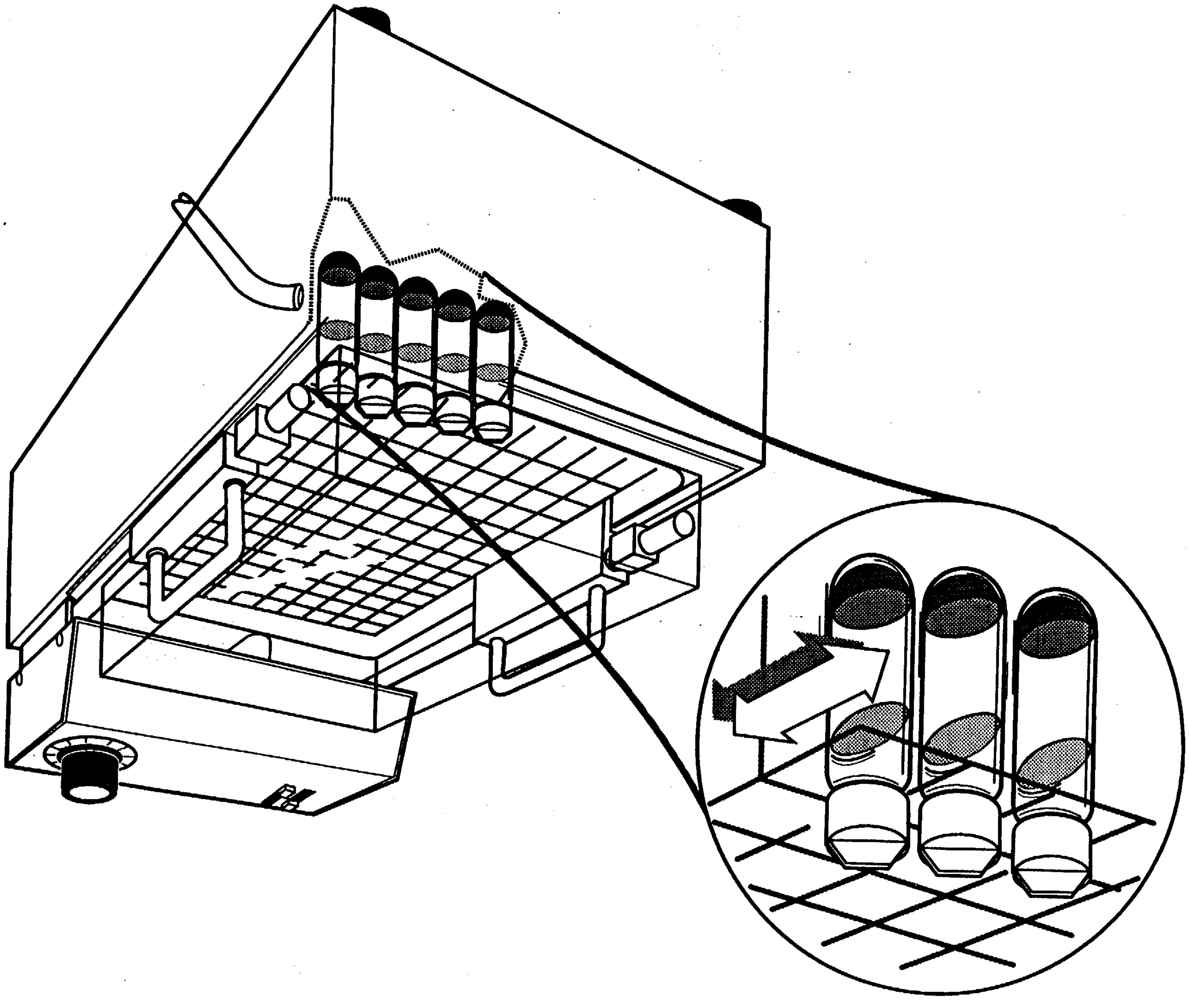
	Kd (ml/g) <u>Range</u>
Devitrified	**0 - 0.6**
Vitric	**0 - 0.4**
Zeolitic	**0.5 - 2.6**

Np Sorption onto Tuffs in UE-25 p#1

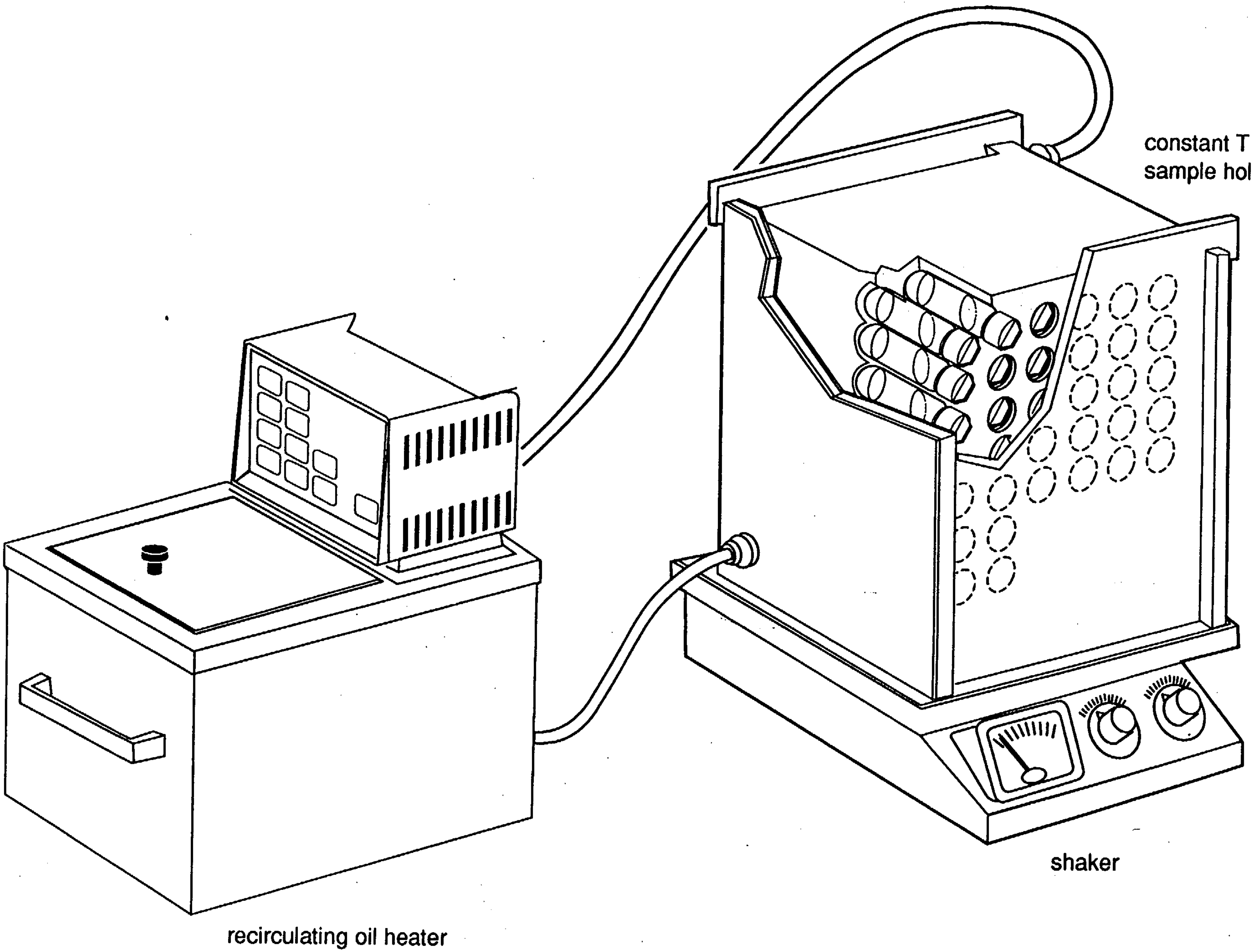
Initial Np Concentration - 5.0 x 10^{-6}M

Sorption pH Range 8.8 - 9.0

	Kd (ml/g) <u>Range</u>
Devitrified	**0 - 0.7**
Vitric	**0 - 0.5**
Zeolitic	**0 - 1.2**



Batch Sorption Equipment for High T Experiments



Results of Batch Sorption Experiments of Np in J-13 Water

	Initial Np Concentration = 6.9×10^{-7}M			Initial Np Concentration = 1.3×10^{-6}M		
	Kd (ml/g)			Kd (ml/g)		
Solid	20	60	80°C	20	60	80°C
quartz	0	4×10^{-1}	5×10^{0}	0	0	
clinoptilolite	3×10^{0}	4×10^{0}	3×10^{0}	3×10^{0}	5×10^{0}	2×10^{0}
hematite, synthetic	2×10^{3}	2×10^{3}	3×10^{3}	2×10^{3}		
G4-270	1×10^{0}	1×10^{0}	1×10^{0}	1×10^{0}	9×10^{-1}	2×10^{0}
G4-1506	3×10^{0}	3×10^{0}	4×10^{0}	4×10^{0}	6×10^{0}	

No loss of Np due to adsorption to walls of containers or precipitation

pH of J-13 after sorption at 20 and 60 °C is 8.4 - 8.6

pH of J-13 after sorption at 90 °C is 8.4 - 8.9

Results of Np Batch Sorption Experiments at 20°C in J-13

Kd (ml/g)

Solid	Initial Np Concentration (M)				
	6.9×10^{-7}	1.3×10^{-6}	2×10^{-5}	3.5×10^{-5}	$4\ .0 \times 10^{-5}$
quartz	0	0		0	0
albite				1×10^{0}	
clinoptilolite	3×10^{0}	3×10^{0}	2×10^{0}	1×10^{0}	
montmorillonite	3×10^{1}	3×10^{1}			
hematite, synthetic	2×10^{3}	2×10^{3}	3×10^{2}	2×10^{2}	7×10^{1}
G4-270	1×10^{0}	1×10^{0}		6×10^{-1}	1×10^{-1}
G4-275			1×10^{0}		
G4-1506	3×10^{0}	4×10^{0}		2×10^{0}	2×10^{0}
G4-1530			2×10^{0}		
GU3-1394	6×10^{-1}	4×10^{-1}		0	3×10^{-1}

Magnetic Separation of Tuff G4-1530

- Iron oxide enriched in magnetic fraction according to chemical analysis
- Sorption experiments performed in different fractions with J-13
- No correlation between Np sorption coefficients determined and amount of iron oxide in tuff fractions

Results of Batch Sorption Experiments of Np in UE-25 p#1 Water

Kd (ml/g)

Solid	Initial Np Concentration = 6.0×10^{-7}M		Initial Np Concentration = 1.4×10^{-6}M	
	20°C	60°C	20°C	60°C
quartz	0	4×10^{0}	0	0
clinoptilolite	1×10^{0}	2×10^{0}	1×10^{0}	1×10^{0}
hematite, synthetic	2×10^{3}	2×10^{3}	8×10^{2}	
G4-270	1×10^{0}	3×10^{0}	1×10^{0}	
G4-1506	1×10^{0}	2×10^{0}	1×10^{0}	

pH of UE-25 p#1 after sorption at 20 and 60 °C is 8.7 - 9.0

Results of Np Batch Sorption Experiments at 20°C in UE-25 p#1

Kd (ml/g)

Initial Np Concentration (M)

Solid	6.0×10^{-7}	1.4×10^{-6}	6.0×10^{-6}	6.7×10^{-6}
quartz	0	0	0	0
albite			2×10^{-1}	
clinoptilolite	1×10^{0}	1×10^{0}	7×10^{-1}	
montmorillonite				1×10^{1}
hematite, synthetic	2×10^{3}	8×10^{2}	6×10^{2}	
G4-270	1×10^{0}	1×10^{0}		5×10^{-1}
G4-1506	1×10^{0}	1×10^{0}	2×10^{-1}	
GU3-1394	8×10^{-1}	9×10^{-1}	2×10^{-1}	

