9311170061 PART 2

DOE-NRC Technical Exchange Radionuclide Migration

Groundwater chemistry modeling

Michael H. Ebinger, LANL

Los Alamos NATIONAL LABORATORY 1943 - 1993

What is the Groundwater Chemistry Model?

One Attempt to Understand Water-Rock Interactions at Yucca Mountain

Conceptual Model (Qualitative-Quantitative)

- Geochemical Processes (Dissolution)
- Reactions (Description of Processes)

What is the Groundwater Chemistry Model?

Mathematical Model

- Quantitative (Uncertainty/Sensitivity)
- Predictive Capability

Purpose of the Groundwater Chemistry Model

SCP Specifies GWC Model (Study 8.3.1.3.1.1)

Predictive Capability (Performance Assessment)

Support Other Investigations

- Sorption
- Radionuclide Solubility

An "Integrating Study"

Progress to Date

Study Plan

- Review Comments Completed
- Revised Draft

Preliminary Modeling

- Processes--Sepiolite Formation
- Reactions--pH Stability
- "Most Active Groundwater"

Review of pH, Eh in Preparation

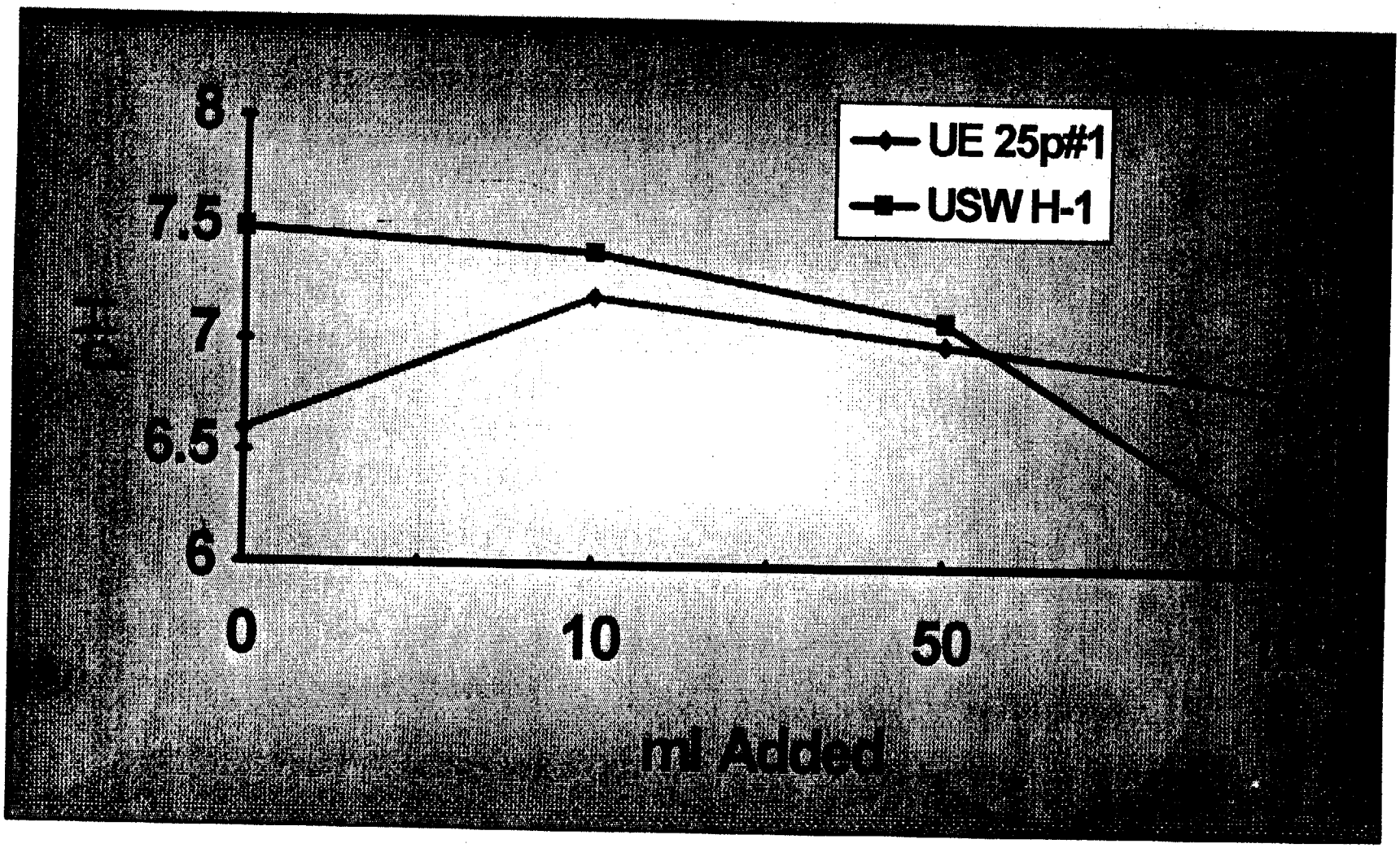
Sepiolite Formation During Evaporation

Evaporation of Well A Water (Tuff)

Concentration Factor	Predicted Minerals
1	C, D
2	C, D
5	C, S, D
10	C, S
50	C, S
100	C, S

C = Calcite, D = Dolomite, and S = Sepiolite

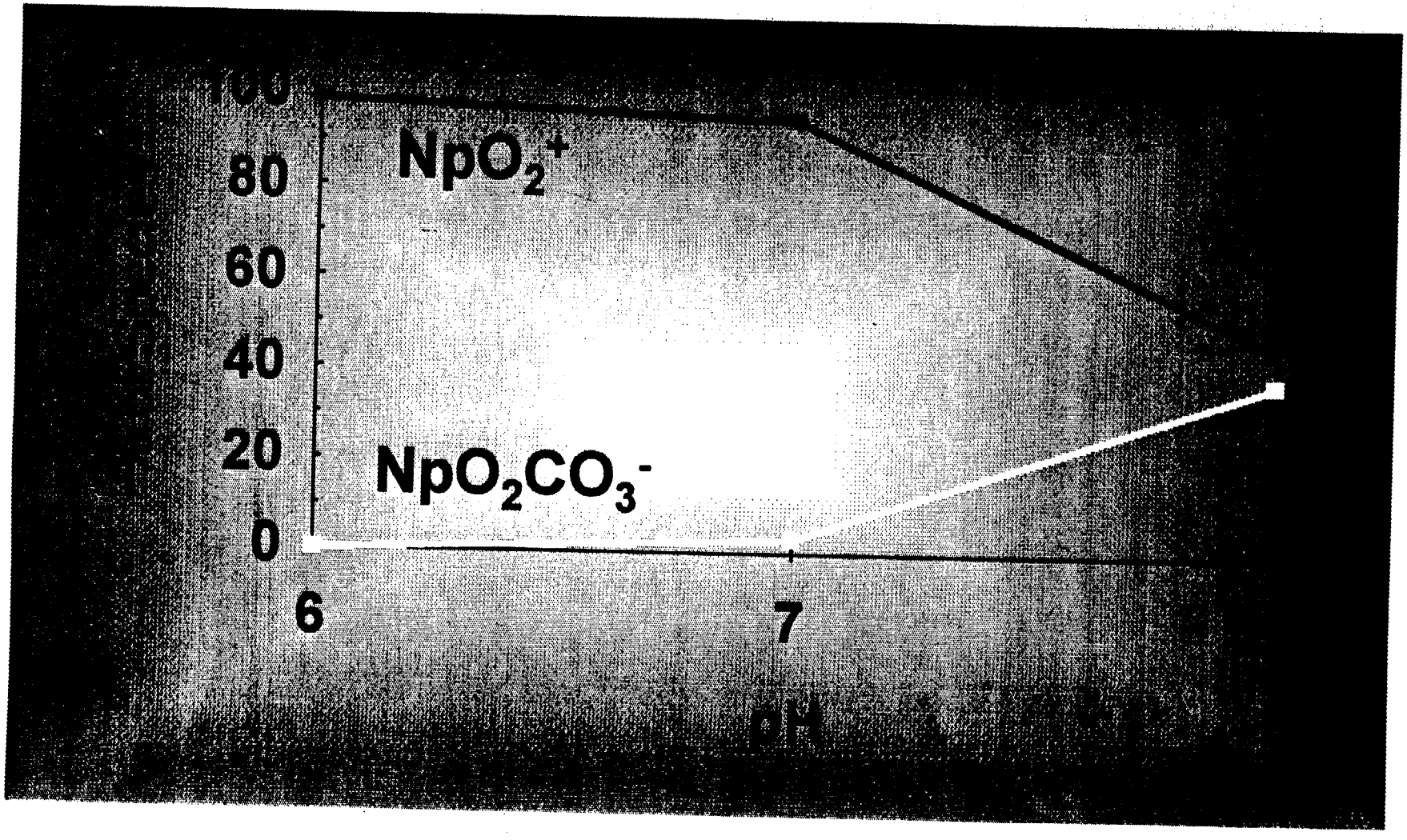
pH vs. UO_2^{2+} Added, USW H-1 & UE 25p#1 Water



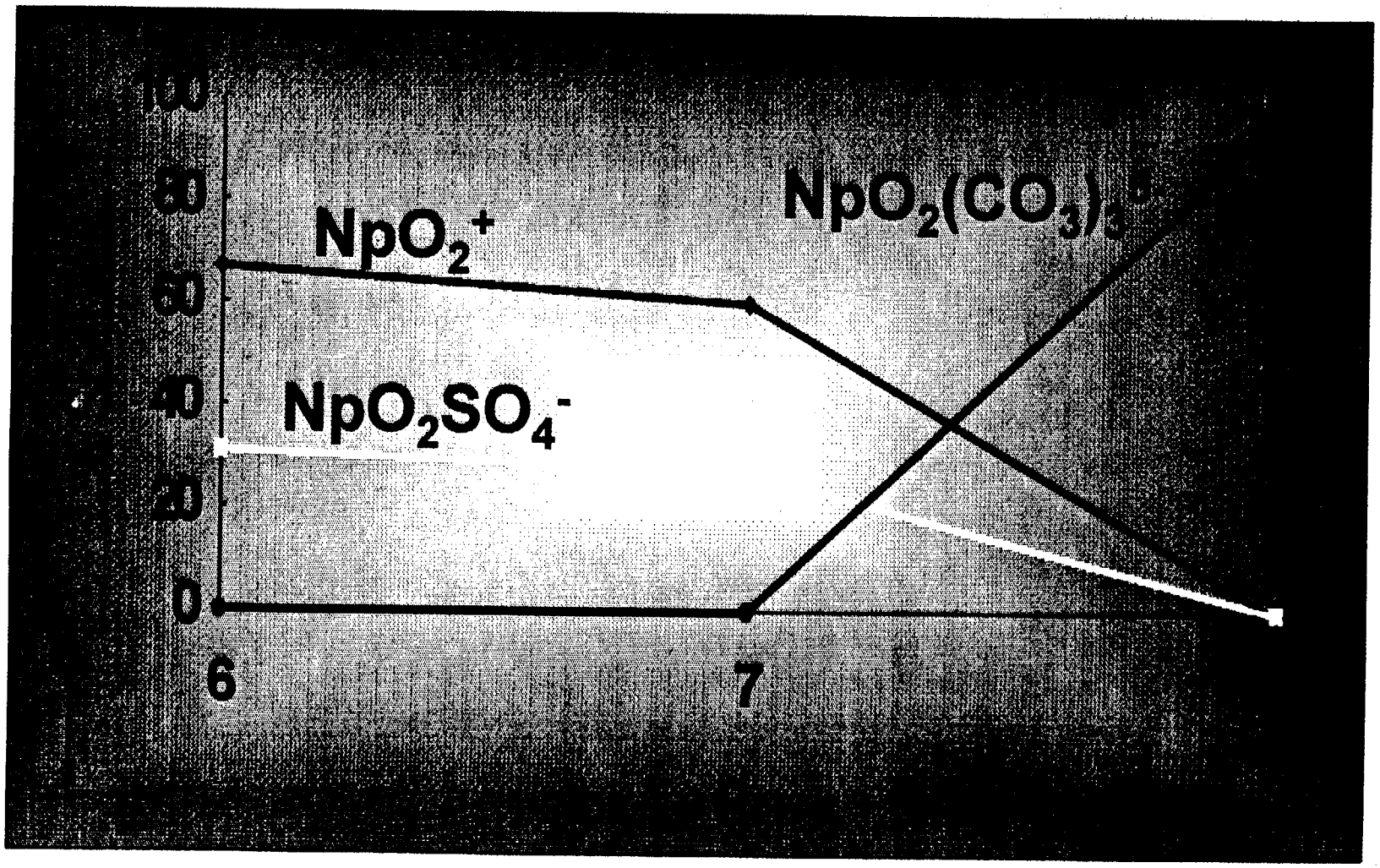
Np Speciation, J-13 and UE 25p#1 Water

pH	J-13	UE 25p#1
6	NpO_2^+ (99%)	NpO_2^+ (67%) $NpO_2SO_4^-$ (31%)
7	NpO_2^+ (95%) $NpO_2CO_3^-$ (3%) $NpO_2CO_3^-$ (3%)	NpO_2^+ (60%) $NpO_2SO_4^-$ (27%)
8.5	NpO_2^+ (46%) $NpO_2CO_3^-$ (38%)	$NpO_2(CO_3)^{-5}$ (97%) $NpO_2(CO_3)^{-5}$ (2%)

Np Speciation, J-13 Water



Np Speciation, UE 25p#1 Water



Planned Work

Study Plan Revisions

Identify Geochemical Processes

Testing

- pH Control (Bicarbonate?)
- Eh (Oxygen Pressure?)
- Mineral/Water Interactions

Planned Work, continued

Develop Conceptual Model(s)

- Hypothesis formulation
- Descriptions of Probable Models

Develop Mathematical Model(s)

- Test Hypotheses
- Uncertainty and Sensitivity

Conclusions

Study Plan Revised

Preliminary Modeling Showing Results

Several Tasks and Tests Planned

Support of Other Investigations

DOE-NRC Technical Exchange

Radionuclide Migration

Actinide Carbonate Speciation Studies by PAS and NMR Spectroscopies

David L. Clark, Scott A. Ekberg, Phillip D. Palmer, and C. Drew Tait

Isotope and Nuclear Chemistry (INC) Division
Los Alamos National Laboratory

PRELIMINARY DRAFT

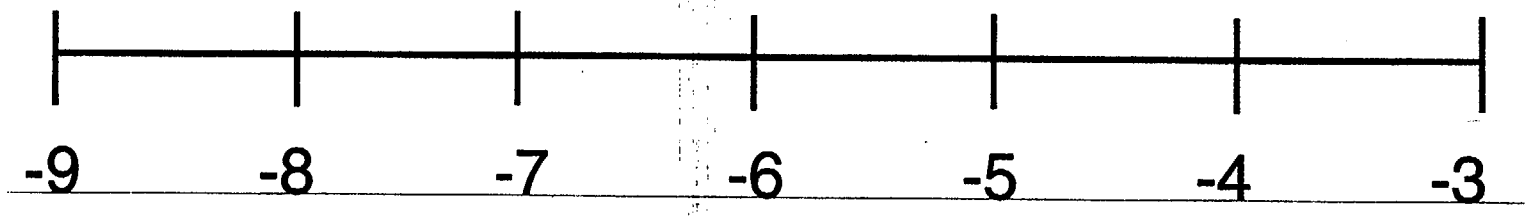
Approach

-repository domain
-minimizes polymerization
-minimizes radiolysis

Photothermal and LIF Spectroscopies

NMR, Vib Spectrosc.

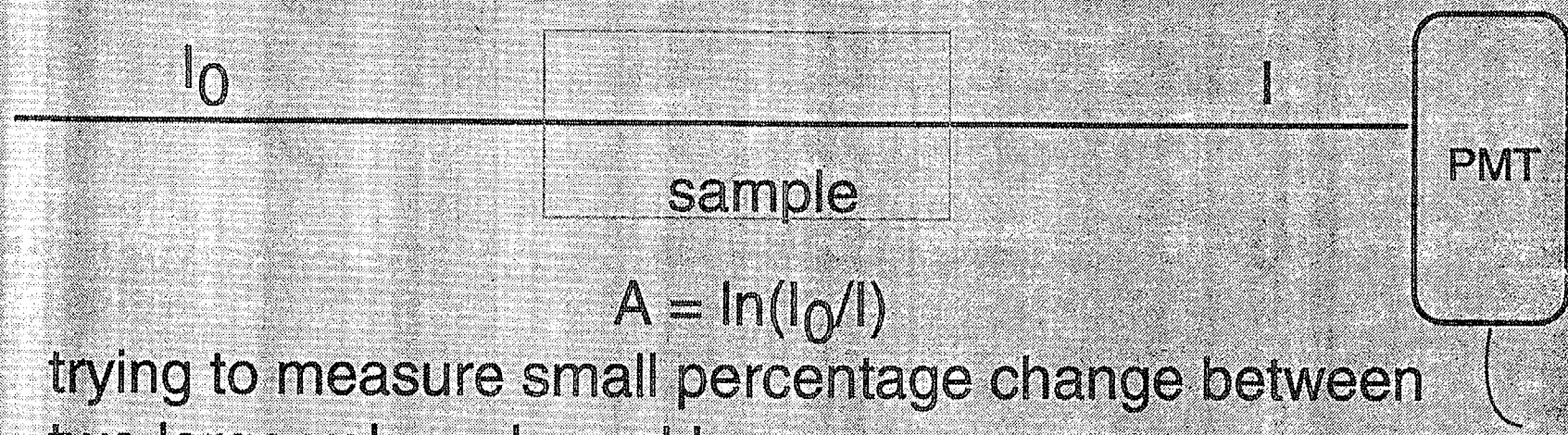
-Explicit Structural Information



log[Radionuclide Concentration]

PRELIMINARY DRAFT

Conventional Absorption Spectroscopy

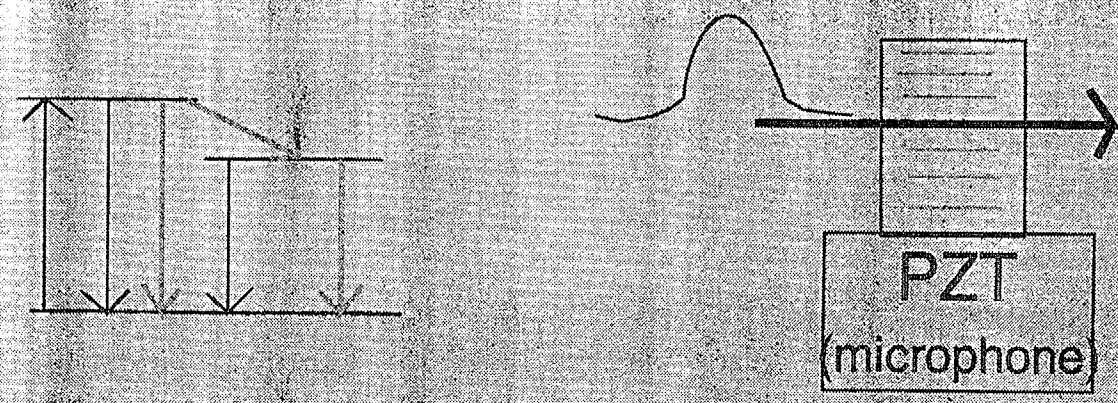


$$A = \ln(I_0/I)$$

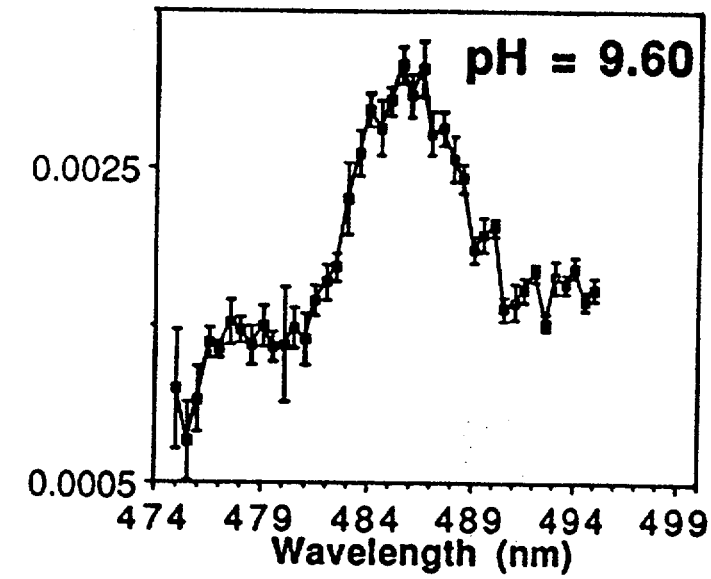
trying to measure small percentage change between two large values, I_0 and I

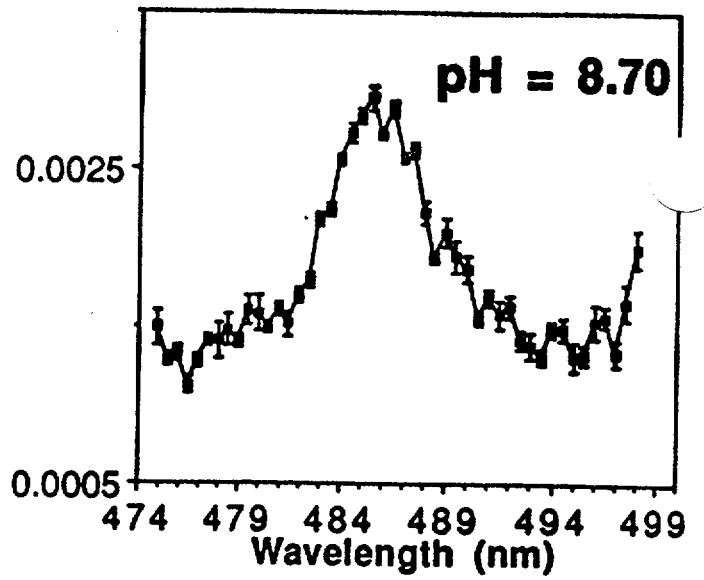
Photothermal Spectroscopies

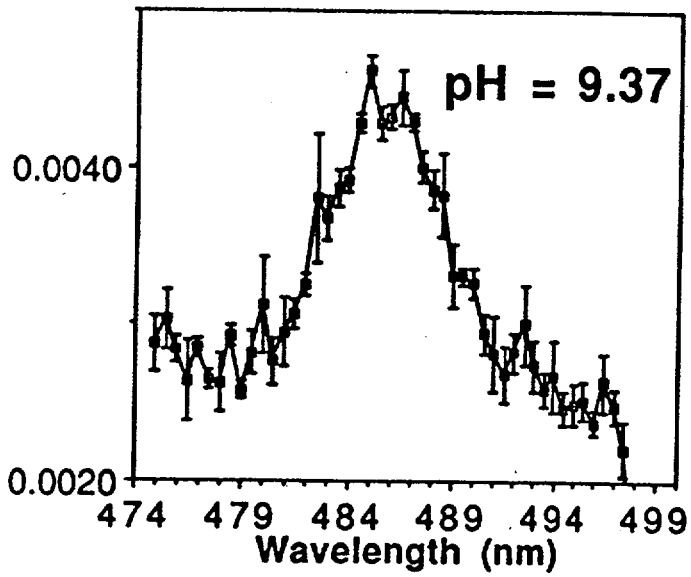
directly measure (small) amounts of energy deposited into sample

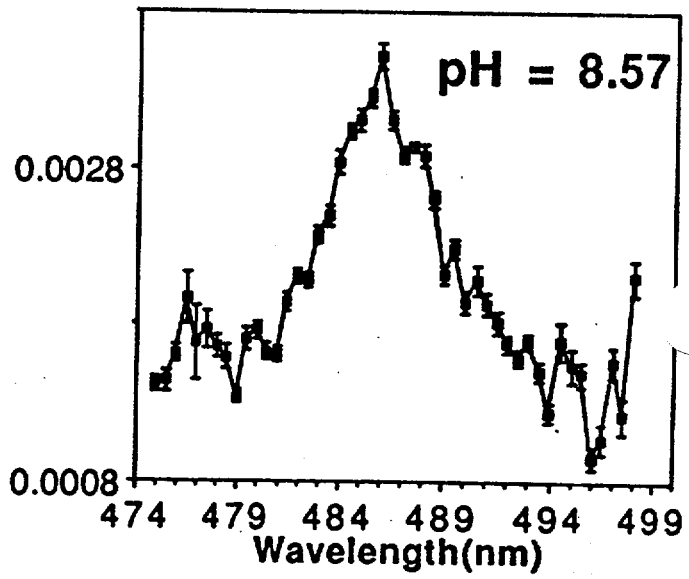


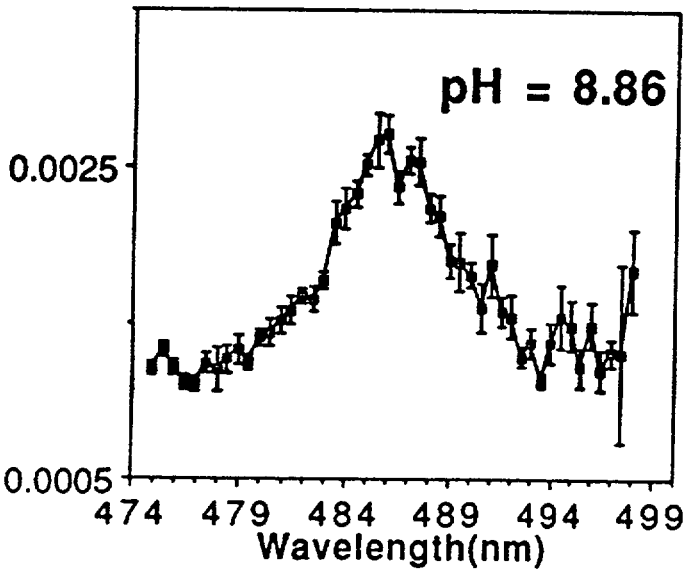
PRELIMINARY DRAFT

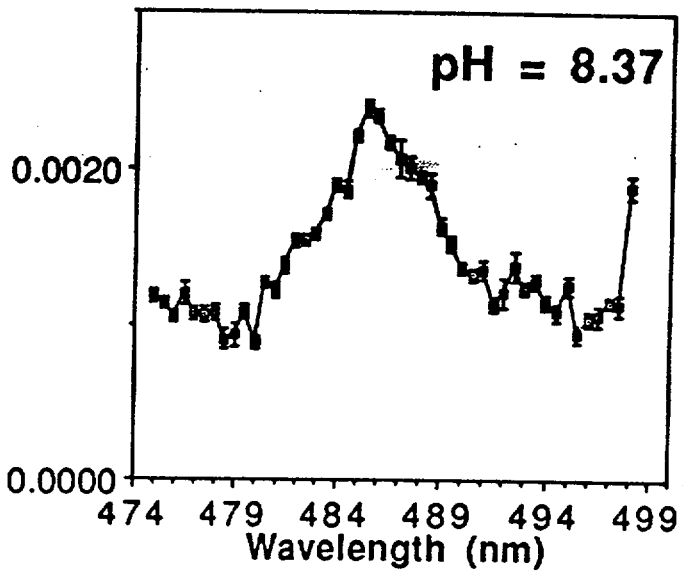












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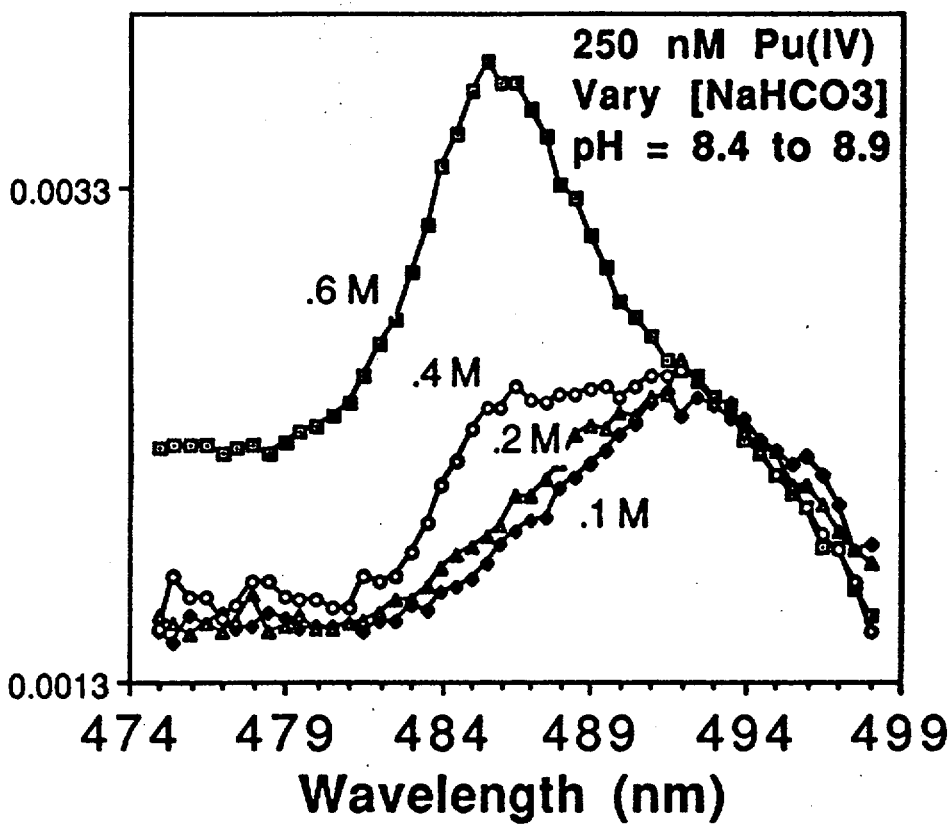

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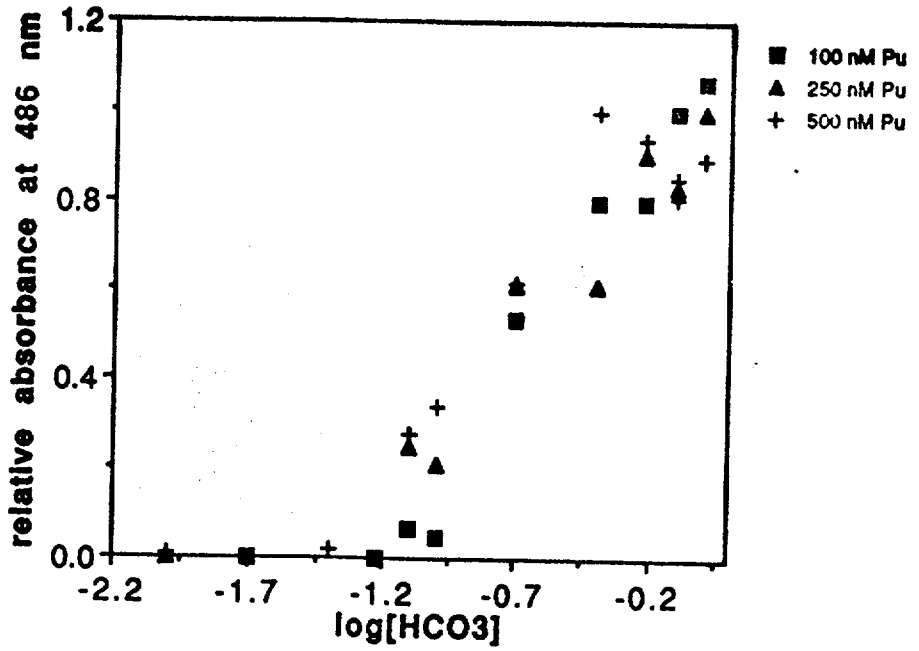

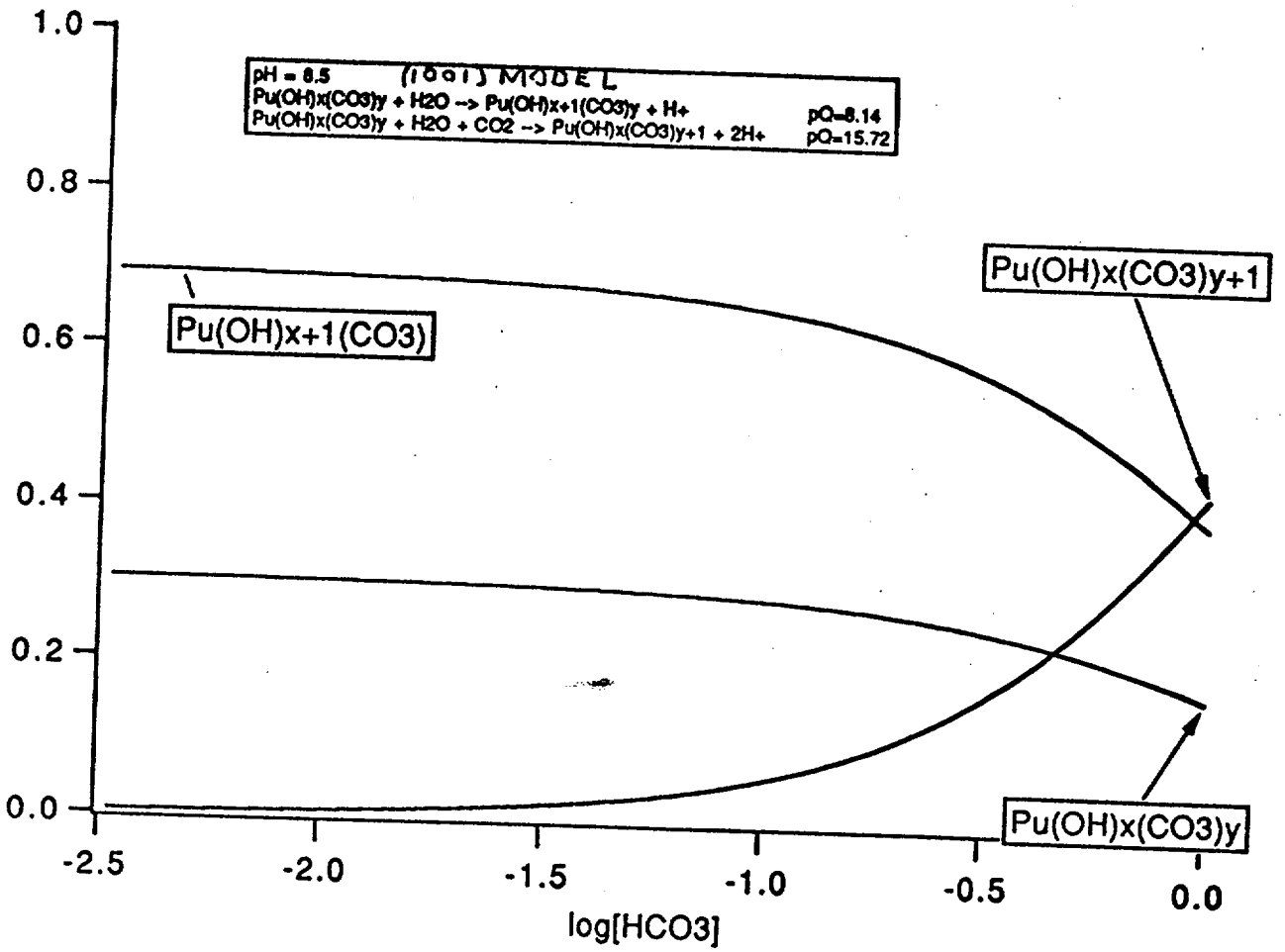

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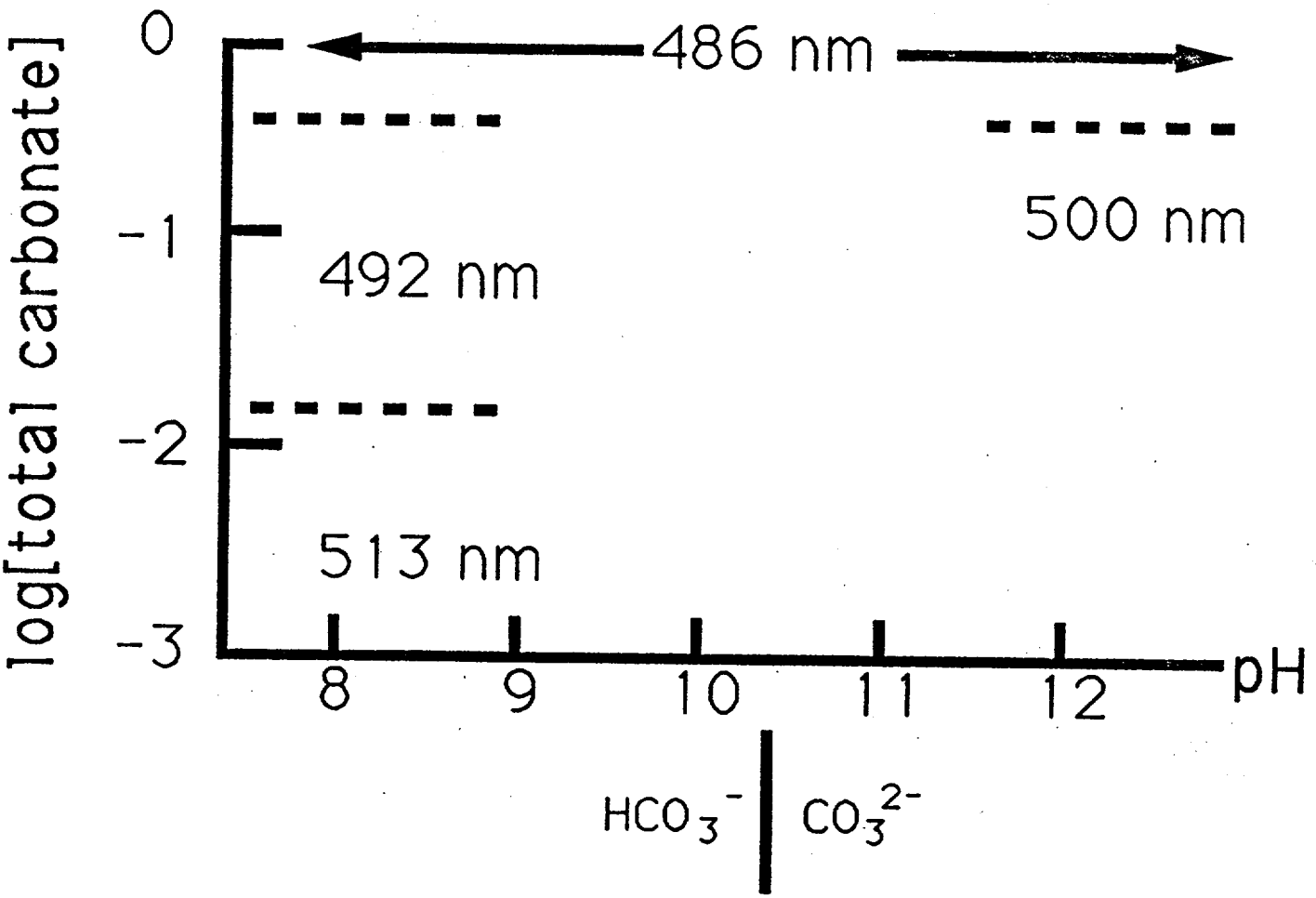

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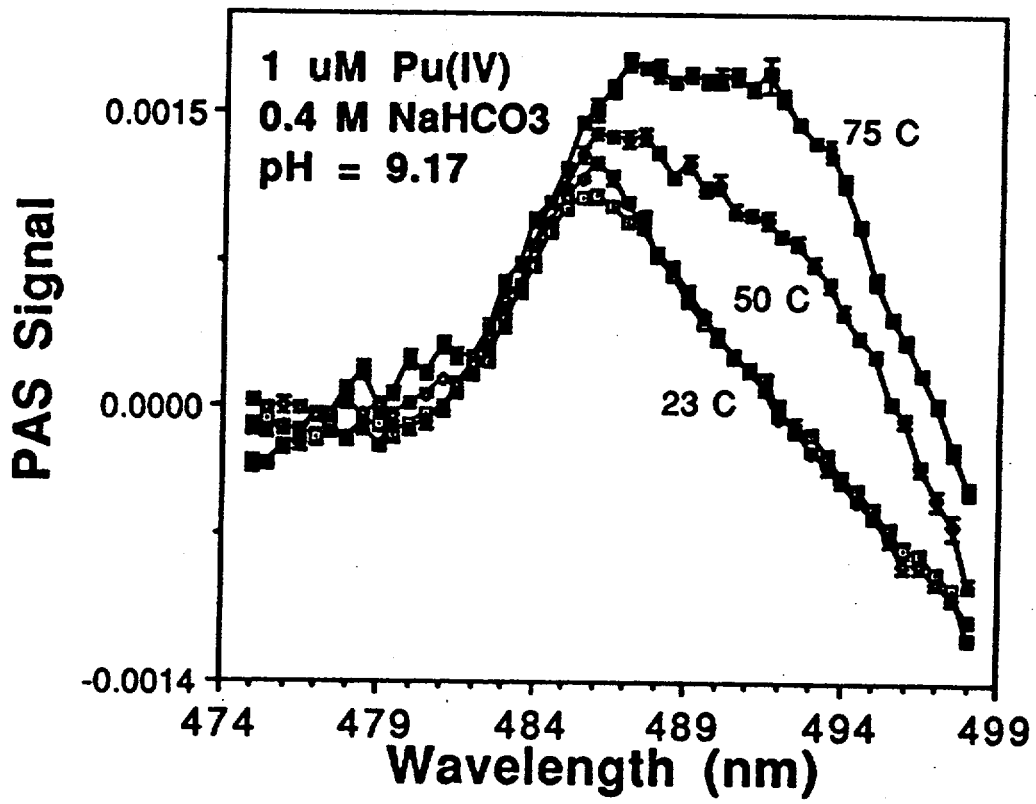
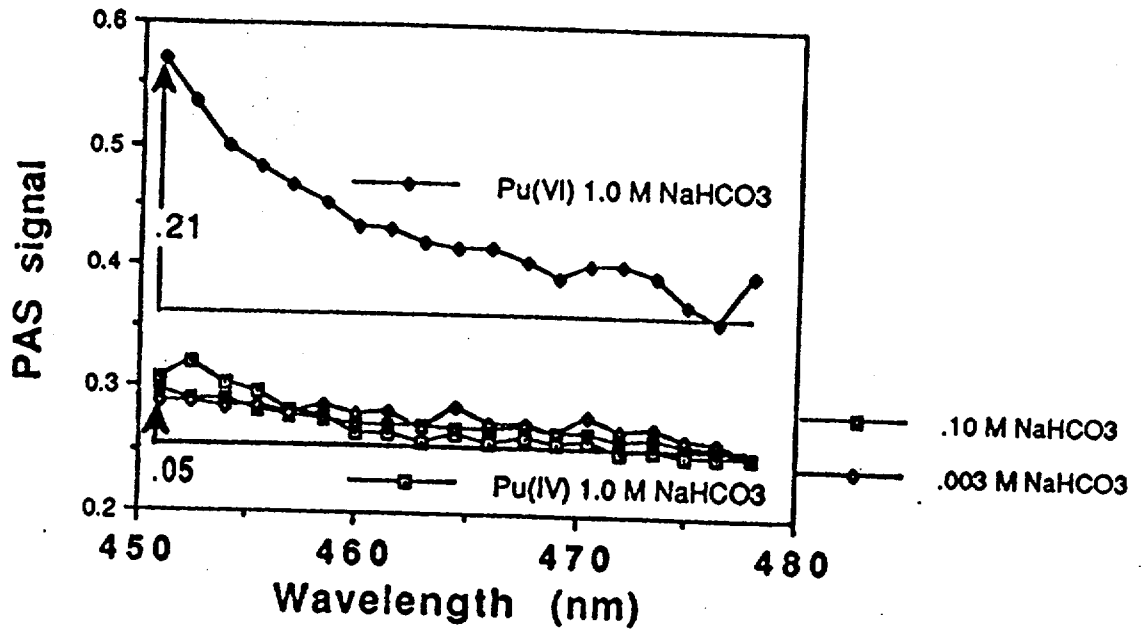
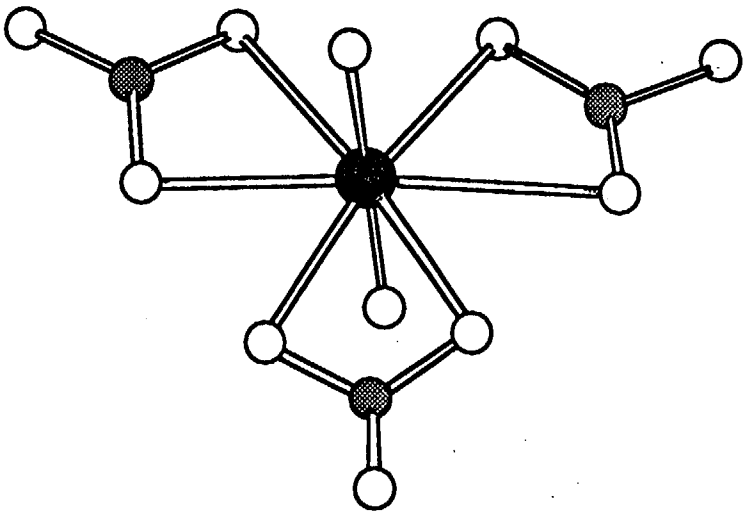