TRANSPORT EQUATION FOR NONREACTIVE SOLUTE IN A SATURATED MEDIUM

$$\nabla \bullet (\mathbf{D} \nabla C - C\mathbf{U}) = \varepsilon \frac{\partial C}{\partial t}$$

D = dispersion tensor

C = concentration of solute

U = Darcy's velocity

ε = porosity

t = time

TRANSPORT EQUATION FOR REACTIVE SOLUTE IN A SATURATED MEDIUM

$$\nabla \bullet (D \, \nabla C - CU) = \varepsilon \frac{\partial C}{\partial t} + Q$$

Q = sink or source term

FOR SORPTION

$$Q = \rho_b \frac{\partial F}{\partial t}$$

ρ_b = rock bulk density

F = amount of solute sorbed per unit mass of solid

MECHANISM OF SORPTION DETERMINES RELATIONSHIP OF F WITH RESPECT TO C

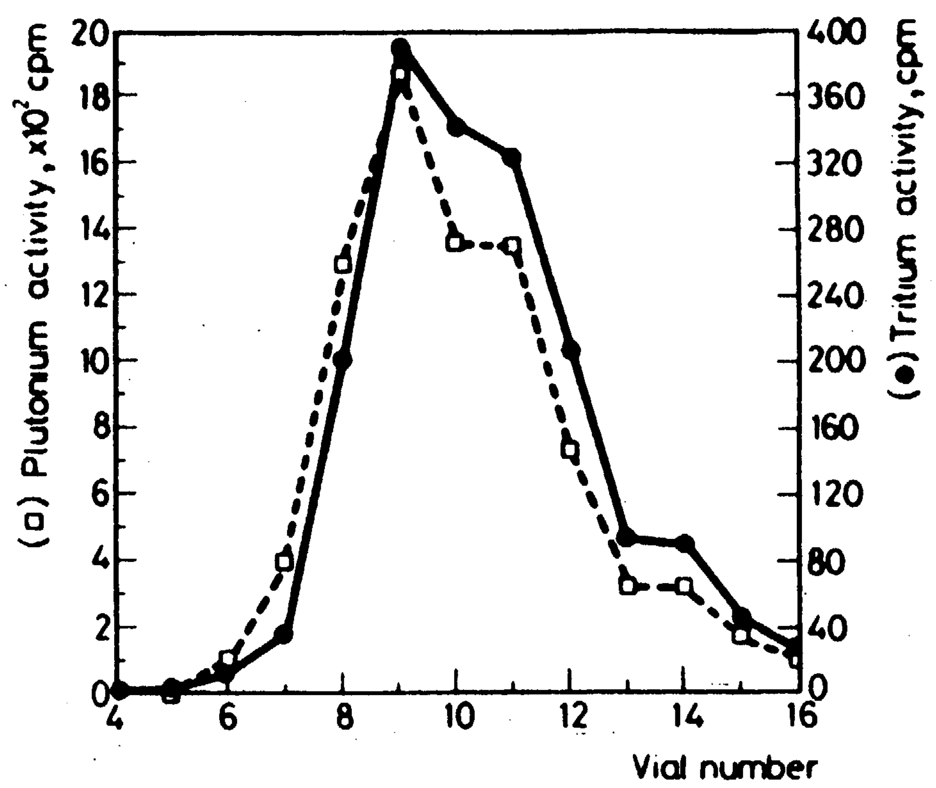
Sorption - linear, reversible, and instantaneous

$$\frac{F}{C} = K_d$$

$$\nabla \bullet (D\,\nabla C - CU) = \varepsilon \frac{\partial C}{\partial t} + \rho_b \frac{\partial F}{\partial t}$$

$$\nabla \bullet (D\,\nabla C - CU) = \varepsilon \left[1 + \frac{\rho_b}{\varepsilon} K_d\right] \frac{\partial C}{\partial t}$$

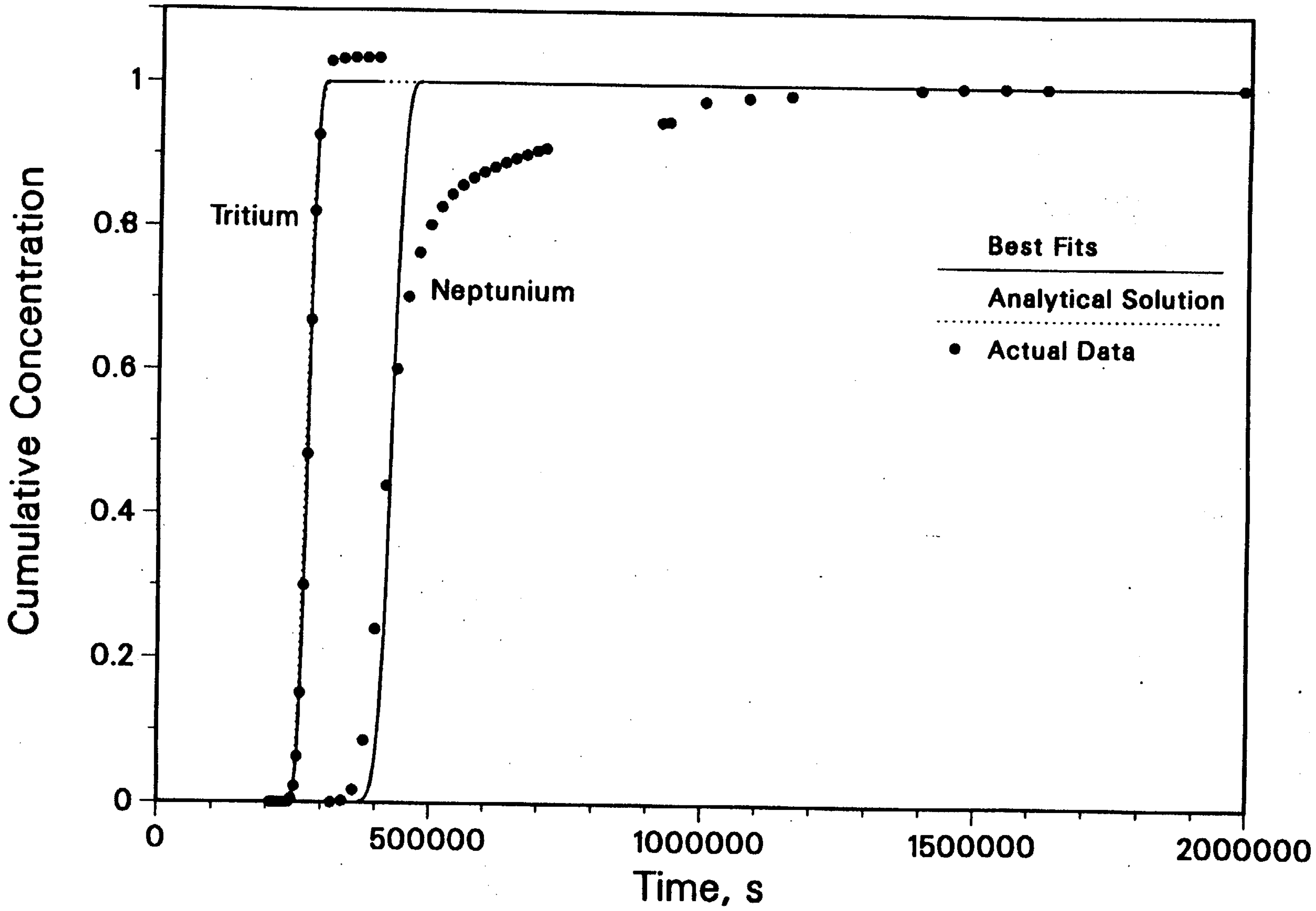
$$R_f = 1 + \frac{\rho_b}{\varepsilon} K_d$$



Elution of tritium (closed circles) and Pu(VI)(open squares). This pattern is typical of Np(V), Pu(V) and Pu(VI)

Breakthrough Curves Through G4-1530

Run 1



Column Experiments for Np Elution

Solid: Tuff G4-1530
Particle Size: 75-500 μm
Water: J-13
pH range: 8.1 - 8.4
Np Batch Kd = 2.4 ml/g

Column Parameters	Column #1	Column #2	Column #3
Length, cm	182	182	183
Diameter, cm	0.5	0.5	0.6
Volume, cm^3	32	32	58
Grams of Tuff	32	33	56
Density, g/ml	1.0	1.0	1.0
Porosity	0.4	0.4	0.4
Volumetric Flow Rate, ml/hr	0.3 for tritiated water 1 for Np	1	1
Interstitial Velocity, m/y	400 for tritiated water 1000 for Np	1000	700
Mean Residence Time, hr	75 for tritiated water 23 for Np	22	36
P_e	1300	970	1500
Dispersivity, cm	0.14	0.19	0.12
Np Kd from fit	1.6	1.7	1.9

Conclusions

- Iron Oxide minerals bind actinides strongly
- There is no obvious correlation between the amount of iron oxides in tuff and the tuff capacity for Np sorption
- Np sorption onto vitric and devitrified tuffs decreases as the pH is decreased from 8.5 to 7; whereas Np sorption onto zeolitic tuffs increases with decreasing pH
- Np sorption onto tuff increases or remains approximately constant as temperature increases
- Neptunium retardation in tuff under flowing conditions can be predicted with a Kd approach

MIGRATION OF RADIONUCLIDES IN POROUS MEDIA

ADVECTION - Dissolved Species are carried along by the movement of the fluid

DIFFUSION - Species are transferred form zones of high concentration to zones of low concentration

KINEMATIC DISPERSION - Mixing phenomenon linked to the heterogeneity of the microscopic velocities inside the medium

DISPERSION

Three components:

D_L is the longitudinal dispersion coefficient (in the direction of the flow)

D_T is the transverse dispersion coeeficient (in the two directions at right angles to the velocity)

$$D_L = \varepsilon d + \alpha_L |U|$$
$$D_T = \varepsilon d + \alpha_T |U|$$

d = diffusion coefficient

α = dispersivity

IRREVERSIBLE SORPTION

NONLINEAR ADSORPTION ISOTHERMS

Langmuir's: $F = \frac{K_1 C}{(1+K_2 C)}$

Freundlich's: $F = K_1 C^{1/n}$

NONINSTANTENOUS ADSORPTION-DESORPTION

DOE-NRC Technical Exchange Radionuclide Migration

Organic Sorption

Stephen Kung, LANL

Los Alamos
NATIONAL LABORATORY
1943 - 1993

DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION

EFFECT OF ORGANIC COATING ON SORPTION

Presented by:
Stephen Kung

PI: Ines Triay

Isotope and Environmental Geochemistry Group (INC-9)
Los Alamos National Laboratory
Los Alamos, New Mexico, 87545

PRELIMINARY DRAFT

OCTOBER 13, 1993

SCOPE OF PRESENTATION

Potential Impact of Organic Coating on Sorption
- Surface Complexation Mechanisms
- Organic Materials in Groundwater

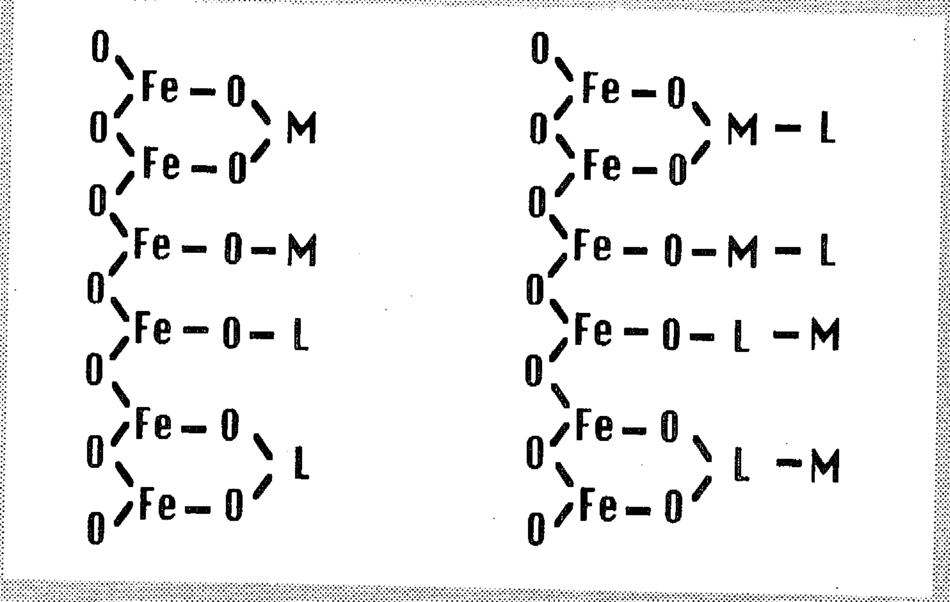
Laboratory Studies of Sorption on Organic Coated Surfaces
- Experimental Setup
- Preliminary Results of Sorption on Coated Surfaces
- Spectroscopic Study of Surface Coordination
- Current Research Activities