PRELIMINARY DRAFT

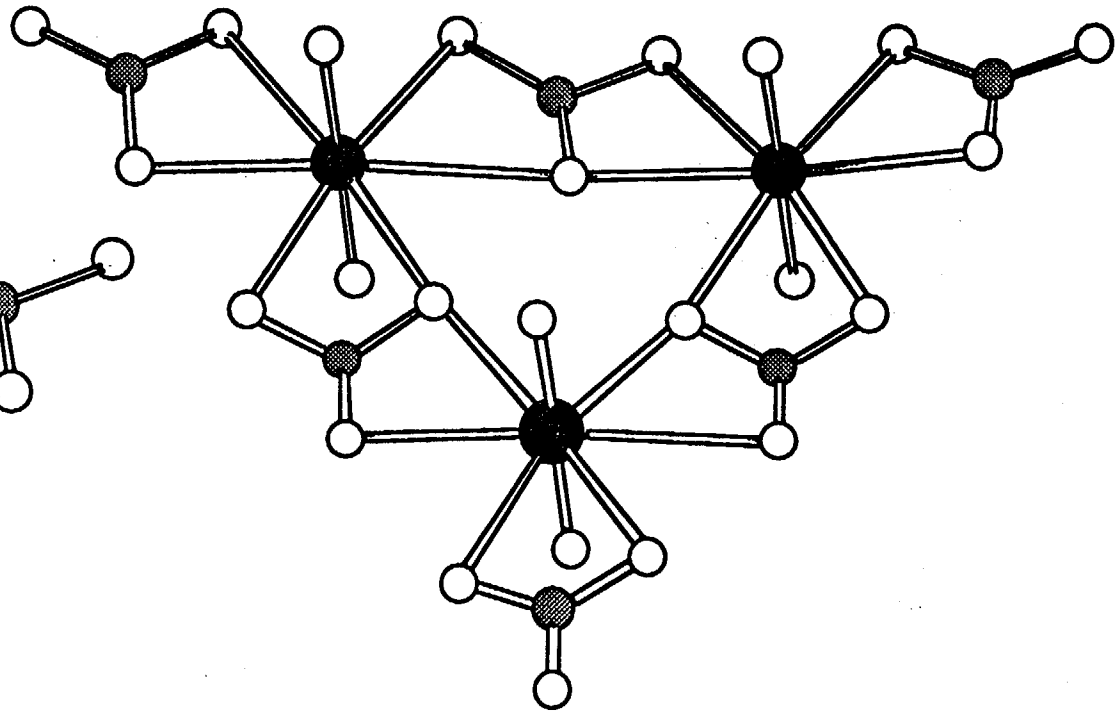


PRELIMINARY DRAFT

Proposed Monomer and Trimer Structures in Uranyl Carbonate System



$UO_2(CO_3)_3^{4-}$

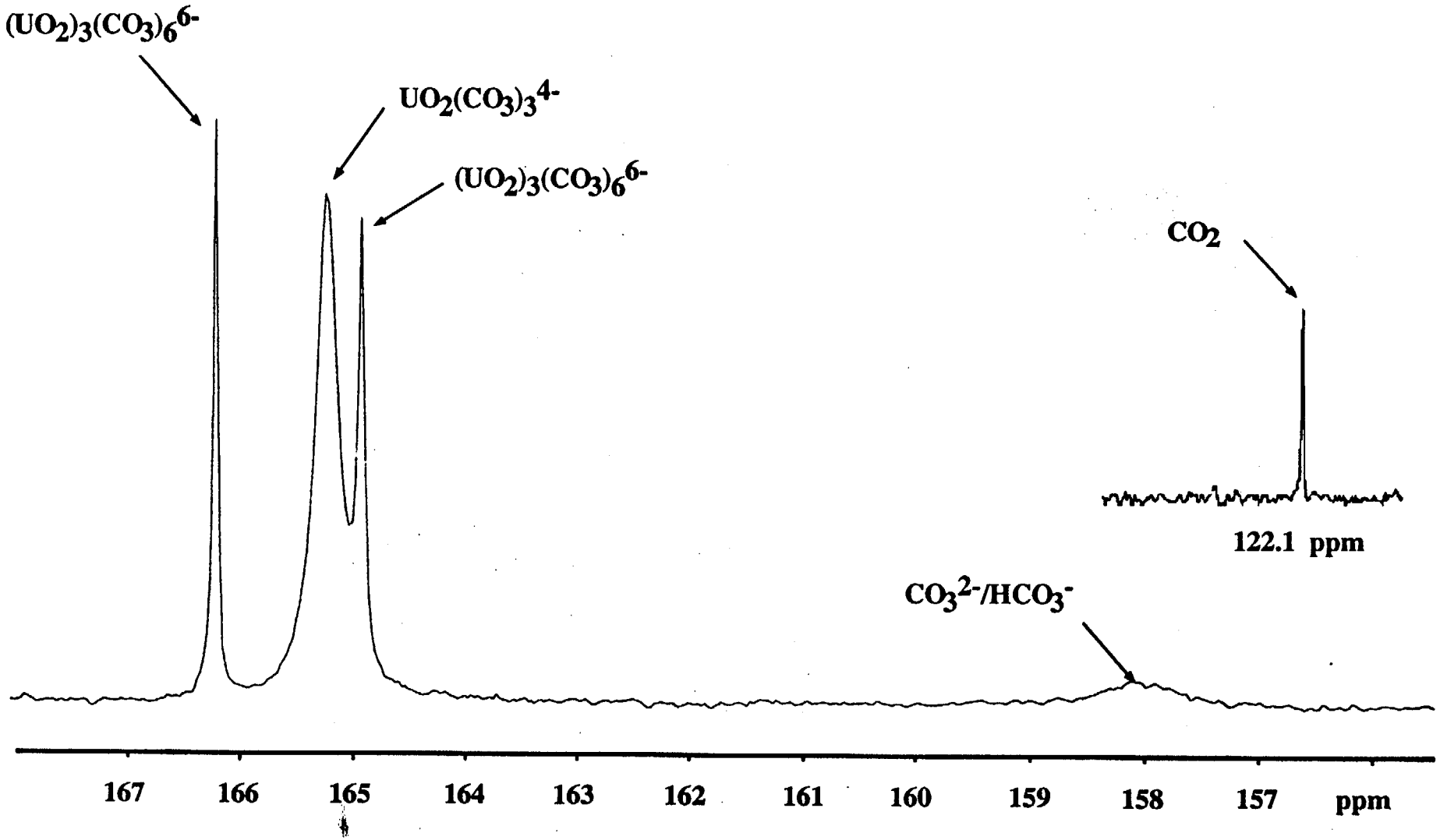


$(UO_2)_3(CO_3)_6^{6-}$

U C O

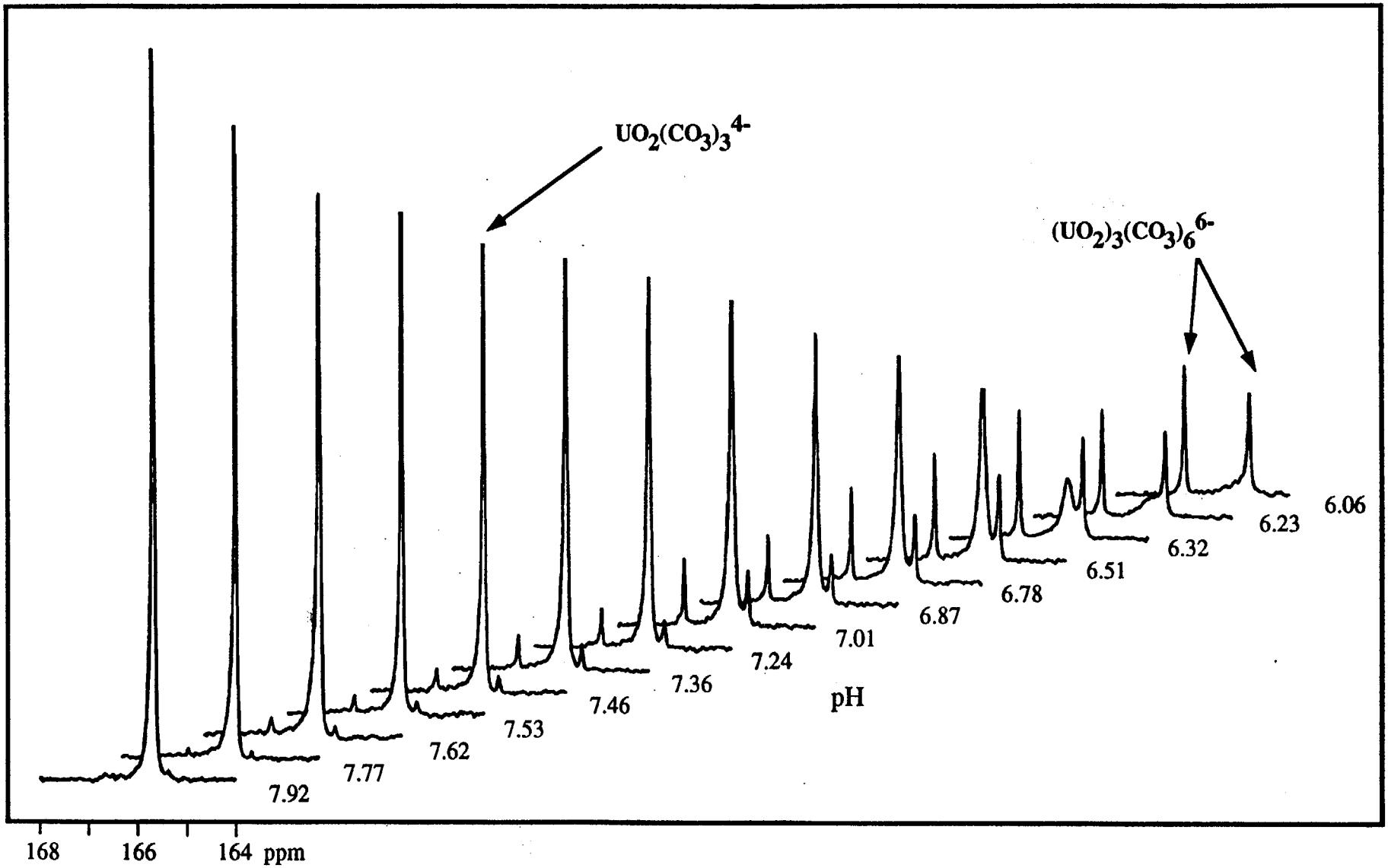
PRELIMINARY DRAFT

62.9 MHz ^{13}C NMR Spectra at 0 °C, and pH 6.5



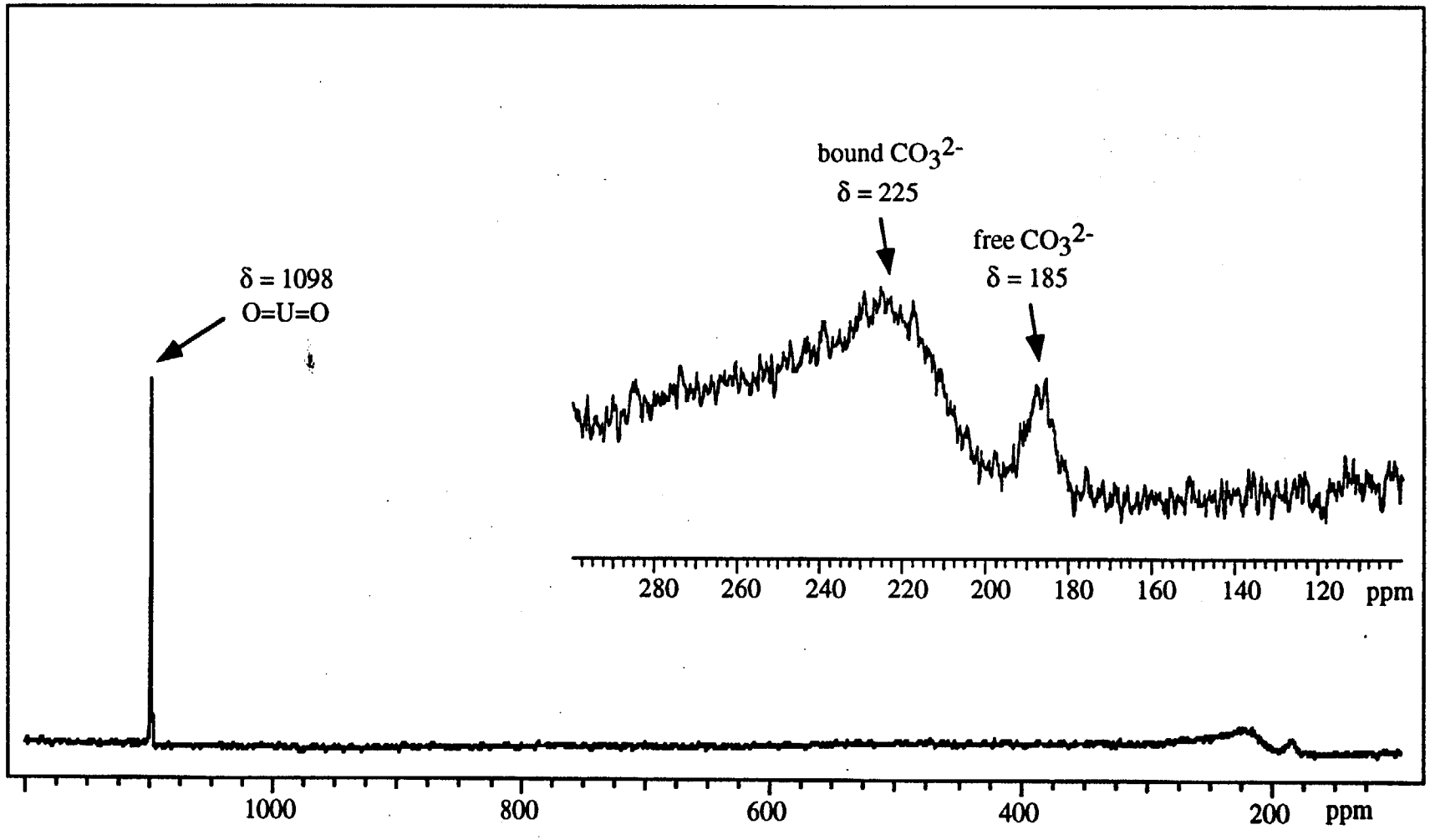
PRELIMINARY DRAFT

^{13}C NMR titration of $UO_2(CO_3)_3^{4-}$ system at 0 °C.



PRELIMINARY DRAFT

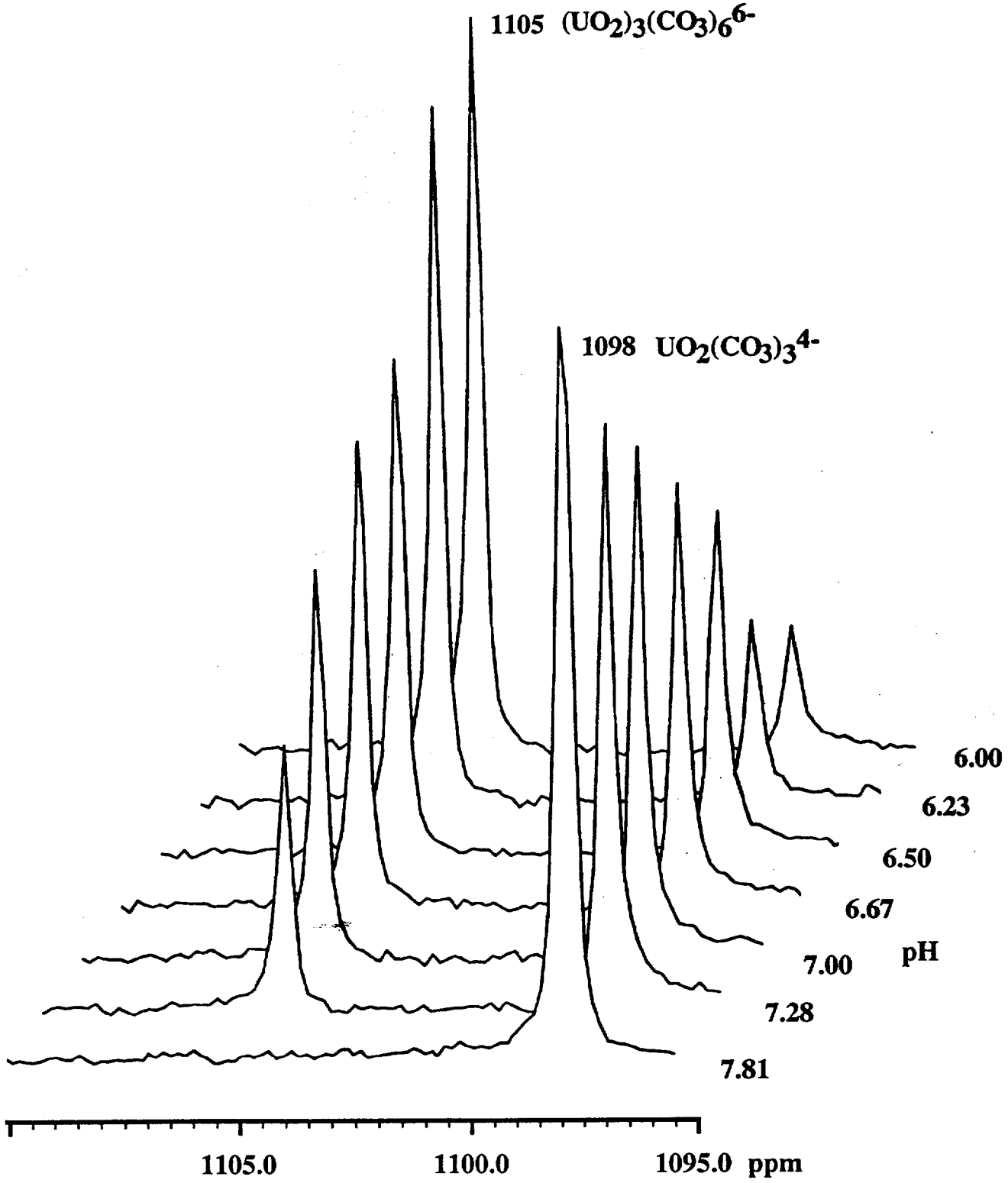
^{17}O NMR spectrum of fully ^{17}O-enriched $UO_2(CO_3)_3^{4-}$ at pH 9.7 and 0 °C.



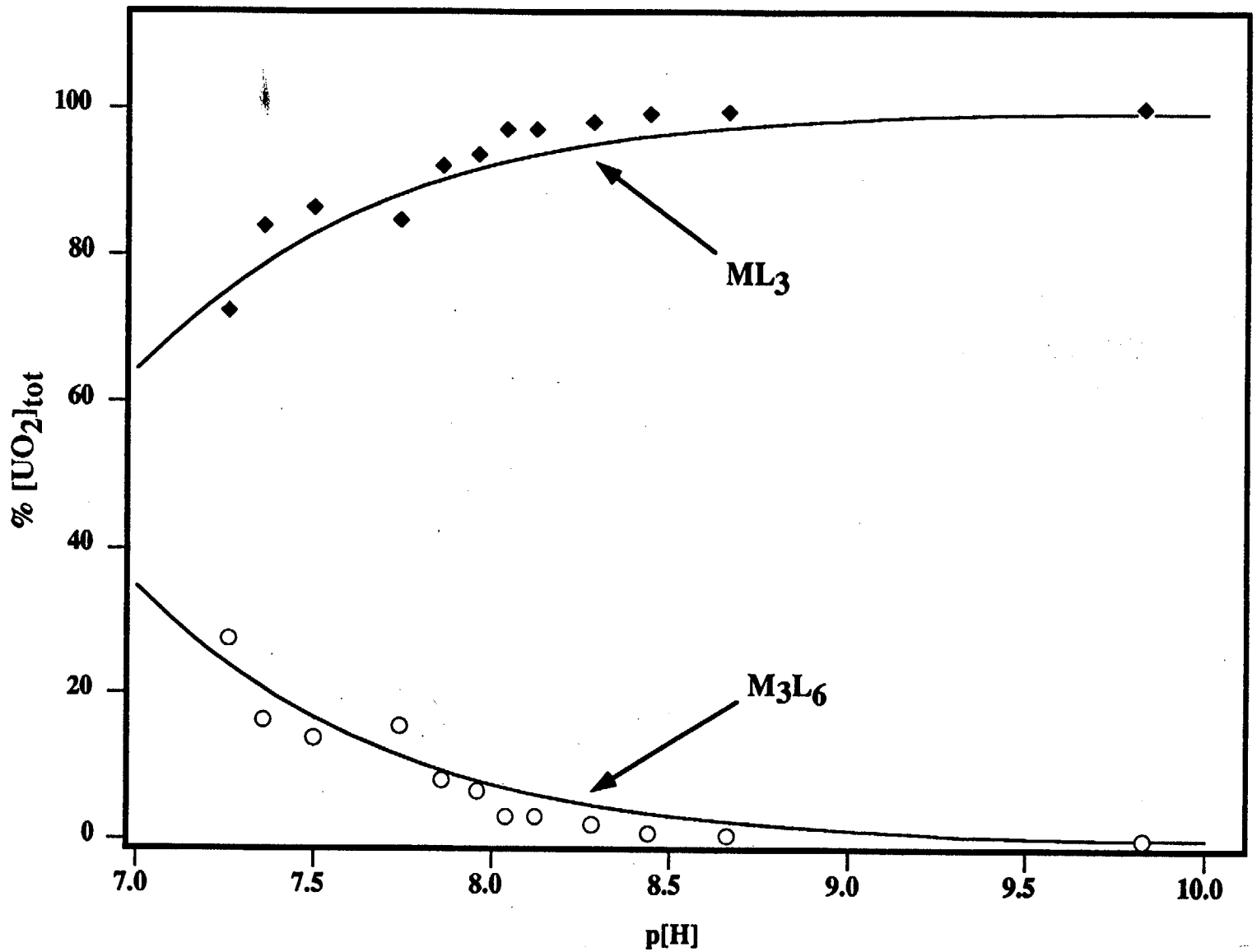
PRELIMINARY DRAFT

33.8 MHz ^{17}O NMR Spectra

$$3\,UO_2(CO_3)_3^{4-} + 6\,H^+ \rightleftharpoons (UO_2)_3(CO_3)_6^{6-} + 3\,CO_2 + 3\,H_2O$$



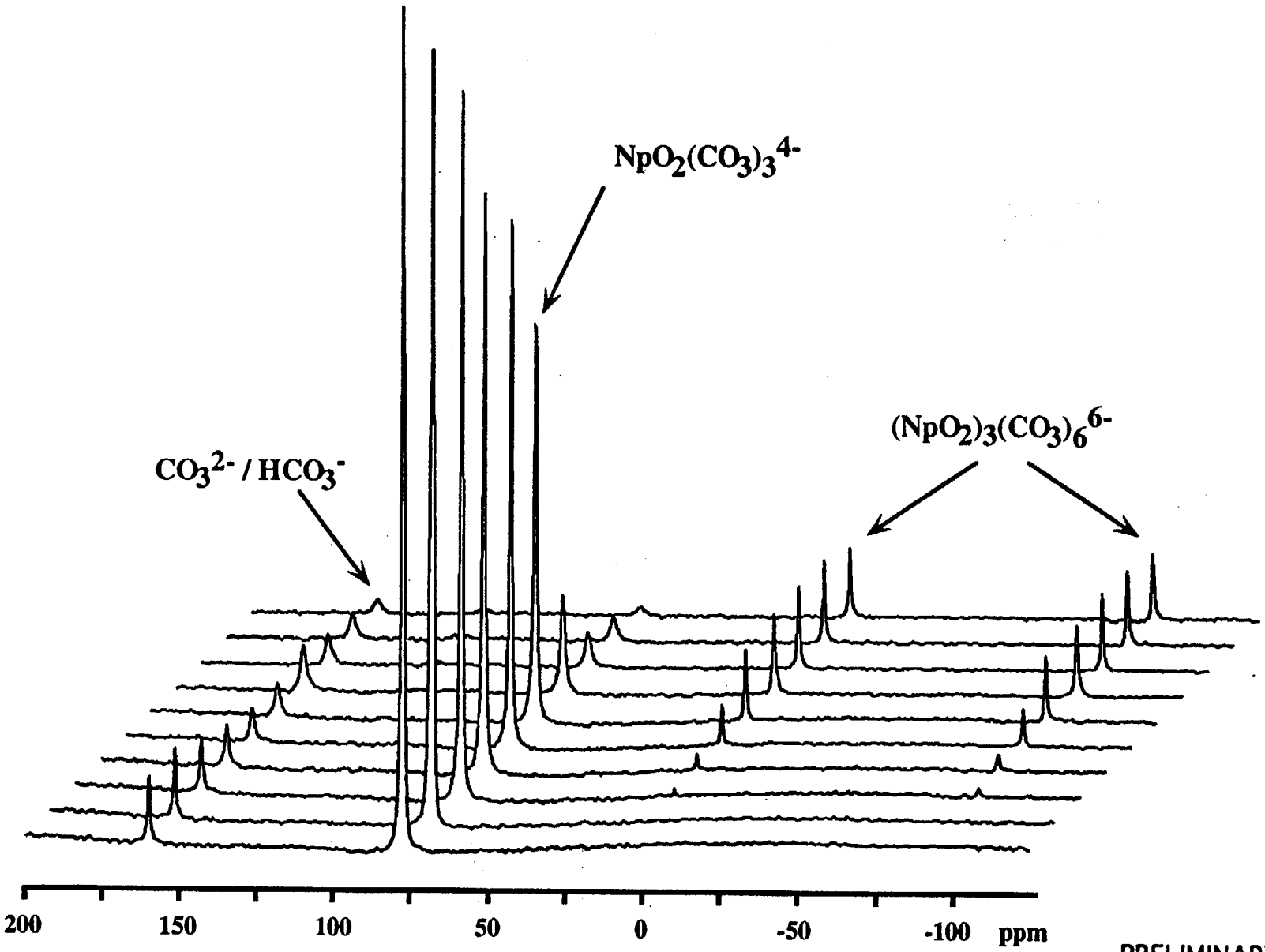
PRELIMINARY DRAF



PRELIMINARY DRAFT

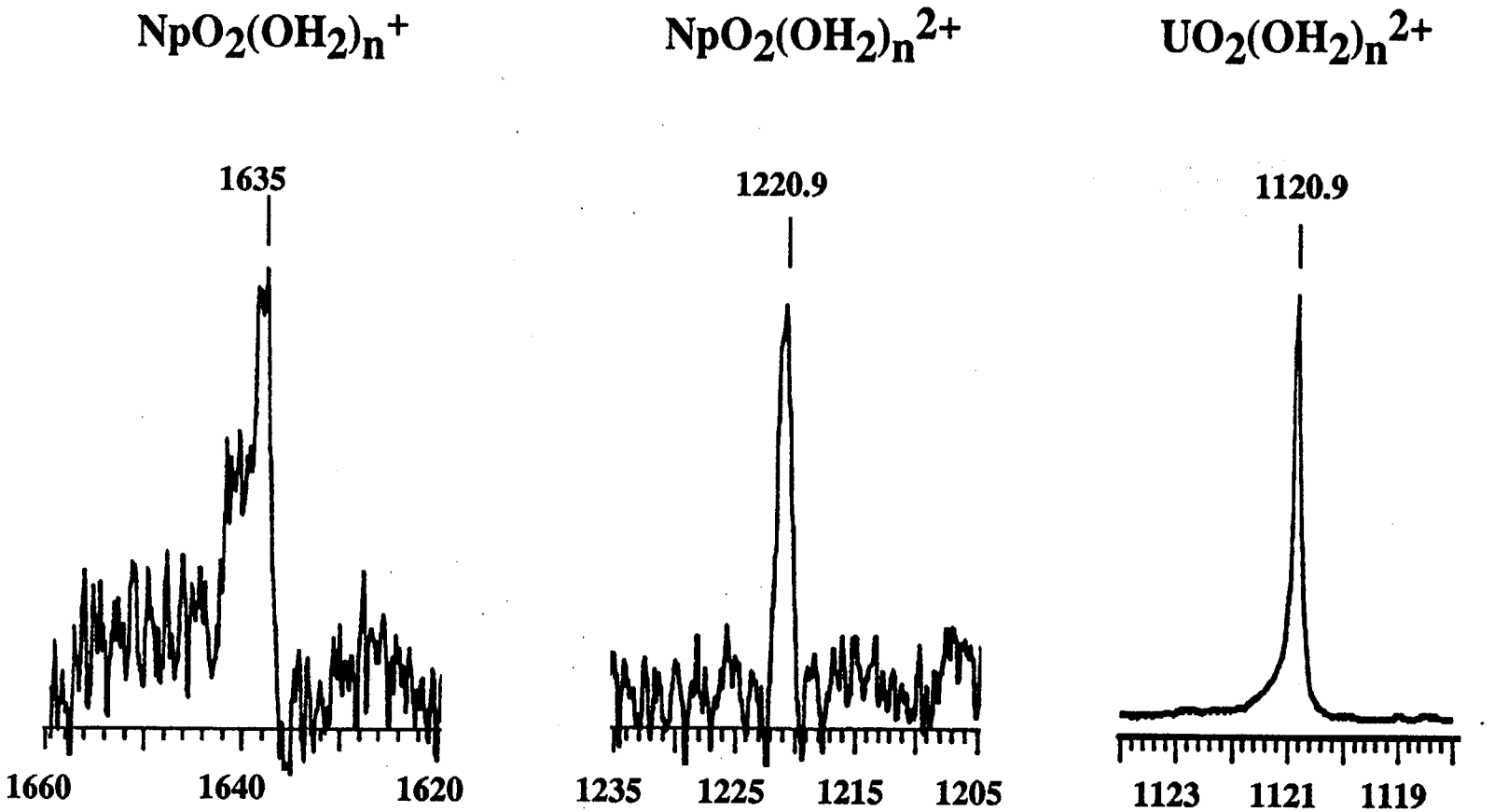
62.9 MHz ^{13}C NMR Spectra at 0 °C

$$3\,NpO_2(CO_3)_3^{4-} + 6\,H^+ \rightleftharpoons (NpO_2)_3(CO_3)_6^{6-} + 3\,CO_2 + 3\,H_2O$$



PRELIMINARY DRAFT

^{17}O NMR Spectra of actinyl ions



PRELIMINARY DRAFRT

FUTURE DIRECTION

(both Absorption and NMR)

NpO_2^+

- un-ambiguous oxidation state in natural environments

- low sorption coefficients

- possible multinuclear species (?)
  analogy to UO_2^{2+} and NpO_2^{2+}, but discounted in lit

some preliminary results from UV/Vis absorption:

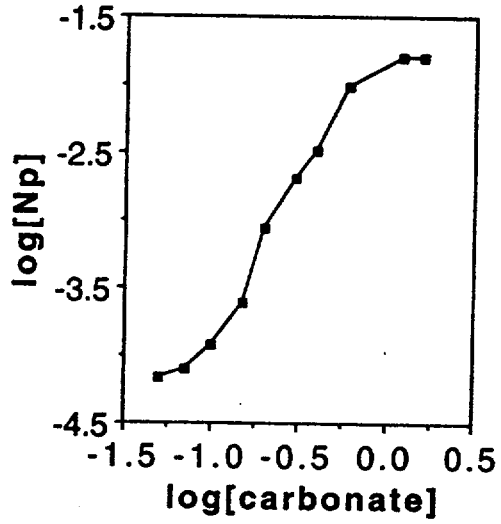
PRELIMINARY DRAFT

Other Studies

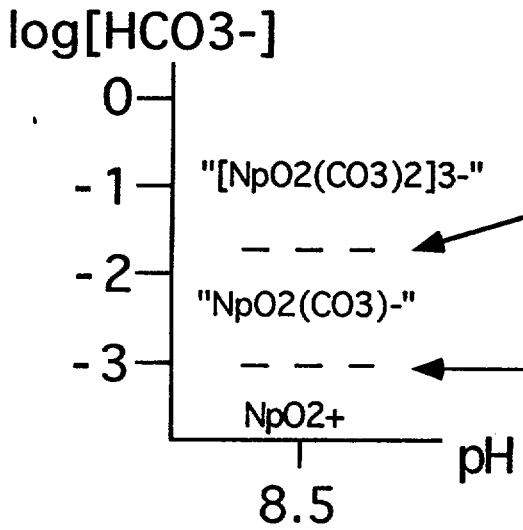
1. Solubility (Double Salts)

from Ueno & Saito (1975):

[carbonate] (M)	Np(V)(M)
1.6	1.6 x 10-2
1.2	1.6 x 10-2
0.6	9.7 x 10-3
0.4	3.2 x 10-3
0.3	2.0 x 10-3
0.2	8.5 x 10-4
0.1	1.2. x 10-4
0.05	6.9 x 10-5



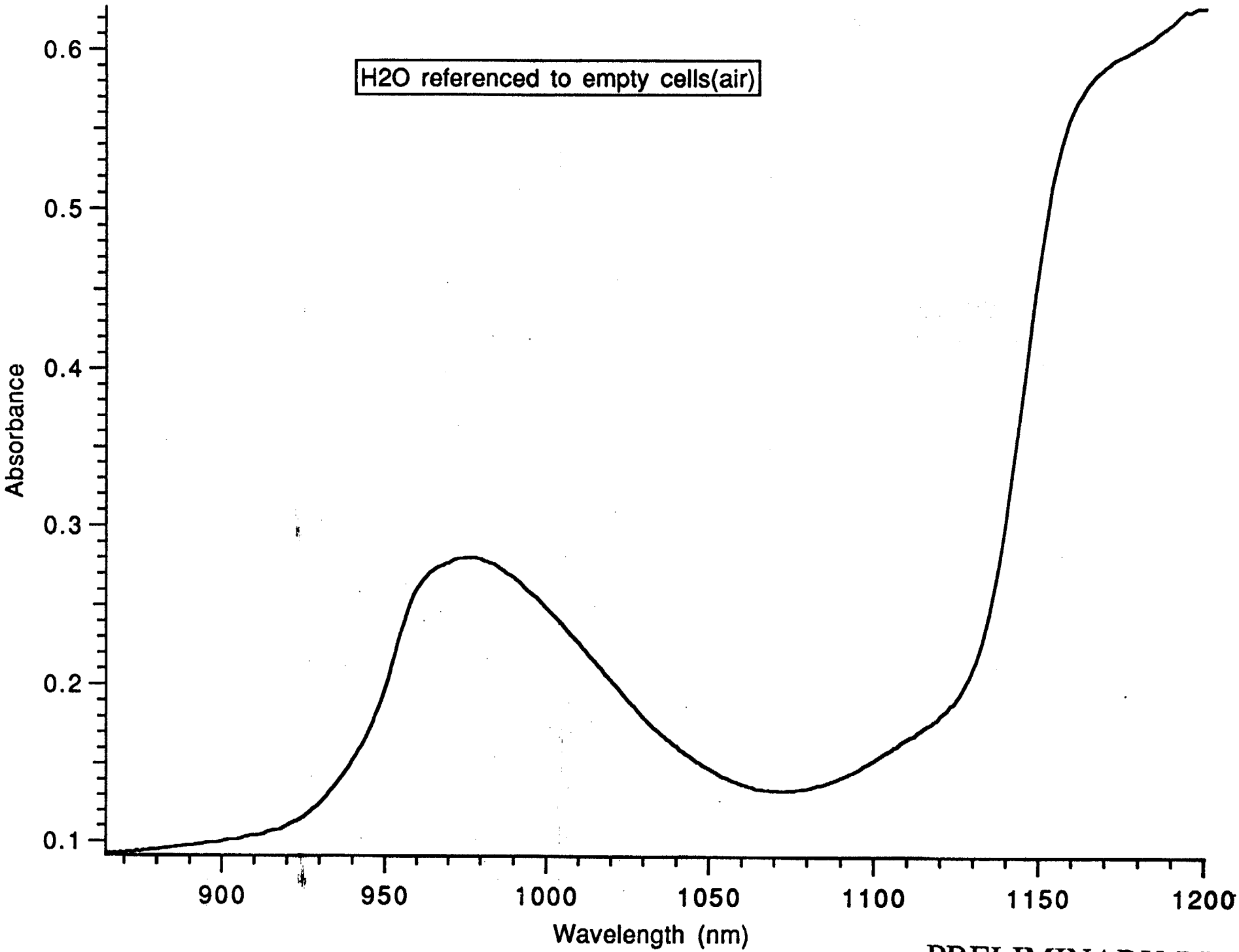
2. At pH = 8.5



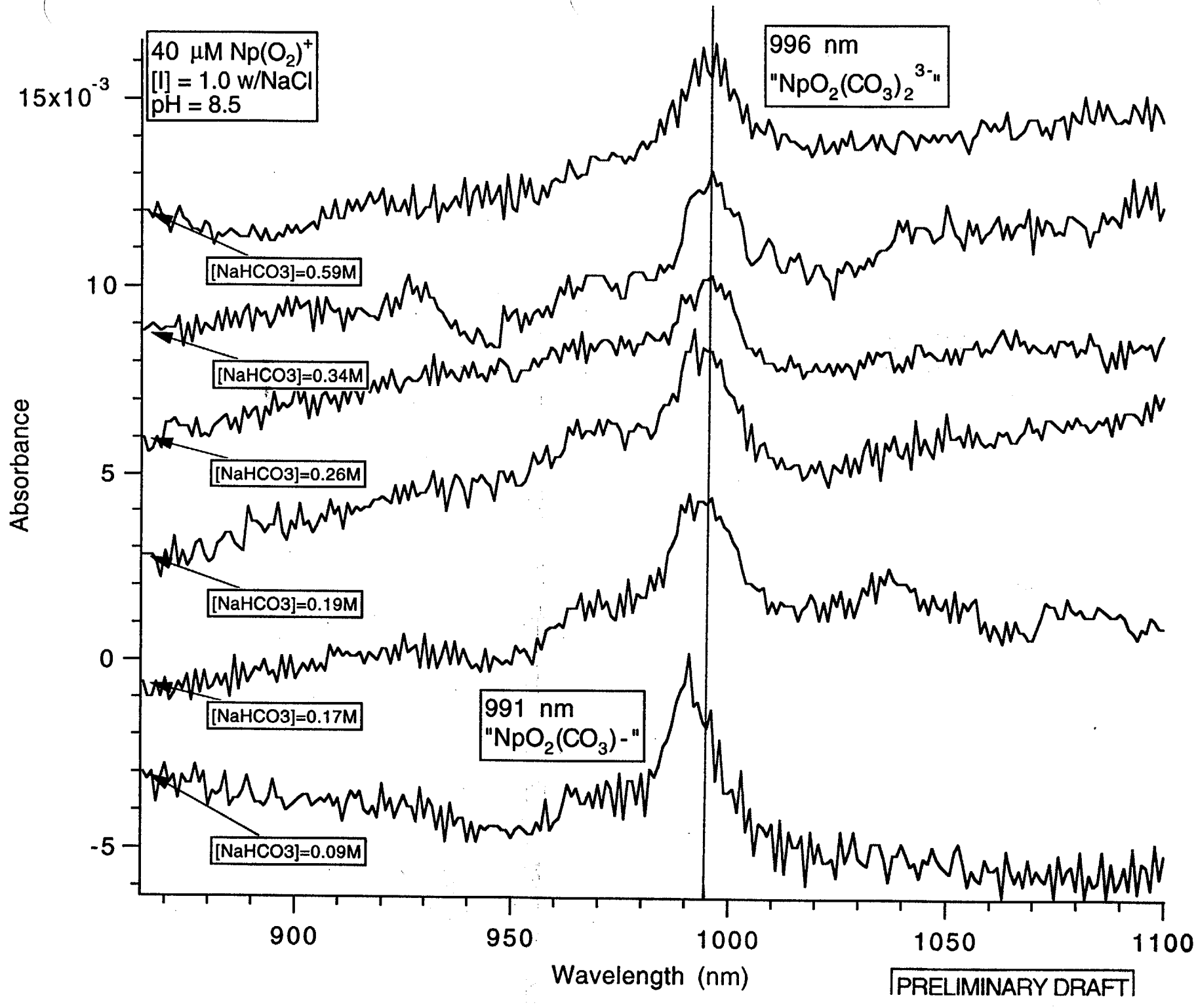
G. Bidoglio, G. Tanet, and A. Chatt (1985) "Studies of neptunium(V) complexes under geologic repository conditions" *Radiochim. Acta* **38**, 21-26. (solvent extractions)

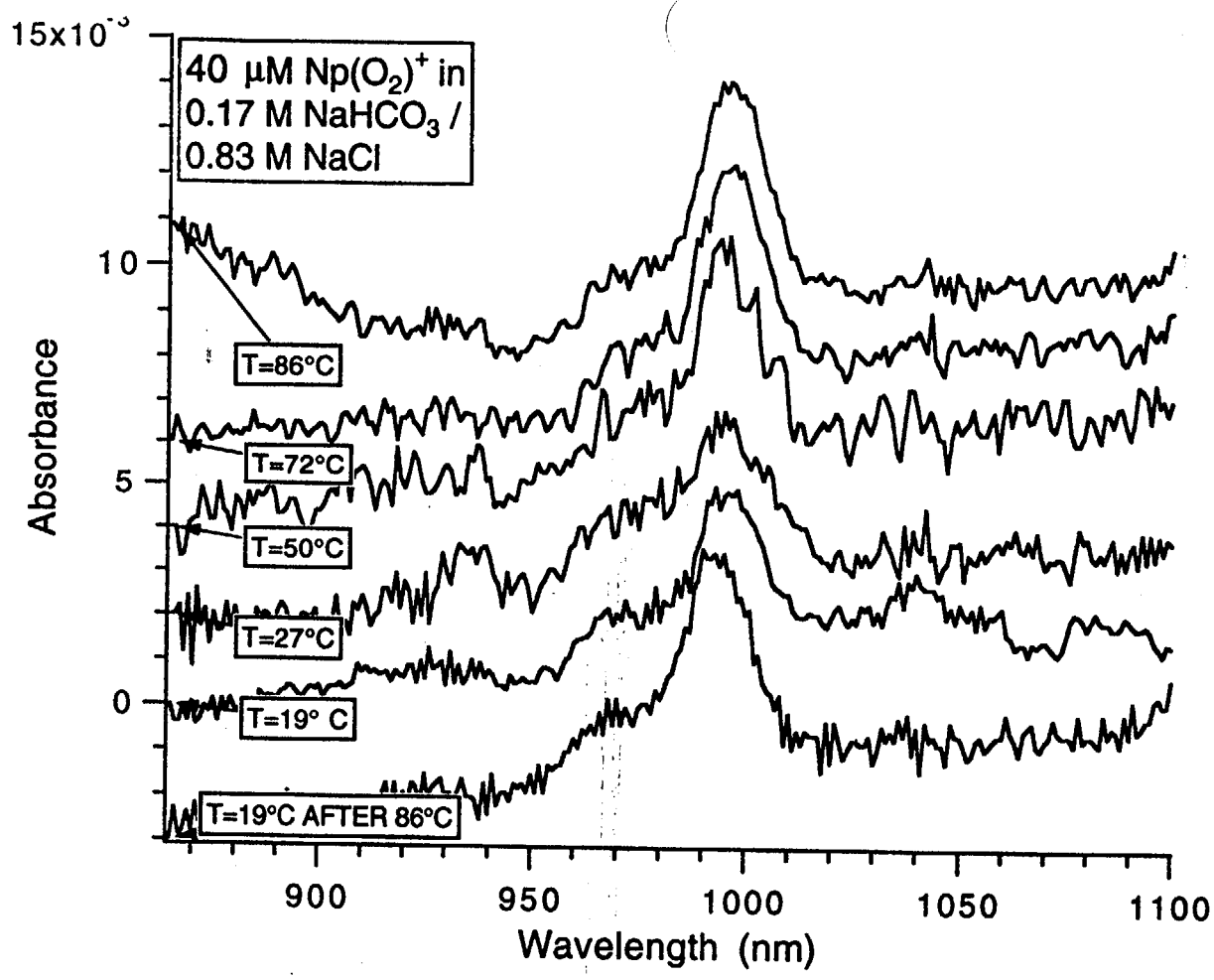
H. Nitsche, E.M. Standifer, and R.J. Silva (1990) "Neptunium(V) complexation with carbonate" *Lanthanide and Actinide Res.* **3**, 203-211. (Absorption study)

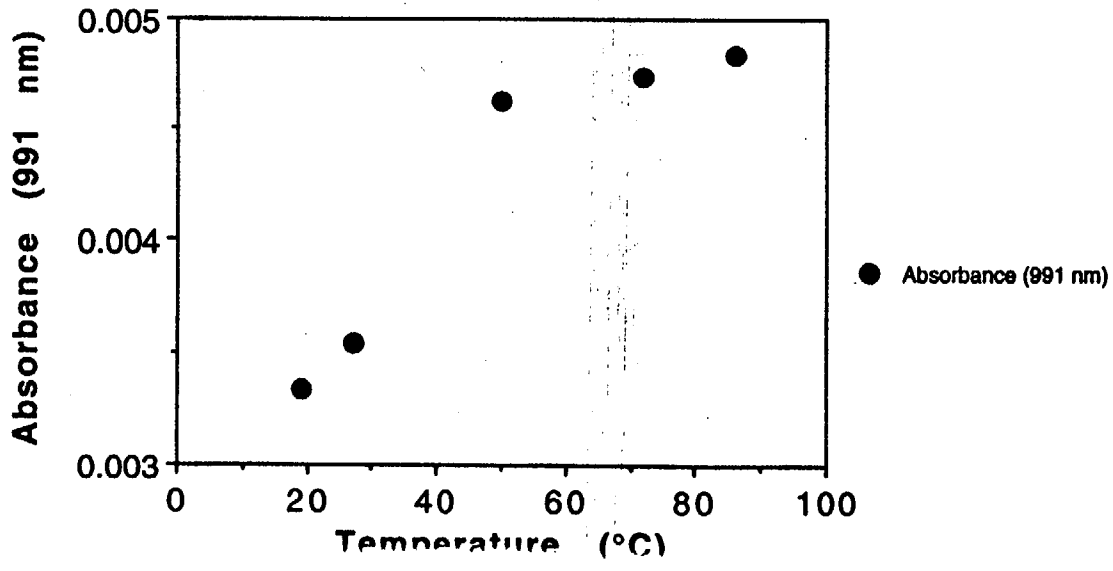
PRELIMINARY DRAFT



PRELIMINARY DRAFT


40 µM Np(O2)+
[I] = 1.0 w/NaCl
pH = 8.5
996 nm
"NpO2(CO3)2 3-"
991 nm
"NpO2(CO3)-"
[NaHCO3]=0.59M
[NaHCO3]=0.34M
[NaHCO3]=0.26M
[NaHCO3]=0.19M
[NaHCO3]=0.17M
[NaHCO3]=0.09M
15x10-3
10
5
0
-5
Absorbance
900
950
1000
1050
1100
Wavelength (nm)
PRELIMINARY DRAFT





PRELIMINARY DRAFT

CONCLUSIONS

PAS of Pu(IV)

1. characterization at dilute concentrations
   - more representative of depository conditions
   - ability to probe species with very low solubilities
   - less polymerization
   - less radiolysis interference
   - less disrpoportionation

PRELIMINARY DRAFT

2. for Pu(IV) carbonates

a. consistent with consecutive reactions: (charges not included for readability)

$Pu(OH)_x(CO_3)_y + H_2O \rightarrow Pu(OH)_{x+1}(CO_3)_y + H^+$ pQ = 8.14

$Pu(OH)_x(CO_3)_y + H_2O + CO_2 \rightarrow Pu(OH)_x(CO_3)_{y+1} + 2H^+$

(492 nm) (486 nm) pQ = 15.72

b. preliminary temperature dependence

c. Pu oxidation state does not change to 6+ during exp't

PRELIMINARY DRAFT

NMR

1. Explicit structure determinations UO_2^{2+} carbonate monomers and trimers directly characterized

2. Equilibrium constants determined from NMR experiments consistent with NEA database

FUTURE - NpO_2^{+} with both Absorption and NMR spectroscopies

PRELIMINARY DRAFT

DOE-NRC Technical Exchange Radionuclide Migration

AFM studies to elucidate sorption

Pam Z. Rogers, LANL

Los Alamos
NATIONAL LABORATORY
1943 - 1993

DOE-NRC TECHNICAL EXCHANGE

RADIONUCLIDE MIGRATION AND
NEAR-FIELD PHENOMENA RELATED TO RADIONUCLIDE
RELEASES
FROM THE ENGINEERED BARRIER SYSTEM

Atomic Force Microscopy Studies of Natural Iron-Oxide Mineral Surfaces

Marilyn Hawley (CMS, LANL)
and
Pamela Rogers (INC-9, LANL)

Purpose: To determine which surface parameters (surface structure, orientation, roughness) have the most influence on sorption properties of iron-oxide minerals.

Approach: Different crystallographic surfaces of goethite and hematite mineral surfaces - both freshly cleaved and weathered - have been imaged in air and **under water.**

Surprises: Many goethite surfaces reacted immediately on contact with water.

The results of such reactions were greatly increased surface roughness,
and hence a **higher surface area** for sorption.

Goals: To extend these measurements to samples of hematite and maghemite from Yucca Mountain and thereby study the differences in surface structure and reactivity between the sample sets.

To determine why pure iron-oxide mineral samples appear to have much higher measured batch sorption capacities than those from Yucca Mountain tuffs.

Several

<u>Color</u> AFM images of surfaces.

Sorry - these will not copy.

Pamela Rogers 9/28/93

Conclusions:

We have published the first atomic resolution AFM scans of goethite surfaces.

AFM imaging of surface reactions **under water** is possible and has lead to some fascinating observations.

PRELIMINARY DRAFT

Conclusions:

Goethite surfaces were seen to react very quickly in water.

Both surface dissolution and precipitation reactions were observed.

The location of surface precipitates was observed to be controlled by the by the underlying crystal structure.

PRELIMINARY DRAFT

Conclusions:

The net result of the reactions was greatly increased local surface area.

This would increase the sorption capacity both by increasing the surface area and by increasing the number of the most reactive sites on the surface.

PRELIMINARY DRAFT

BUT

More (non-AFM) compositional measurements are needed to confirm that the reacting surface really was goethite and not a very thin covering of some other mineral.

PRELIMINARY DRAFT

Conclusions:

The size regime most important for sorption reactions is on the scale of step heights, or generally 10 angstroms .

This is precisely the spatial resolution readily obtained in an AFM scan.

PRELIMINARY DRAFT

Conclusions:

Rapid surface reactivity probably precludes easy imaging of sorbates on goethite at the level of atomic resolution - the surfaces just become too rough.

However, lower resolution methods of gauging site reactivity are being tested.

PRELIMINARY DRAFT

The burning question:

"How do the surface structure and reactivity of mineral separates from Yucca Mountain compare with these, and how might that influence sorptive capacity?".

We are presently working with small samples of maghemite from Yucca Mountain to try to resolve this issue.

PRELIMINARY DRAFT

DOE-NRC Technical Exchange Radionuclide Migration

Surface complexation models

James Leckie, Stanford University

Los Alamos NATIONAL LABORATORY 1943 · 1993

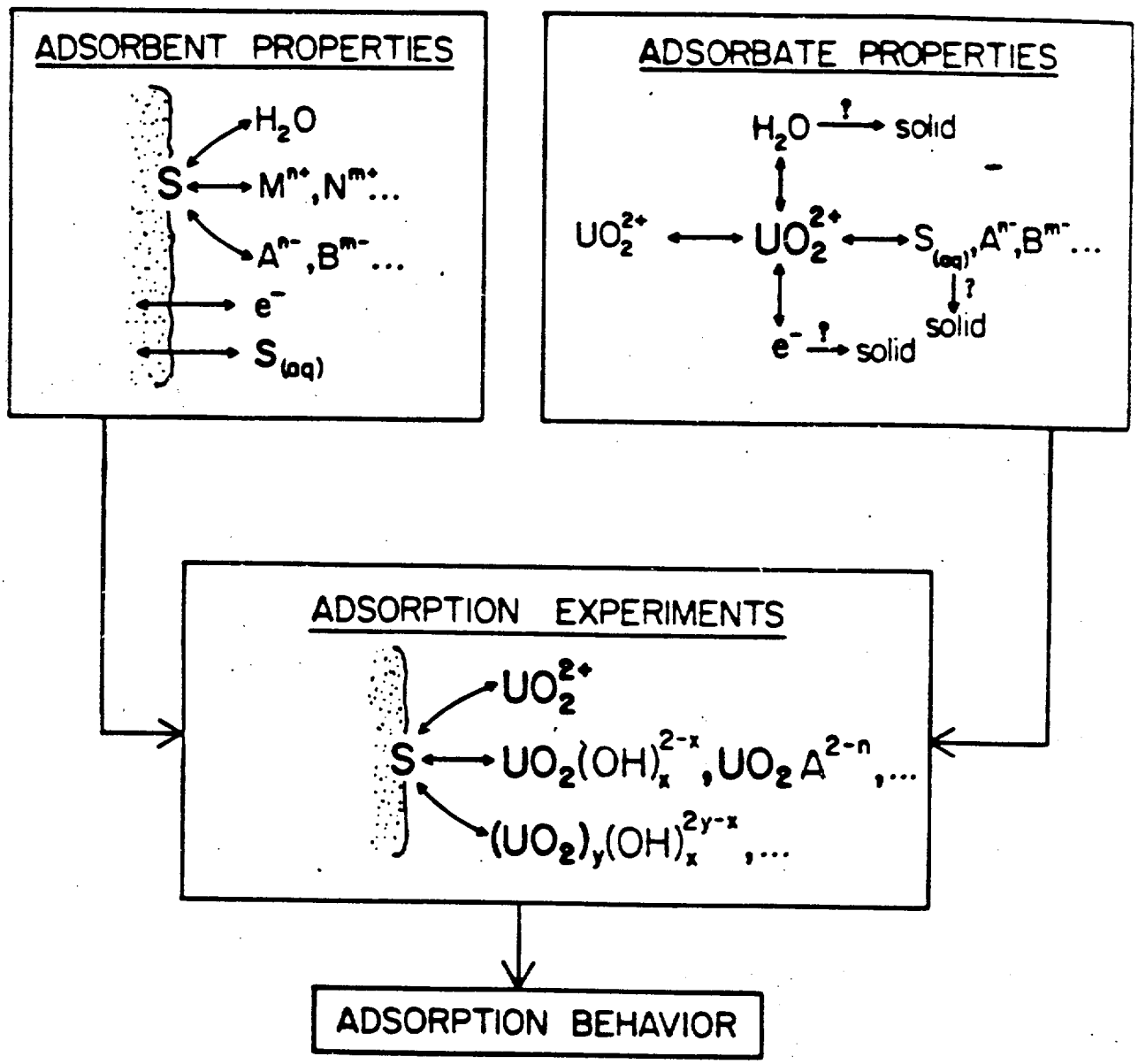

ADSORBENT PROPERTIES
S
H_2O
M^{n+}, N^{m+}...
A^{n-}, B^{m-}...
e^-
$S_{(aq)}$
ADSORBATE PROPERTIES
H_2O ? solid
UO_2^{2+}
UO_2^{2+}
$S_{(aq)}, A^{n-}, B^{m-}$...
?
solid
e^- ? solid
ADSORPTION EXPERIMENTS
S
UO_2^{2+}
$UO_2(OH)_x^{2-x}, UO_2A^{2-n}$,...
$(UO_2)_y(OH)_x^{2y-x}$,...
ADSORPTION BEHAVIOR

Table 2

Characteristics of Soil Samples

Parameter	N16	N21	N33
Surface Area m2/g(dry wt)	3.7	9.0	8.0
Water Content % (wet wt)	21	47	37
Extractable Organic mg/g	3.6	18.8	6.8
Total Organic* mg/g(dry wt)	11	260	17

*Based on 50 percent carbon content.

Table 3

Range of Site Densities for Soil Components*

Minerals	Site Densities sites/nm^2	Site Densities moles/m^2	Percent Carbon
Clays	0.5 - 4	0.8 - 6.6x 10^{-6}	
Oxides	3 - 17	5 - 28 x 10^{-6}	
Organics**	mole sites/g		
Humic	3 - 11 x 10^{-3}		54 -59
Fulvic	7 - 16 x 10^{-3}		40 - 53
Polysaccharide	0.5 - 6 x 10^{-3}		45

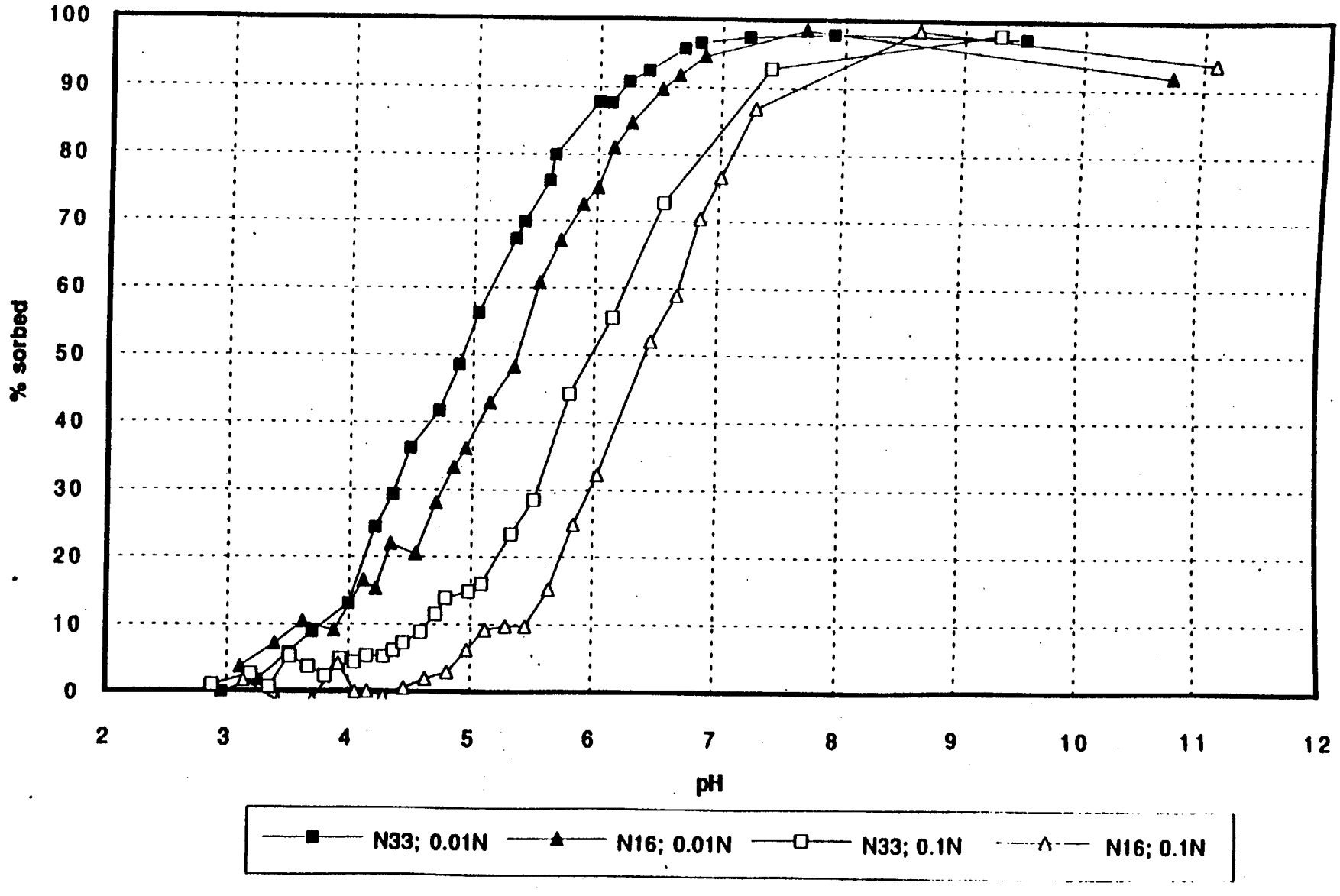
*From Buffle (1988)

**Carboxylic and phenolic sites

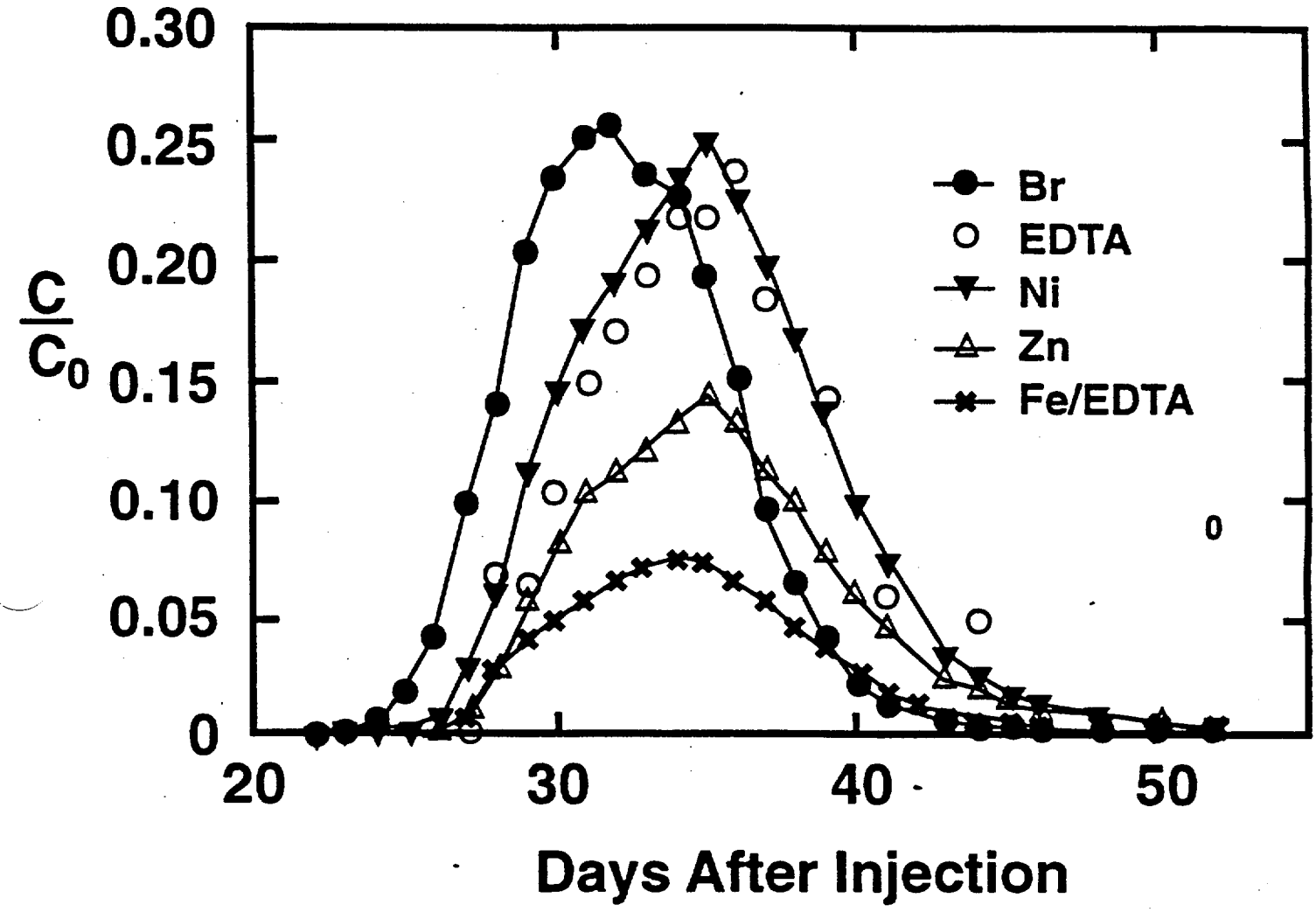
Table 2

Parameter	N16	N21	N33
Surface Area m2/g	3.7	9.0	8.0
% Organic mg/g	1.8	9.4	3.4
Mineral Sites moles/g	30x10-6	75x10-6	66x10-6
Organic Sites moles/g	9.0x10-6	47x10-6	17x10-6
Percent Organic	23%	39%	20%
Total:moles/g	39x10-6	122x10-6	83x10-6

Cadmium sorption to soil N4-33(6.3g/l) and N4-16(13.5g/l); 1.5x10-6M total cadmium; 0.01N and 0.1N NaCl



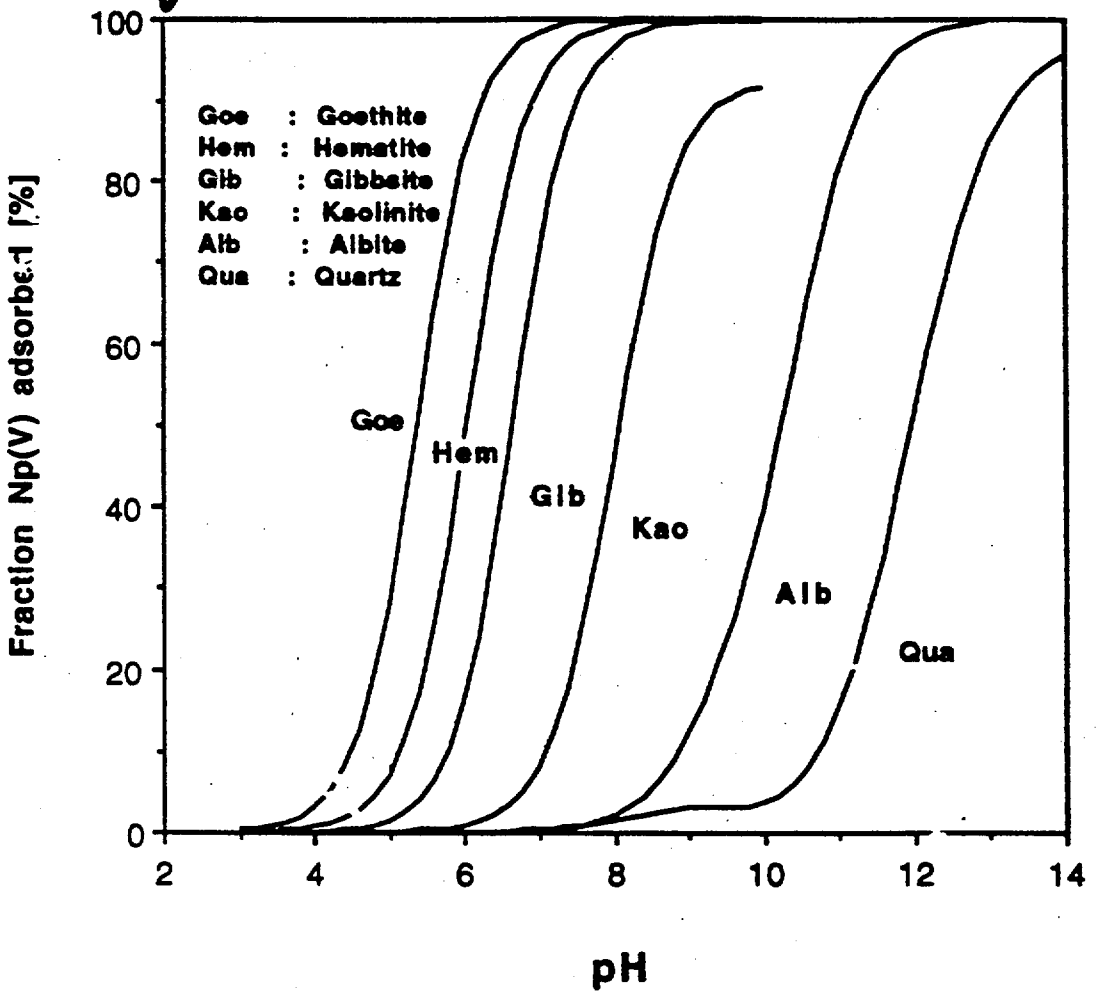
Kent, Davis, Anderson and Rea (1992)

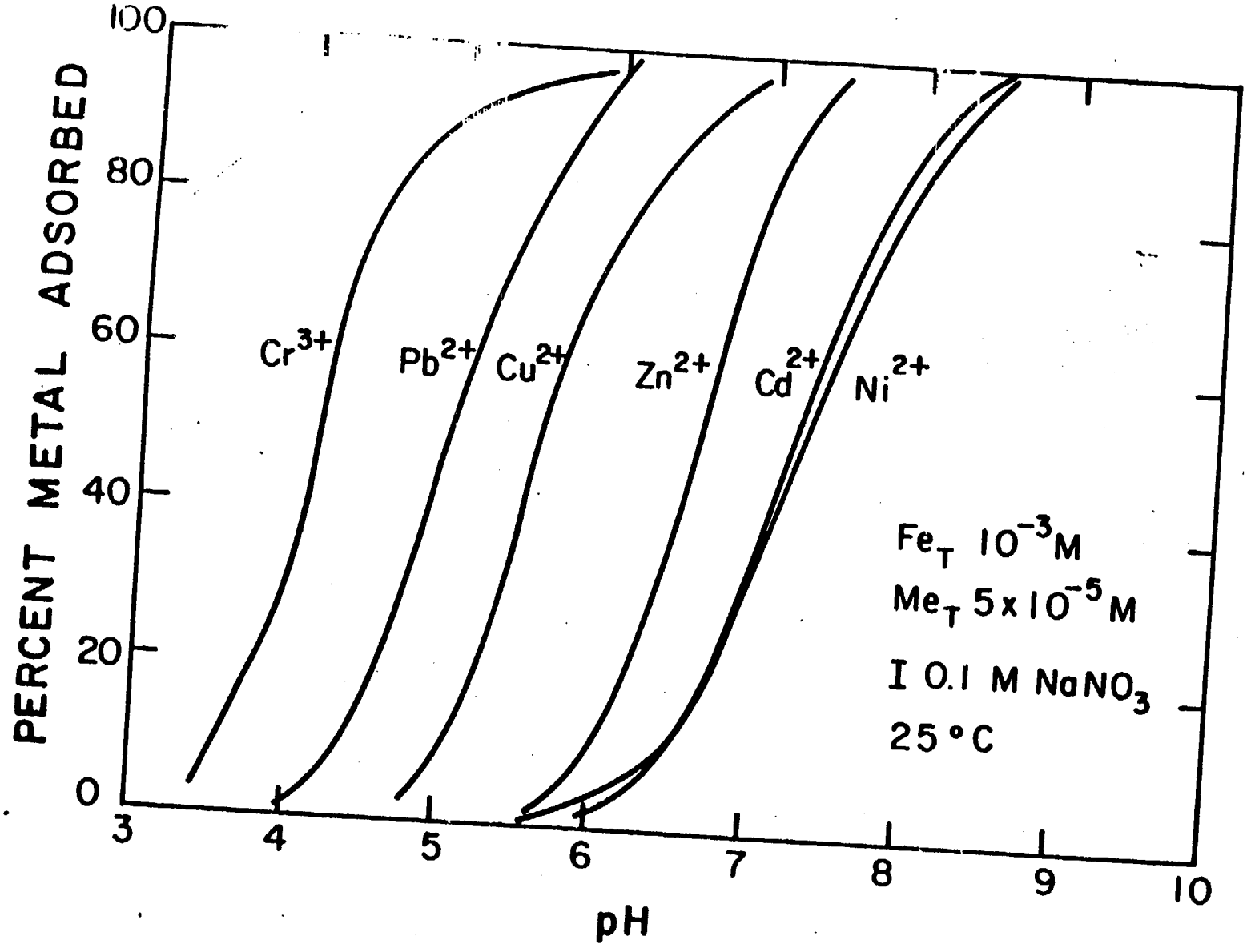


$$Fe(OH)_3\,(s) + ZnEDTA^{2-} + SOH + 2H^+ = FeEDTA + SOZn^+ + 3H_2O$$

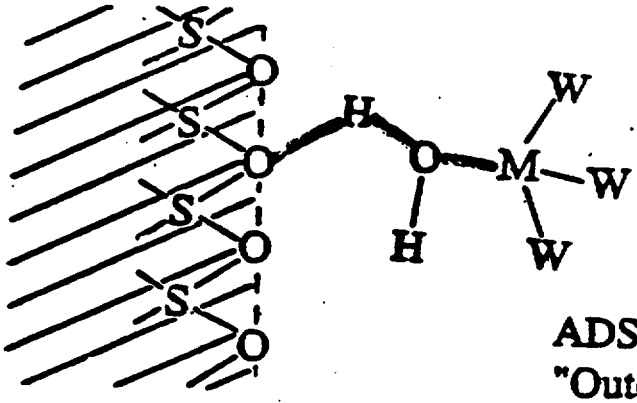
$Np(V)_T$ 1×10^{-7} M

Equimolar Surface Sites 5×10^{-4} M

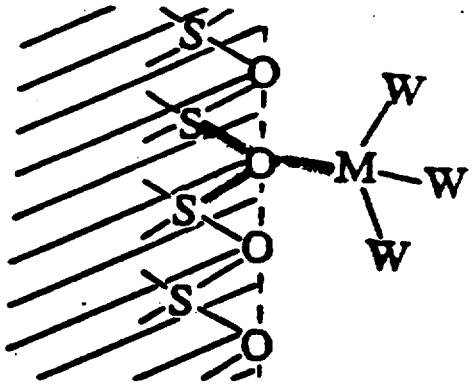



PERCENT METAL ADSORBED
100
80
60
40
20
0
3
4
5
6
7
8
9
10
pH
Cr^{3+}
Pb^{2+}
Cu^{2+}
Zn^{2+}
Cd^{2+}
Ni^{2+}
Fe_T 10^{-3}M
Me_T 5×10^{-5}M
I 0.1 M $NaNO_3$
25 °C

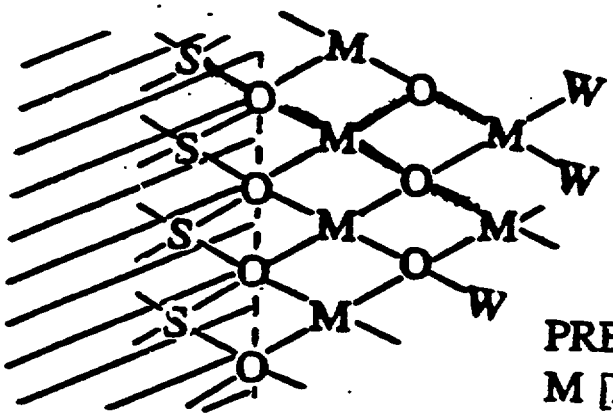
SORPTION COMPLEXES



ADSORPTION
"Outer sphere complex"
No metal ions in 2nd CN Shell



ADSORPTION
"Inner Sphere Complex"
S [= Fe] in 2nd CN Shell



PRECIPITATE
M [Pb] in 2nd CN Shell

Figure 2

TYPE OF SURFACE COMPLEX

INNER SPHERE

$$SOH + M^{2+} = SOM^{+} + H^{+}$$

$$SOH + L^{2-} + H^{+} = SL^{-} + H_2O$$

OUTER SPHERE

$$SOH + M^{2+} = SO^{-}\text{-}M^{2+} + H^{+}$$

$$SOH + L^{2-} + H^{+} = SOH_2^{+}\text{-}L^{2-}$$

COMPETITIVE REACTIONS IN ADSORPTION

COMPETITIVE ADSORPTION

SOA + B = SOB + A

COMPETITIVE LIGAND

SOM + L = SO + ML

COMPETITIVE SURFACE

SOM + TO = SO + TOM

LIGAND EFFECTS ON CATION ADSORPTION

COMPETITION FOR SURFACE SITES

$$SOH + M = SOM + H$$

$$SOH + L + H = SL + H_2O$$

COMPETITION WITH SURFACE SITES

$$SOM + L = SO + ML$$

FORMATION OF TERNARY SURFACE COMPLEXES

$$SOH + ML = SOML + H$$

$$SOH + ML + H = SLM + H_2O$$

OVERALL REACTIONS STOICHIOMETRY

<u>Exchange with proton</u>

$$SO_aH_a + bM^{m+} + cL^{l-} + dH^+ + eH_2O = (SO)_aM_b(OH)_eH_dL_c^{\delta} + (a+e)H^+,$$

$$K = \frac{\left((SO)_aM_b(OH)_eH_dL_c^{\delta}\right)(H^+)^{(a+e)}}{(SO_aH_a)(M^{m+})^b(L^{l-})^c(H^+)^d(H_2O)^e},$$

<u>Exchange with hydroxyl</u>

$$S_a(OH)_a + bM^{m+} + cL^{l-} + dH^+ + eH_2O = S_aH_dL_cM_b(OH)_e^{\delta} + (a+e)OH^-,$$

$$K = \frac{\left((S_aH_dL_cM_b(OH)_e^{\delta}\right)(H^+)^{(a+e)}}{(S_a(OH)_a)(M^{m+})^b(L^{l-})^c(H^+)^d(H_2O)^e},$$

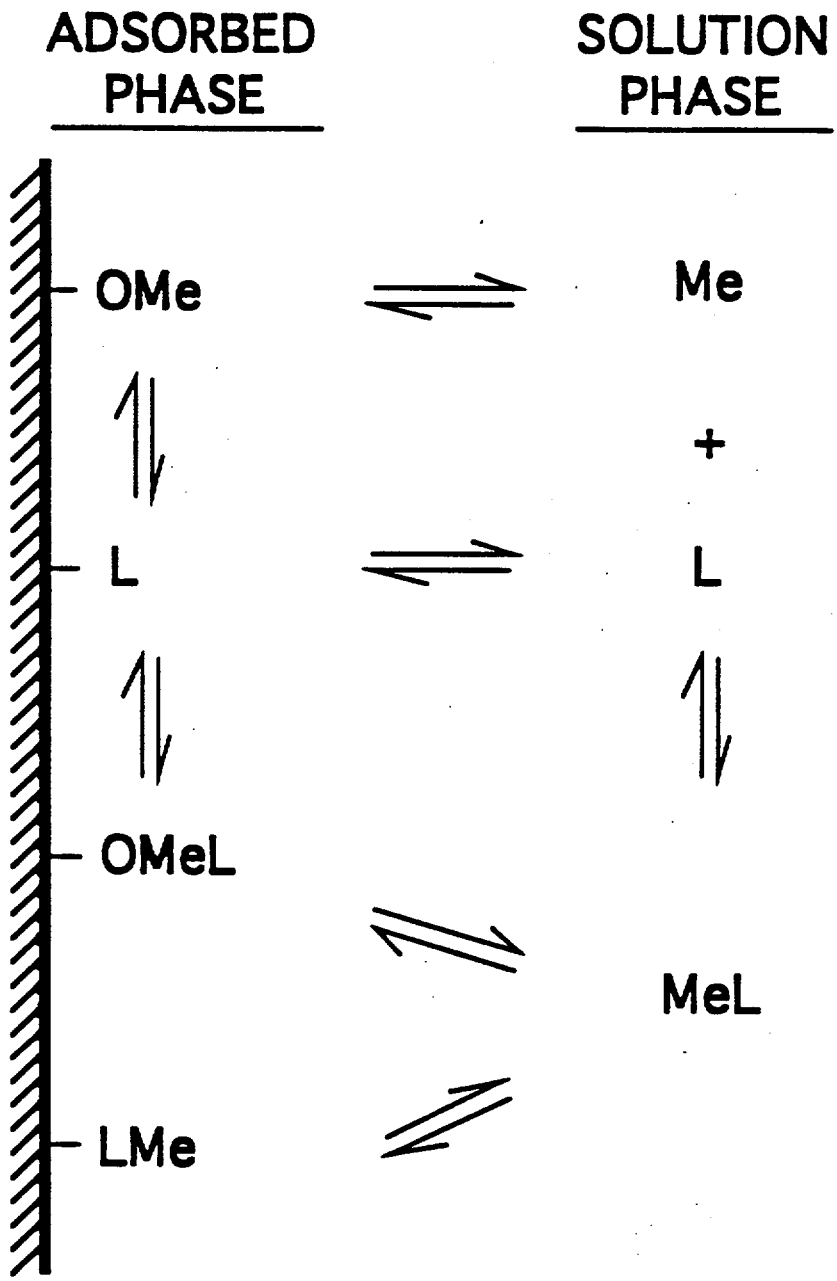
PROTON STOICHIOMETRY

Cation Binding

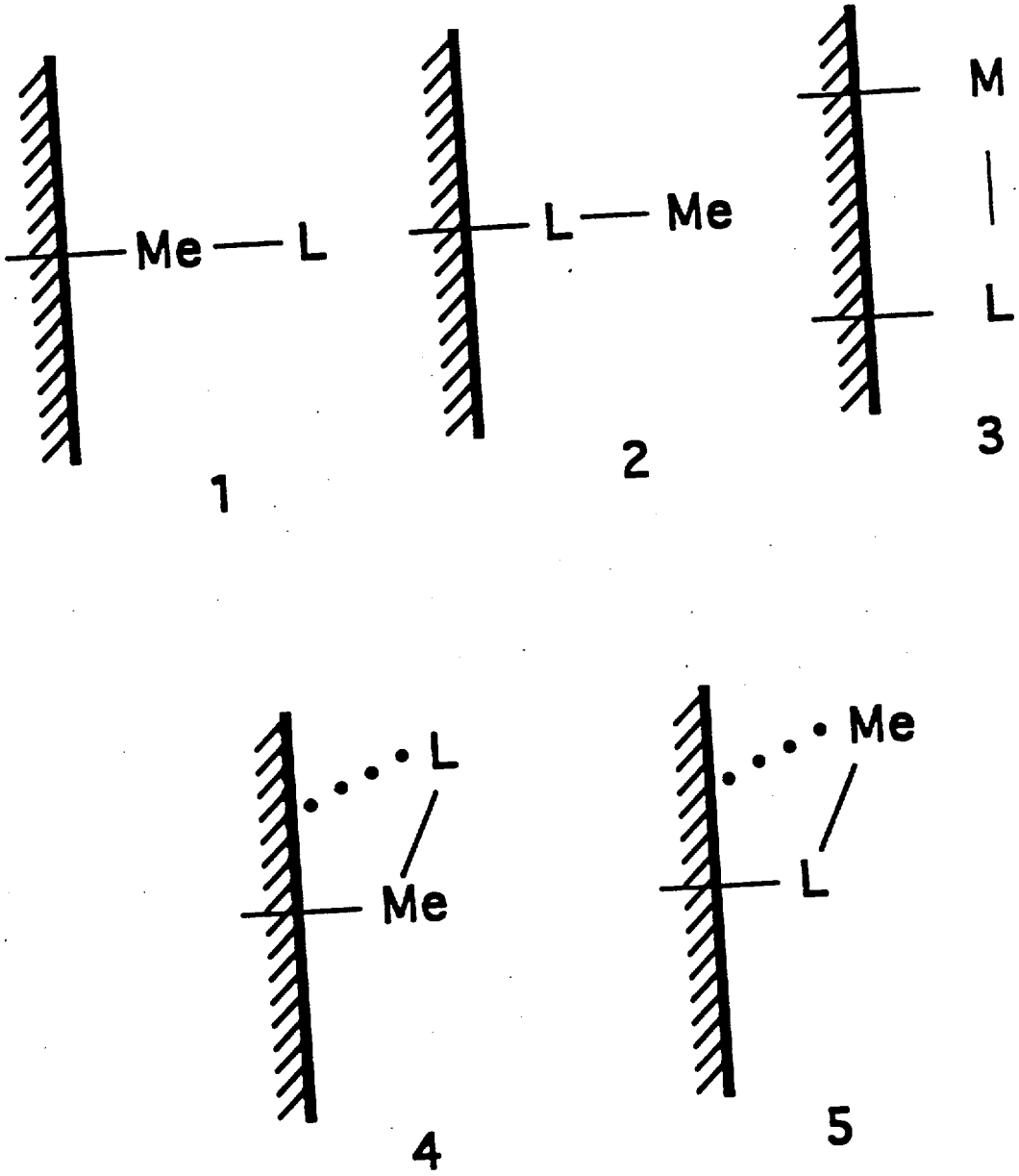
$$SH_{\chi} + M \overset{{}^{c}K_{M}}{=\!=} SM + \chi H$$