PRELIMINARY DRAFT

POTENTIAL IMPACT OF ORGANICS ON SORPTION

Potential Surface Coordination Mechanism Affecting Sorption

Competition for surface reactive sites
Enhancement through ternary or multilayer complexation
Formation of unsorbable species in solution



PRELIMINARY DRAFT

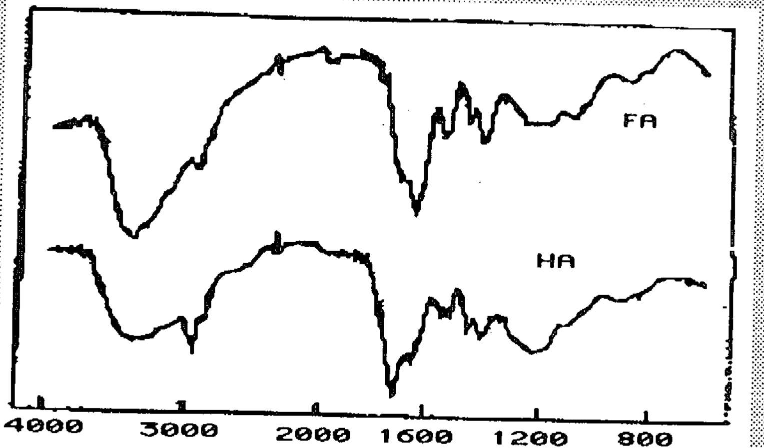
POTENTIAL IMPACT OF ORGANIC ON SORPTION

Natural Organic Materials in Groundwater

Groundwater Generally Contains < 10 ppm of Total Organic Carbon
Usually Between 0.1 and 2 ppm; Median ~0.7 ppm (Drever, 1988)

J-13 well water 0.15 ppm (Means et al., 1983)
NTS groundwater 0.54 ppm (Hall et al., unpublished data)

Humic material (HA, FA) isolated from J-13 water (Minai et al., 1992)



PRELIMINARY DRAFT

Laboratory Studies of Sorption on Organic Coated Surfaces

Experimental Setup

Materials

Synthetic Fe Oxide-Goethite FeOOH
Synthetic Al Oxide-Boehmite AlOOH
Fumed Silica-Amorphous SiO_2
Crushed Tuff from Yucca Mountain-USW G-4 270
  ~30% Silica (~25% Tridymite & ~5% Cristobolite)
  ~68% Feldspar
  ~1% Hematite and trace level of Mica & Smectite
DOPA 3-(3,4-dihydroxyphenyl)-DL-alanine

Method

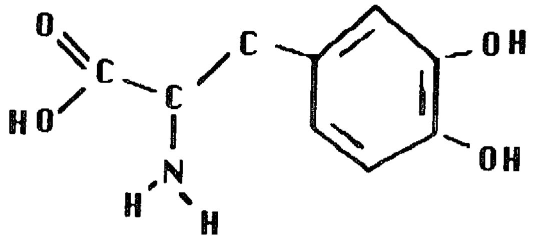
Batch sorption method was used to obtain sorption isotherms.

Tuff was treated with 15% H_2O_2 to remove organic.

Surface coordination mechanism was studied by FTIR.

PRELIMINARY DRAFT

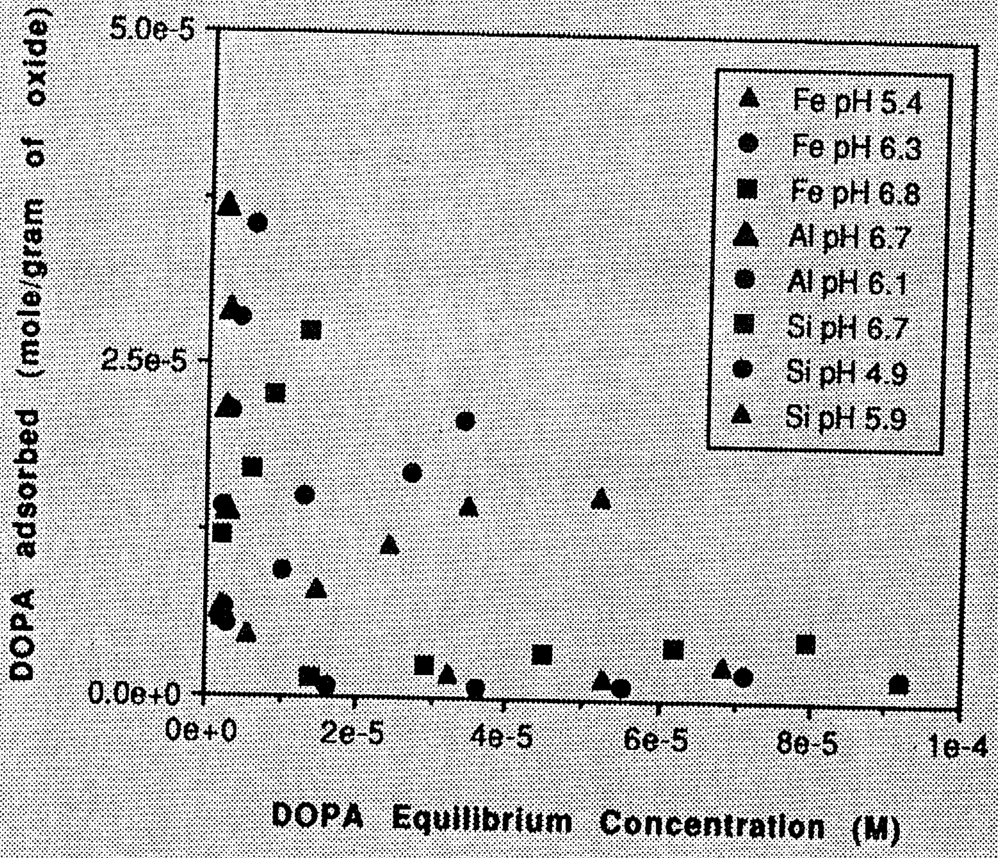
3-(3,4-dihydroxyphenyl)-DL-alanine



PRELIMINARY DRAFT

DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION

DOPA Adsorbed on Oxide Surfaces

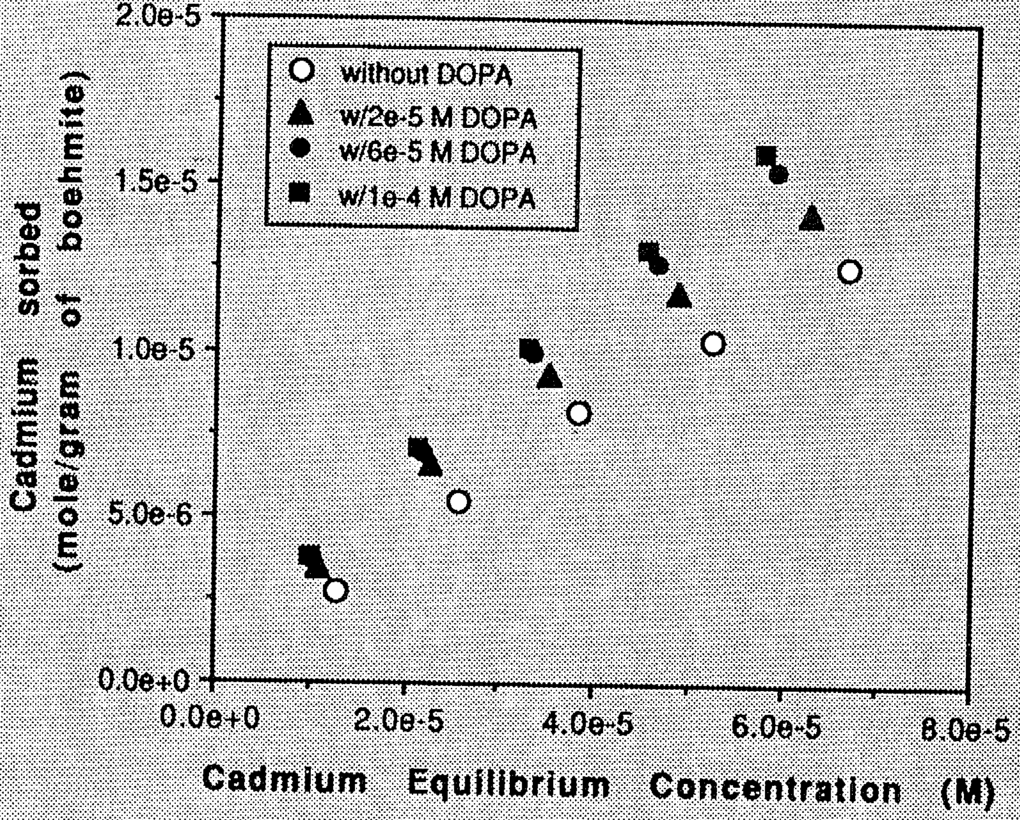


PRELIMINARY DRAFT

Effect of Organics on Sorption
Los Alamos National Laboratory

DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION

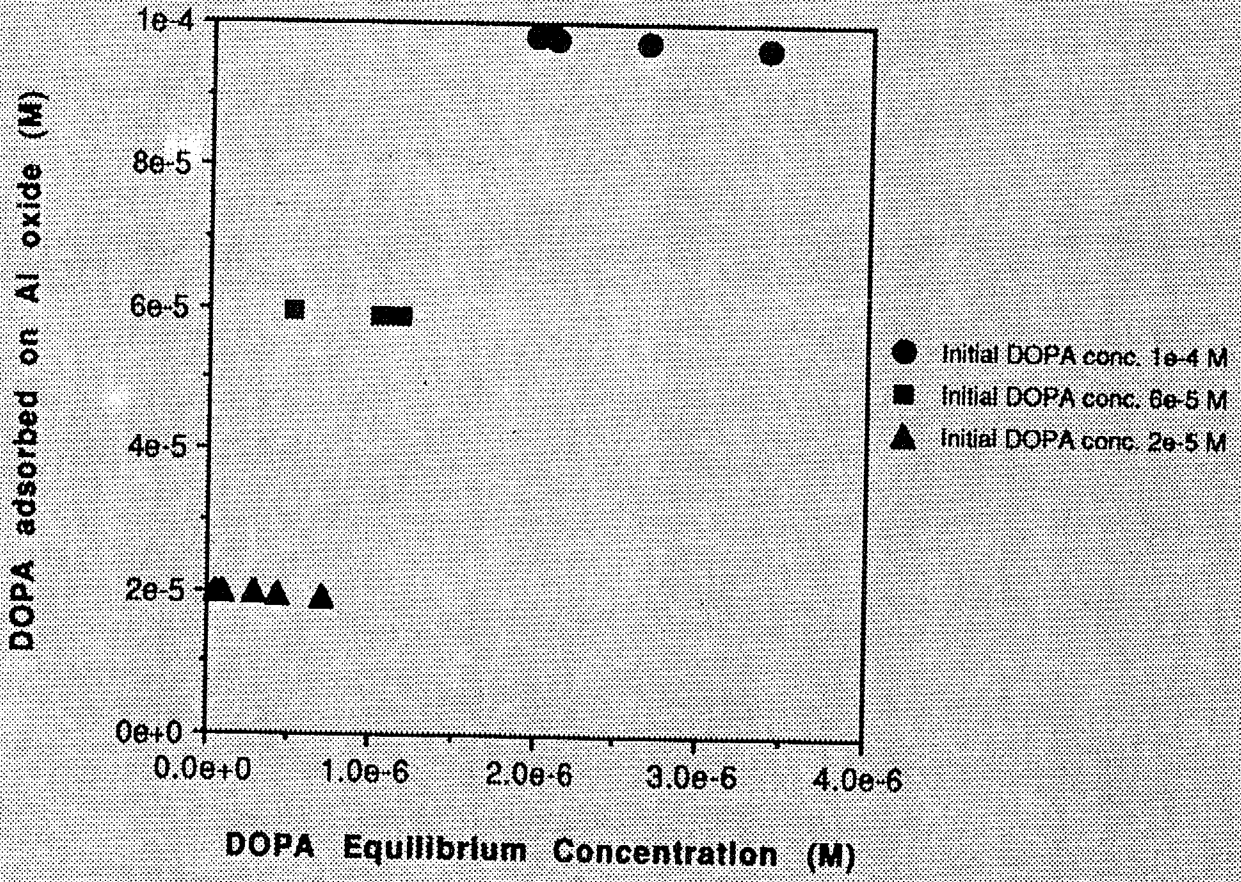
Sorption of Cd on Al Oxide with and without DOPA



PRELIMINARY DRAFT

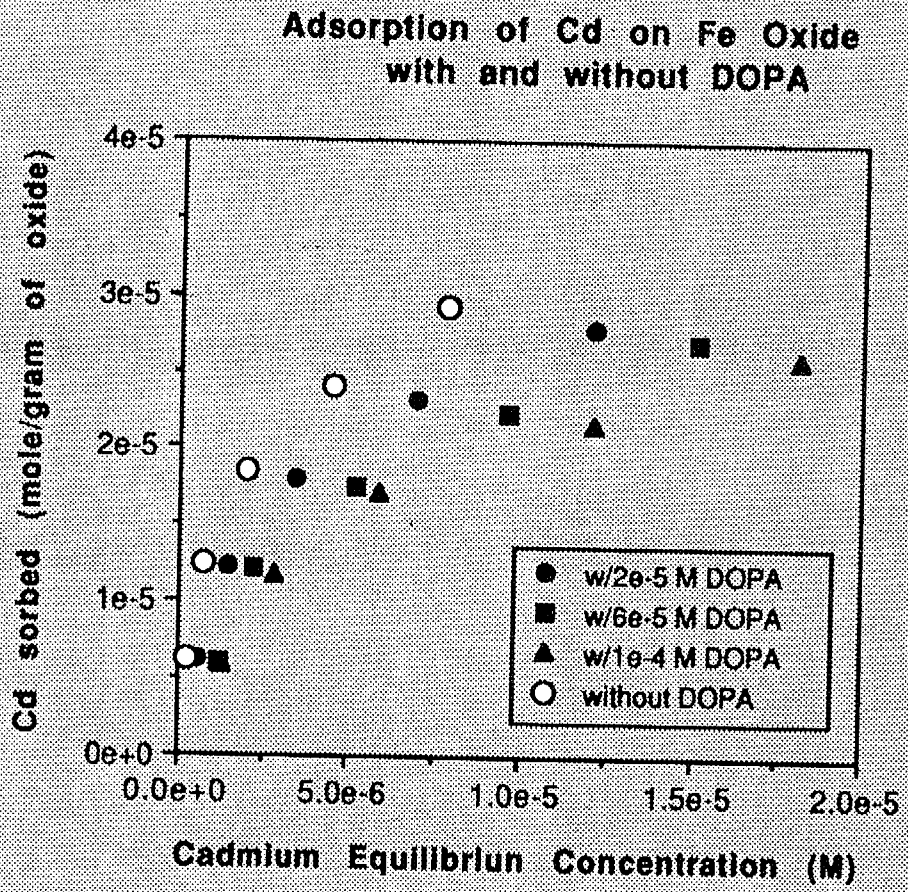
Effect of Organics on Sorption
Los Alamos National Laboratory

Adsorption of DOPA on Al Oxide With Cd (II)



PRELIMINARY DRAFT

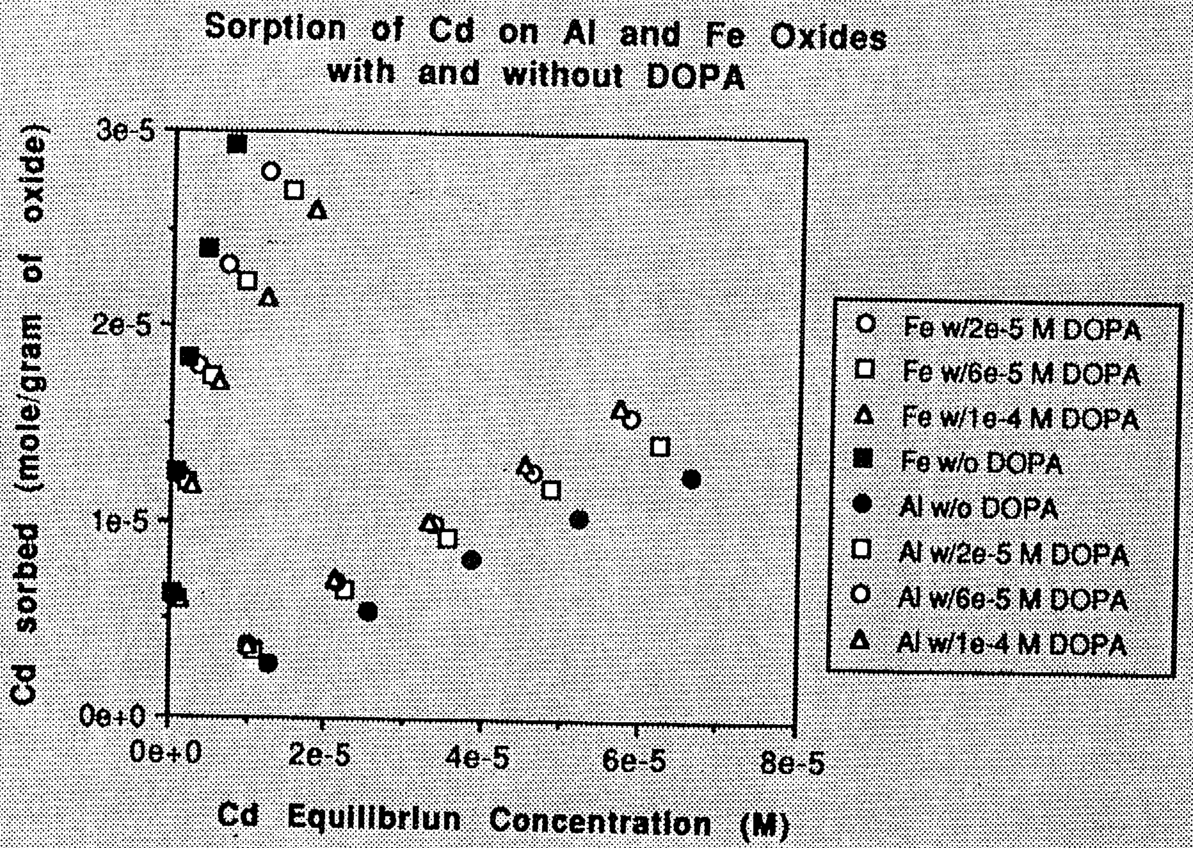
DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION



PRELIMINARY DRAFT

Effect of Organics on Sorption
Los Alamos National Laboratory

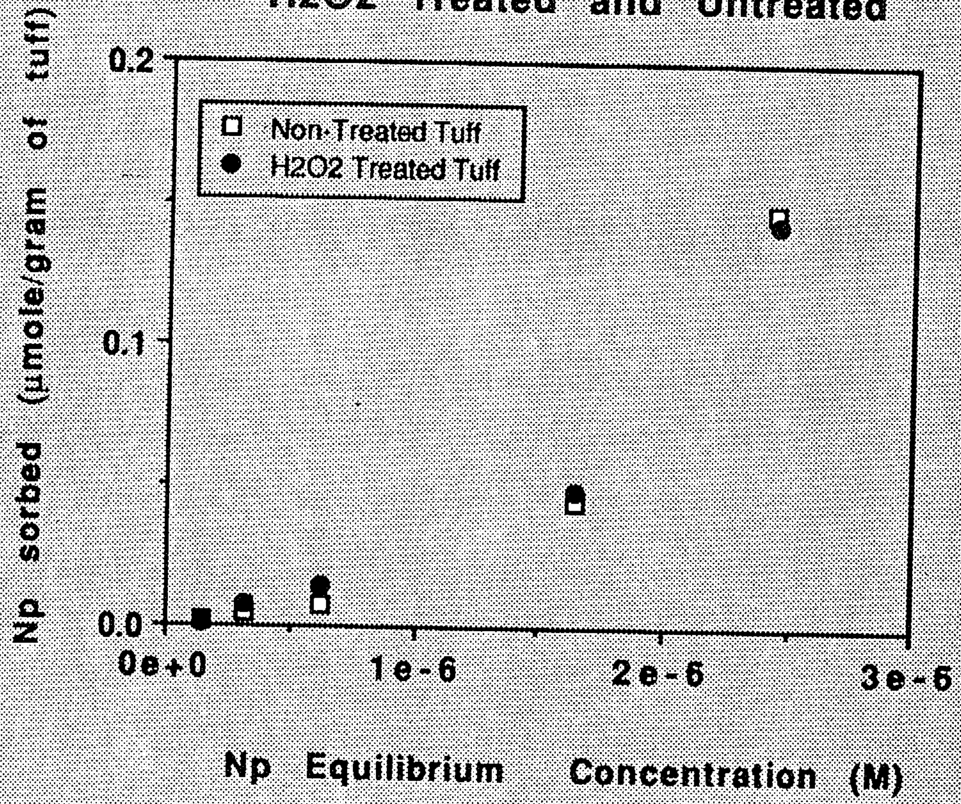
DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION



PRELIMINARY DRAFT

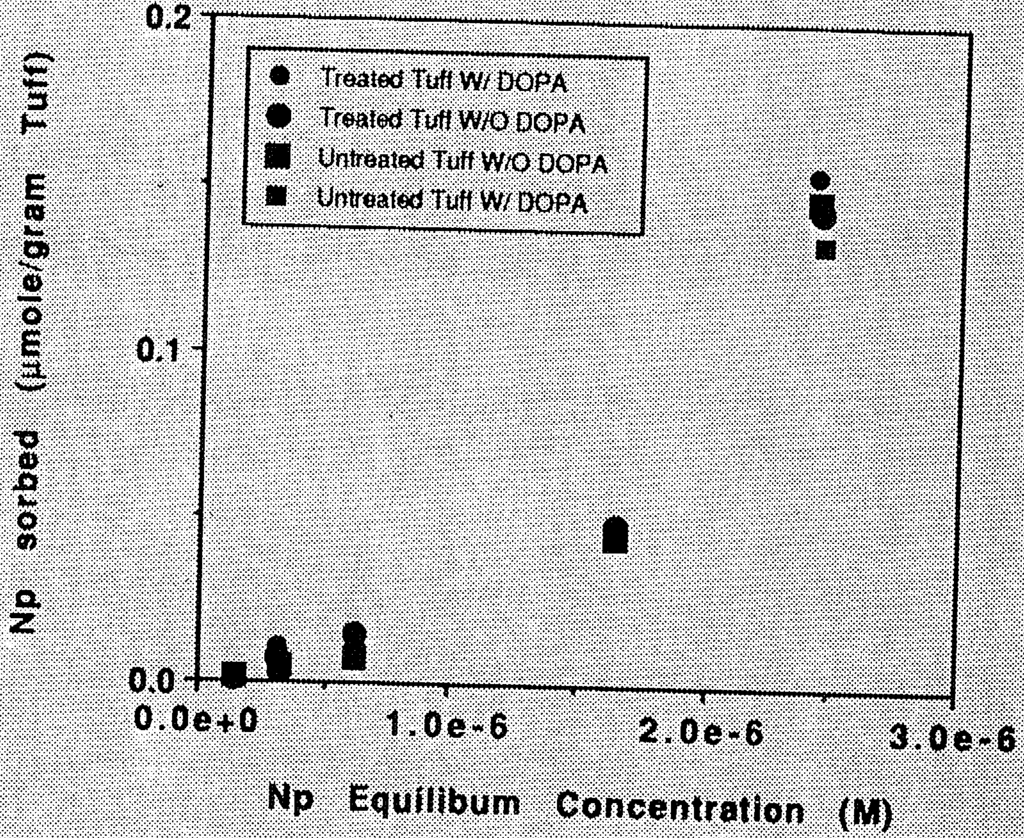
Effect of Organics on Sorption
Los Alamos National Laboratory