Anion Binding

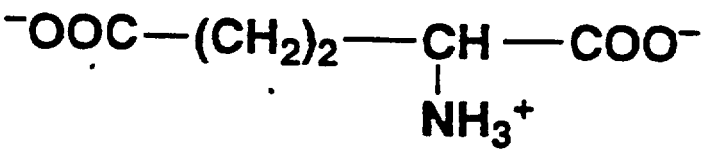
$$SH + \chi H + A \overset{{}^{c}K_{A}}{=\!=} SH_{(1+\chi)}A$$



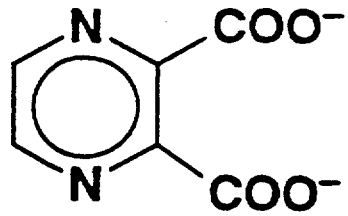
SCHEMATIC REPRESENTATION OF SURFACE COMPLEXATION REACTIONS



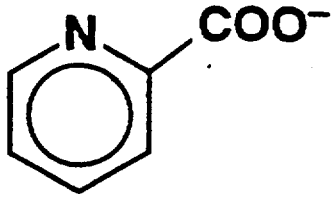
POSSIBLE CONFORMATIONS FOR TERNARY SURFACE COMPLEXES



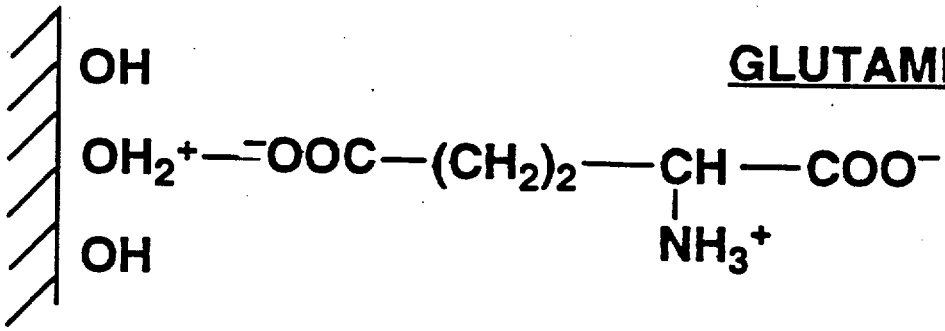
glutamic acid
in mid-pH region



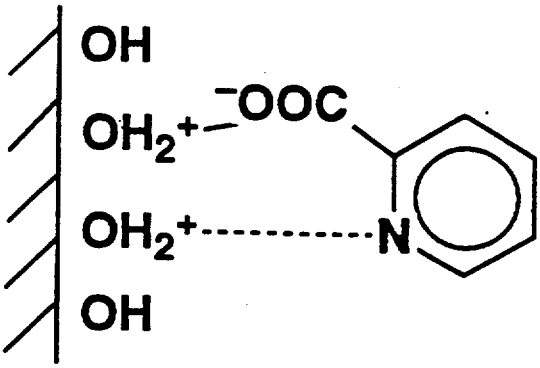
2, 3-PDCA
in mid-pH region



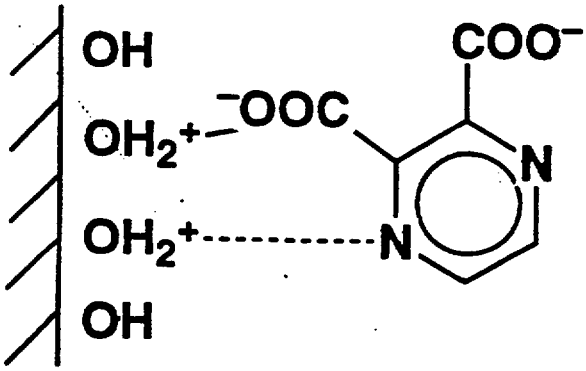
picolinic acid
in mid-pH region



GLUTAMIC ACID

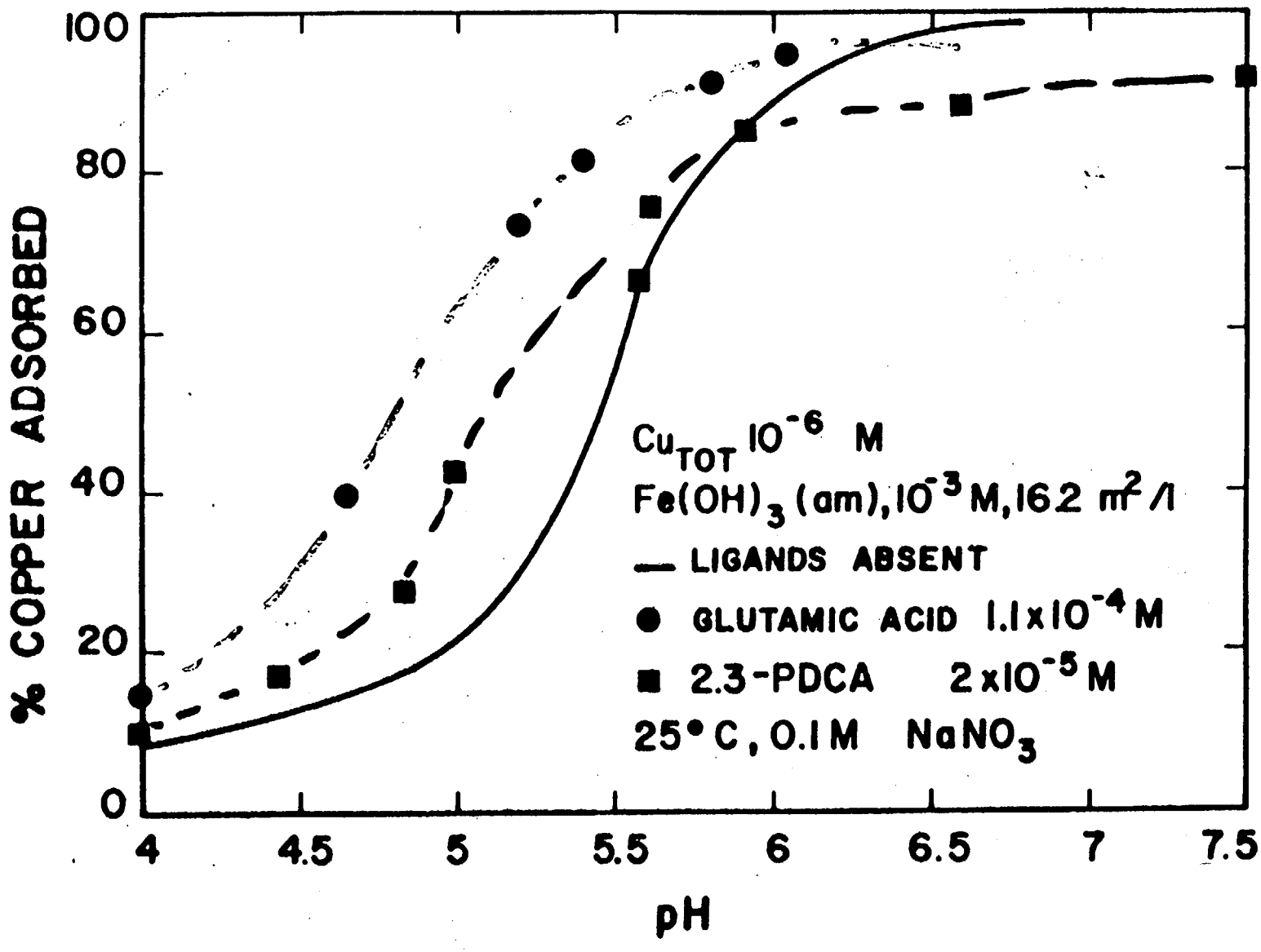


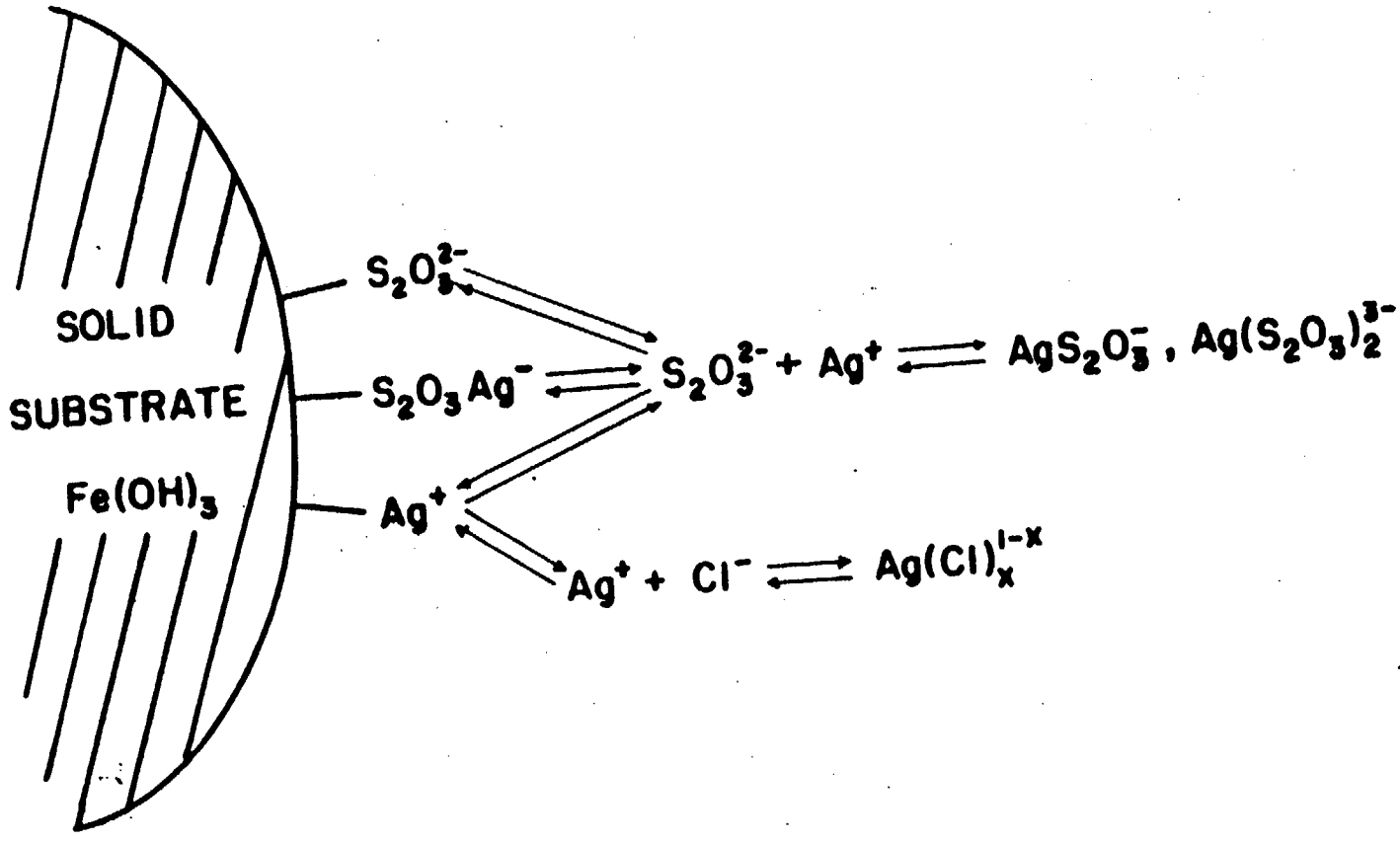
PICOLINIC ACID



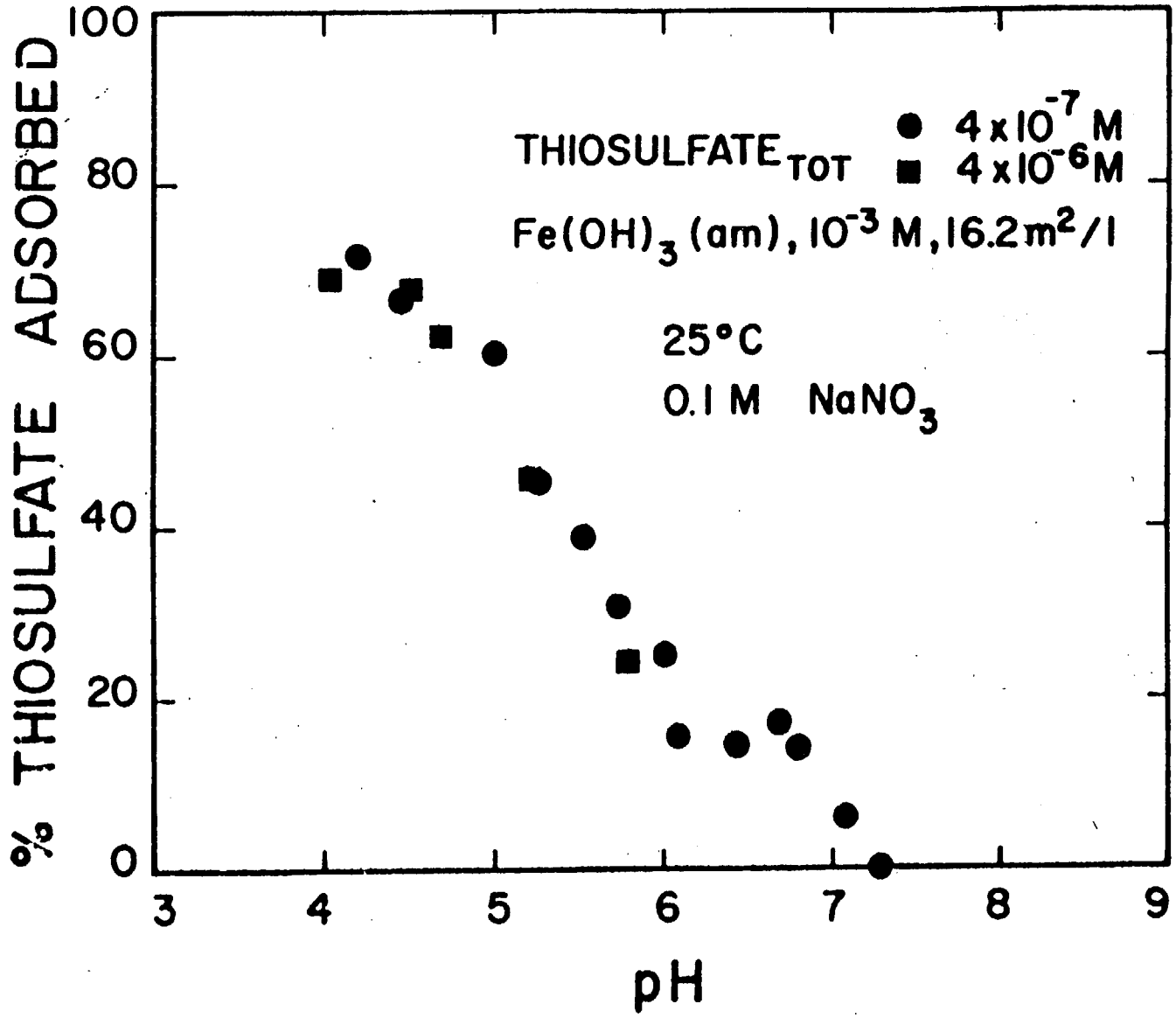
2, 3-PDCA

Davis and Leckie (1978)

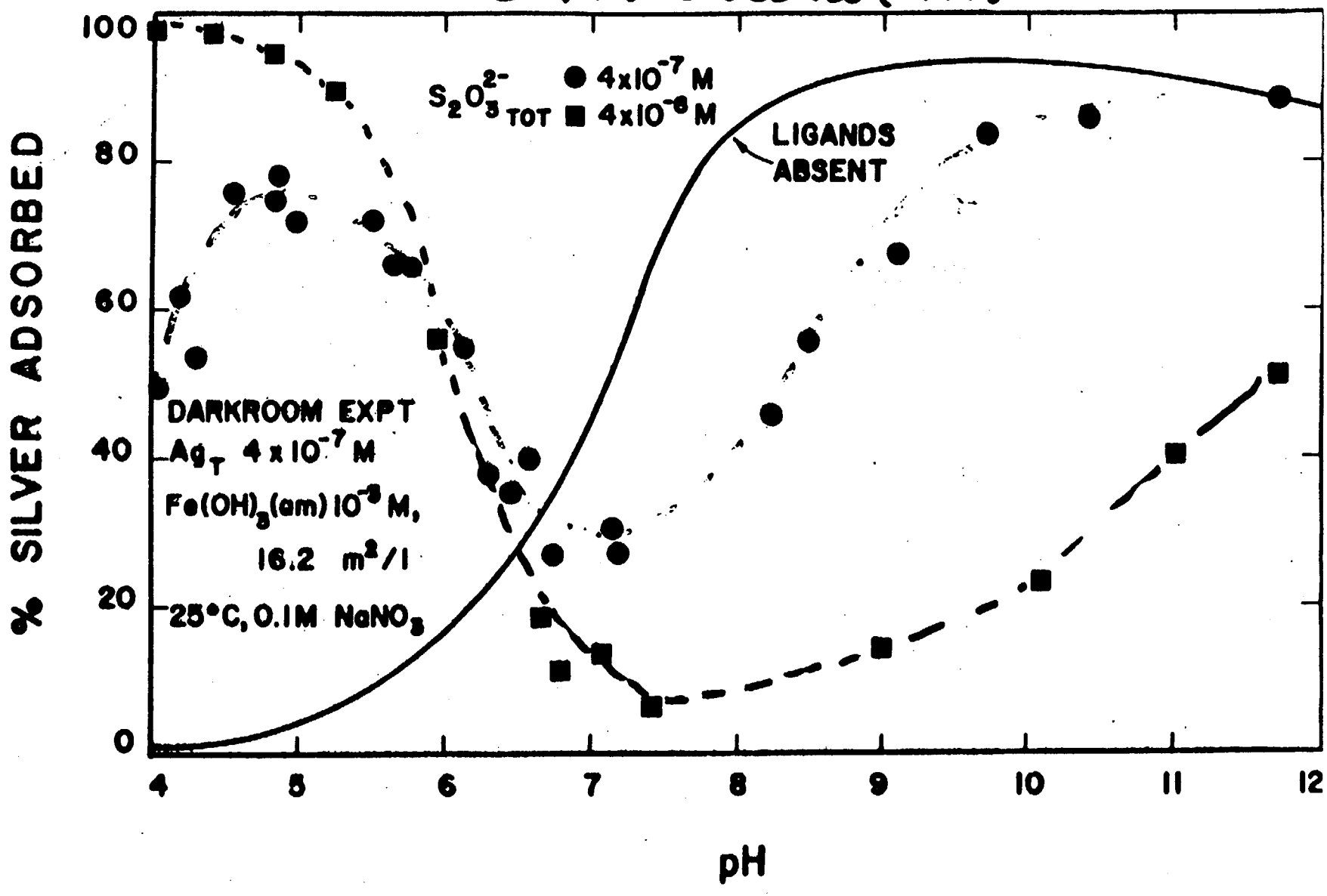



SOLID
SUBSTRATE
Fe(OH)3
S2O3 2-
S2O3Ag-
Ag+
S2O3 2- + Ag+
AgS2O3-, Ag(S2O3)2 3-
Ag+ + Cl-
Ag(Cl)x 1-x

Davis and Leckie (1978)



Davis and Leckie (1978)

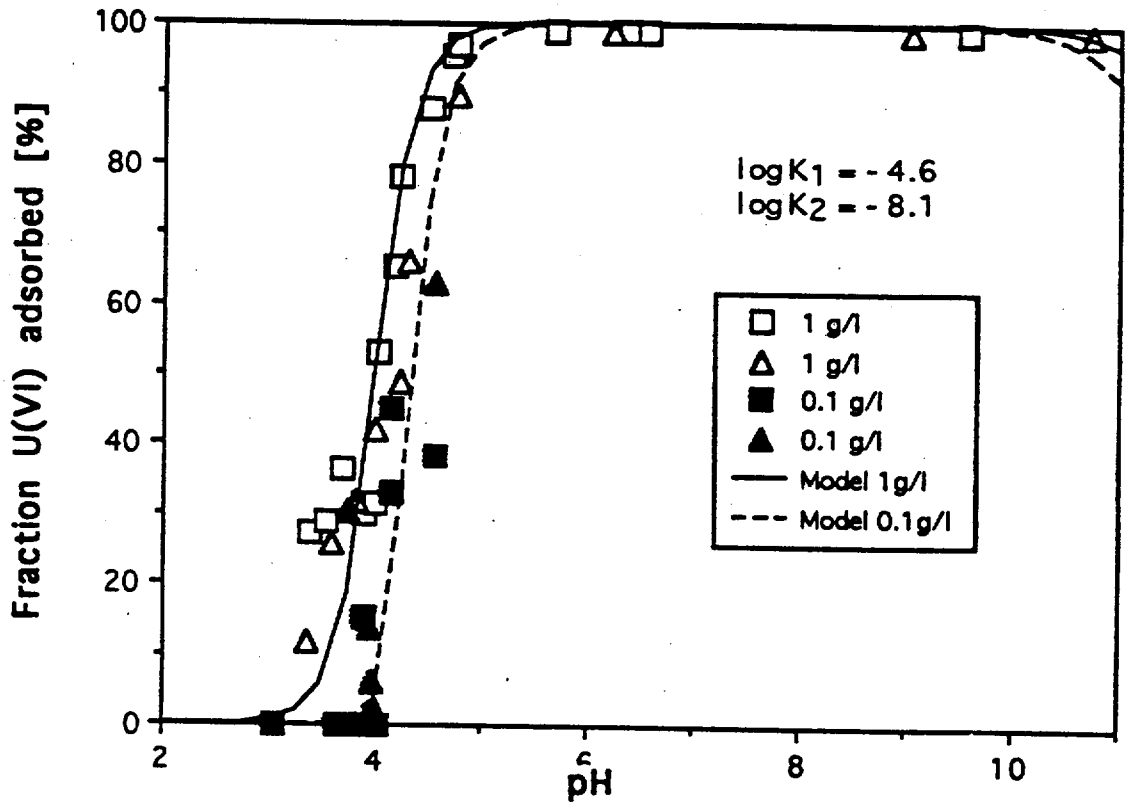


Adsorption of U(VI) onto 1g/l Goethite

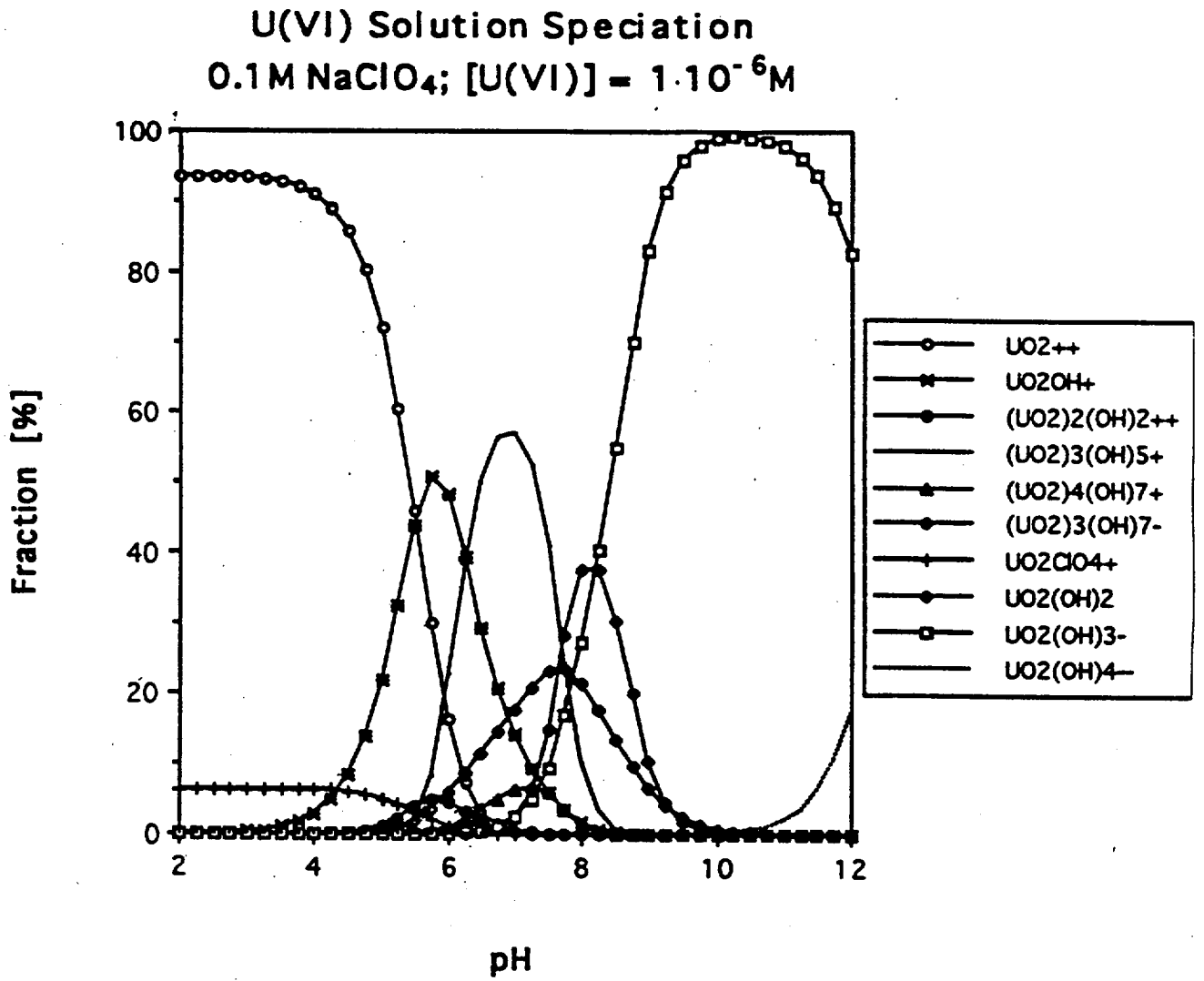
I = 0.1M $NaClO_4$; [U(VI)] = $1 \cdot 10^{-6}$M (STD)

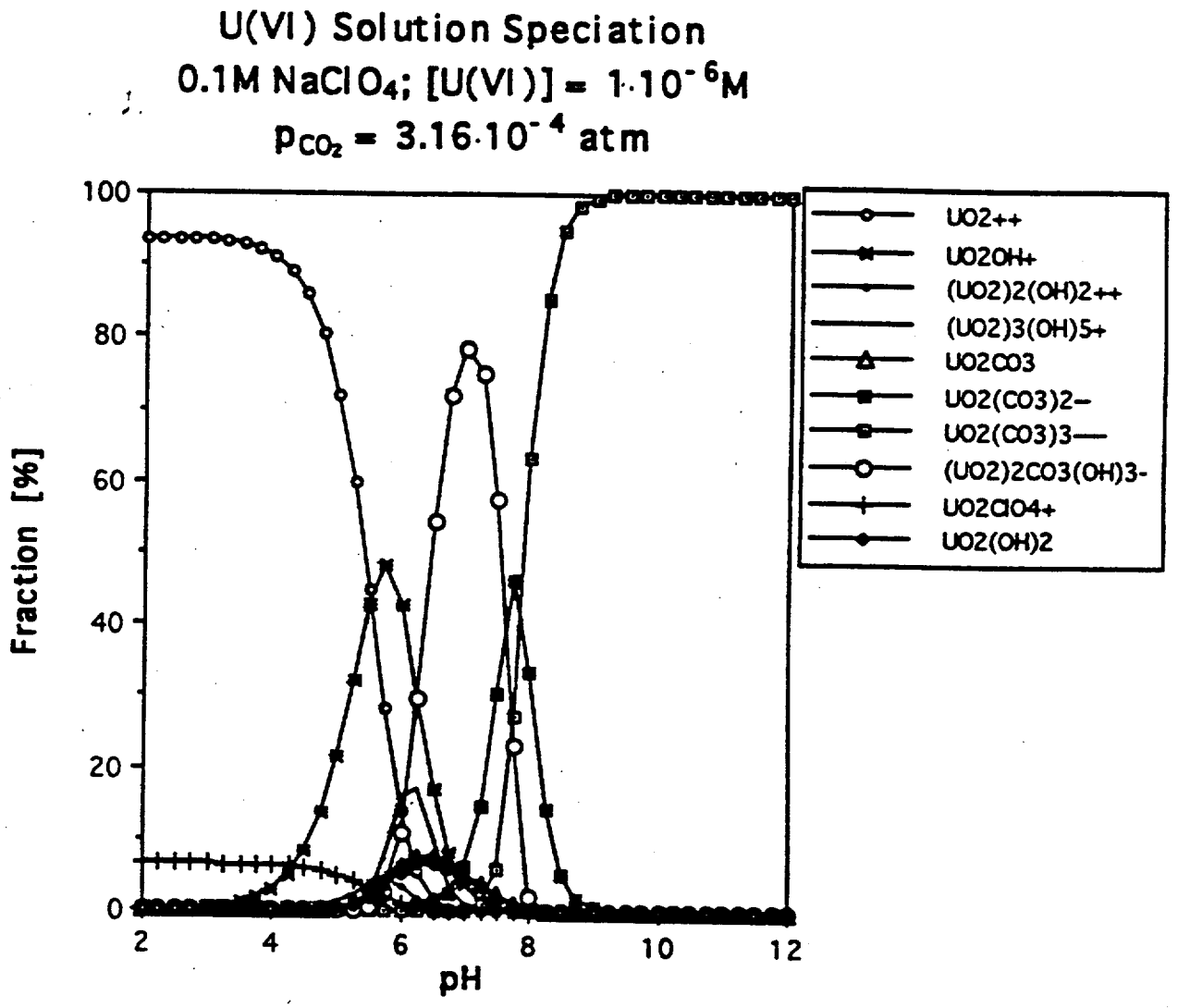
(R1): $SOH + UO_2^{2+} + H_2O \leftrightarrow SOUO_2OH + 2H^+$

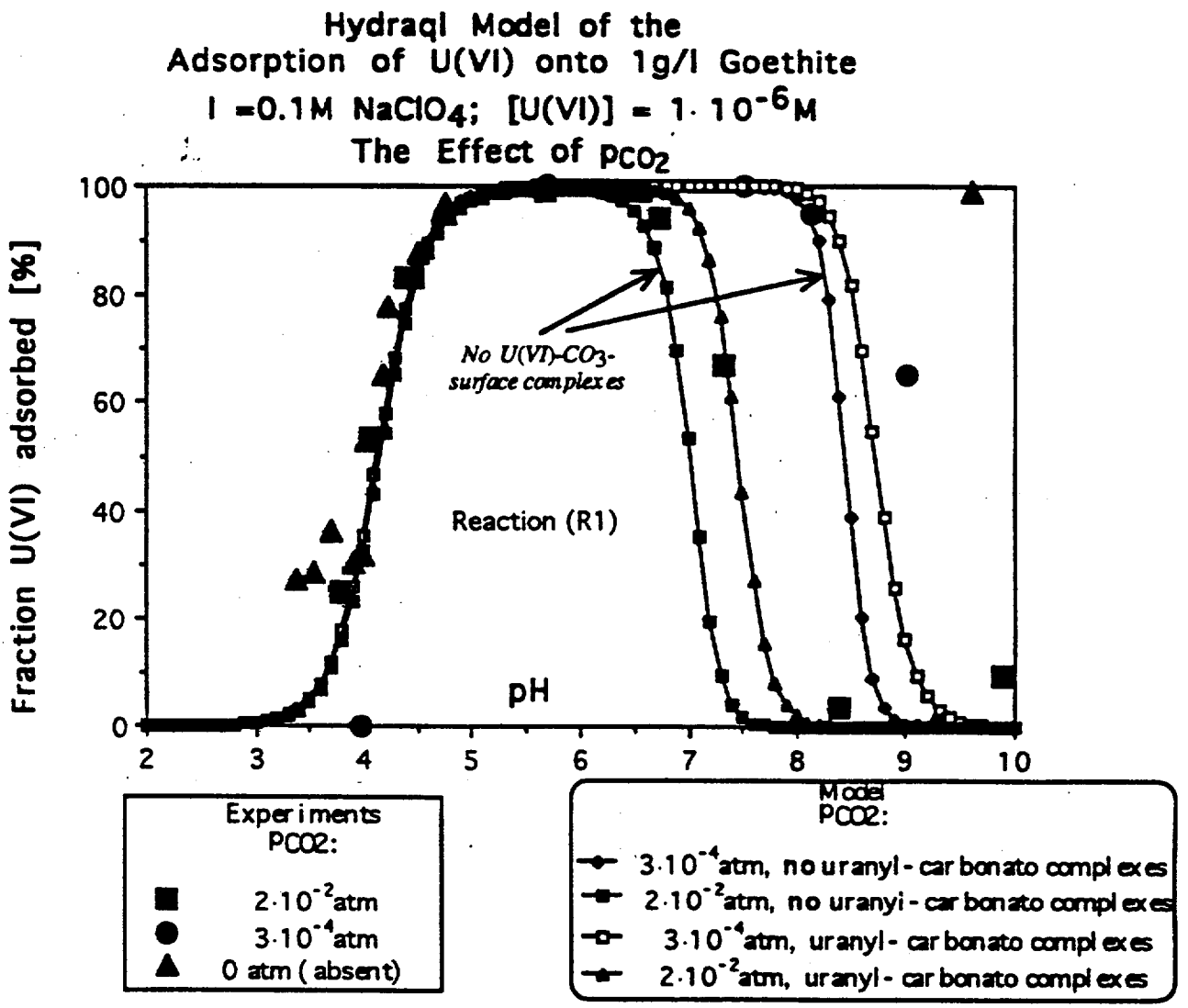
+ (R2): $SOH + 3UO_2^{2+} + 5H_2O \leftrightarrow SO(UO_2)_3(OH)_5 + 6H^+$



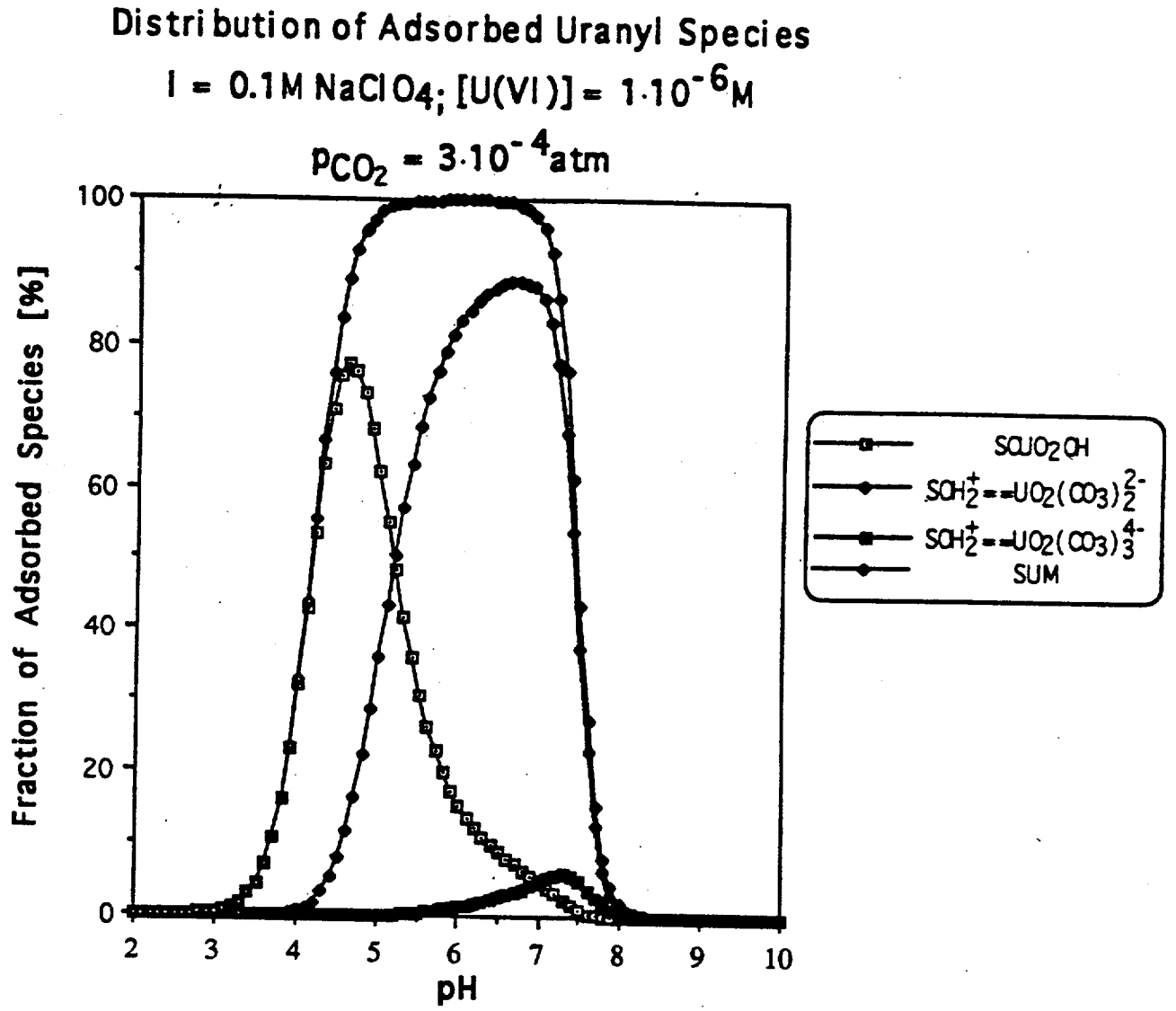
Kohler, Honeyman and Leckie (in prep)


U(VI) Solution Speciation
0.1M NaClO4; [U(VI)] = 1·10-6M
Fraction [%]
100
80
60
40
20
0
2
4
6
8
10
12
pH
UO2++
UO2OH+
(UO2)2(OH)2++
(UO2)3(OH)5+
(UO2)4(OH)7+
(UO2)3(OH)7-
UO2ClO4+
UO2(OH)2
UO2(OH)3-
UO2(OH)4--

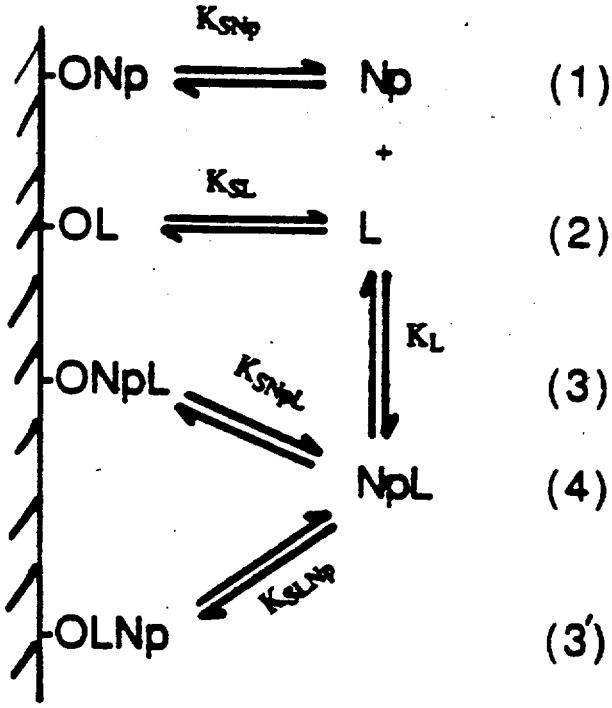

U(VI) Solution Speciation
0.1M NaClO4; [U(VI)] = 1·10^-6 M
pCO2 = 3.16·10^-4 atm
Fraction [%]
pH
100
80
60
40
20
0
2
4
6
8
10
12
UO2++
UO2OH+
(UO2)2(OH)2++
(UO2)3(OH)5+
UO2CO3
UO2(CO3)2--
UO2(CO3)3---
(UO2)2CO3(OH)3-
UO2ClO4+
UO2(OH)2