Np Sorption on Tuff Material
H2O2 Treated and Untreated



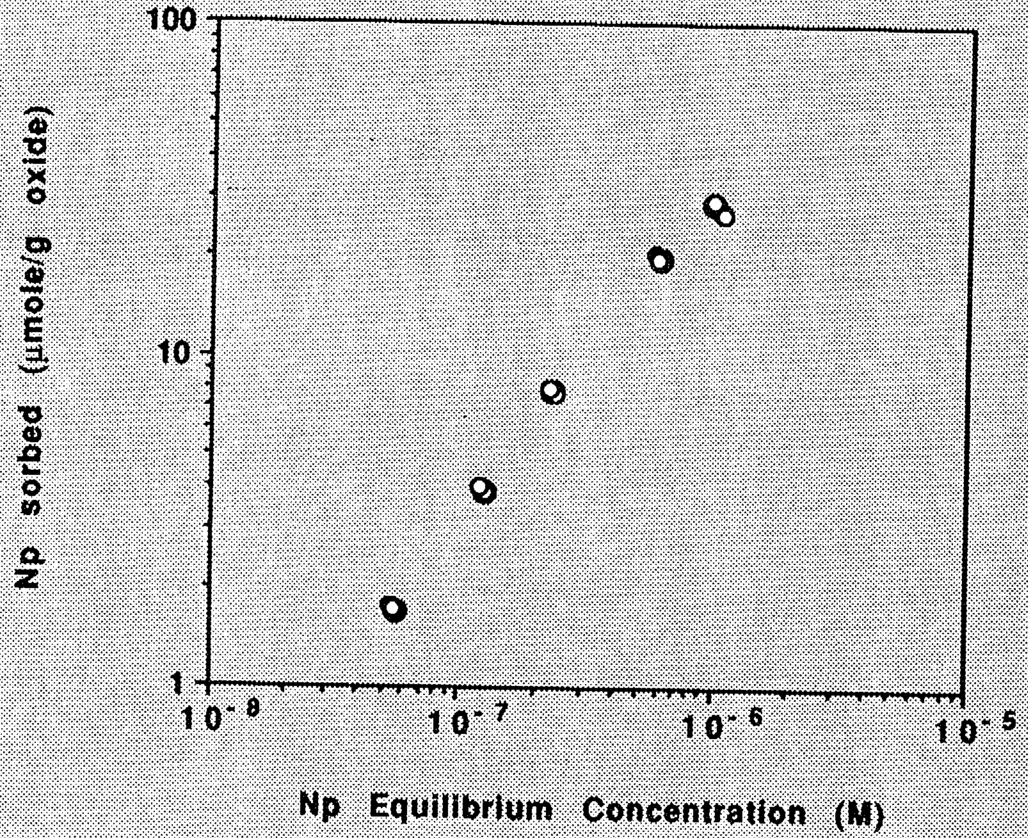
PRELIMINARY DRAFT

Np Sorption on Tuff With and Without DOPA



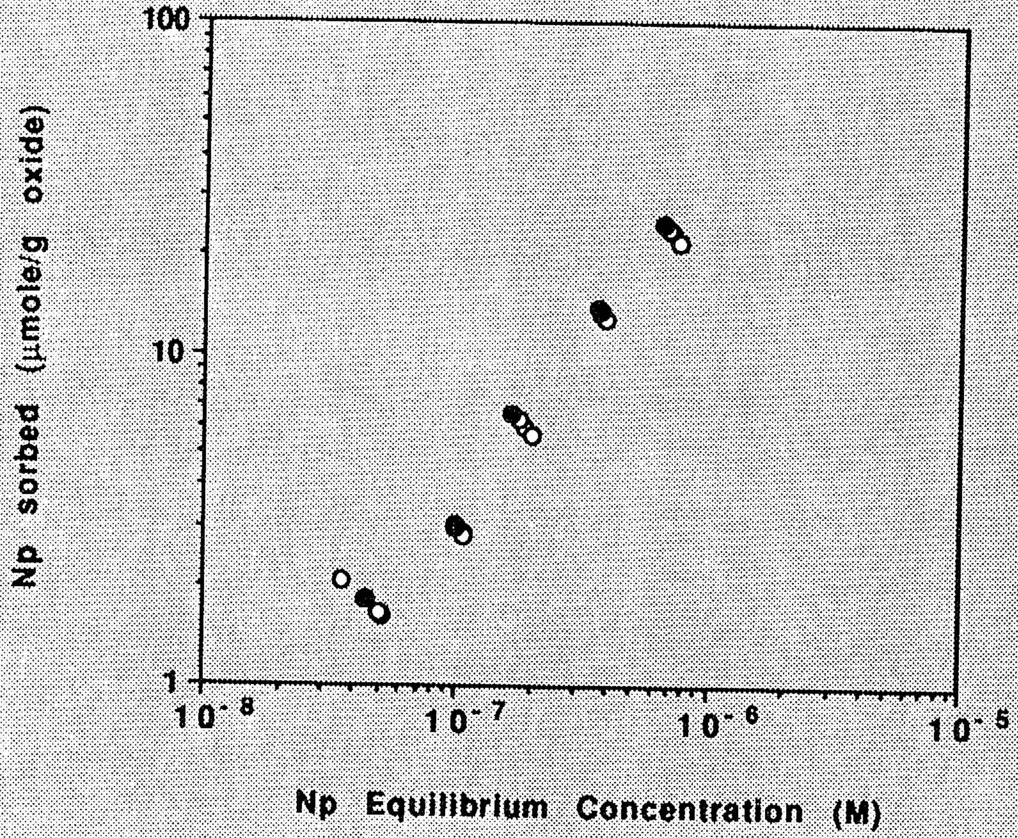
PRELIMINARY DRAFT

Np Sorption on Fe oxide With and Without DOPA



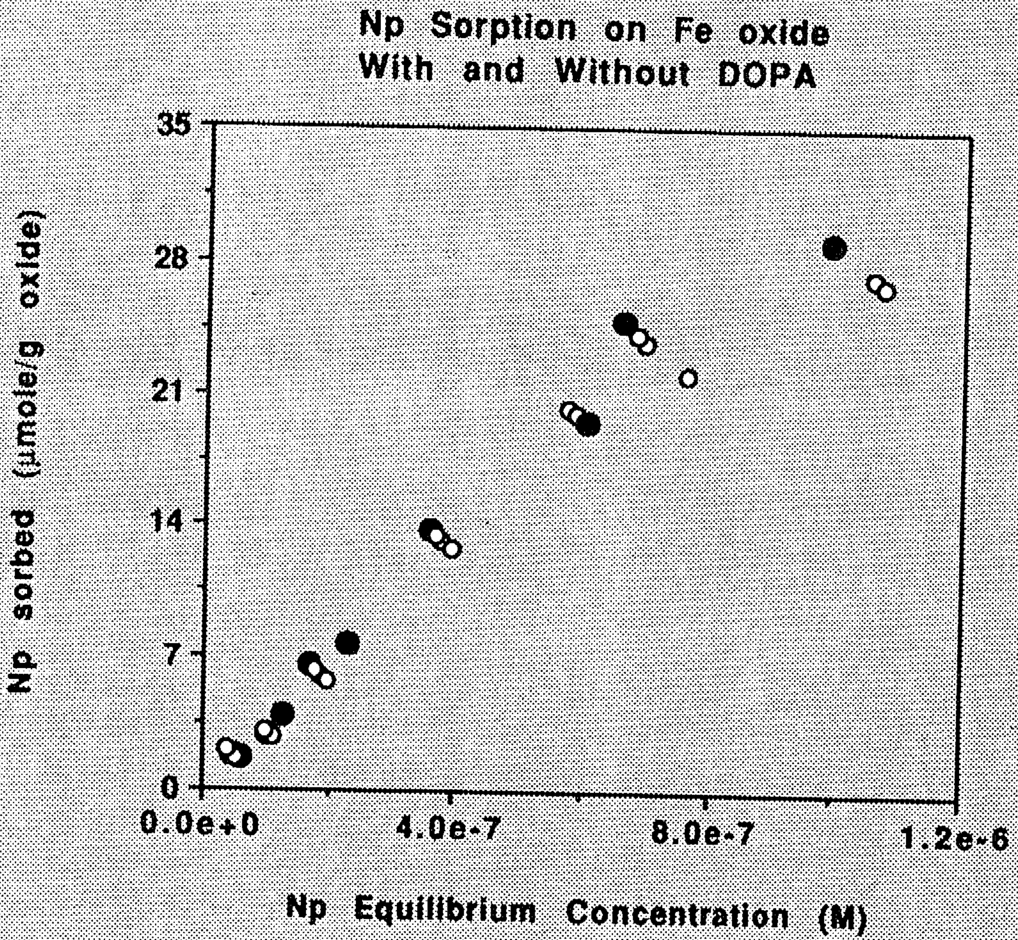
PRELIMINARY DRAFT

Np Sorption on Fe oxide With and Without DOPA



PRELIMINARY DRAFT

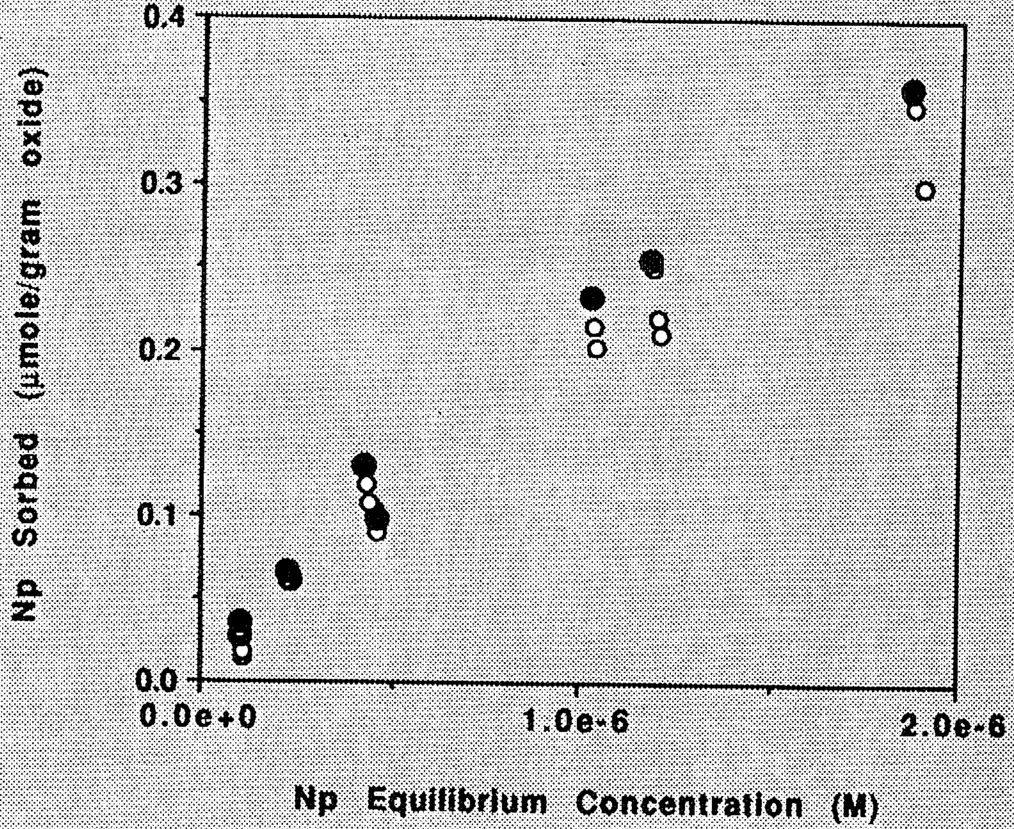
DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION



PRELIMINARY DRAFT

Effect of Organics on Sorption
Los Alamos National Laboratory

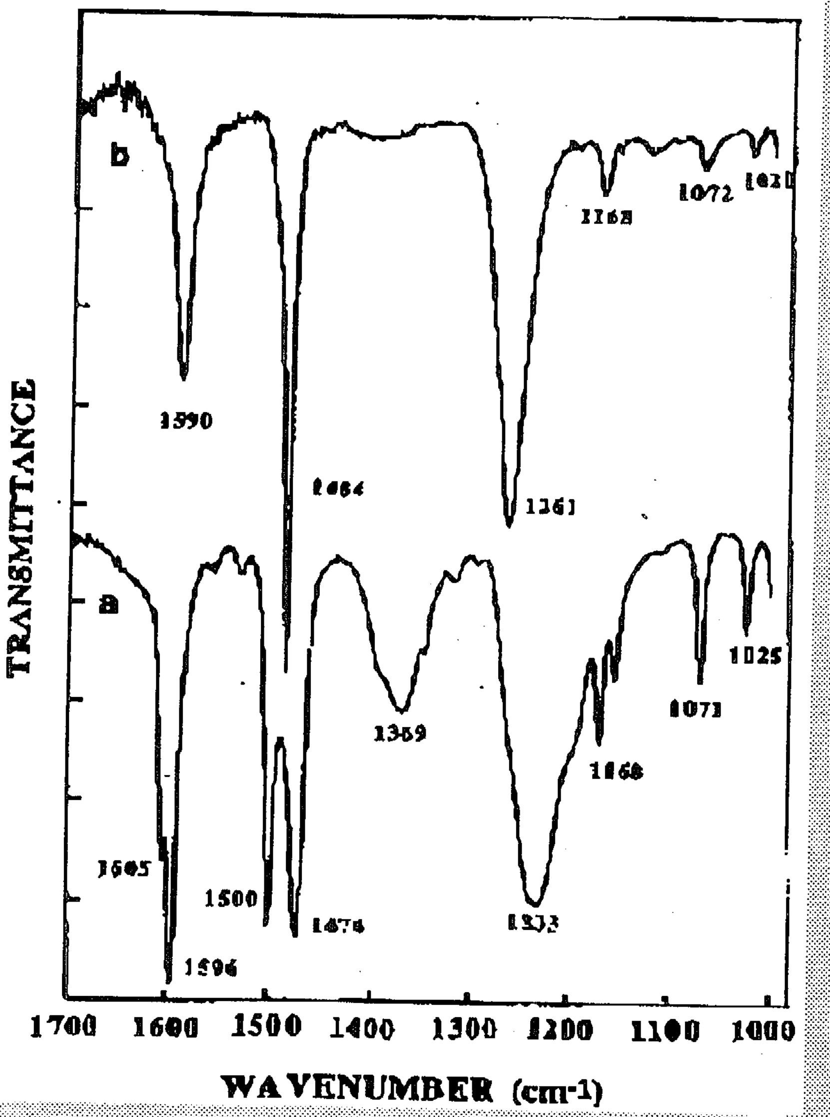
Np Sorption on Al Oxide With and Without DOPA

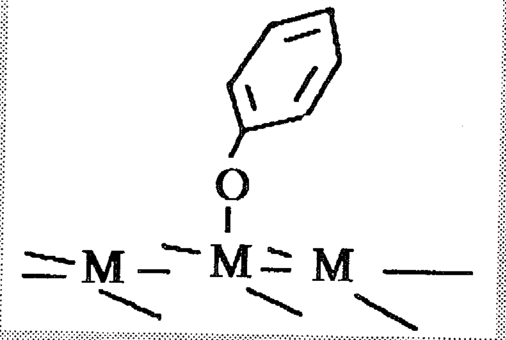


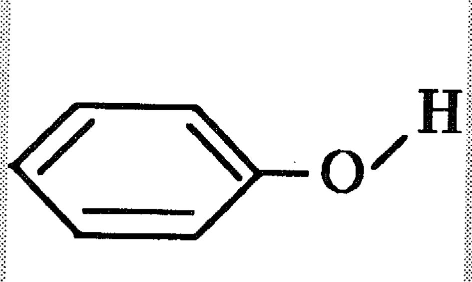
PRELIMINARY DRAFT

DOE-NRC TECHNICAL EXCHANGE
RADIONUCLIDE MIGRATION

Mechanistic Study of Surface Coordination





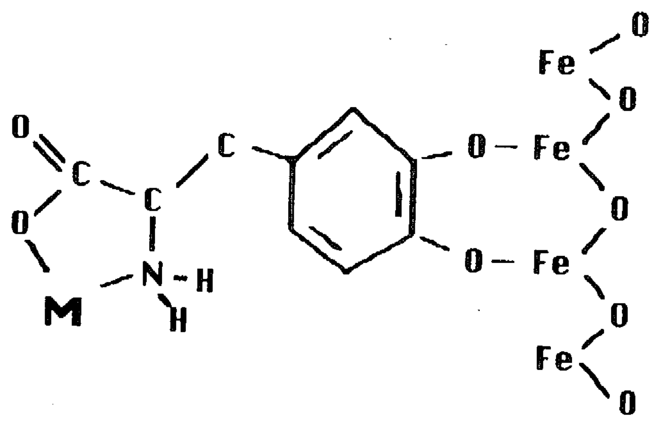


PRELIMINARY DRAFT

Effect of Organics on Sorption
Los Alamos National Laboratory

Current Research Activities and Effort

To characterize surface organic coating and identify sorption mechanism



To extend the developed methodology to natural organic material (humic and fulvic acids)

Colloid Transport Experiments and Calculations

- perform laboratory-scale column experiments involving elution of well characterized colloids (such as polystyrene spheres), degradation colloids, radiocolloids, and pseudocolloids through porous and fractured tuff media under various degree of saturation

- elute colloids through a lysimeter (filled with porous media) and large blocks (~ 1 m^3) of fractured tuff to bridge the gap between the laboratory and field scales

- perform field-scale colloid transport study in unsaturated, fractured tuff by evaluating whether radionuclides leached beneath a weapon's test (fired above water table) at NTS

- perform field-scale colloid transport experiment involving injection of polystyrene microspheres during a cross-hole hydraulic testing at a well complex at Yucca Mountain (C-Wells)

- validate colloid transport code

- use validated code to address the importance of colloid-facilitated radionuclide transport at the proposed repository at Yucca Mountain

DOE-NRC Technical Exchange
Radionuclide Migration

Matrix diffusion affecting mobility in fracture flow conditions

Inés R. Triay, LANL

Los Alamos
NATIONAL LABORATORY
1943 - 1993

DOE-NRC Technical Exchange
Radionuclide Migration

Diffusion

Inés Triay, LANL
Robert Lopez, LANL
Jim Conca, WSU Tri-Cities

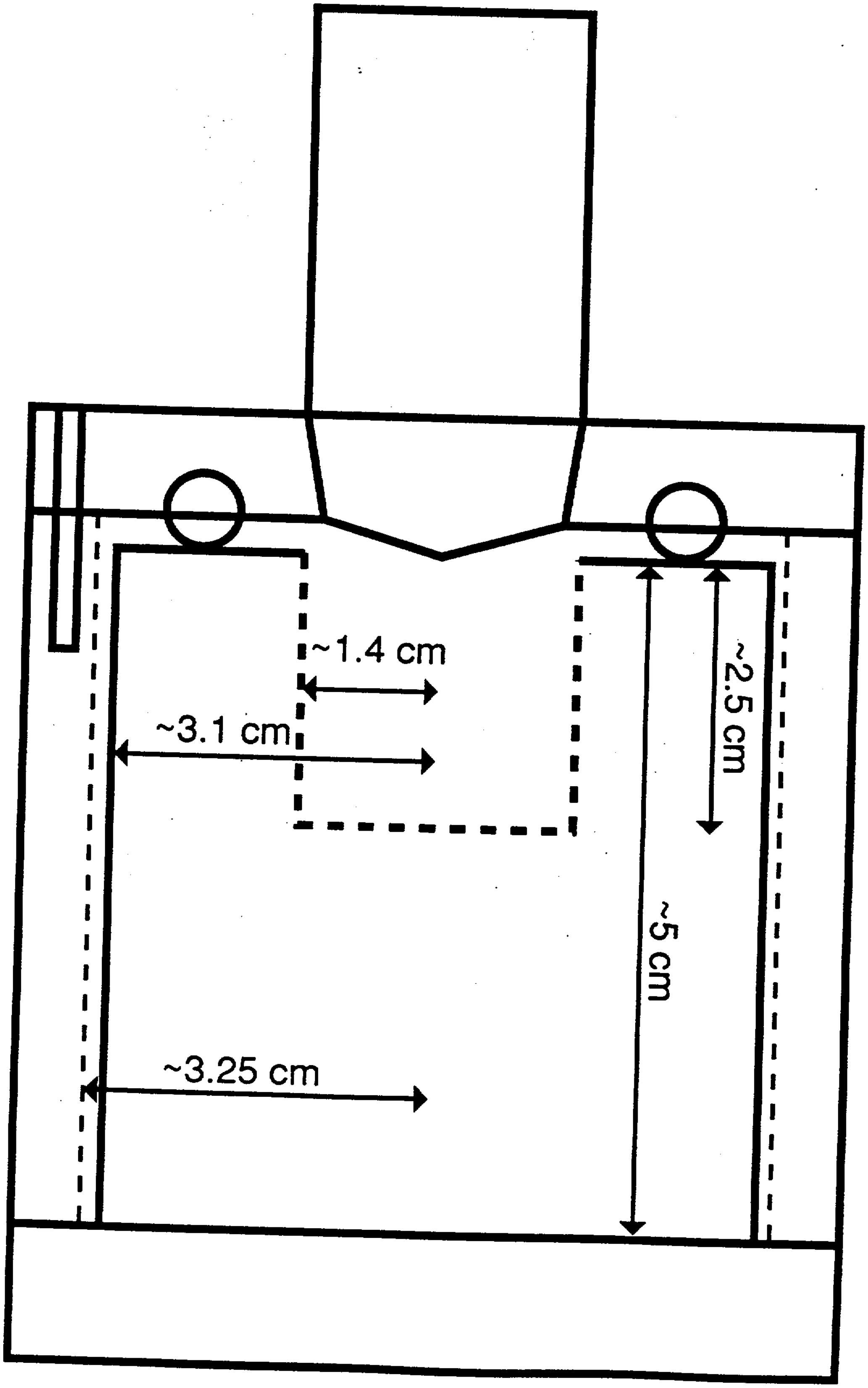
Radionuclide Migration Under Diffusive Conditions

Objective: Study the diffusion of radionuclides in Yucca Mountain tuffs under varying degrees of saturation