Kohler, Honeyman and Leckie (in prep)

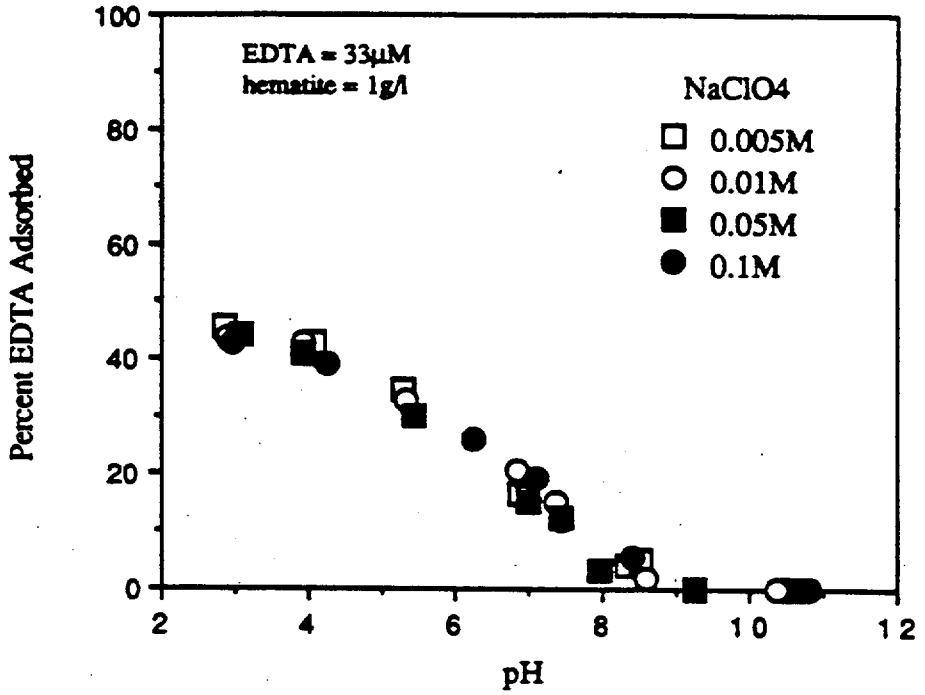

Distribution of Adsorbed Uranyl Species
I = 0.1M NaClO4; [U(VI)] = 1·10^-6 M
pCO2 = 3·10^-4 atm
Fraction of Adsorbed Species [%]
100
80
60
40
20
0
2
3
4
5
6
7
8
9
10
pH
SOUO2OH
SOH2+=UO2(CO3)2 2-
SOH2+=UO2(CO3)3 4-
SUM

Schematic illustration of hypothetical neptunyl reactions



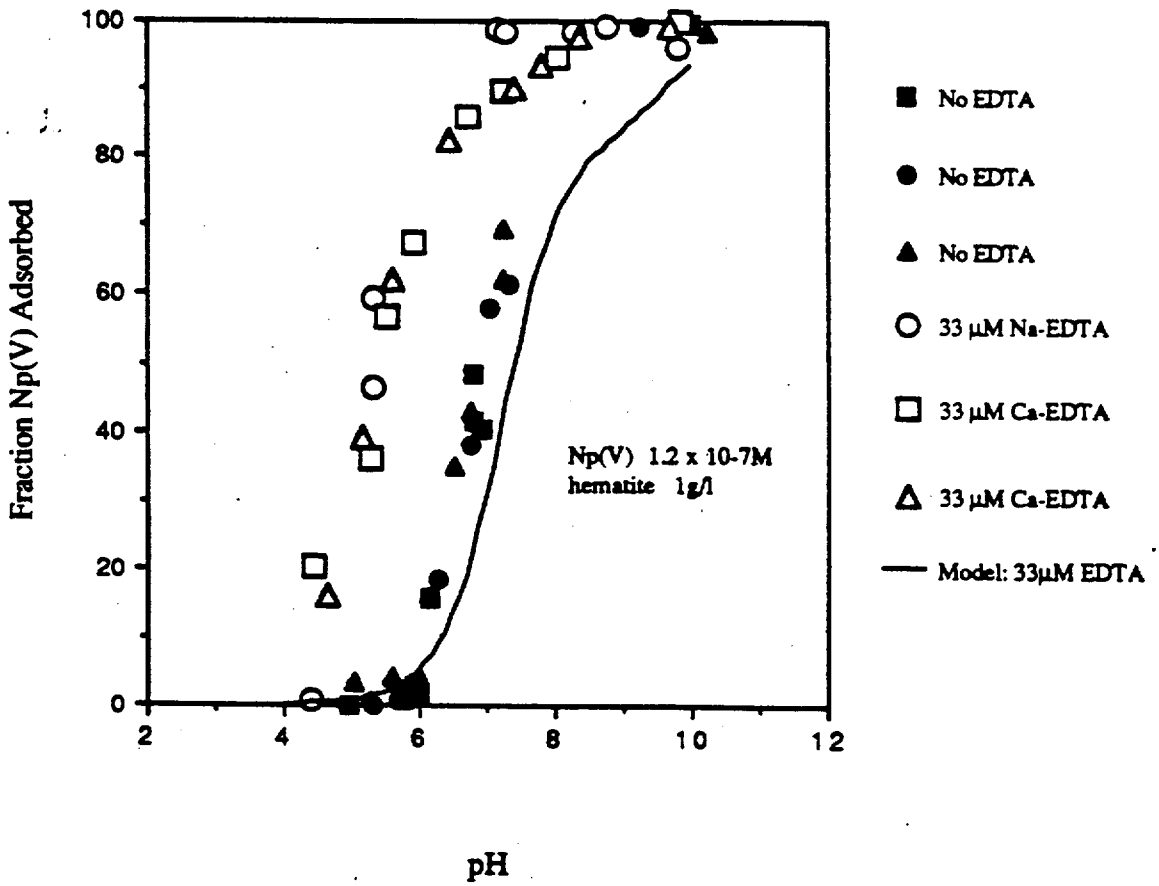
L = carbonate, EDTA

EDTA Sorption onto hematite:
effect of variation in ionic strength



Kohler, Honeyman and Leckie (in prep)

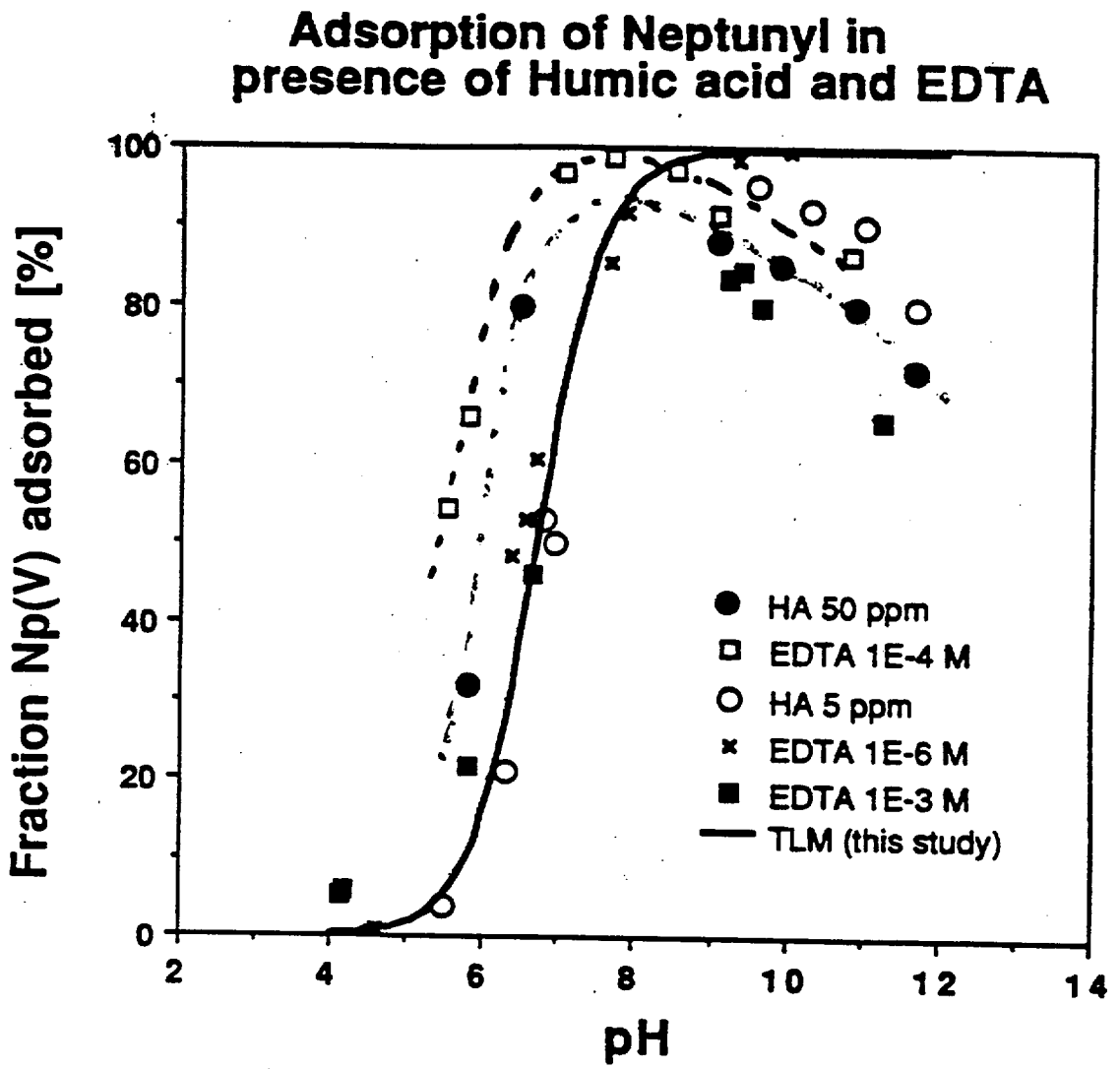
Effect of EDTA on Neptunyl Sorption



Kohler, Honeyman and Lochie (in prep)

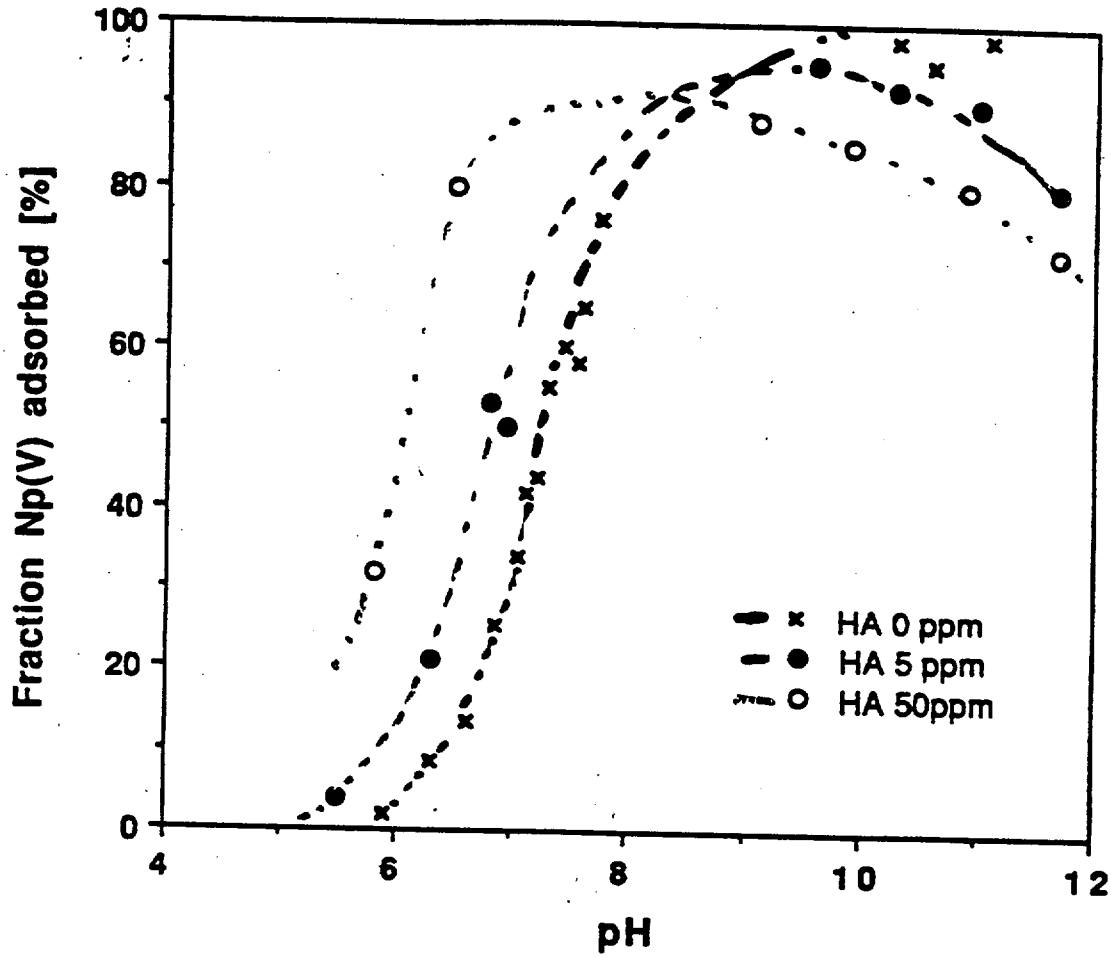
EDTA solution complexes considered:

$$NpO_2^+ + EDTA^{4-} = NpO_2EDTA^{3-}$$
$$NpO_2^+ + HEDTA^{3-} = NpO_2HEDTA^{2-}$$



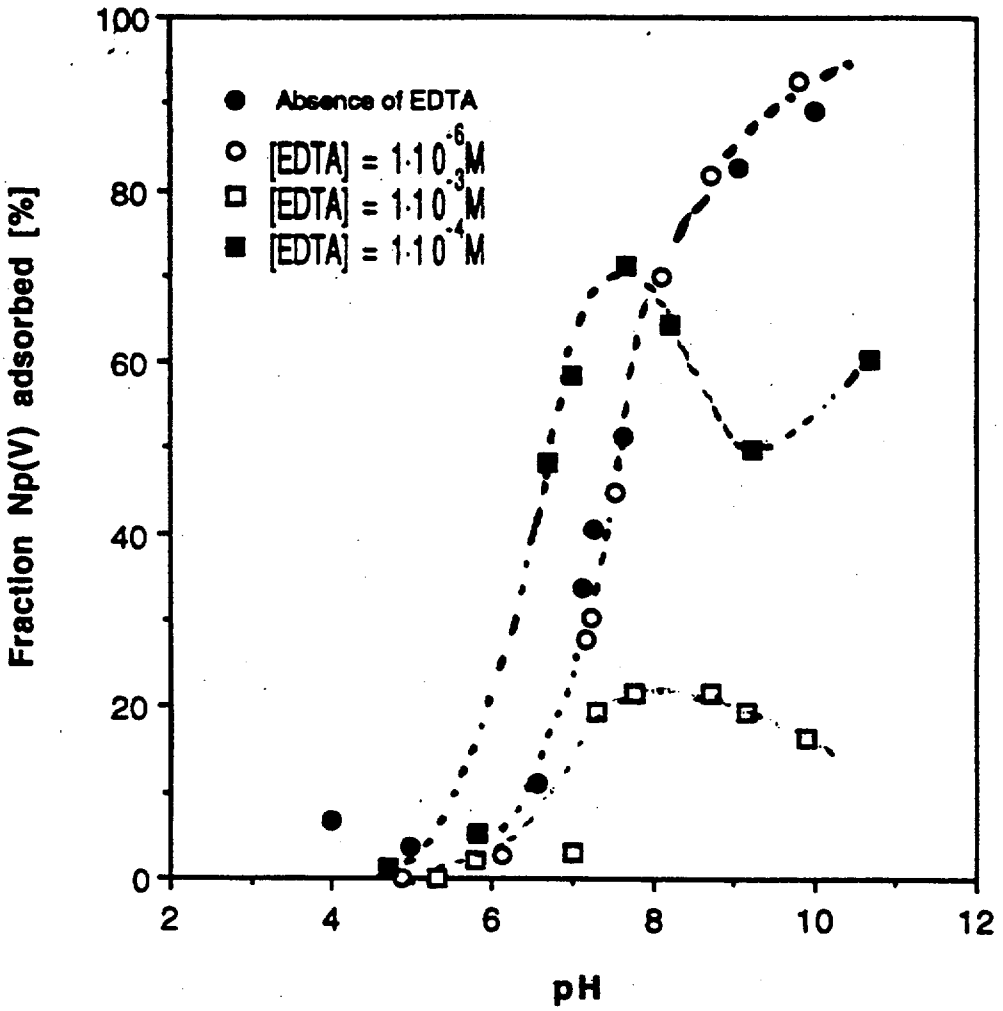
Wieland and Lackie (in prep)

Adsorption of Neptunyl on Gibbsite in presence of Humic acid (data from Rhigetto et al., 1991)



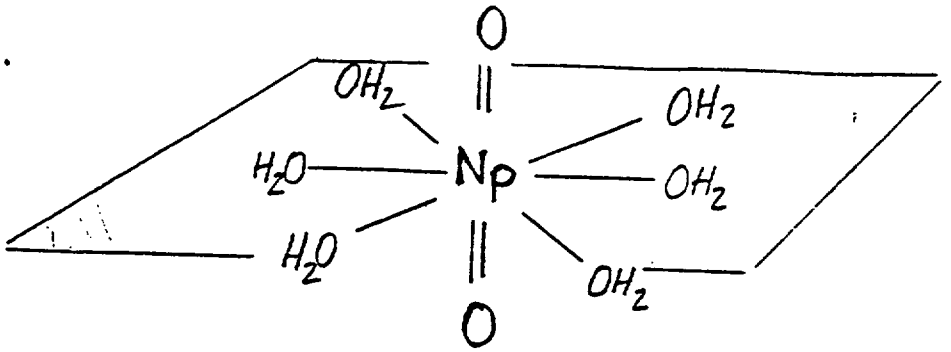
Ternary Complexes with EDTA

Np(V) 1×10^{-7} M Kaolinite 50 m^2/l

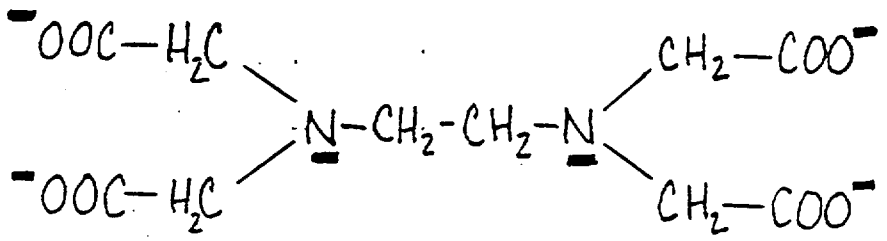


Wieland, Kohler and Leckie (in prep)

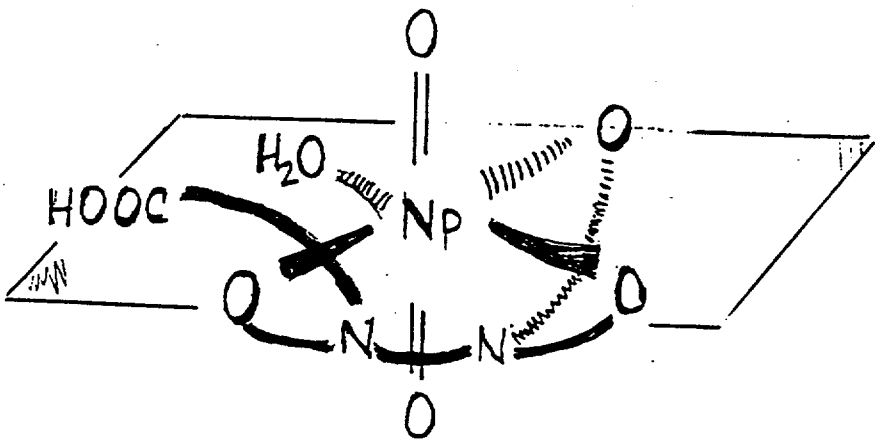
$NpO_2^+(H_2O)_6$



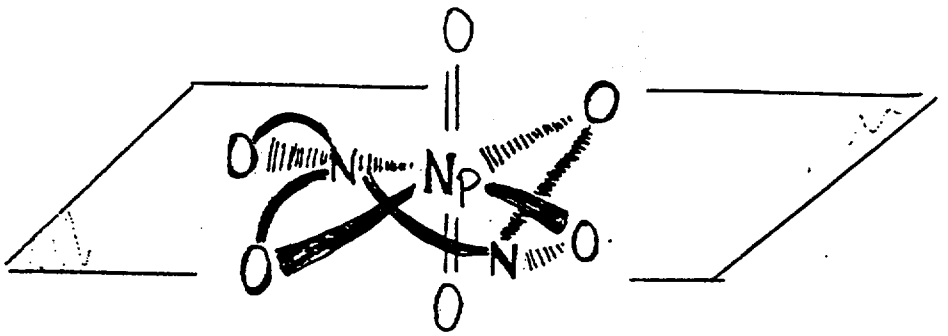
$EDTA^{4-}$



NpO_2HY^{2-}

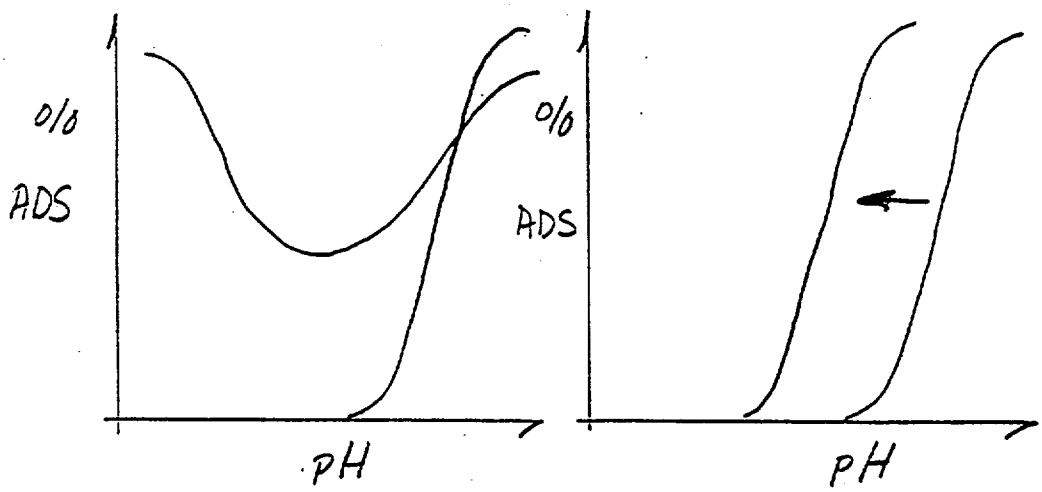


NpO_2Y^{3-}



TERNARY SURFACE COMPLEXES

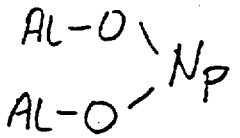
	CASE 1	CASE 2
Metal Group	NpO_2HY^{2-}	NpO_2^+
Surface Group	Al-OH	Al_2Y^{2-}
Adsorption	"Ligand-like"	"Metal-Like"

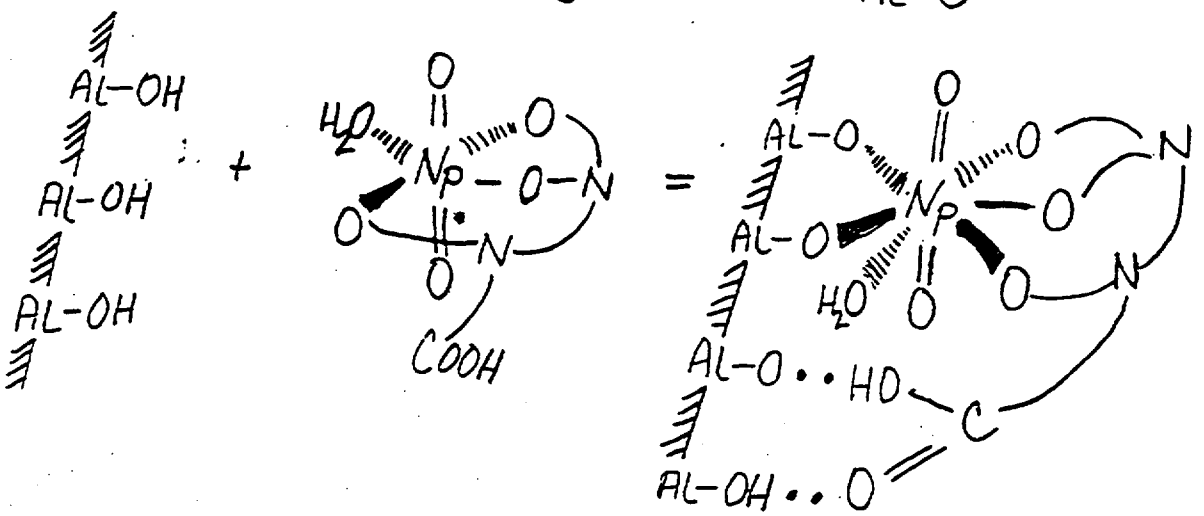


TERNARY SURFACE COMPLEXES

"METAL-LIKE" COORDINATION

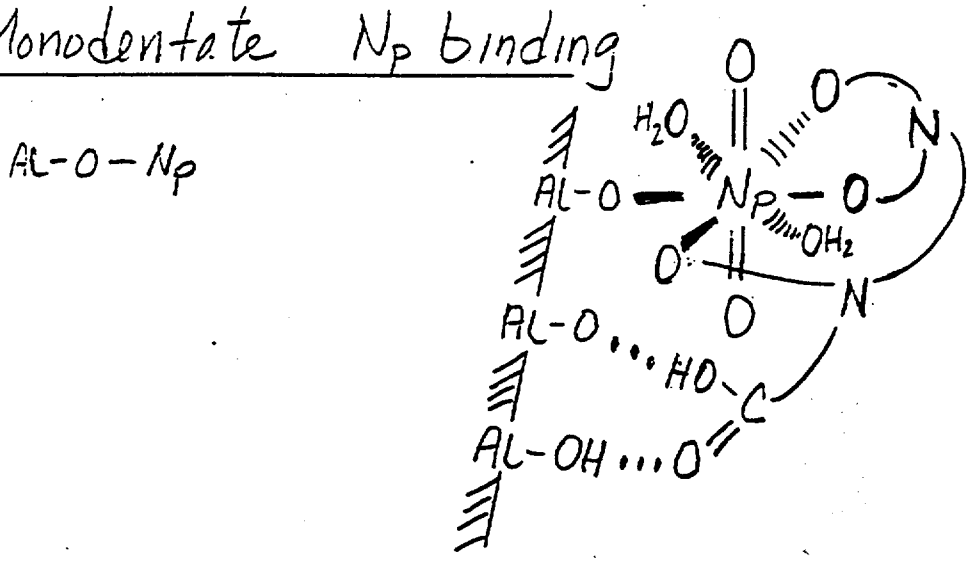
Bidentate Np binding





$$(SOH)_2 + NpO_2HY^{2-} = (SO)_2NpO_2HY^{4-} + 2H^+$$

Monodentate Np binding

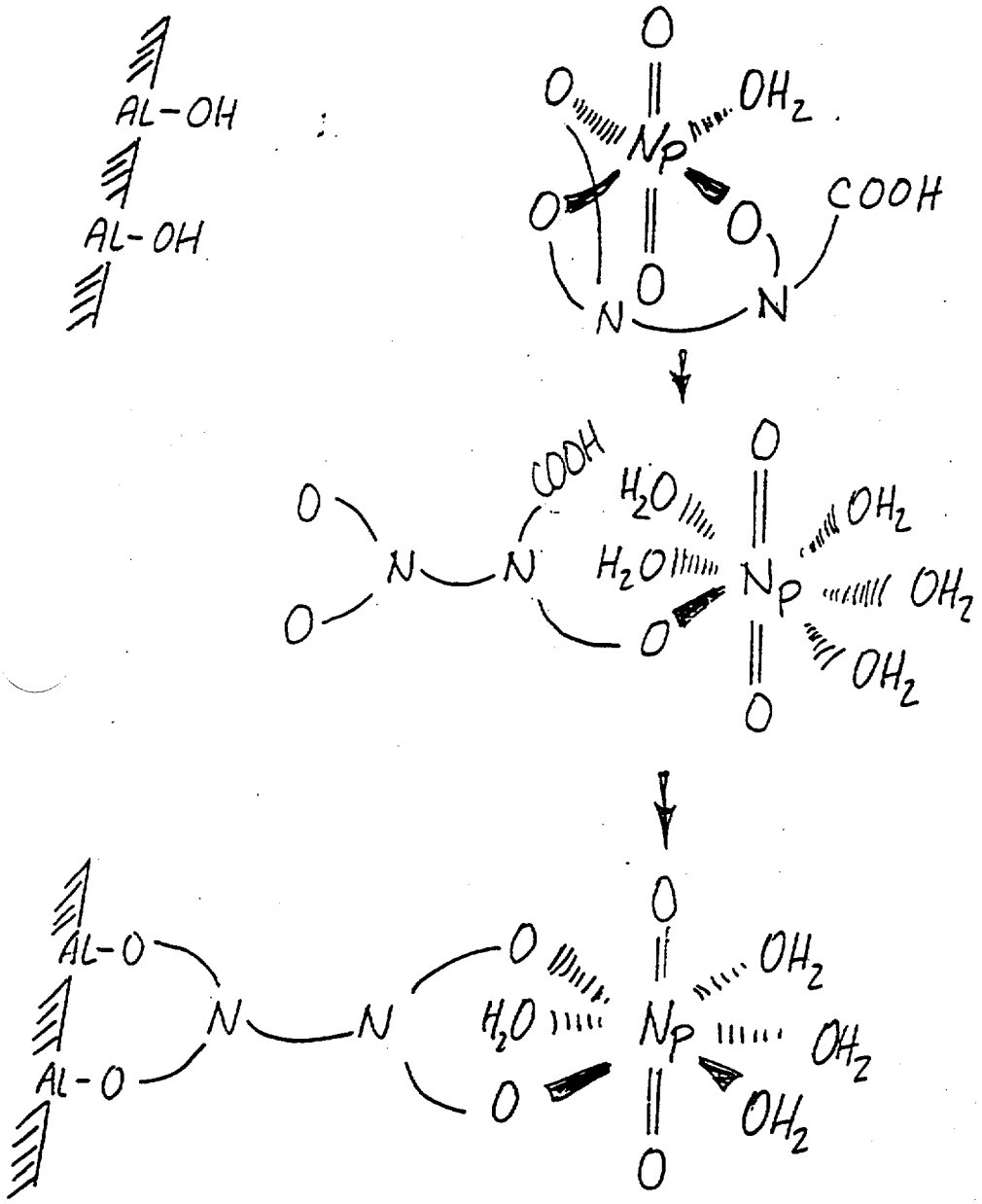


$$SOH + NpO_2HY^{2-} = SONpO_2HY^{3-} + H^+$$

TERNARY SURFACE COMPLEXES

"LIGAND-LIKE" COORDINATION

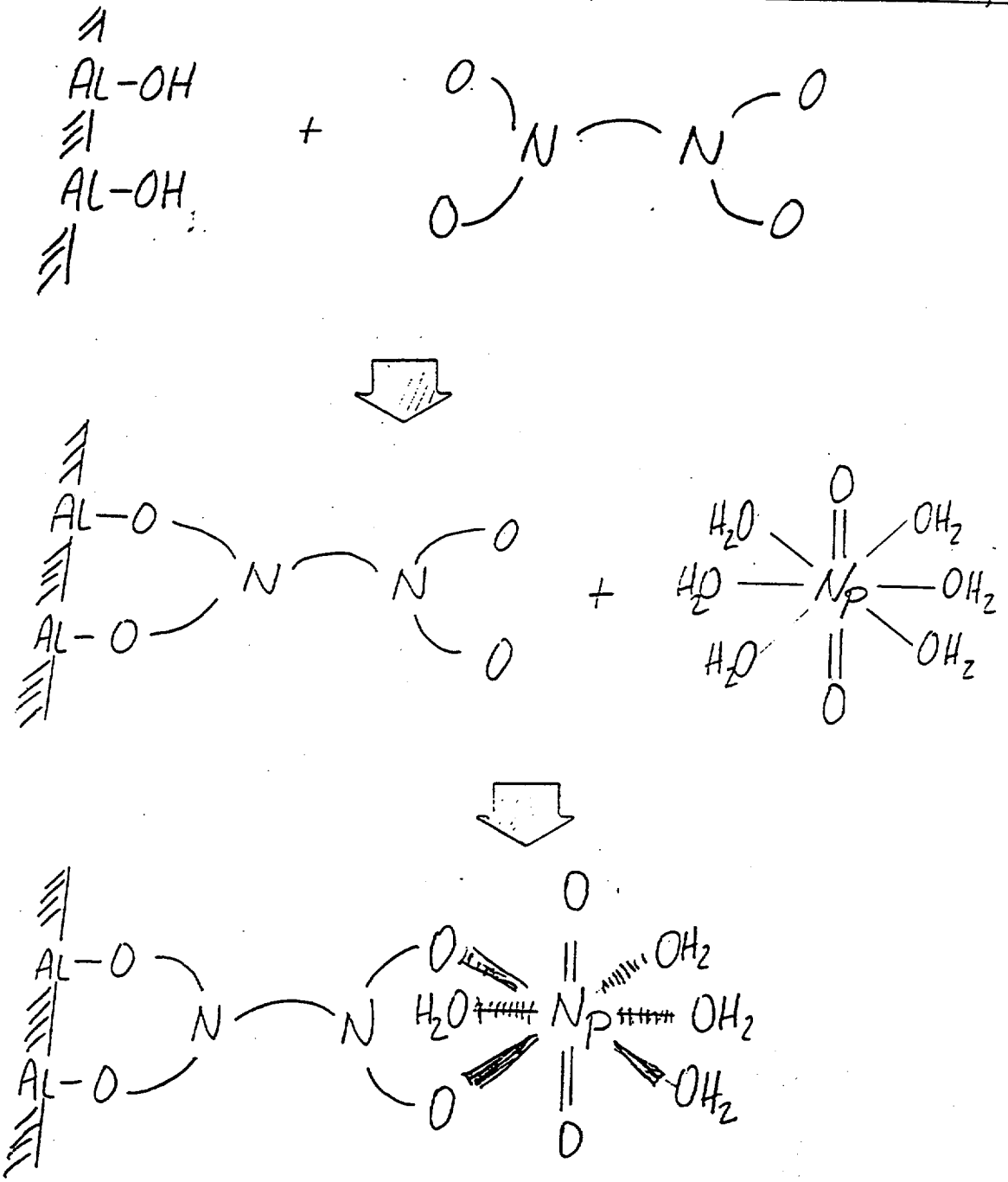
CASE 1



$$(SOH)_2 + ML = S_2L\text{-}M + 2H_2O$$

$$\Delta G(Ads) \gg \Delta G(chelate)$$

CASE 2 "New" Surface-Site Type (Modified Surface)



Modified Surface

$$(SOH)_2 + L = S_2\text{-}L + 2H^+$$

"Metal-Like" COORDINATION

$$S_2\text{-}L + M = S_2\text{-}L\text{-}M$$

CONCLUSIONS

Np / EDTA SYSTEM

Ternary Surface Complexes

- "Metal-Like" adsorption behavior of ternary surface complexes
- Two Possible adsorption mechanisms

1. Adsorption of NpO_2HY^{2-} on Al-OH sites with additional stabilization

2. Adsorption of NpO_2^+ on Al_2Y^{2-} sites

DOE-NRC Technical Exchange Radionuclide Migration

Retardation sensitivity analysis

George A. Zyvoloski, LANL

Los Alamos NATIONAL LABORATORY 1943 - 1993

Bottom Line -

Prevent Radionuclide escape to the environment

Groundwater Flow at Yucca Mountain -

1) ***Uncertainty in Infiltration rates***

2) ***Fracture flow important***

3) ***Stratigraphy and faults can be important***

Issues Affecting Radionuclide Transport -

1) ***Release rates***

2) ***Sorption***
   - ***Geochemistry***

3) ***Air flow (C^{14})***

4) ***Ground water flow***

Porous Flow and Fracture

CODE PHYSICS - George Zyvoloski and Bryan Travis

FEHM Finite element heat, mass (and stress)

- 3-D geometry
- Flow of air, water and heat
- Multiple chemically reacting and sorbing tracers
- Coupled stress solution
- Saturated and unsaturated media
- Double porosity, double permeability treatment
- Finite element/finite volume formulation
- Algorithms:
  - Preconditioned conjugate gradient solution of coupled linear equations;
  - Newton-Raphson solution of nonlinear equations

Porous Flow and Fracture

CODE PHYSICS - George Zyvoloski and Bryan Travis

(continued)

TRACR3D

- 3-D geometry
- Flow of air and water
- Multiple chemically reacting and sorbing tracers
- Saturated and unsaturated media
- Biokinetics
- Adjoint sensivity capbilities
- Finite difference formulation
- Algorithms:
  - Preconditioned conjugate gradient solution of coupled linear equations;
  - Newton-Raphson solution of nonlinear equations

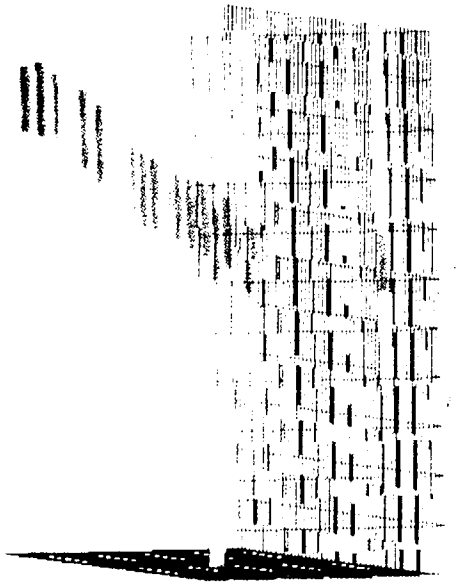
Construction of Flow Model -

1) *Use information from the Sandia Data Base*

2) *Block values identified with hydrogeologic units*

3) *Structured or Unstructured meshs*

a)

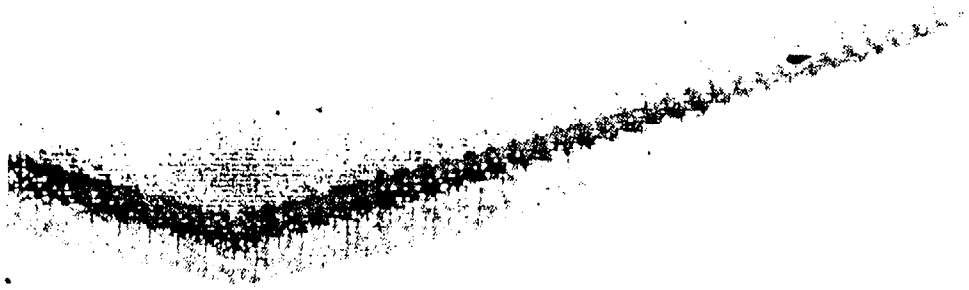


b)

c)

a)Well Log Data
b)Model of Stratigraphy
c)2D Computational Mesh
d)3D Computational Mesh

d)

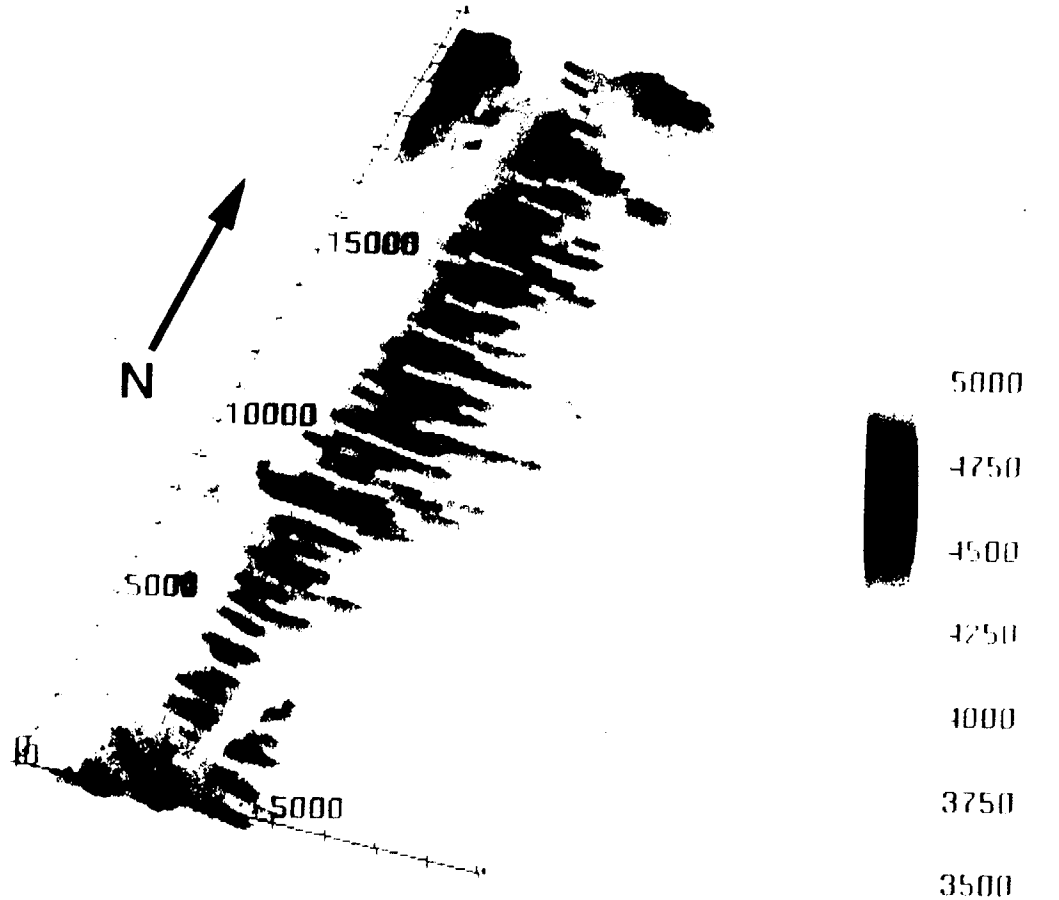


Air Flow at Yucca Mountain –

1) ***Needed for C^{14} transport calculations***

2) ***Thermal convection and barometric changes are the driving forces***

Yucca Mountain topography on a grid with 250ft. centers.