Experimental Techniques

- Wafers
- Diffusion Cells
- Rock Beakers
- Blocks of Tuff

Sample Rock Beaker



Rock Beaker Experimental Technique

- Actinide solutions prepared in J-13 water from well characterized $^{237}Np(V)$ and $^{241}Am(III)$ acidic solutions
- pH of solutions adjusted to 8
- Tracers utilized: ^{3}H, ^{95m}Tc, ^{237}Np, ^{241}Am, ^{85}Sr, ^{137}Cs, ^{133}Ba
- Tracer solutions placed in tuff beakers
- Aliquots of tracer solution taken as a function of time and analyzed for tracer concentration
- After diffusion of tracers, beakers will be sectioned and tracer concentration will be determined in the tuff

Batch Sorption Experimental Procedure

Pre-treatment Step

- 1g of tuff equilibrated with 20 ml of J-13 water for two weeks
- Phases separated by centrifugation

Sorption Step

- Pre-treated tuff equilibrated for three weeks with 20 ml of solution containing radionuclide
- Phases separated by centrifugation
- Amount of radionuclides in liquid phase determined by radioanalytical techniques
- Amount of radionuclide in solid phase calculated by difference

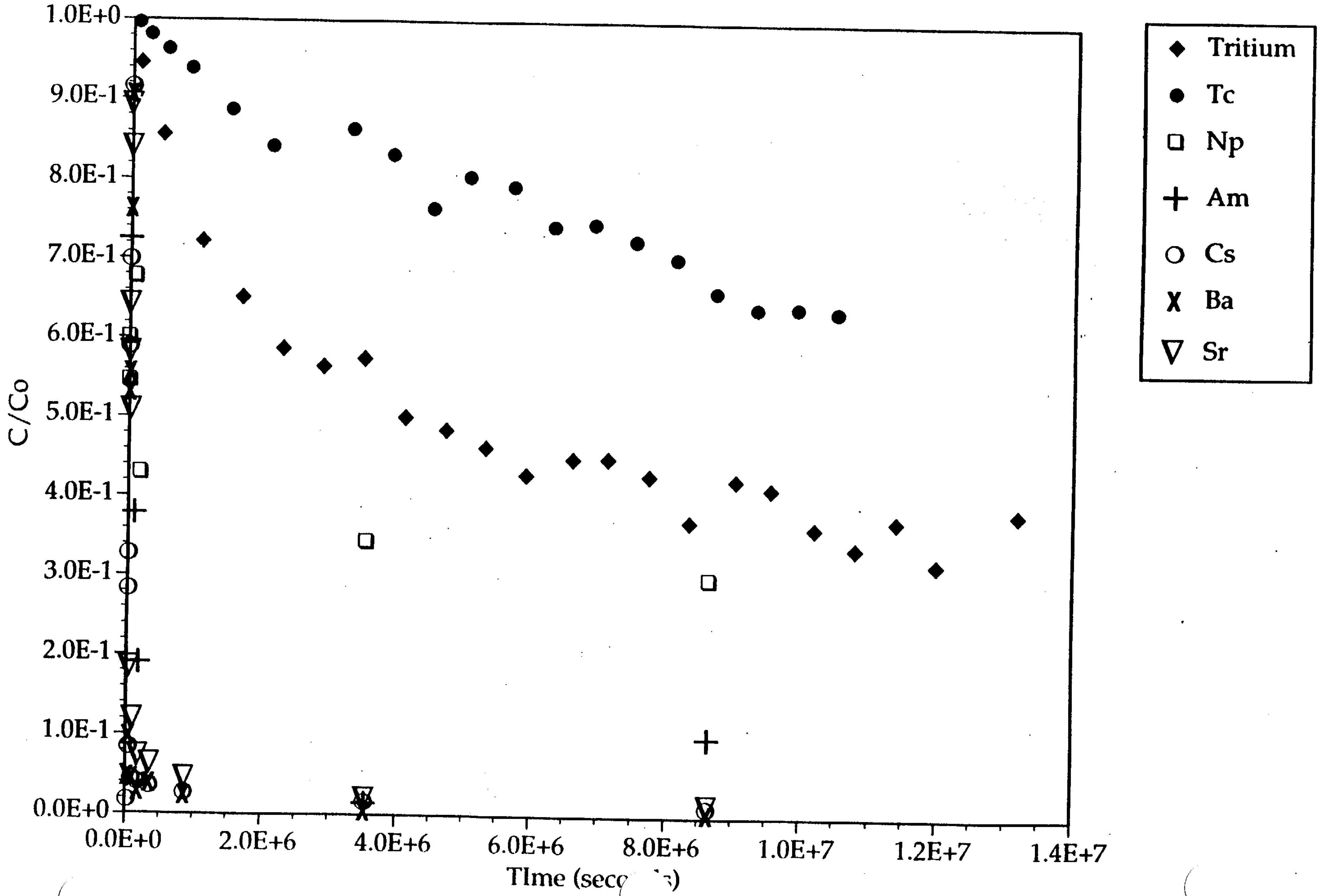
Controls

- Containers without tuff utilized to monitor radionuclide precipitation and/or sorption onto walls

Sorption Results

Tuff Sample	Major Mineral, %	K_d (ml/g)				
				Cs	Sr	Ba
G4-737	alkali feldspar, 68 cristobalite, 28			532	52	28
GU3-304	alkali feldspar, 75 cristobalite, 25			342	18	19
GU3-433	alkali feldspar, 76 cristobalite, 15			1264	20	61
GU3-1119	alkali feldspar, 70 quartz, 19			494	42	27
Topopah Outcrop	alkali feldspar, 59 cristobalite, 23 quartz, 12			465	20	25

G4-737


1.0E+0
9.0E-1
8.0E-1
7.0E-1
6.0E-1
5.0E-1
4.0E-1
3.0E-1
2.0E-1
1.0E-1
0.0E+0
C/Co
0.0E+0
2.0E+6
4.0E+6
6.0E+6
8.0E+6
1.0E+7
1.2E+7
1.4E+7
TIme (seconds)
◆ Tritium
● Tc
□ Np
+ Am
○ Cs
X Ba
▽ Sr

Diffusion Equation

$$\nabla \bullet (\varepsilon D \nabla C) = \varepsilon \frac{\partial C}{\partial t} + Q$$

$$Q = 0 \text{ (nonreactive)}$$

$$Q = (1 - \varepsilon)\, \rho_s \frac{\partial F}{\partial t} \text{ (sorbing)}$$

D = diffusion coefficient

C = concentration of solute

ε = porosity

t = time

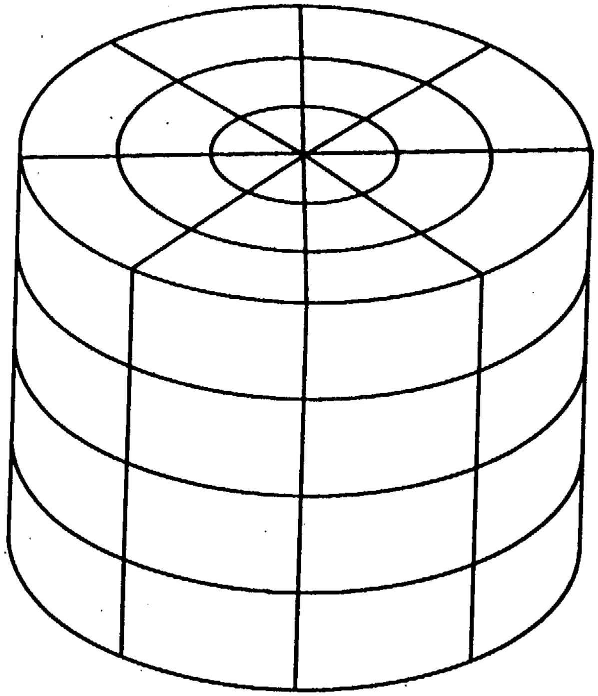
Q = sink or source term

ρ_s = density of the solid particles

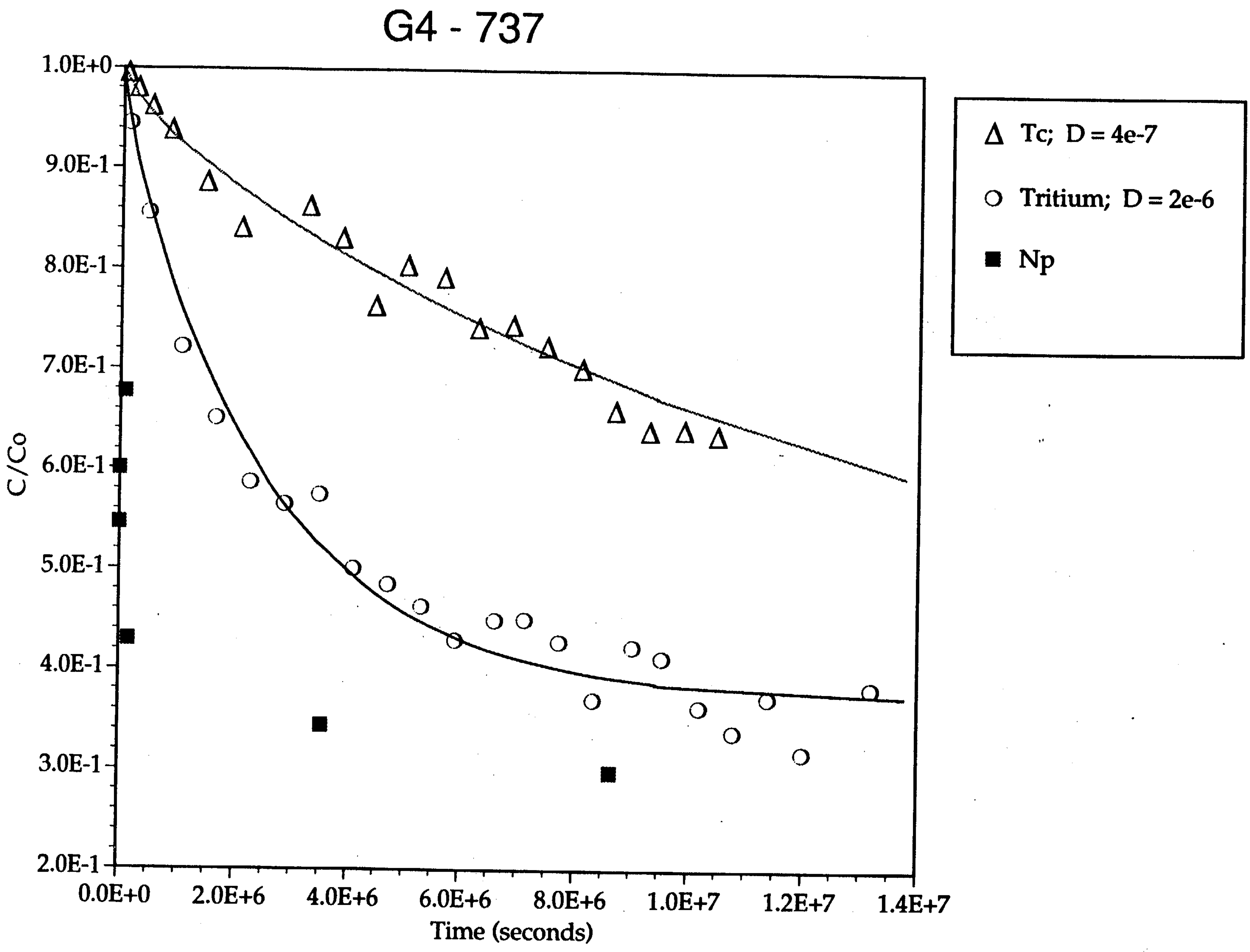
$$F = \frac{\text{mass of solute sorbed}}{\text{unit mass of solid}}$$

Modeling Performed with TRACR3D

- Using Cylindrical Coordinates



- Implicit Finite Difference Scheme


G4 - 737
1.0E+0
9.0E-1
8.0E-1
7.0E-1
6.0E-1
5.0E-1
4.0E-1
3.0E-1
2.0E-1
C/Co
0.0E+0
2.0E+6
4.0E+6
6.0E+6
8.0E+6
1.0E+7
1.2E+7
1.4E+7
Time (seconds)
Δ Tc; D = 4e-7
○ Tritium; D = 2e-6
■ Np