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Coupled flow and Geochemistry -

1) ***Important to understanding processes at Yucca Mountain***

2) ***Interaction with Ebinger's task***

Multiple Reaction Module -

- ***User specifies a system of chemical reactions involving one or more components***
  - ***Stoiciometry***
  - ***Reaction rate laws***
  - ***Identification of phase(s) participating in reaction (fluid, sorbed, etc.)***
- ***Code solves transport equation with reaction for each component at each time step***

Types of Chemical Species -

- ***Liquid Phase***
- ***Vapor Phase***
- ***Solid Phase (chemical reaction only)***
- ***Henry's Law-solute partitions between liquid and vapor subject to Henry's Law equilibrium***
- ***Sorption is included through the use of linear and nonlinear sorption isotherm (equilibrium) models***

Students

Activities Related to Flow and Transport

New Mexico Tech
- Colarullo (Philips)
  - heterogeneities, flow, transport

University of Illinois
- Viswanathan (Valocchi)
  - flow and coupled geochemistry

University of Utah
- Snelgrove (Forester)
  - vapor transport, air flow

University of Arizona
- Levin (Neuman)
  - heterogeneities, flow, transport

DOE-NRC Technical Exchange
Radionuclide Migration

Retardation sensitivity analysis

George A. Zyvoloski, LANL

<Supplement>

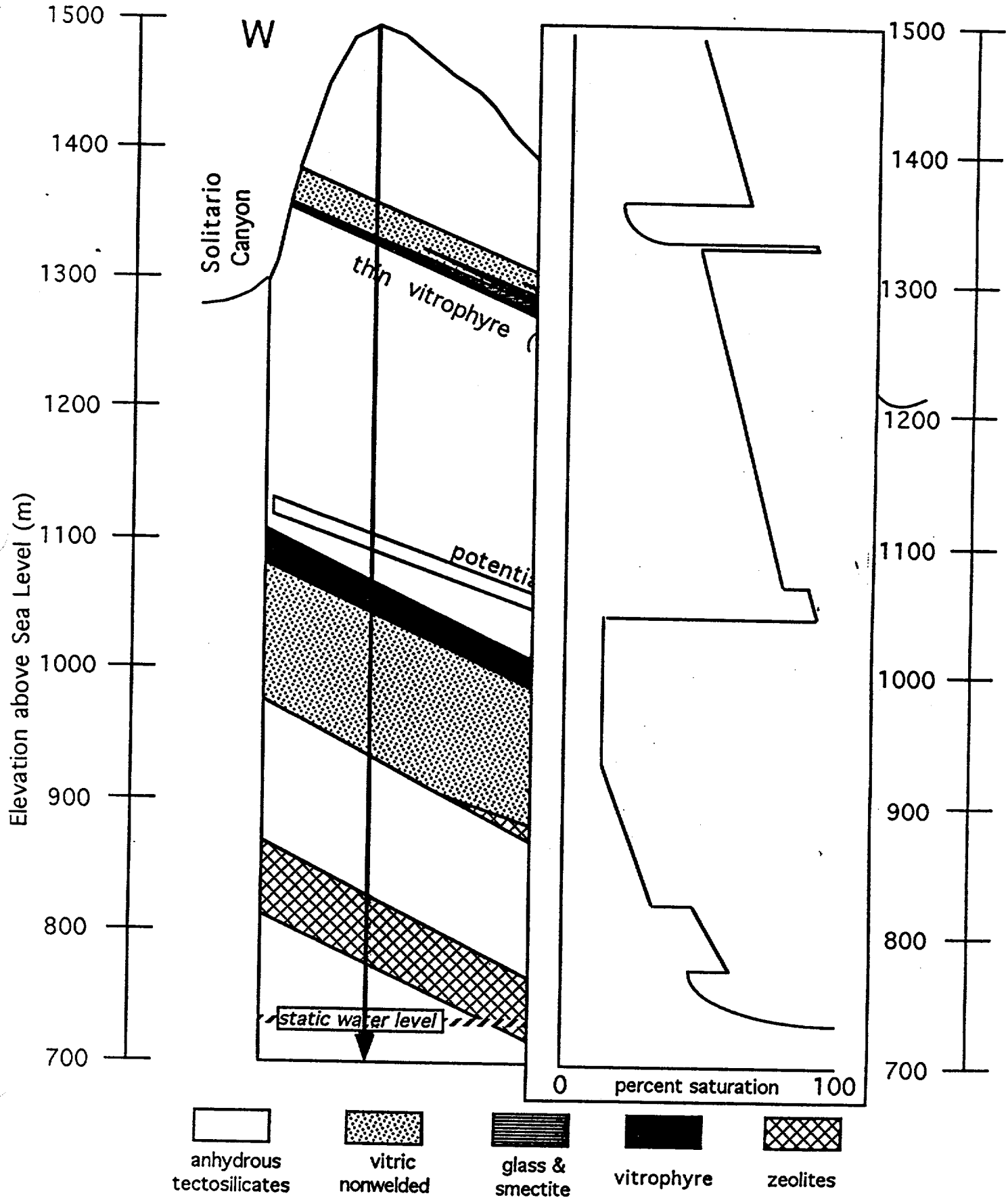
Los Alamos
NATIONAL LABORATORY
1943 - 1993

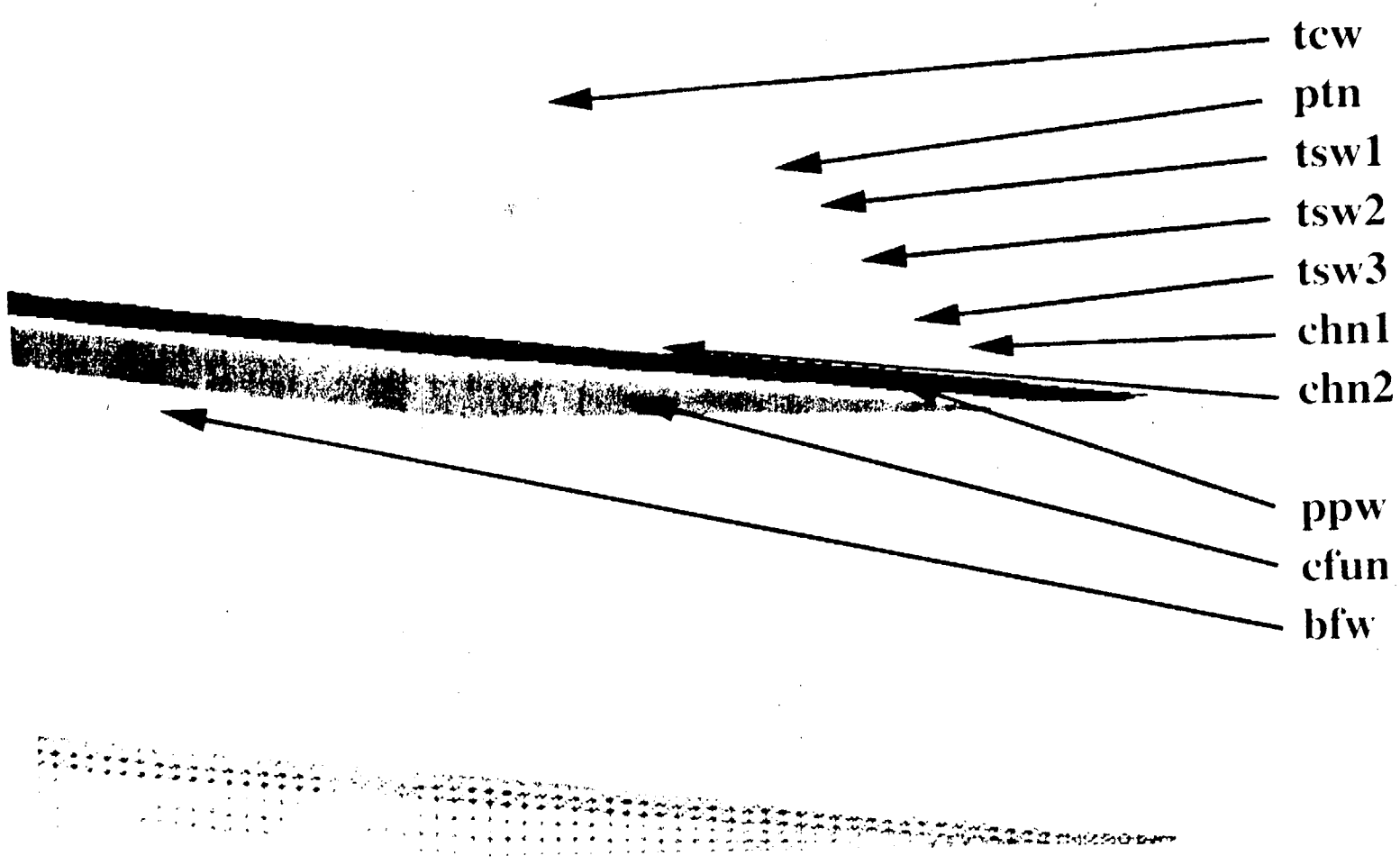
FLOW MODEL

- 76 m (250 ft) by 152 m (500 ft) plan view
- 35 vertical nodes (10 meters)
- 2 - phase flow
- Uniform flow (0.1 mm/yr)
- Finite element / finite volume

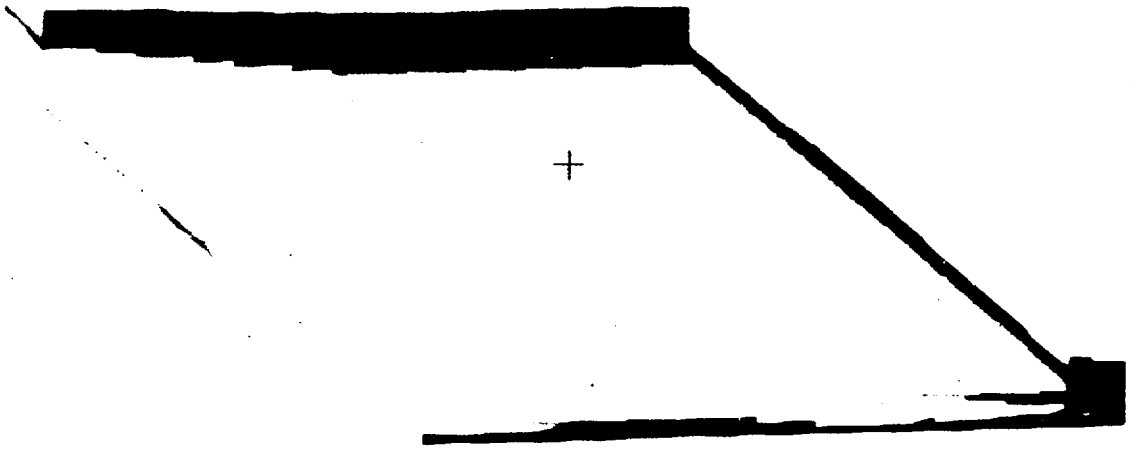
Fig. 3

CROSS-SECTION OF YUCCA MOUNTAIN ALONG ANTLER RIDGE
(5x vertical exaggeration)

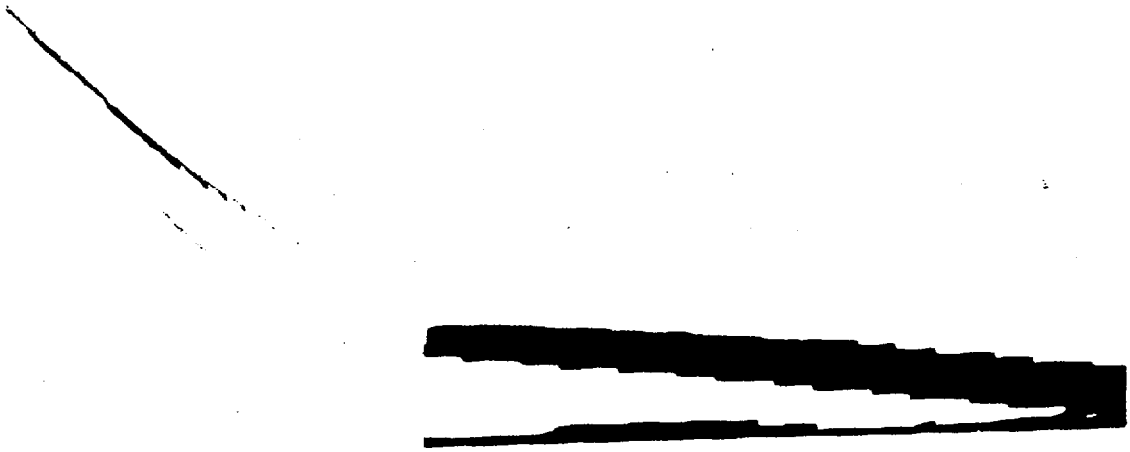




Yucca Mountian Stratigraphy and
Finite Element Mesh



Steady State Saturation Field



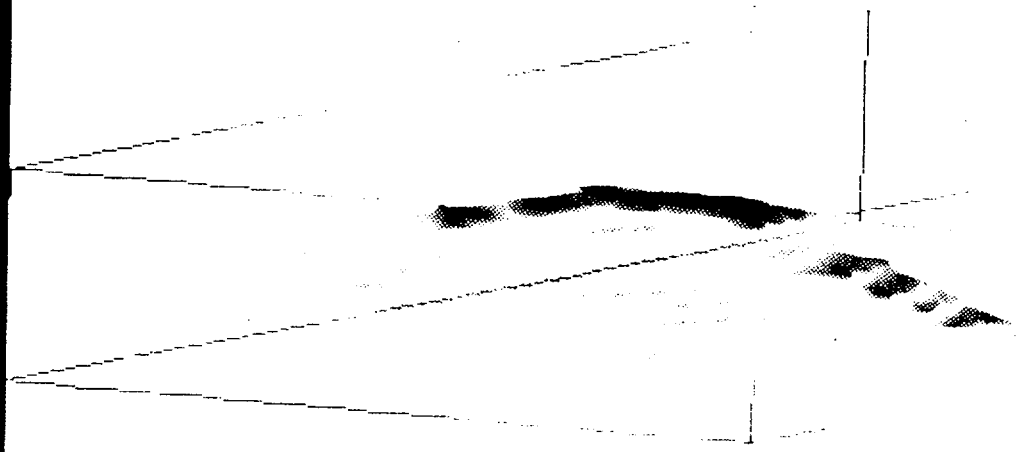
0.0 Saturation 1.0

CLEAR TOPPER

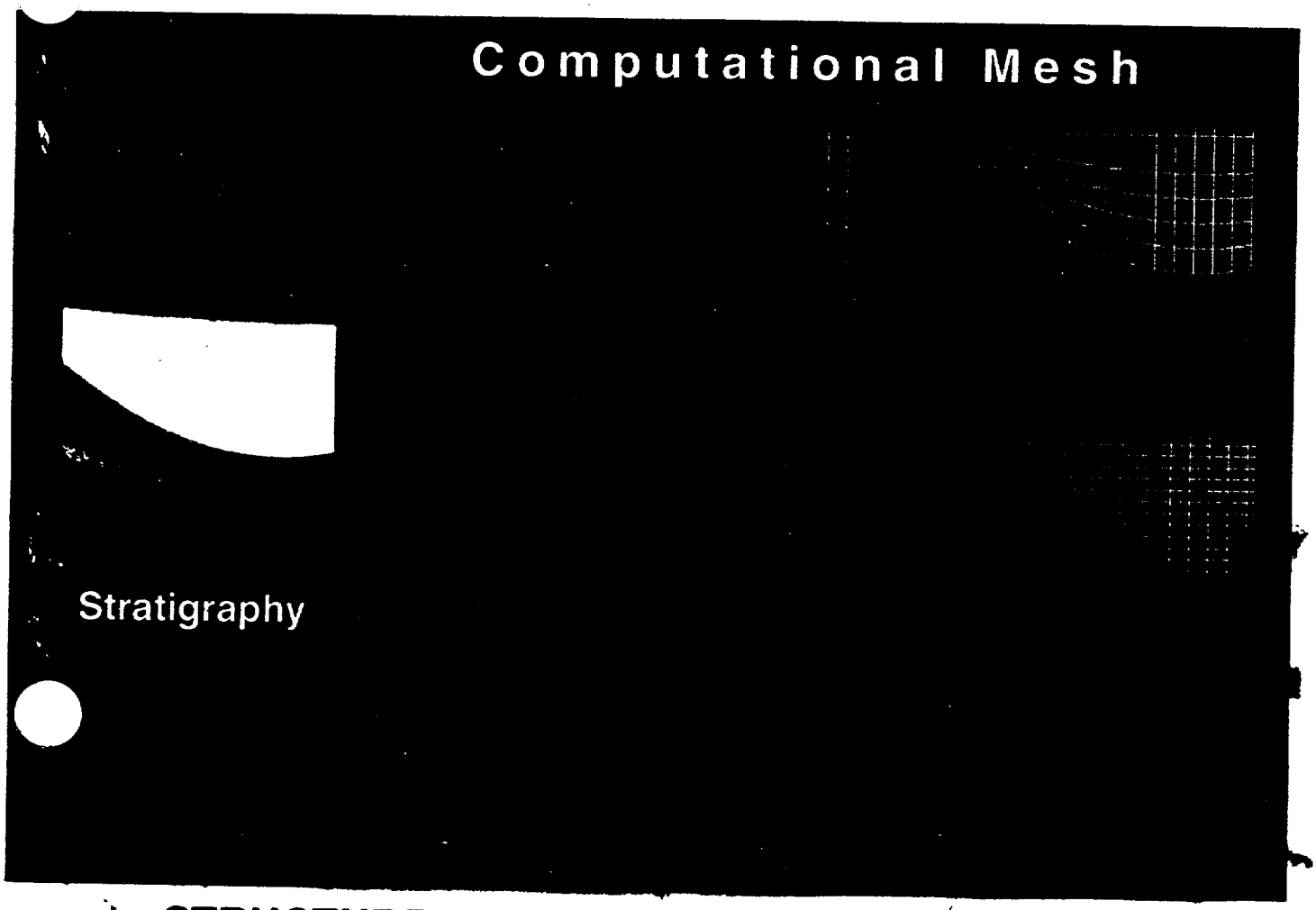
Concentration ([redacted]onditions)

Concentration (2500 Years)

Concentration ([redacted]l Conditions)



Concentration (10,000 Years)



STRUCTURED VERSUS UNSTRUCTURED GRID

Issues Affecting Radionuclide Transport -

1) ***Release rates***

2) ***Sorption***
   - ***Geochemistry***

3) ***Air flow (C^{14})***

4) ***Ground water flow***

IMPORTANT ISSUES FOR THE FUTURE

- **Distributed flow**
- **Model faults better**
- **Dual porosity/dual permeability**
- **Thermal repository**
  - **Affects gas and liquid flow**

TRANSPORT MODEL

- K_d values from PACE - 90
  - Radioactive decay
  - Coupled geochemistry
  - Gas phase tracers

DOE-NRC Technical Exchange Radionuclide Migration

International Programs

Robert S. Rundberg and David B. Curtis, LANL

Los Alamos

Np Sorption Onto Iron Oxides

NAGRA/USDOE TECHNICAL COOPERATIVE PROJECT

MECHANISTIC APPROACHES TO SORPTION

Objectives

1. Determine the mechanisms for adsorption of radionuclides onto minerals and rocks.

2. Indentify critical parameters affecting sorption in the field. These parameters can be mineral composition, pH, groundwater carbonate concentration, and cation composition.

3. Measure the adsorption isotherms for minerals and rocks. The reasons for measuring isotherms are twofold. One is to determine the limit of applicability of the linear isotherm (Kd concept). The other is to get insight into the mechanism.

4. Develop improved methods for characterizing mineral and rock surfaces

5. Develop a model that will predict radionuclide sorption under field conditions.

NEPTUNIUM (V) ADSORPTION ONTO GOETHITE AND HEMATITE

Robert S. Rundberg, Los Alamos National Laboratory

Yngve Albinsson, Chalmers University of Technology

Karl Vannerberg, Chalmers University of Technology

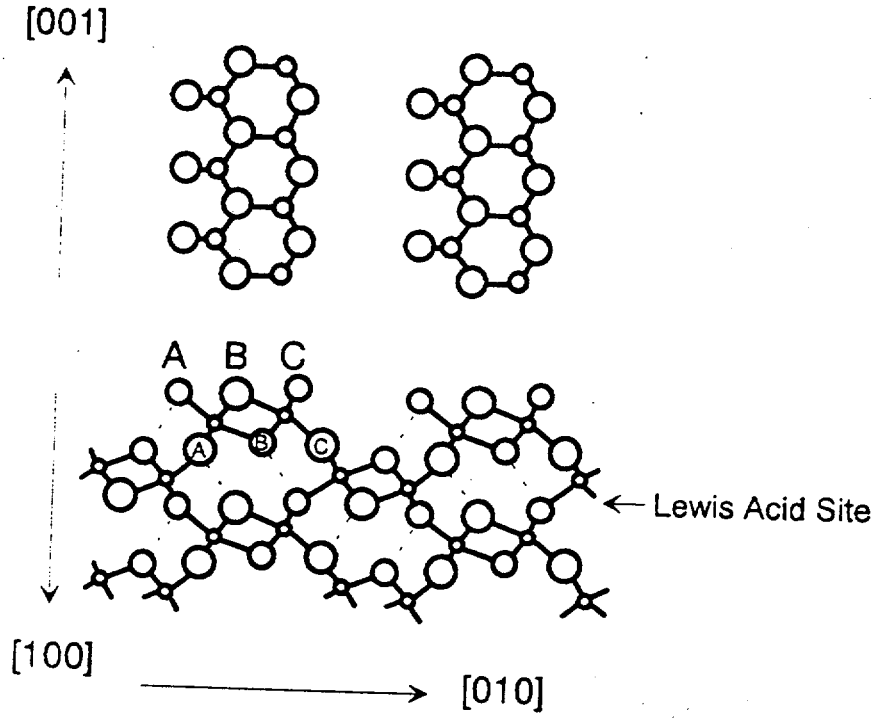
presented at ACTINIDES-93, Santa Fe, New Mexico
September 20, 1993

Definition of Sorption Coefficients

$$K_d = \frac{\text{Concentration in solid phase per unit mass}}{\text{Concentration in the aqueous phase}}$$

$$K_a = \frac{\text{Concentration in solid phase per unit area}}{\text{Concentration in the aqueous phase}}$$

Crystallographic Structure of Goethite Showing the A-type, B-type, C-type oxygens and Lewis Acid Site in the C plane..



EXPERIMENTAL

Preparation of Goethite, FeOOH

- Goethite was prepared according to a method of Atkinson et al. as described in more detail by Machesky and Anderson.
- The goethite was prepared from A.R. quality reagents using a OH/Fe ratio of 2 in the preliminary aging step.
- The goethite was repeatedly washed with >16 megaOhm water until the conductivity no longer decreased with further washing. The conductivity of the rinse water in the last washing was less than or equal to 30 microSiemens (measured with a Philips PW-9529 conductivity meter).
- The N_2 BET surface area was 76.2 m^2/g. Suspensions were prepared as needed from freeze-dried solid.

Preparation of Hematite, Fe_2O_3

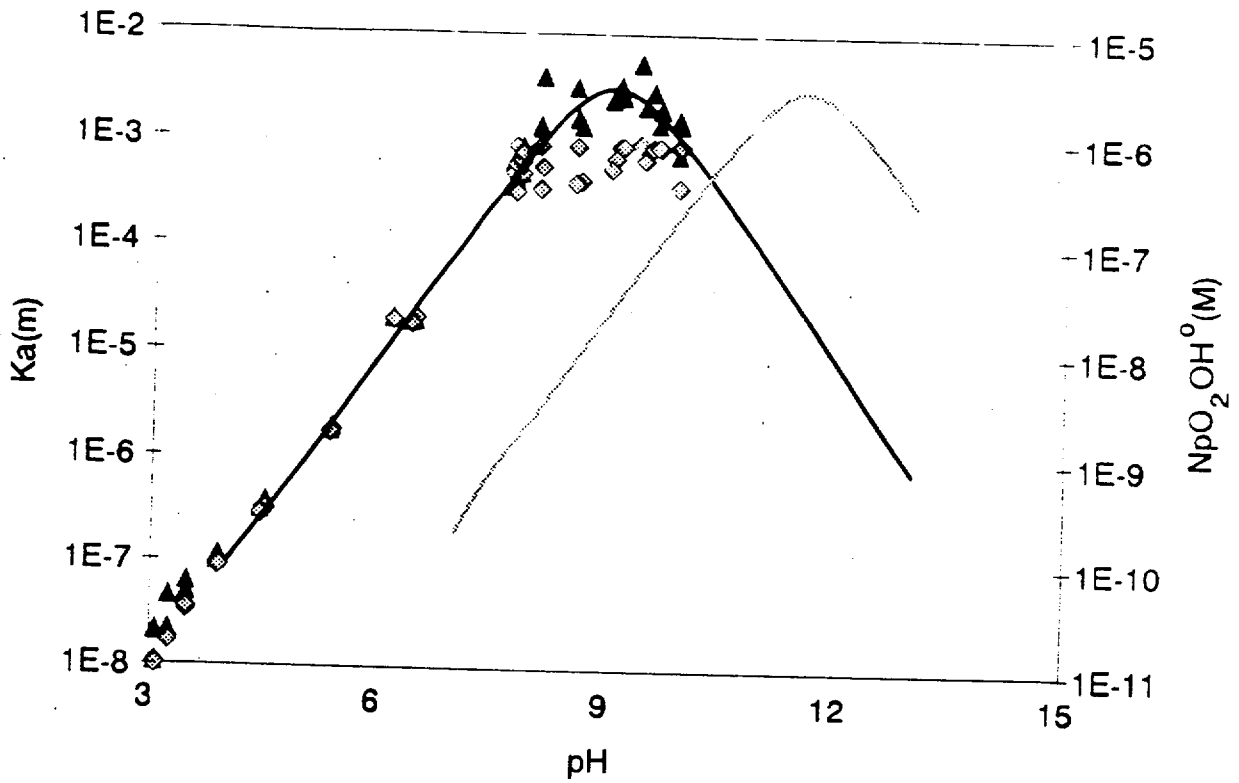
- The hematite was analytical reagent grade Fe_2O_3 (Merck).
- The N_2 BET surface area was 3.8 m^2/g.

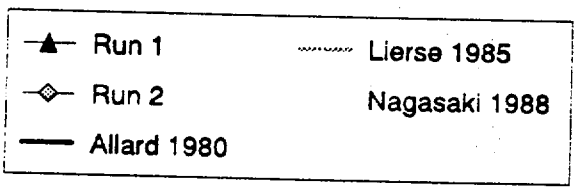
EXPERIMENTAL

- A 0.5 M stock solution of ^{237}Np was prepared by dissolving Neptunium in 1 M $HClO_4$. A secondary stock solution was prepared by diluting with deionized water to 5×10^{-4} M. Each sample was prepared by adding 0.2 ml of the secondary stock to 10 ml of emulsion.

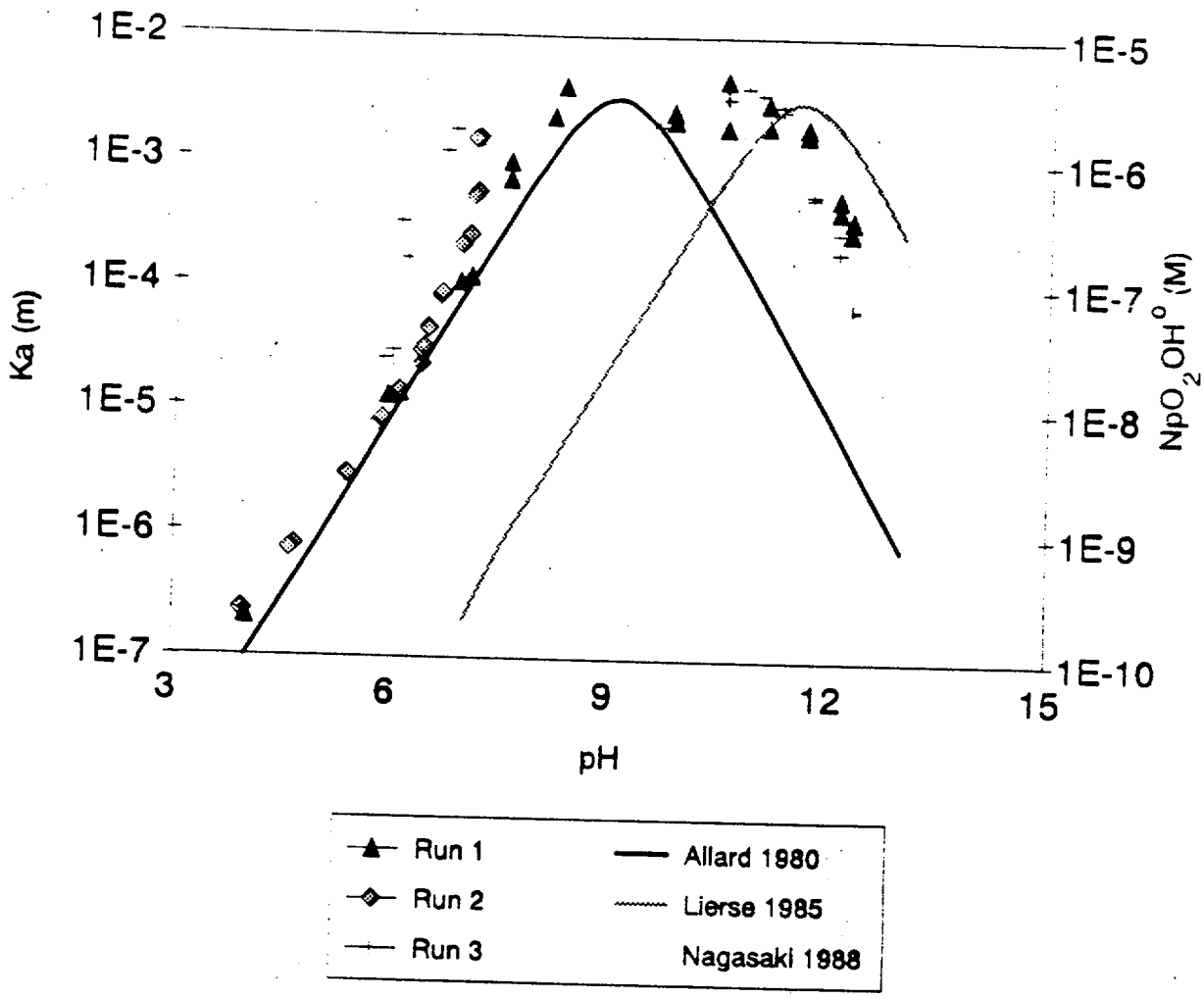
- The sorption measurements were made holding electrolyte concentrations to 0.01M or 0.10 M with sodium perchlorate.
- The pH was adjusted by adding perchloric acid or sodium hydroxide.
- The suspensions were made to a concentration of 0.2 grams of goethite per 10 ml.
- The solutions were contacted with goethite in hermetically sealed vials for 2 days before phase separation. The solid phase was separated by centrifugation at 12000 RPM for 1 hour using a Beckman model J2-21 centrifuge with a type JA-20.1 rotor.
- The aqueous phase was sampled by taking a 1 ml aliquot immediately after centrifugation. Solution concentrations were determined by liquid scintillation counting
- The ^{237}Np alpha activity was determined by setting a energy window on the liquid scintillation counter discriminating nearly all of the beta activity from the ^{233}Pa daughter of ^{237}Np.
- The measurements were checked by measuring the ^{233}Pa activity using a gamma counter after 6 months to ensure that secular equilibrium was established.

Np(V) Sorption onto Goethite, 0.01M $NaClO_4$

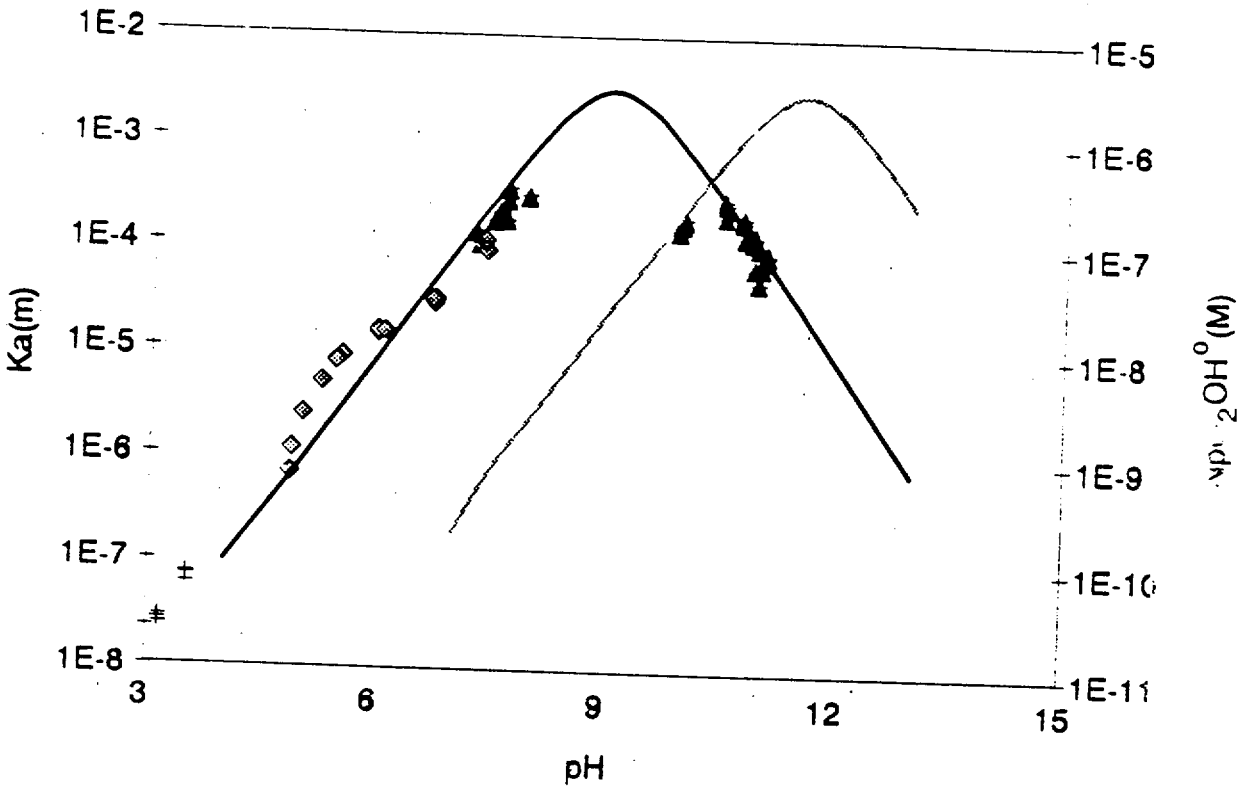




Np(V) Sorption onto Goethite, 0.10 M $NaClO_4$

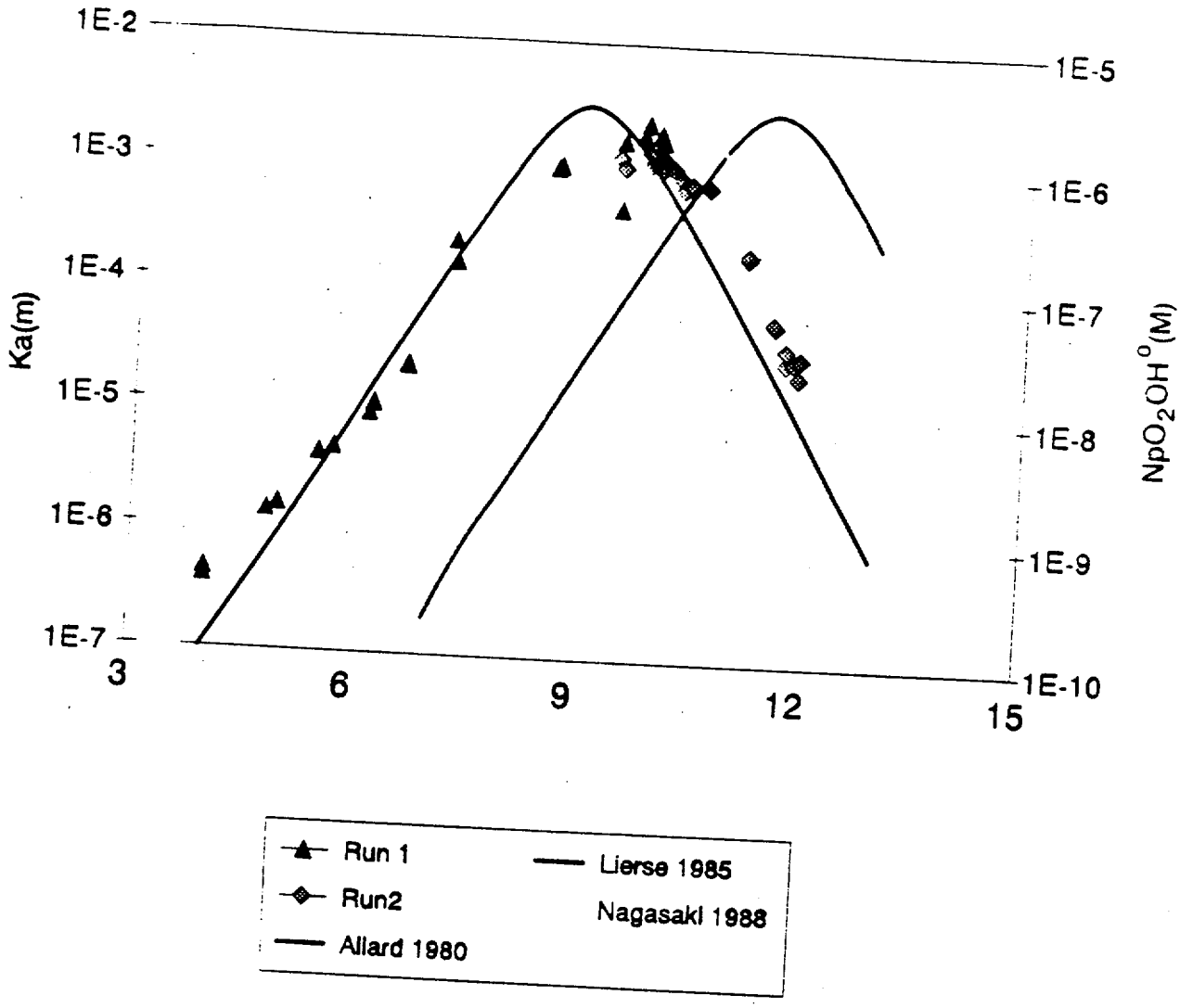


Np(V) Sorption onto Hematite, 0,01 M $NaClO_4$



Run 1	Allard 1980
Run 2	Lierse 1985
Run 1x	Nagasaki 1988

Np(V) sorption onto hematite



The hydrolysis constants listed are defined as follows:

$$\beta_i = \frac{[NpO_2(OH)_i^{2-i}]}{[NpO_2^{+}][OH^-]}$$

Hydrolysis Constants used in EQ3 calculations

Reference	log β_1	log β_2
Allard 1980	5.1±0.8	(10±2)[a]
Lierse 1985	2.3±.6	4.89±0.05
Nagasaki 1988	6.0	9.9

EQ3 fixed input parameters

Parameter	Input Value
Temperature	25 C
log (O2 fugacity)	-.6794
$[NpO_2^+]$	1.0 x 10-5 M
[Na+]	0.01, 0.1 M
$[ClO_4^-]$	0.01, 0.1 M

[a] Estimated

Langmuir Adsorption Isotherm

$$q = \frac{KQ_{max}c}{c_s + (K-1)c}$$

$$K_d = \frac{q}{c} = \frac{KQ_{max}}{c_s + (K-1)c} \cong \frac{KQ_{max}}{1 + Kc}$$

Langmuir Adsorption Constant for NpO_2OH

	K' (m^3/mole)
Goethite, 0.01M $NaClO_4$	3108
Goethite, 0.1M $NaClO_4$	12870
Hematite, 0.01M $NaClO_4$	7136
Hematite, 0.1M $NaClO_4$	4437
Average	7000 ±3000

CONCLUSIONS

- Neptunium (V) adsorption onto iron oxides does not depend electrolyte concentration
- Neptunium (V) adsorption onto iron oxides goes an inner sphere surface complexation mechanism
- The magnitude of the sorption coefficient, K_a, does not depend strongly on the crystal structure of the oxide.
- The sorption coefficient is inversely proportional to the hydrogen ion concentration suggesting neptunyl hydrolysis is involved.
- There are discrepancies in the neptunyl hydrolysis stability constants between potentiometric titrations and solubility measurements. This disagreement makes the interpretation of the surface complexation mechanism equivocal.