Diffusion Results

Tuff Sample	Major Minerals, %	Porosity	D (cm^2/s)	
			HTO	TcO_4^-
G4-737	alkali feldspar, 68 cristobalite, 28	0.07	2.2×10^{-6}	3.9×10^{-7}
GU3-304 #1	alkali feldspar, 75	0.06	1.5×10^{-6}	3.0×10^{-7}
GU3-304 #2	cristobalite, 25		1.6×10^{-6}	3.0×10^{-7}
GU3-433	alkali feldspar, 76 cristobalite, 15	0.10	3.5×10^{-6}	
GU3-1119	alkali feldspar, 70 quartz, 19	0.10	2.0×10^{-6}	4.9×10^{-7}
Topopah Outcrop	alkali feldspar, 59 cristobalite, 23 quartz, 12	0.07	1.0×10^{-6}	1.0×10^{-7}

Diffusion Results (Continued)

Tuff Sample	Major Minerals, %	Porosity	D (cm^2/s)	
			HTO	TcO_4^-
†G4-1067 #1 †G4-1067 #2 †G4-1067 #3	alkali feldspar, 61 quartz, 12 cristobalite, 10 tridymite, 10	~0.1	1.1×10^{-6} 1.1×10^{-6} 1.0×10^{-6}	
†G4-1502	clinoptilolite, 71 opal-CT, 15	~0.3	1.6×10^{-6}	*4.8×10^{-7}
†G4-1607 #1 †G4-1607 #2	clinoptilolite, 63 opal-CT, 18	~0.3	2.0×10^{-6} 2.0×10^{-6}	*2.1×10^{-7} *3.2×10^{-7}
†G4-1608	clinoptilolite, 63 opal-CT, 18	~0.3	1.6×10^{-6}	*3.0×10^{-7}

† from YMP Milestone R524

* values calculated from YMP Milestone R524 assuming unitary retardation factors

Diffusion Equation

$$\nabla \bullet (\varepsilon D \, \nabla C) = \varepsilon \frac{\partial C}{\partial t} + Q$$

$Q = 0$ (nonreactive)

$Q = (1 - \varepsilon)\, \rho_s \, \frac{\partial F}{\partial t}$ (sorbing)

D = diffusion coefficient

C = concentration of solute

ε = porosity

t = time

Q = sink or source term

ρ_s = density of the solid particles

$$F = \frac{\text{mass of solute sorbed}}{\text{unit mass of solid}}$$

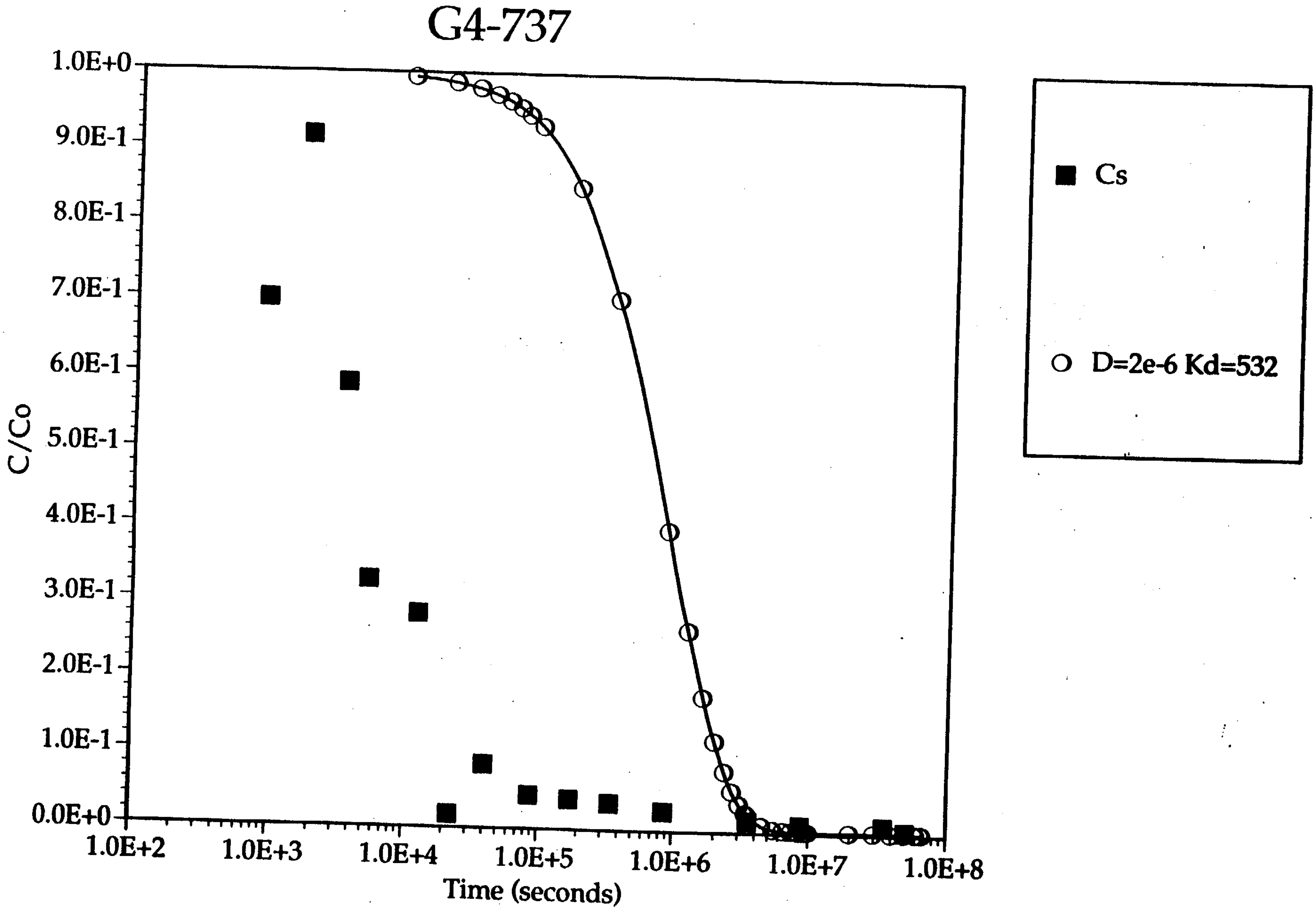
Mechanism of Sorption Determines Relationship of F with Respect to C

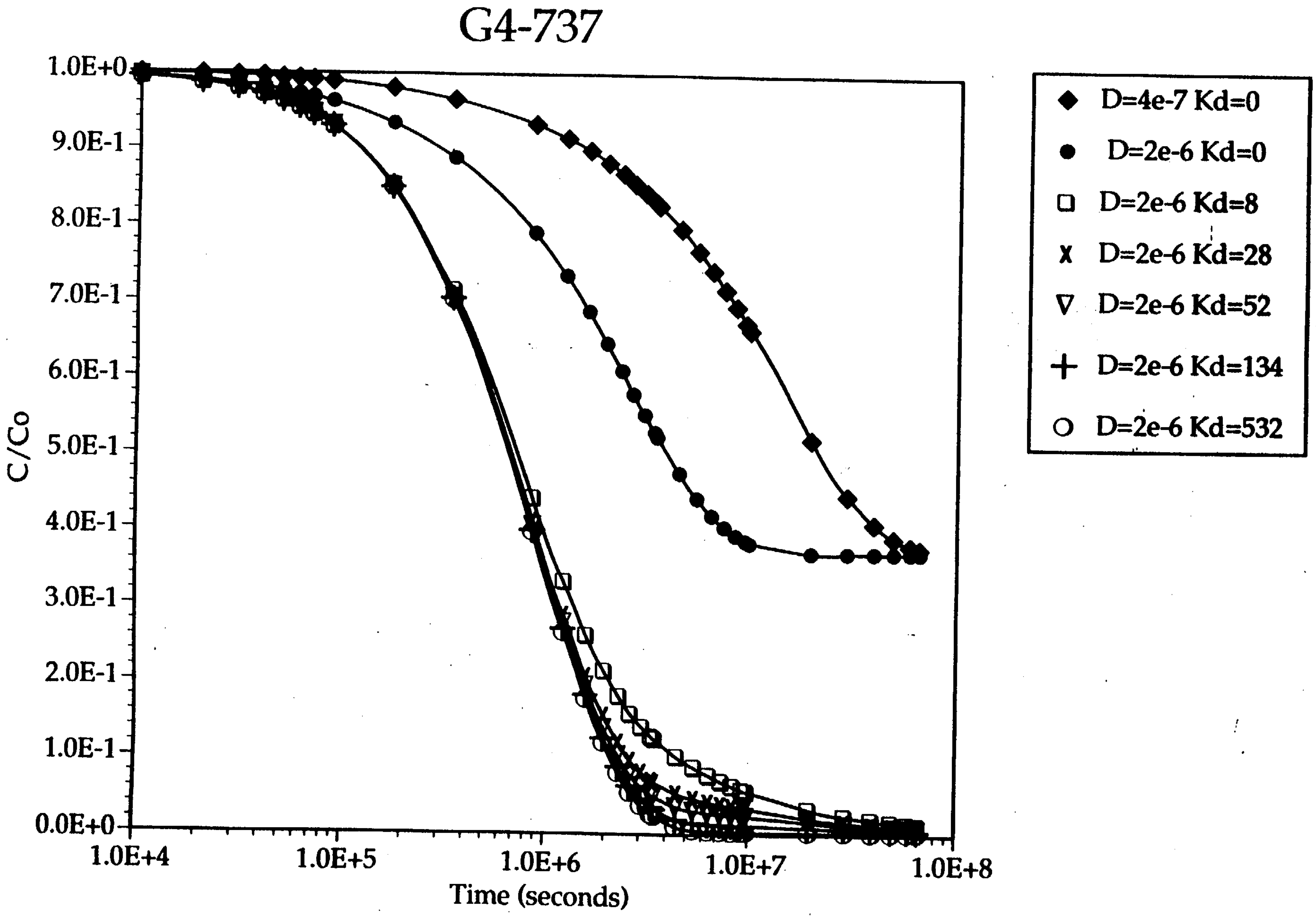
Sorption - linear, reversible, and instantaneous

$$\frac{F}{C} = K_d$$

$$\nabla \bullet (D \nabla C) = \frac{\partial C}{\partial t} + \frac{(1-\varepsilon)\rho_s}{\varepsilon} \frac{\partial F}{\partial t}$$

$$\nabla \bullet (D \nabla C) = \left[1 + \frac{(1-\varepsilon)}{\varepsilon} \rho_s K_d\right] \frac{\partial C}{\partial t}$$


G4-737
1.0E+0
9.0E-1
8.0E-1
7.0E-1
6.0E-1
5.0E-1
4.0E-1
3.0E-1
2.0E-1
1.0E-1
0.0E+0
C/Co
1.0E+2
1.0E+3
1.0E+4
1.0E+5
1.0E+6
1.0E+7
1.0E+8
Time (seconds)
■ Cs
○ D=2e-6 Kd=532


G4-737
C/Co
1.0E+0
9.0E-1
8.0E-1
7.0E-1
6.0E-1
5.0E-1
4.0E-1
3.0E-1
2.0E-1
1.0E-1
0.0E+0
1.0E+4
1.0E+5
1.0E+6
1.0E+7
1.0E+8
Time (seconds)
◆ D=4e-7 Kd=0
● D=2e-6 Kd=0
□ D=2e-6 Kd=8
x D=2e-6 Kd=28
∇ D=2e-6 Kd=52
+ D=2e-6 Kd=134
○ D=2e-6 Kd=532

Summary

- Diffusion coefficients in tuff under saturated conditions were determined
- Large anions such as TcO_4^-, excluded from tuff pores
- Diffusion data from sorbers can not be fit assuming reversible, instantaneous and linear sorption
- Conservative transport calculations will result from available parameters
- Future research efforts will concentrate on elucidating the sorption kinetics of actinides via experiments under advective and diffusive conditions