Application of Neptunyl Surface Complexation Data to Tuff and J-13 ground water

Predictions of Neptunium(V) Sorption onto Tuff

Data

Iron Content ~ 1%
pH ≈ 8.4
Alkalinity ≈ 1.0 e -3 M
Estimated crystal size of oxide = 0.01 to 1 micrometer

Calculation

Iron oxide surface area = 0.011- 1.1 m^2 / g tuff

EQ3NR calculations for J-13 water

	$NpO_2OH(aq)$	NpO_2^+	Ka	Kd
pH 6.3	0.2331E-07	0.9896E-05	6.5 E-6	0.07 - 7.2
pH 6.8	0.7230E-07	0.9706E-05	2.0 E-5	.22 - 22
pH 7.8	0.5794E-06	0.7779E-05	1.6 E-4	1.8 - 180
pH 8.4	0.1423E-05	0.4799E-05	4.0 E-4	4.4 - 440
pH 8.9	0.2293E-05	0.2445E-05	6.8 E-4	7.5 - 750

Measured Ka/Kd in J-13 (Triay et al., Thomas, and Schroeder and Meijer)

	pH	Ka	Tuff	pH	Kd
Goethite	7.1	6.0 E-5	Zeolitic	8.4	6
	8.5	1.5 E-3		6.5	7
Hematite	7.1	9.2 E-5	Devitrified	8.5	2
	8.5	3.5 E-4		8.3	.5

Predicted Neptunyl Adsorption with a CO_2 Atmosphere

Conditions	pH	Ka measured[1] (m)	Ka predicted (m)
Hematite 2% CO_2	7.0	9.0 E-5	8.9 E-5
	7.5	2.1 E -4	1.9 E-4
	8.0	1.6 E-4	9.7 E-5
	8.5	6 E-5	7 E-7
	9.0	2 E -7	1 E-10
Hematite .03% CO_2	7.0	9.0 E-4	9.4 E -5
	7.5	4.9 E -4	2.9 E -4
	8.0	6.9 E -4	8.1 E -4
	8.5	>7.0 E-4	1.4 E -3
	9.0	>7.0 E-4	6.1 E -4

[1] Kohler, Honeyman and Leckie

RESULTS OF NEPTUNIUM SORPTION ON TUFFS TREATED WITH THE BORGAARD METHOD

Sample	Dithionite + EDTA		EDTA		Untreated	
G1-1941	3.62	3.15	7.69	7	1.8	1.9
G4-270	1.3	1.55	0.38	1.51	0	0.2
G2-770			1.17	1.39	0.2	-0.1
G4-1067	2.94	2.84	3.3	3.09	0.2	0.4
G4-1506	11.17	9.73	7.29	6.21	3.9	3.6
G2-1813	5.93	6.14	1.7	1.35	1	1
YM-22	2.43	2.75	2.23	1.84	0.4	0.5
G1-1271			13.76	4.99	1	0.1

Triple Layer Model of Surface Complexation

I. Site activation

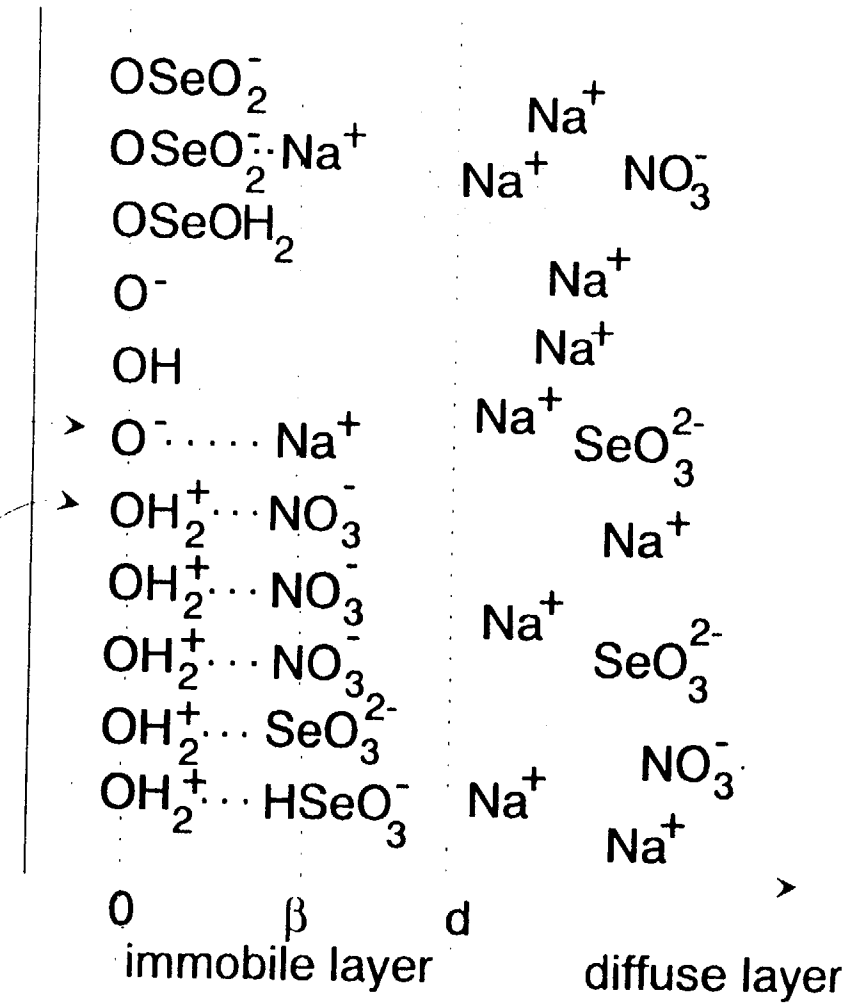
$$SOH_2^+ \overset{K_1}{\rightleftharpoons} SOH + H^+_{(s)}$$

$$SOH \overset{K_2}{\rightleftharpoons} SO^- + H^+_{(s)}$$

II. Surface Complex formation

$$SO^- + Na^+_{(s)} \overset{K^{int}_{Na^+}}{\rightleftharpoons} SO^- \; Na^+$$

$$SOH_2^+ + NO^-_{3\,(s)} \overset{K^{int}_{NO_3^-}}{\rightleftharpoons} SOH_2^+ \; NO_3^-$$



Triple Layer Model Capacitance

Gouy-Chapman Double Layer

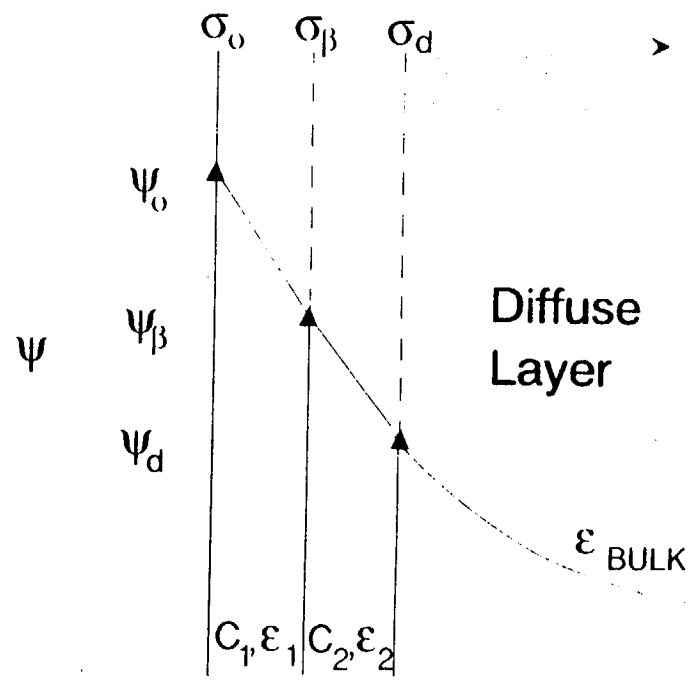
$$\sigma_d = -11.74C^{1/2}\sinh\left(\frac{ze\,\psi_d}{2kT}\right)$$

Concentrations in double layer

$$[H^+]_s = [H^+]\exp(-e\psi_o/kT)$$

$$[Na^+]_s = [Na^+]\exp(-e\psi_\beta/kT)$$

$$[NO_3^-]_s = [NO_3^-]\exp(+e\psi_\beta/kT)$$



Equations Which Comprise the Surface Complexation Model

1. $$K_{a1}^{int} = \frac{[SOH][H^+][\exp(-e\psi_0/kT)]}{[SOH_2^+]}$$

2. $$K_{a2}^{int} = \frac{[SO^-][H^+][\exp(-e\psi_0/kT)]}{[SOH]}$$

3. $$^*K_{Na}^{int} = \frac{[SO^-\text{-}Na^+][H^+]\exp[e(\psi_\beta - \psi_0)/kT]}{[SOH][Na^+]}$$

4. $$^*K_{Cl^-}^{int} = \frac{[SOH][H^+][Cl^-]\exp[e(\psi_\beta - \psi_0)/kT]}{[SOH_2^+ - Cl^-]}$$

5. $$\sigma_d = -11.74\, C^{1/2} \sinh\left(\frac{ze\psi_d}{2kT}\right) \mu C/cm^2$$

Equations Which Comprise the
Surface Complexation Model

6. Mass Balance

$$N_s = B\,([SOH_2^+] + [SOH_2^+\text{-}Cl^-] + [SOH] + [SO^-] + [SO^-\text{-}Na^+])$$

7. Charge and Charge Balance

$$\sigma_0 = B\,([SOH_2^+] + [SOH_2^+\text{-}Cl^-] + [SO^-] + [SO^-\text{-}Na^+])$$

$$\sigma_\beta = B\,([SO^-\text{-}Na^+] + [SOH_2^+\text{-}Cl^-])$$

$$\sigma_0 + \sigma_\beta + \sigma_d = 0$$

8. Charge and Capacitance

$$\psi_0 - \psi_\beta = \sigma_0 / C_1$$

$$\psi_\beta - \psi_d = -\sigma_d / C_2$$

Cation Exchange

Consider the general case of cation B, valence Z_B, in the aqueous phase exchanging with cation A, valence Z_A, bound to the clay mineral surface, the exchange reaction can be written as follows:

$$z_B \cdot A\text{-}Clay + z_A \cdot B \rightleftarrows z_A \cdot B\text{-}Clay + z_B \cdot A \qquad (5a)$$

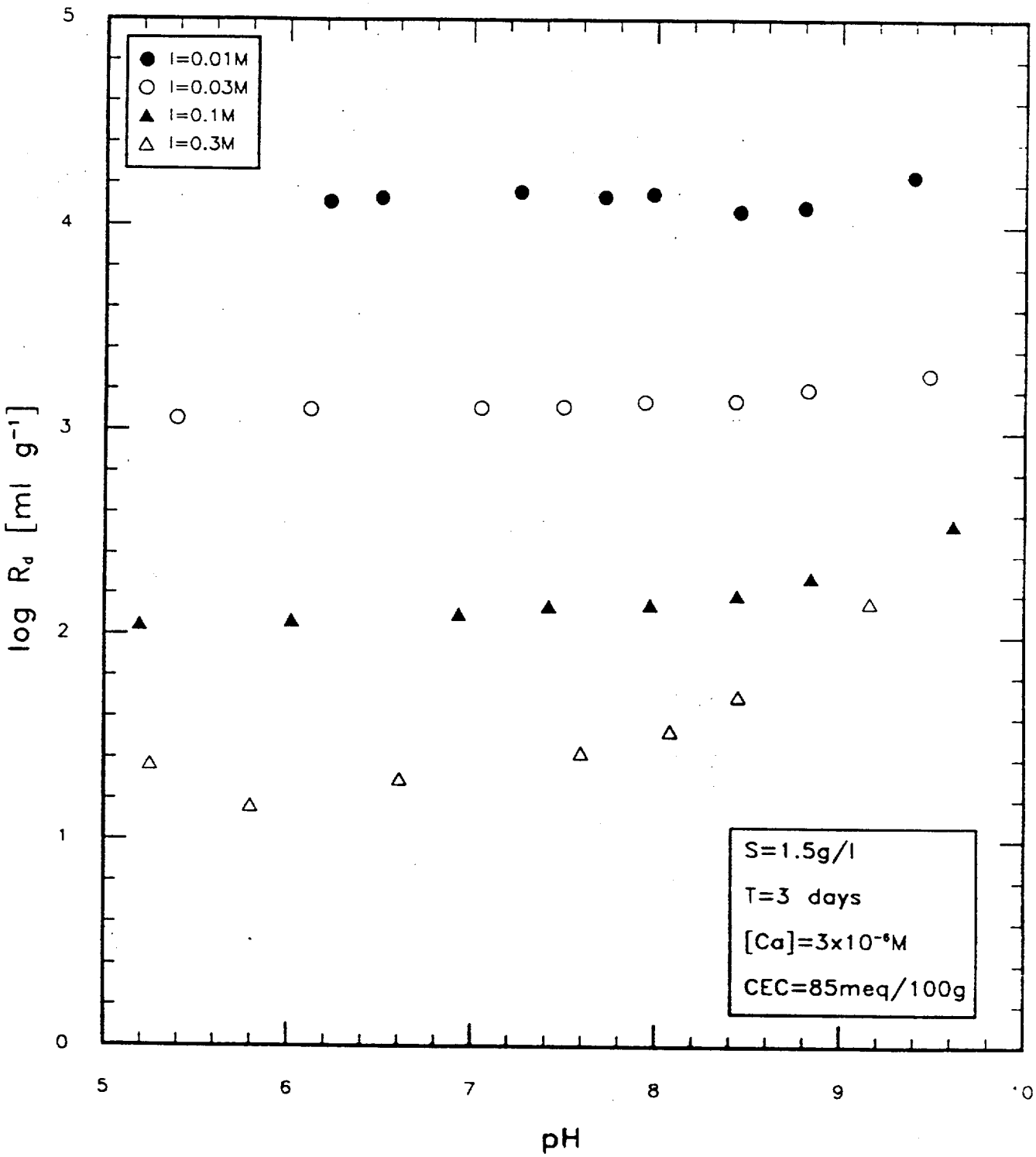
$$ {}^{B}_{A}K_C = \frac{N_B^{Z_A}}{N_A^{Z_B}} \cdot \frac{a_A^{Z_B}}{a_B^{Z_A}} \qquad (5b)$$

a_A and a_B are the solution activities of nuclides A and B, respectively. N_A and N_B are equivalent fractional occupancies defined as the equivalents of A (or B) sorbed per unit mass divided by the cation exchange capacity, in equivalents per unit mass.

ENTSORGUNG

Ca sorption on Na-montmorillonite

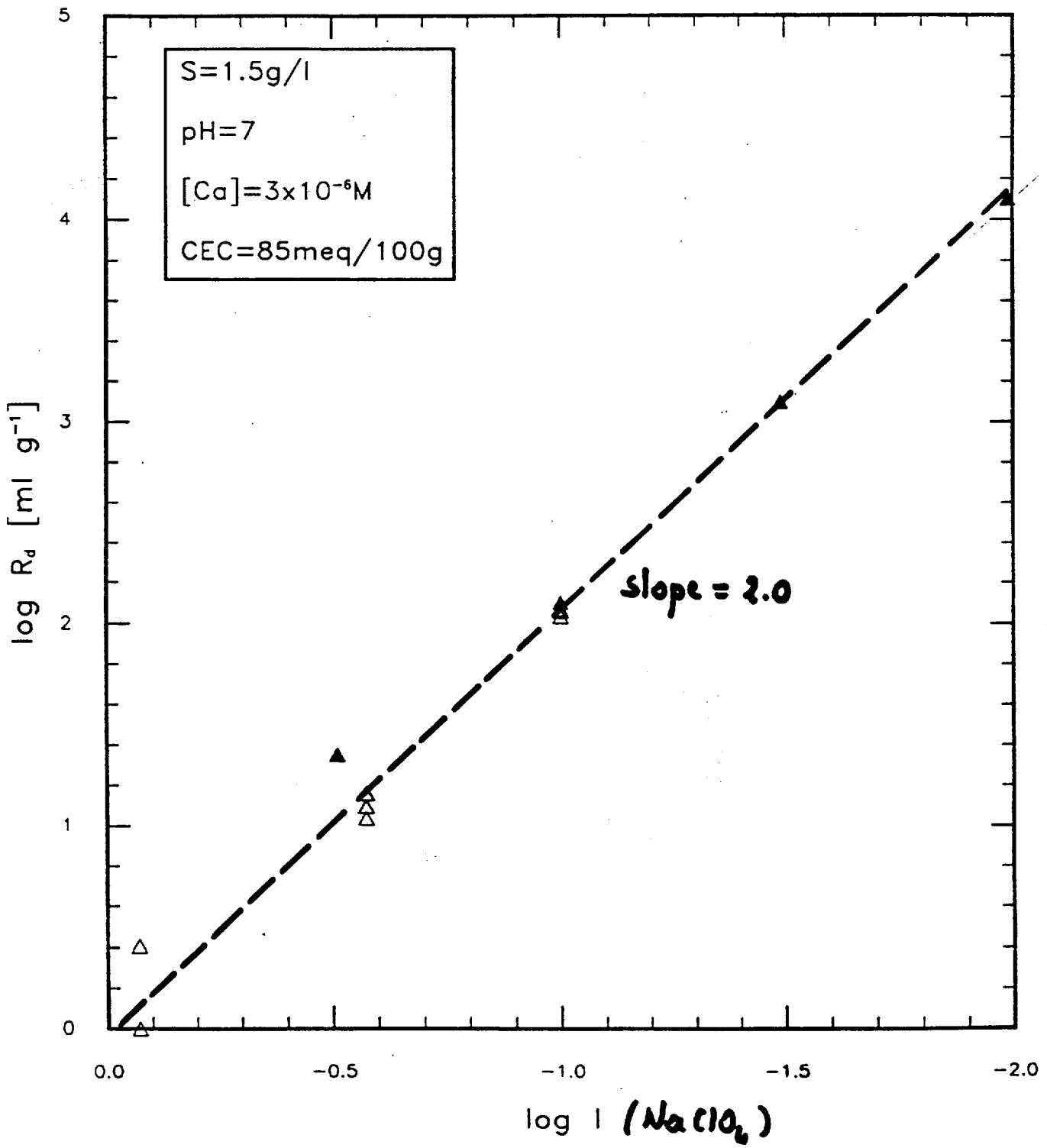
Effect of ionic strength and pH



ENTSORGUNG

Ca sorption on Na–montmorillonite

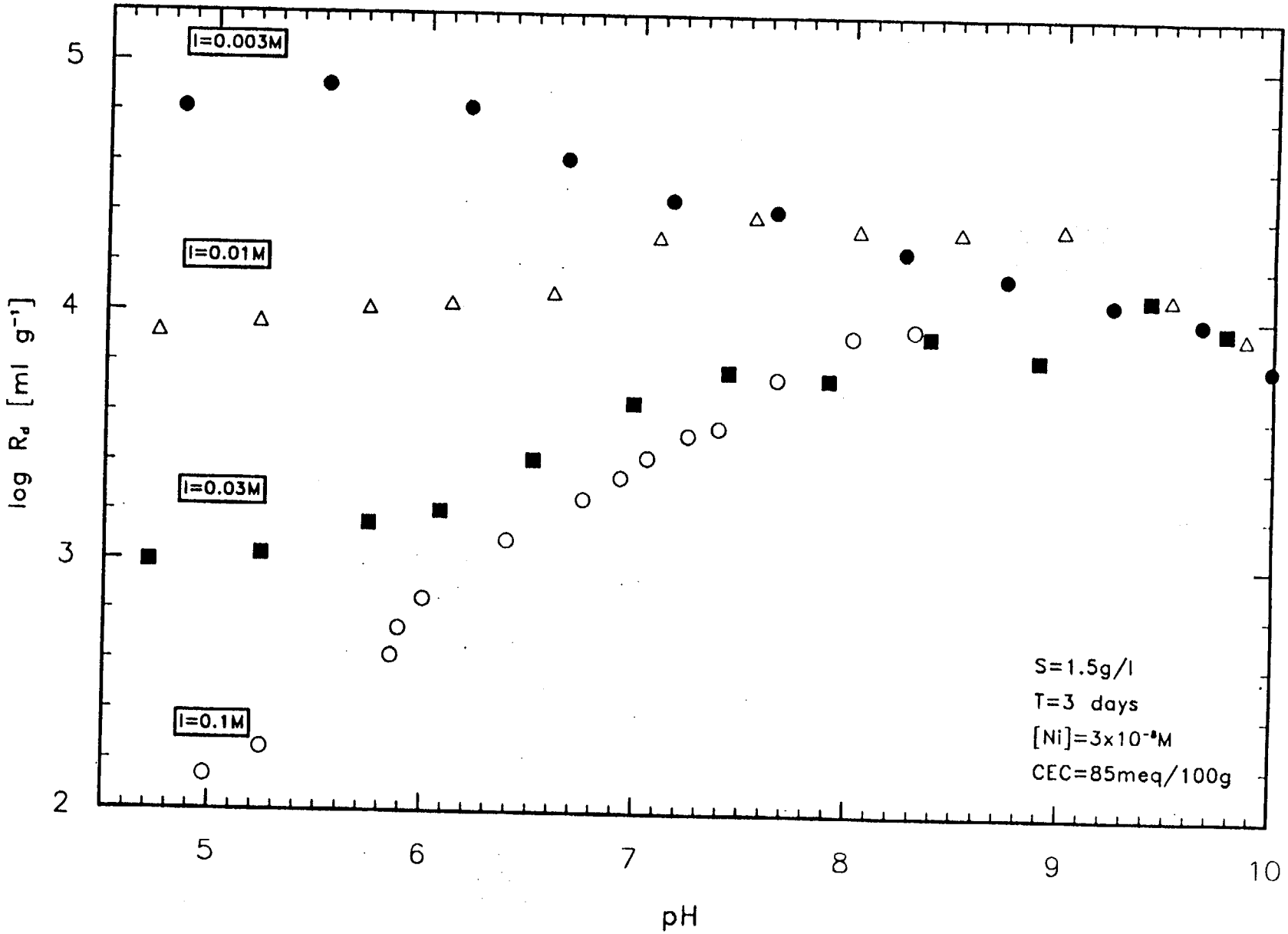
Effect of ionic strength at fixed pH



ENTSORGUNG

Ni sorption on Na-montmorillonite

Effect of ionic strength and pH

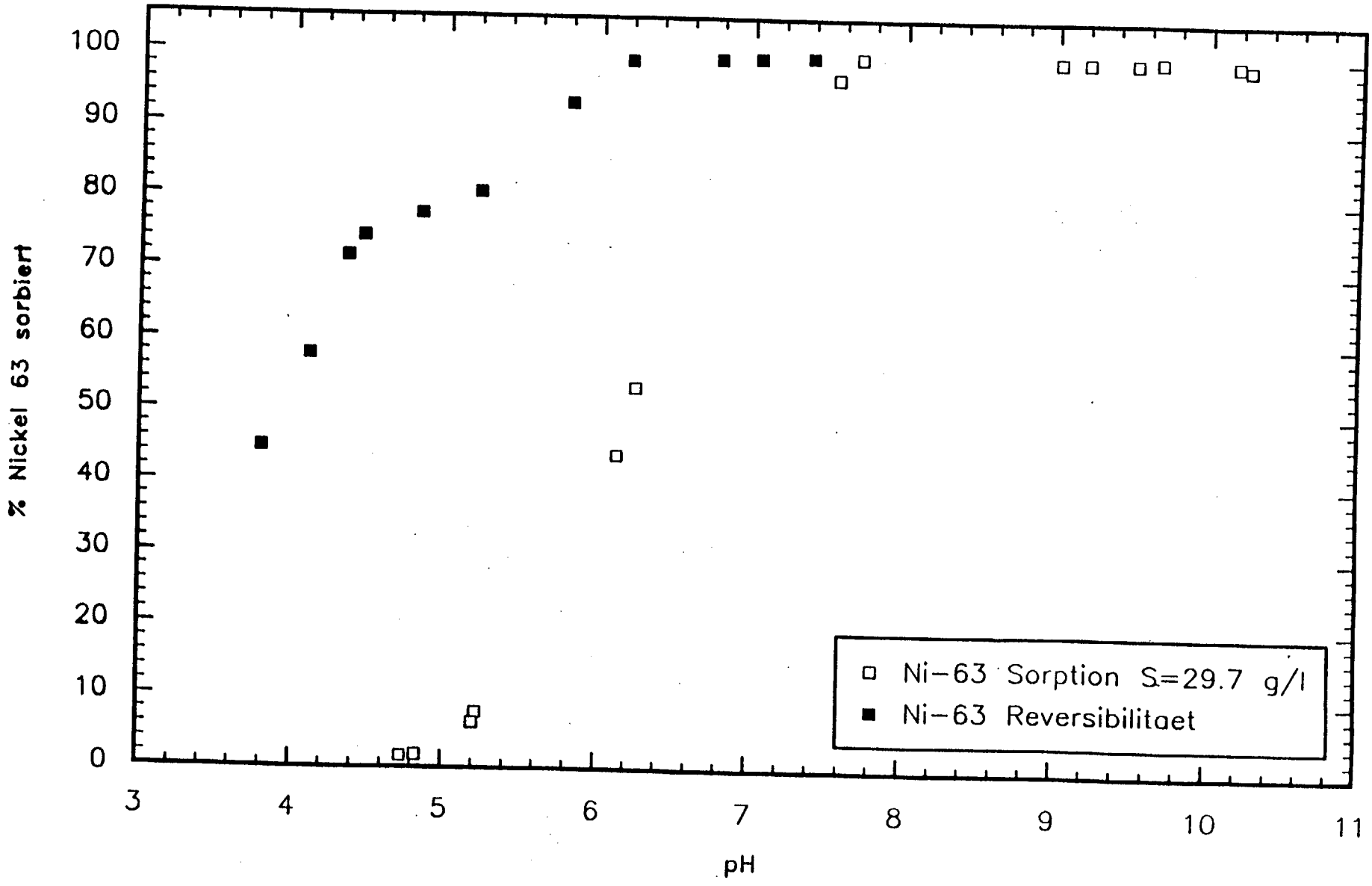


NI2.PIC

HOTLABOR

Sorption und Reversibilitaet von Ni-63 auf Mylonit

NiTOT=5*10^{-6}M Zeit: 21 Tage



rever.plc

CONCLUSIONS

- Neptunium sorption ratios for zeolitic tuff increase after treatment with EDTA and increase still further with dithionite + EDTA. This suggests either opening of detritus plugged channels and/or removal of competing species (i.e., calcium and rare earths)

- Neptunium sorption ratios for zeolitic tuff do not exhibit a pH dependence consistent with surface complexation.

- Some devitrified tuffs exhibit an increase in Kd with EDTA stripping and a decrease with the dithionite + EDTA treatment. This suggests both removal of competing species and removal of surface complexation site.

- The adsorption of Np in tuffs cannot be attributed to iron oxides alone.

- Iron oxides appear to be passivated in Yucca Mountain tuffs.

- The method of iron oxide extraction alone is not adequate to determine the mechanism of Np sorption in tuff.

- Competetive isotherms similar to those done under the NAGRA program should be applied to actinide adsorption in tuff.

K&M Company PO
Torrance, CA 90503 # P

NATURAL NUCLEAR REACTION PRODUCT GEOCHEMISTRY

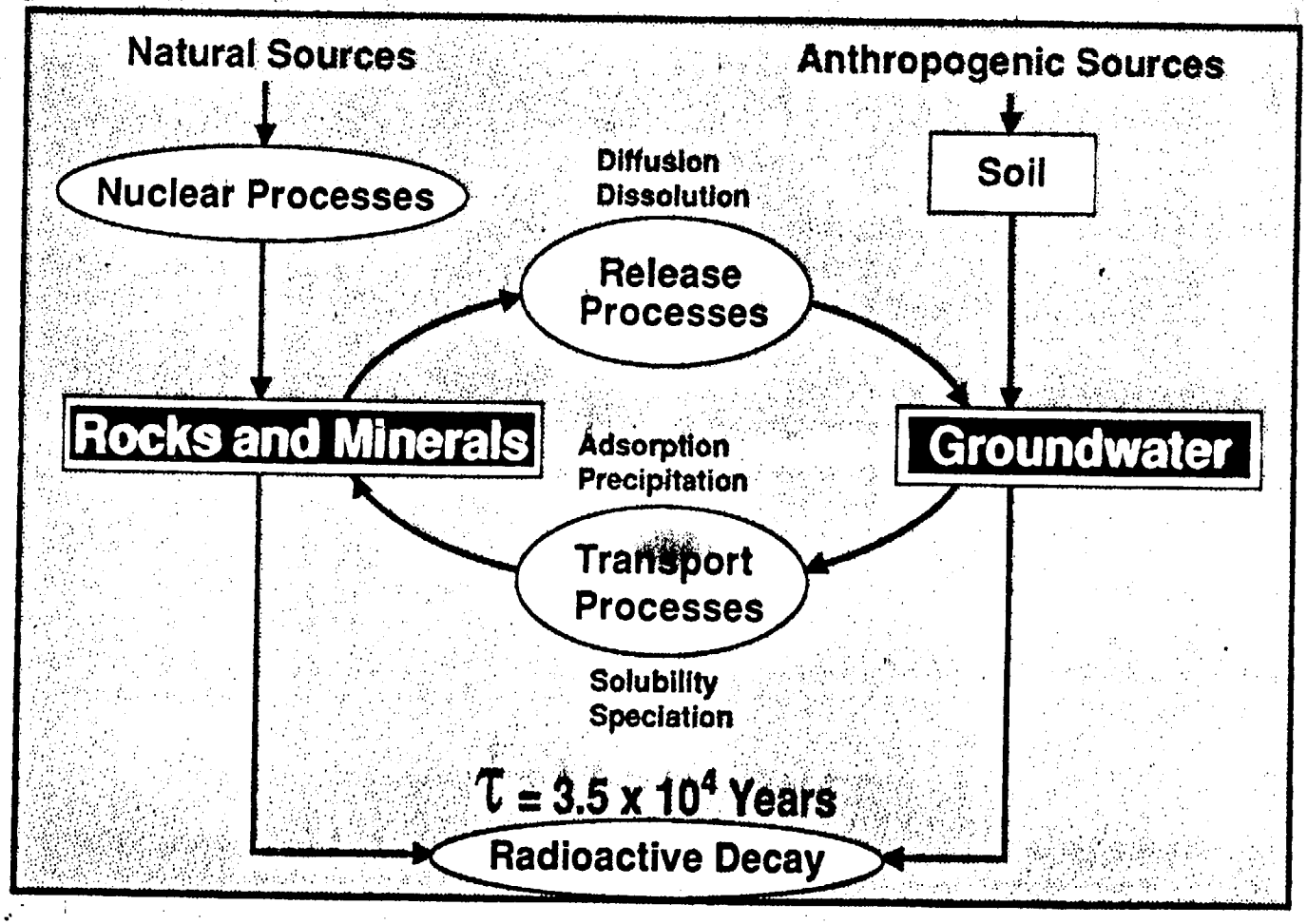
Natural Analogue Project Consortium

Presented by
David B. Curtis

ATOMIC ENERGY OF CANADA LTD.
AUSTRALIAN NUCLEAR SCIENCE & TECHNOLOGY ORG.
LOS ALAMOS NATIONAL LABORATORY
LAWRENCE LIVERMORE NATIONAL LABORATORY
UNIVERSITY OF ROCHESTER

512/92/21-DO

Actinide and Fission-Product Geochemical Cycle



NATURAL NUCLEAR REACTION PRODUCT GEOCHEMISTRY

Objective:

Characterize the timing, rates, and chemical effects of processes affecting radionuclide release, transport, and retention in geologic systems.

K&M Company POLY-VU
Torrance, CA 90503 # PV119G

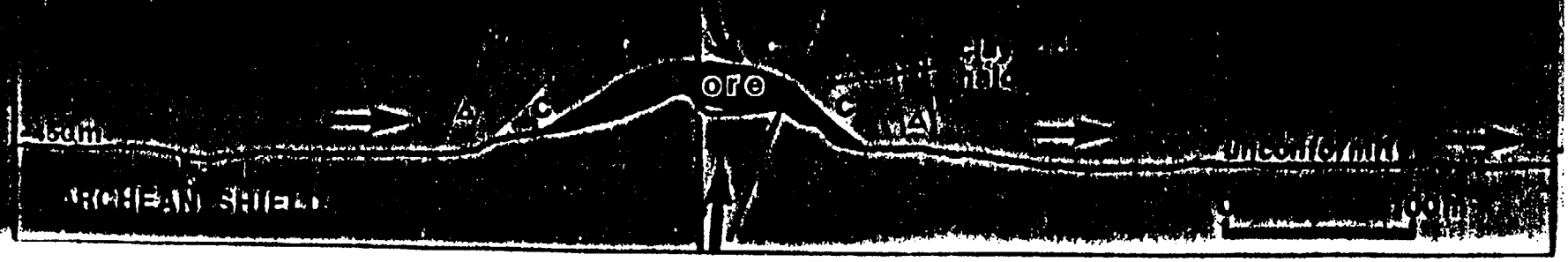
NUCLEAR PRODUCTION OF RADIONUCLIDES

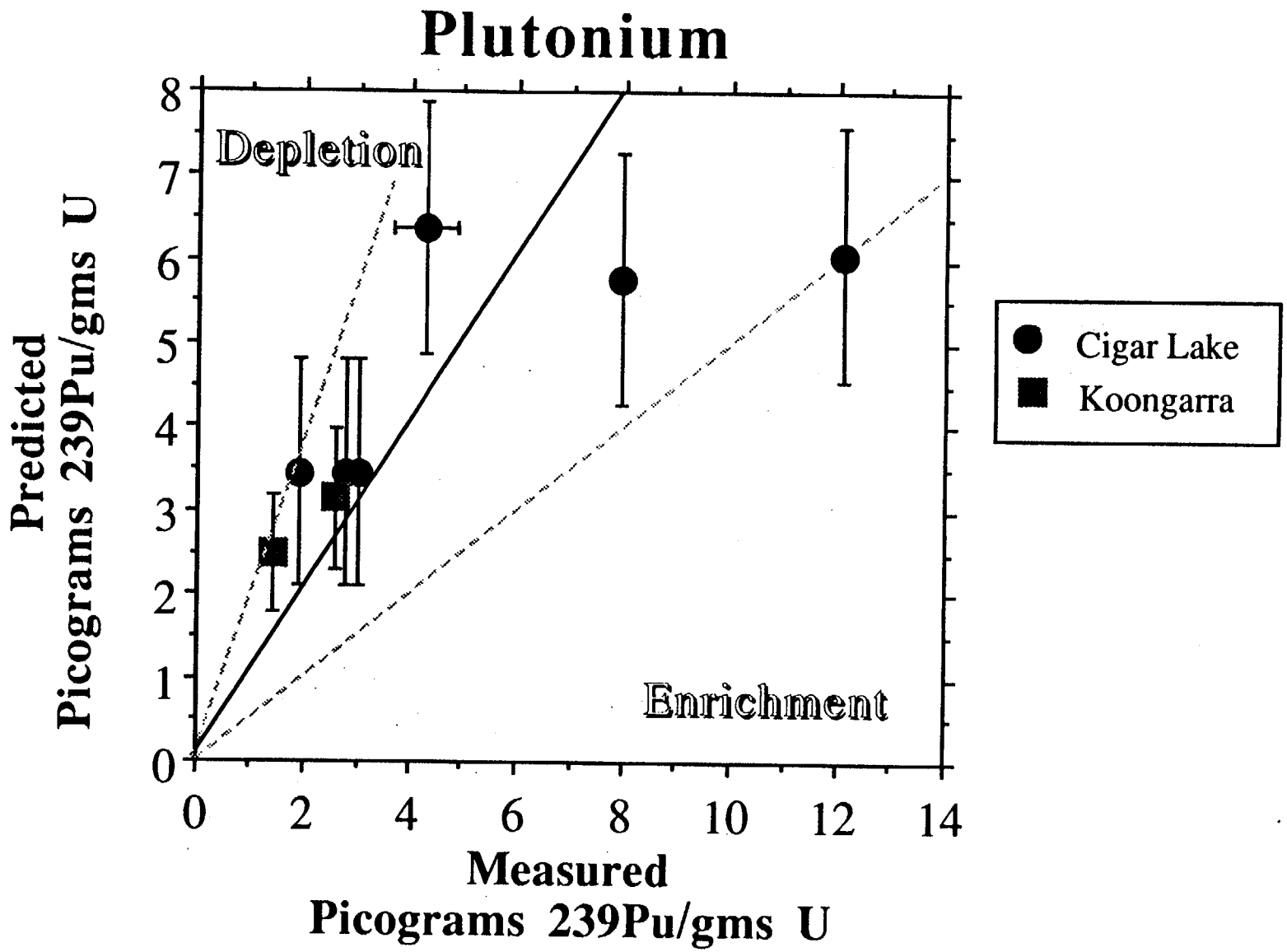
Uranium $\xrightarrow{\text{Fission}}$ $^{99}Tc + {}^{129}I$ $\xrightarrow{\text{Decay}}$

Uranium $\xrightarrow{\text{Neutron Capture}}$ ^{239}Pu $\xrightarrow{\text{Decay}}$

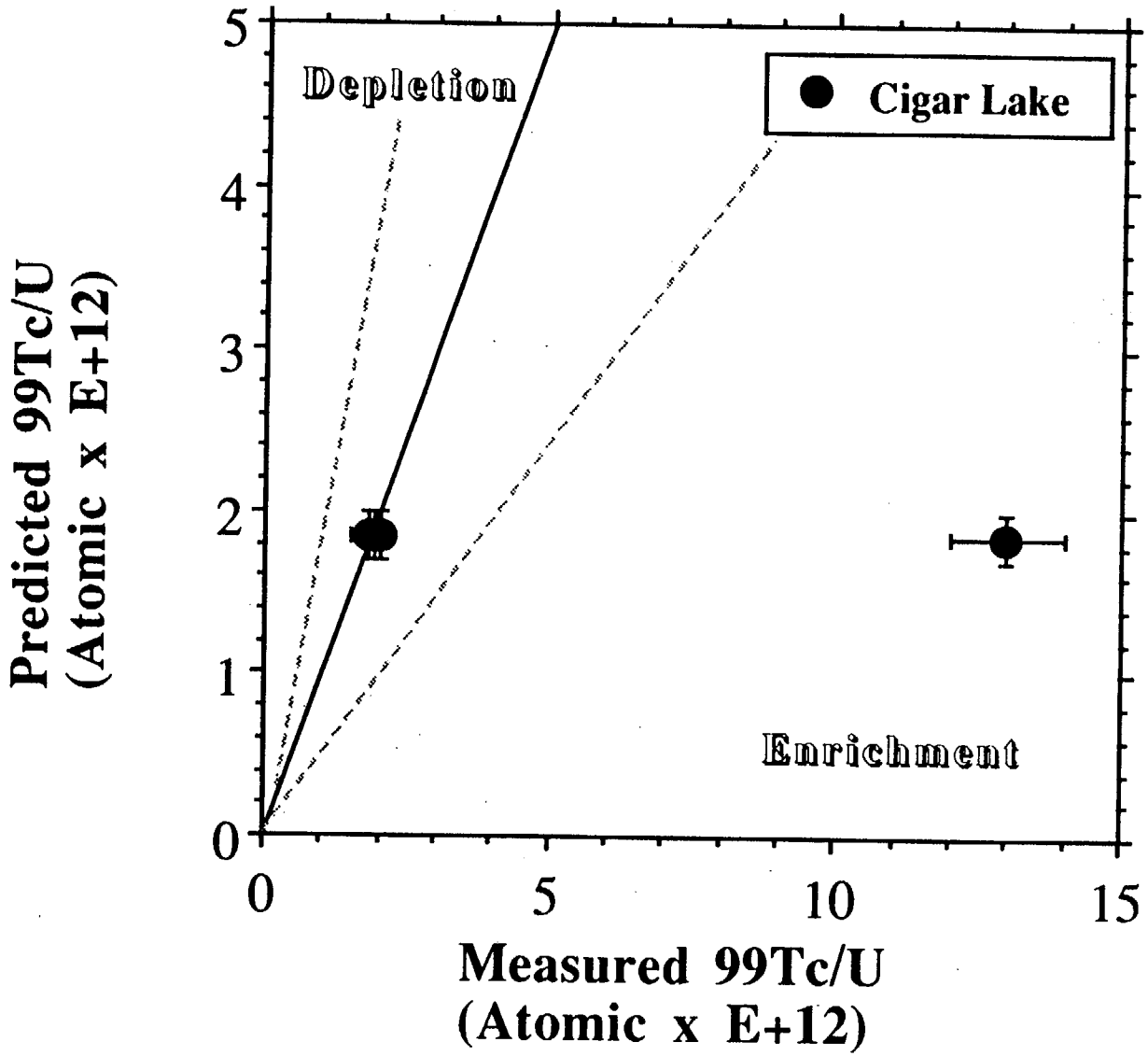
$$\alpha \text{ (Disequilibrium Factor)} = \frac{(\text{Daughter/Parent})_{\text{Meas}}}{(\text{Daughter/Parent})_{\text{Equil}}}$$

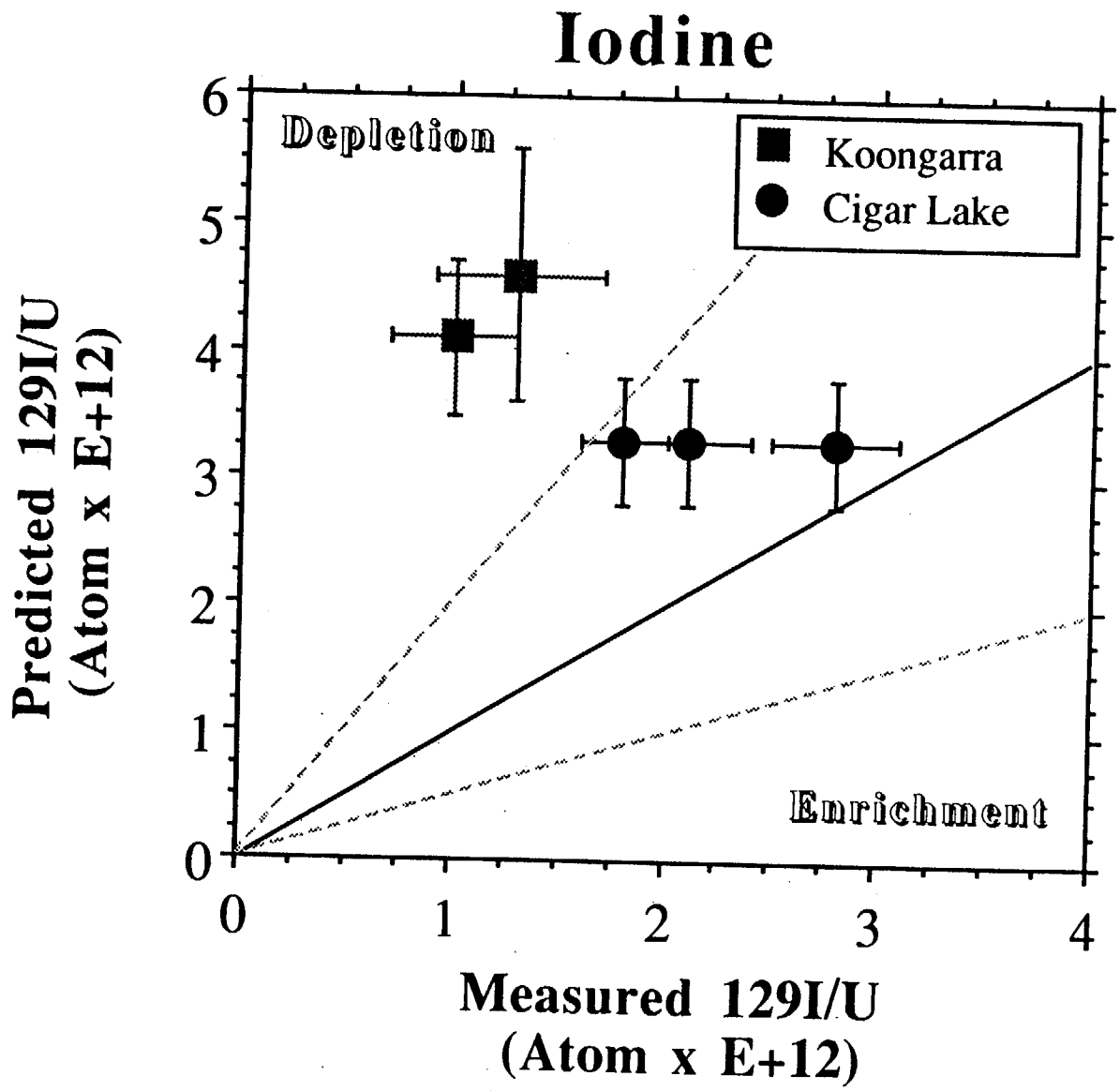
CLEAR LAKE U DEPOSIT

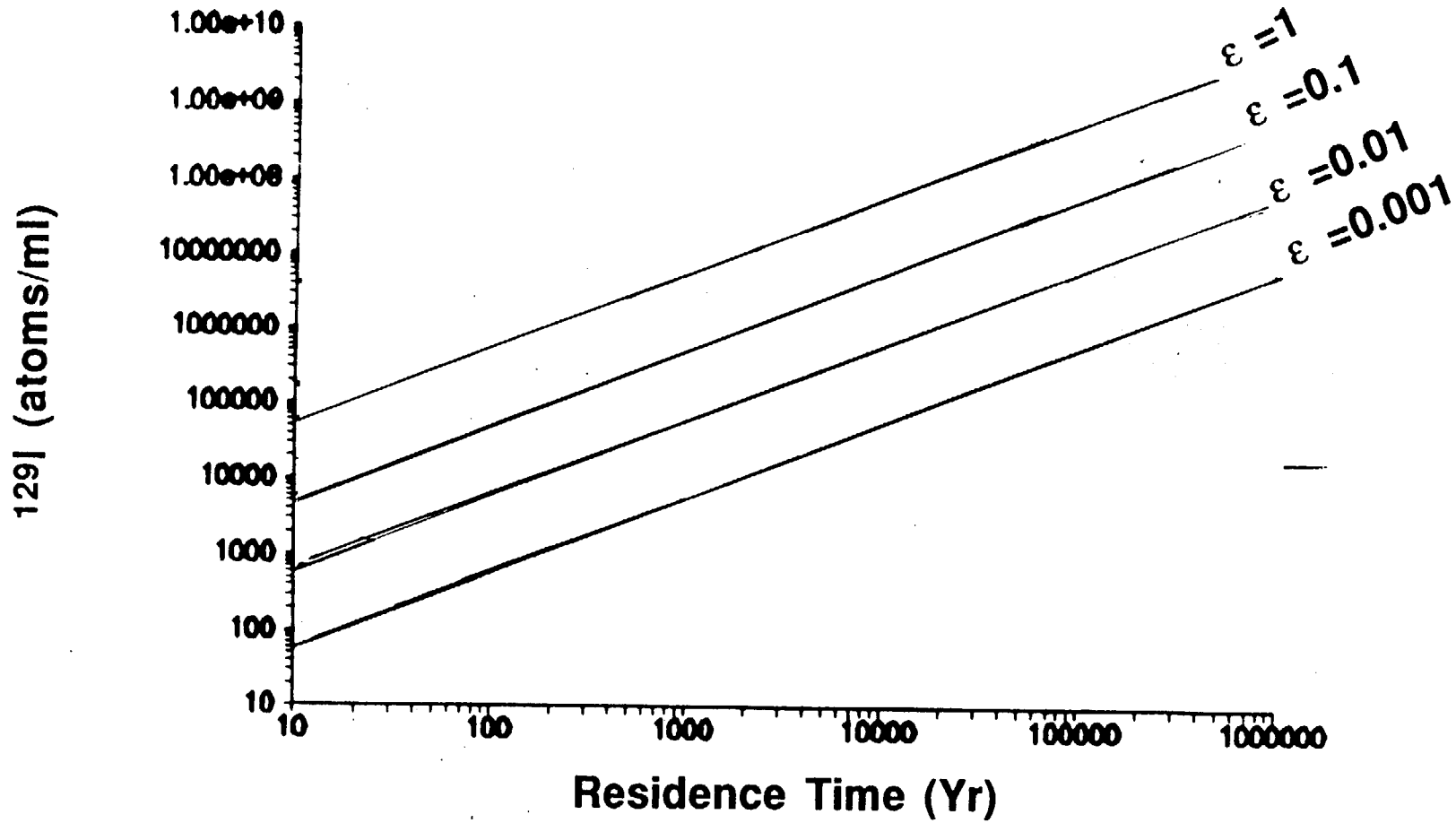



Plutonium
Depletion
Enrichment
Predicted
Picograms 239Pu/gms U
Measured
Picograms 239Pu/gms U
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
Cigar Lake
Koongarra

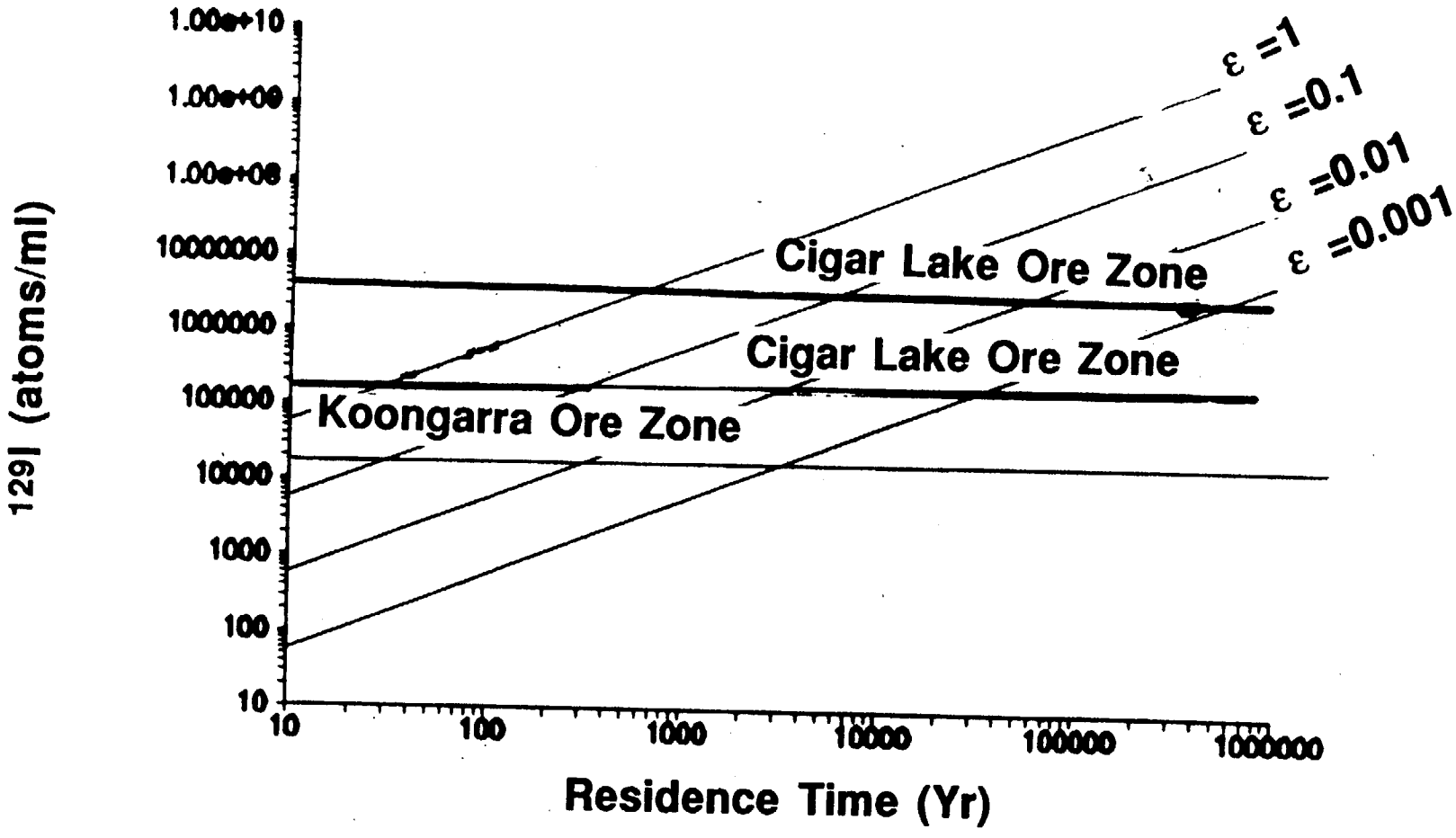
TECHNETIUM


Depletion
Cigar Lake
Enrichment
Predicted 99Tc/U
(Atomic x E+12)
Measured 99Tc/U
(Atomic x E+12)
0
1
2
3
4
5
0
5
10
15

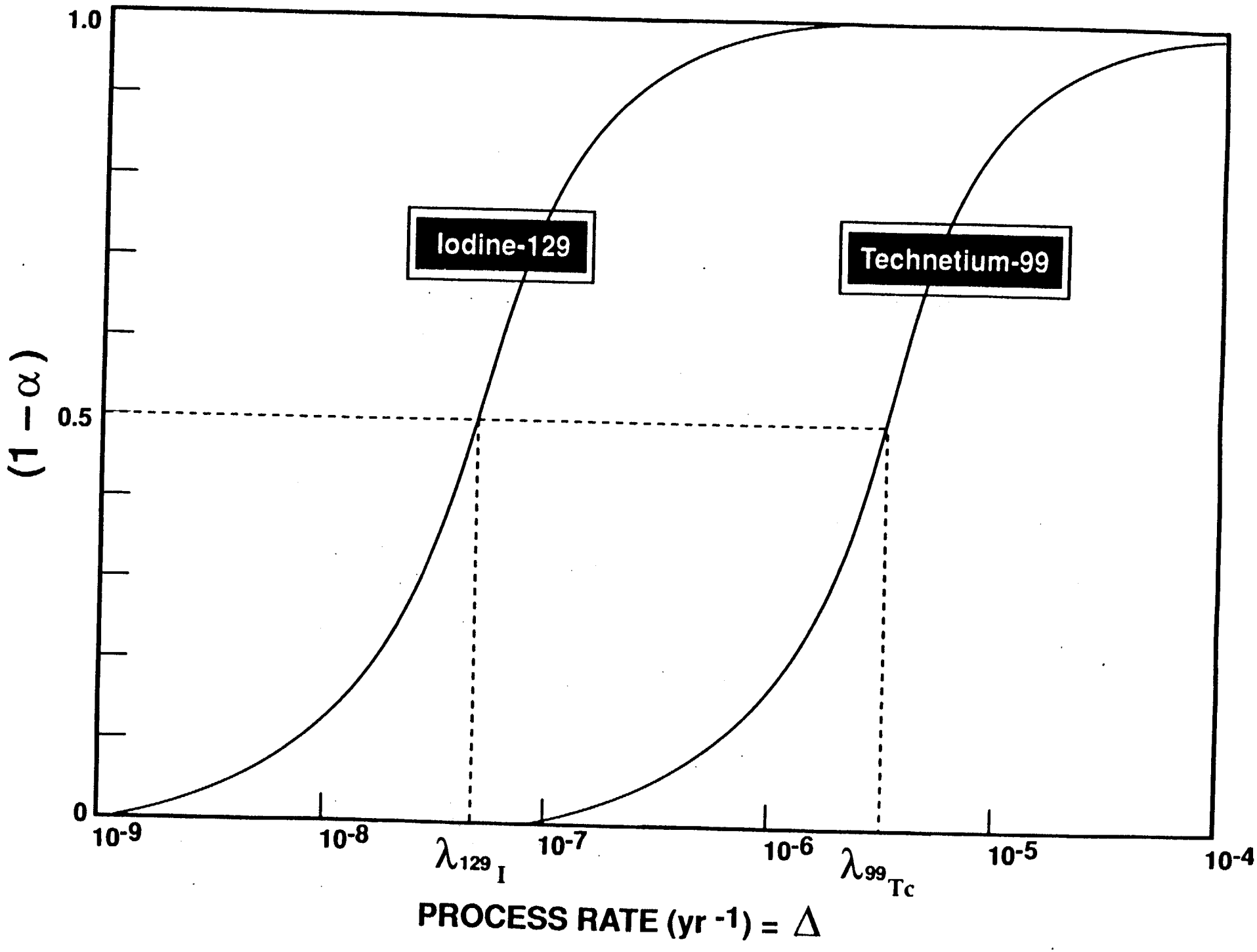

Iodine
Depletion
Enrichment
Koongarra
Cigar Lake
Predicted 129I/U
(Atom x E+12)
Measured 129I/U
(Atom x E+12)
0
1
2
3
4
5
6

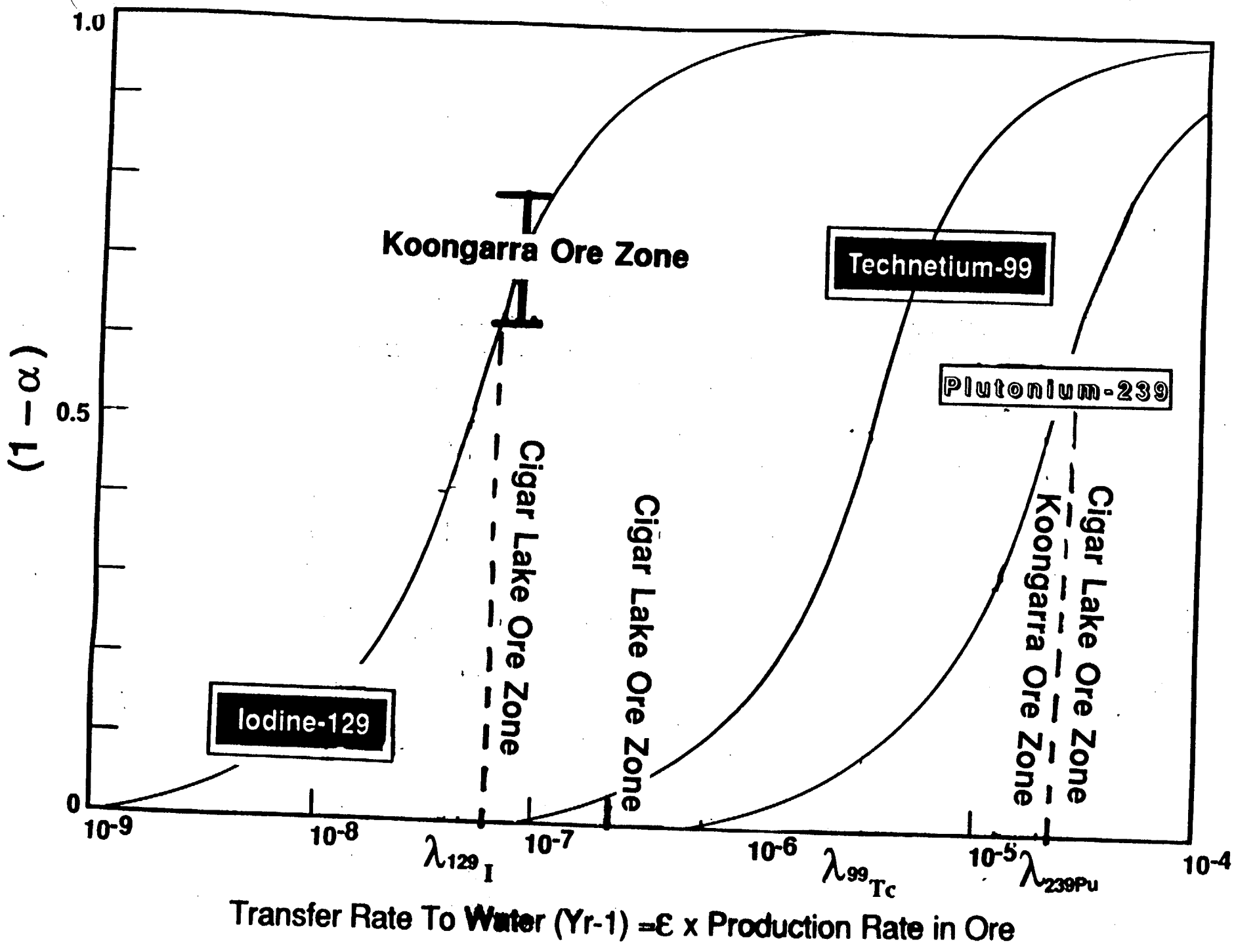


Emanation Rate (ε) =Transfer Rate to Water/Production Rate in Ore



Emanation Rate (ε) =Transfer Rate to Water/Production Rate in Ore


1.0
0.5
0
(1 − α)
Iodine-129
Technetium-99
10-9
10-8
λ129 I
10-7
10-6
λ99 Tc
10-5
10-4
PROCESS RATE (yr -1) = Δ


1.0
0.5
0
(1 − α)
Koongarra Ore Zone
Technetium-99
Plutonium-239
Iodine-129
Cigar Lake Ore Zone
Cigar Lake Ore Zone
Cigar Lake Ore Zone
Koongarra Ore Zone
10-9
10-8
10-7
10-6
10-5
10-4
λ129 I
λ99 Tc
λ239Pu
Transfer Rate To Water (Yr-1) =ε x Production Rate in Ore

CONCLUSIONS

1) Processes that release and transport radionuclides from uranium minerals are operative in geologic systems representing a wide range of hydrogeochemical conditions.

2) These processes have been operative in the time domain between the present and 10^8 years ago.

3) Release processes for ^{129}I are orders of magnitude faster than for uranium.

4) Water residence times at Cigar Lake are more than an order of magnitude longer than at Koongarra.

5) Radionuclide release rates are smaller at Cigar Lake than at Koongarra.

6) Processes operative at Cigar Lake concentrate ^{99}Tc and and possibly ^{239}Pu in rock.

Natural Nuclear Product Geochemistry

David Curtis, June Fabryka-Martin, Paul Dixon, Don Rokop; Los Alamos National Laboratory. Carol Bruton, Lawrence Livermore Laboratory, and Jan Cramer; AECL Whiteshell Laboratory.

An understanding of processes involving radionuclide distribution and transport is inherent to safety assessment protocol. Such assessments associated with the development of geologic repositories for high-level radioactive wastes are uncertain because of uncertainties inherent in our understanding of fundamental processes in relevant environments and over relevant time scales. To aid in constraining the results of safety assessments of these geologic repositories,we are developing information from studies of uranium deposits to enhance our understanding of radionuclide behavior, rates at which key processes proceed, and factors influencing changes in these rates in geologic environments. Uranium deposits represent natural analogues of processes associated with the release and transport of radionuclides from spent fuel.

Our work involves measurement abundances of the natural radionuclides ^{99}Tc, ^{129}I, and ^{239}Pu in rock, water, and minerals from uranium deposits. Measured abundances are compared with those produced by nuclear reactions to determine the nature and extent of radionuclide enrichment or depletion. No enrichment or depletion indicates that the system has been undisturbed over relevant time domains (10^6 yr for ^{99}Tc, 10^8 yr for ^{129}I, and 10^5 yr. for ^{239}Pu), **or** processes rates were significantly less than rates of radionuclide production, **or** processes did not chemically enrich or deplete parent from daughter element. Conversely, measures of enrichment or depletion show that the system has been disturbed in the relevant time domain **and** the rate of the disruptive process was significant relative to the rate of radionuclide production, **and** the processes chemically fractionated parent from daughter. We then seek to resolve our interpretations regarding the timing, rate, and chemical effects with our understanding of system parameters believed to control processes that influence these properties in the system being examined.

We have studied uranium deposits in two extremely different hydrogeochemical settings. The Cigar Lake deposit is an impermeable deposit in a reduced environment. It appears to have been largely undisturbed for most of the 1.3 x 10^9 yr since its formation. The

Koongarra deposit can be considered as two zones, with an intervening transitional zone. The near surface zone is weathered rock in an oxidizing environment. Uranium has been dispersed by water flow. The sub-surface zone is unweathered, but has been altered from primary ore at some time in the geologic past. There is no obvious evidence for uranium dispersion in the unweathered zone at Koongarra.

At this time interpretations of our measurements suggest the following conclusions:

1) Processes that release and transport radionuclides from uranium minerals are operative in both the Koongarra and Cigar Lake deposits.

2) These processes have been operative in the time domain between the present and 10^8 years ago.

3) Release processes are orders of magnitude faster for ^{129}I than for U.

4) Water residence times at Cigar Lake are more than an order of magnitude longer than at Koongarra.

5) Radionuclide release rates are slower at Cigar Lake than at Koongarra.

6) Processes operative at Cigar Lake concentrate ^{99}Tc and possibly ^{239}Pu in rock.

K_d Modeling

John W. Bradbury

Hydrology and Systems Performance Branch
Division of High-Level Waste Management
U. S. Nuclear Regulatory Commission

presented at

NRC/DOE Technical Exchange

Radionuclide Migration

and

Near-Field Phenomena Related to Radionuclide Releases
From the Engineered Barrier System

Los Alamos National Laboratory
October 13 - 15, 1993

K_D Approximation Testing

When is it appropriate to use K_D to calculate retardation?

$$R_f = \frac{v_w}{v_m} = 1 + \frac{\rho}{\theta} K_D$$

Equation is valid when

1) **Isotherm is linear**
2) **Sorption/desorption is fast and reversible**
   (Freeze and Cherry, 1979)

Why must the isotherm be linear?

What effect does the shape of the isotherm have on radionuclide transport?

Method of Testing

Simulate ion exchange (a sorption mechanism)

PHREEQM, a mixing cell code

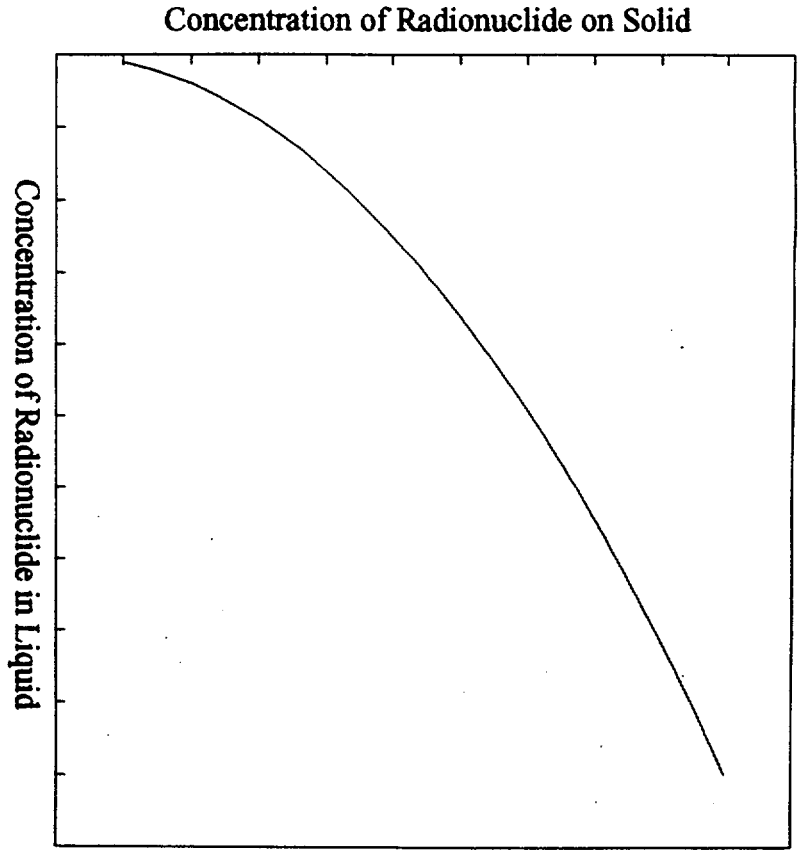
Flow–through column experiment

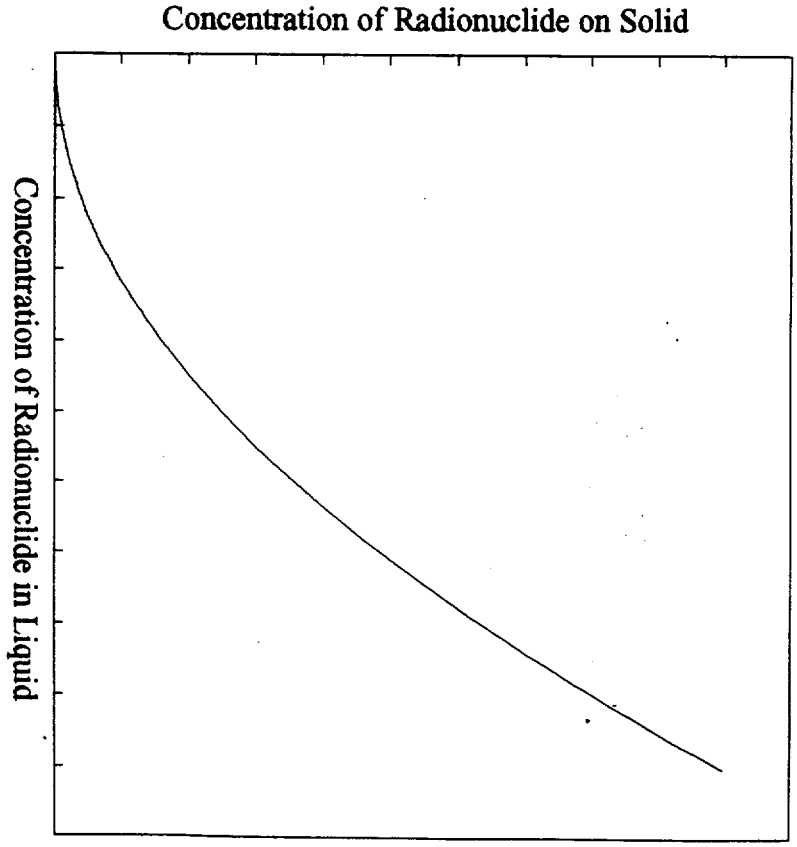
$$K^{+}+NaX=Na^{+}+KX$$

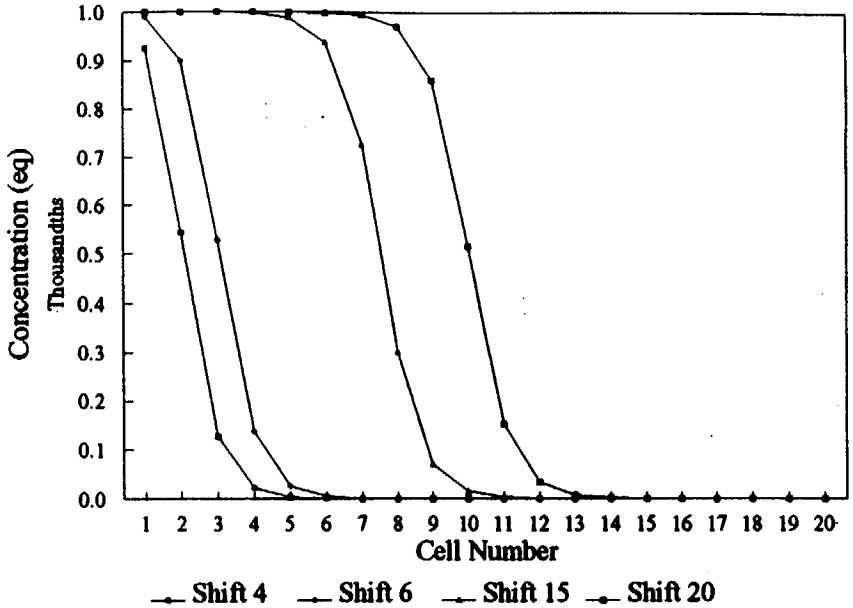
K^+, Na^+ can be considered analogs for radionuclides

K^+ is more strongly sorbed than Na^+

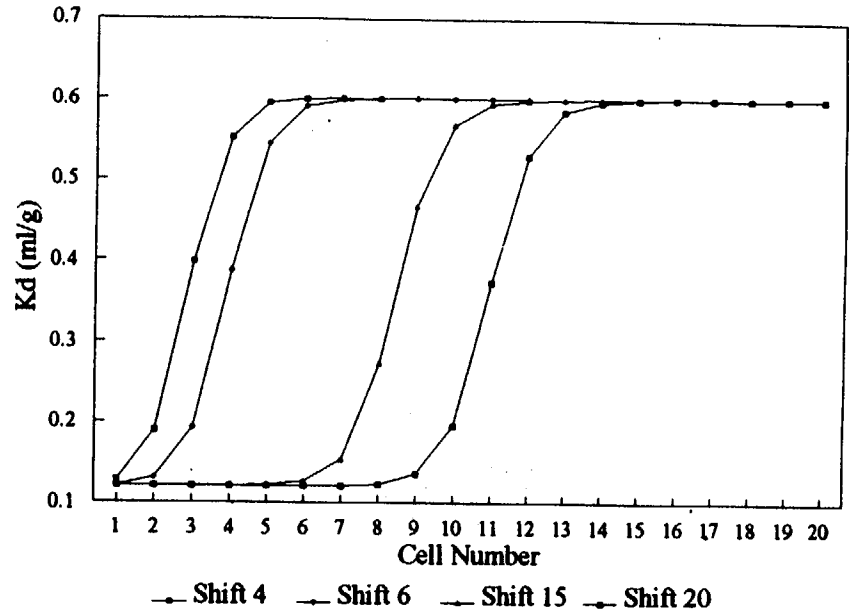
Varied concentrations and flushing solution


Concentration of Radionuclide on Solid
Concentration of Radionuclide in Liquid

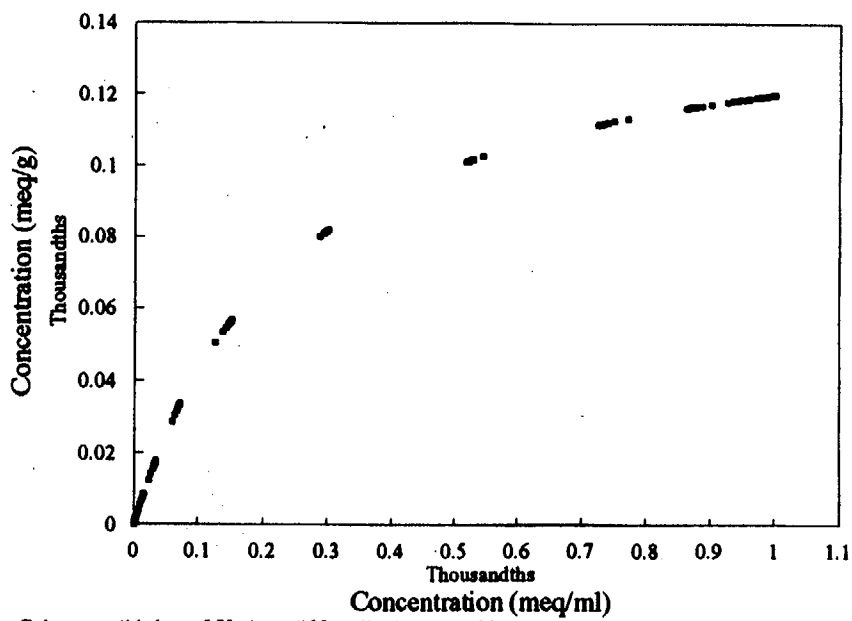

Concentration of Radionuclide on Solid
Concentration of Radionuclide in Liquid



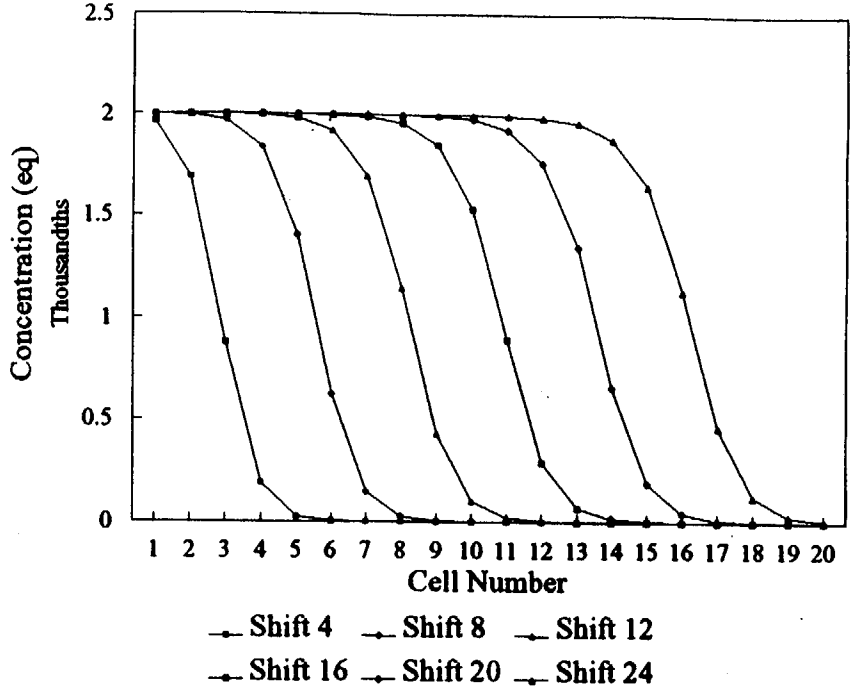
Column: solid, 1 meq/l X- 1 meq/l Na+; liquid, 1meq/l Na+
Flushing solution: 1meq/l K+



Column: solid, 1meq/l X- 1meq/l Na+; liquid, 1 meq/l Na+
Flushing solution: 1meq/l K+



Column: solid, 1meq/l X- 1meq/l Na+; liquid 1meq/l Na+
Flushing solution: 1 meq/l K+



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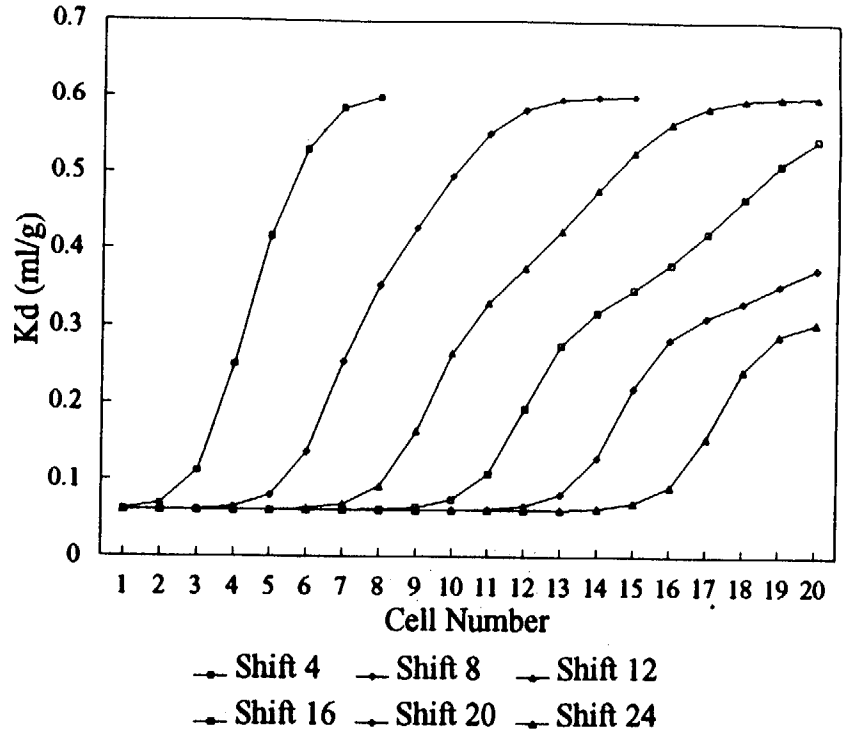
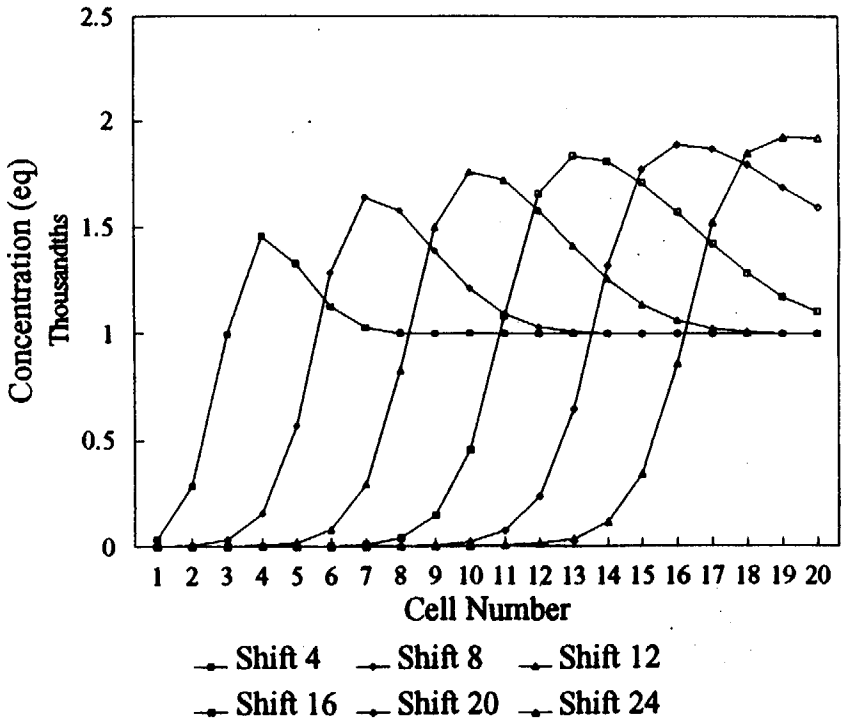
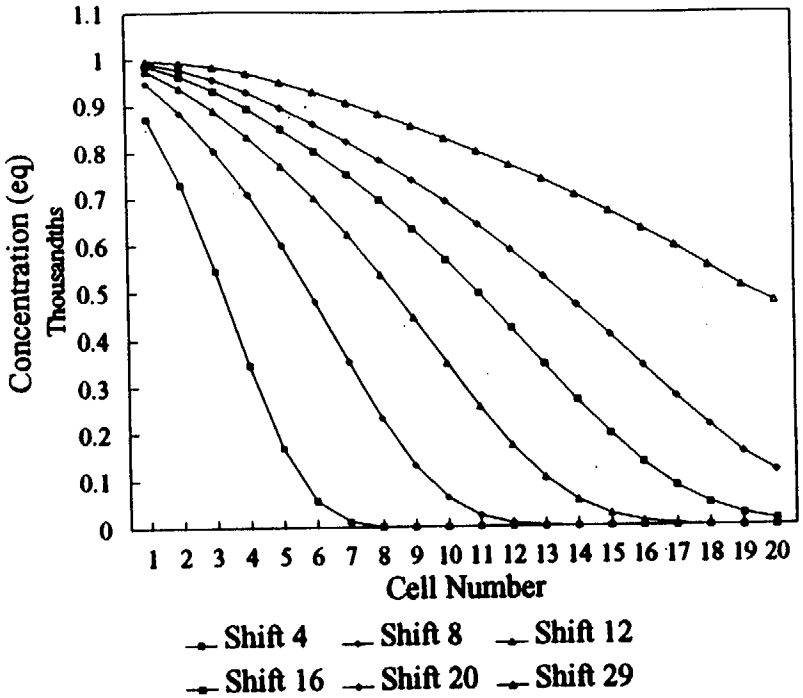
Flushing solution: 2 meq/l K+



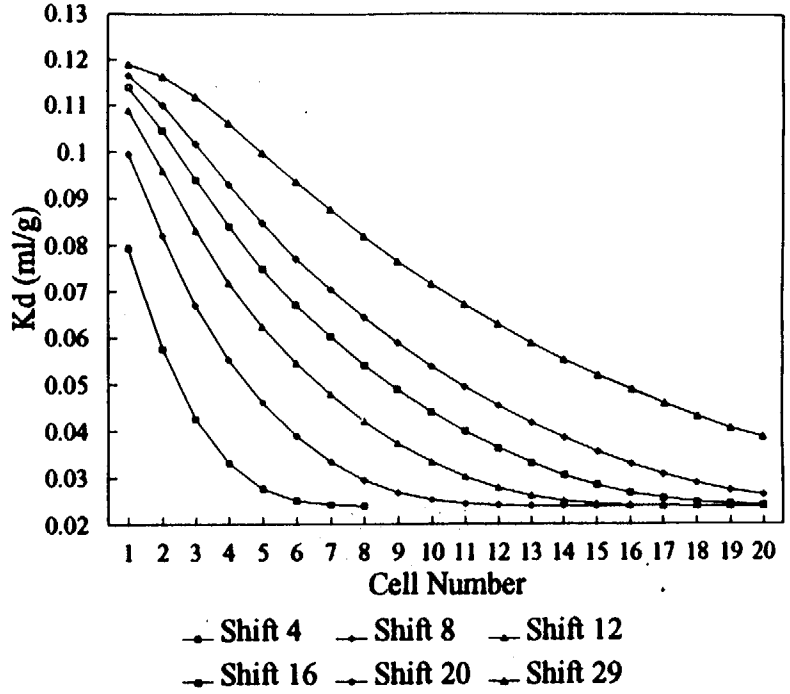
Column: solid, 1 meq X- 1meq Na+; liquid, 1 meq/l Na+
Flushing solution: 2 meq/l K+



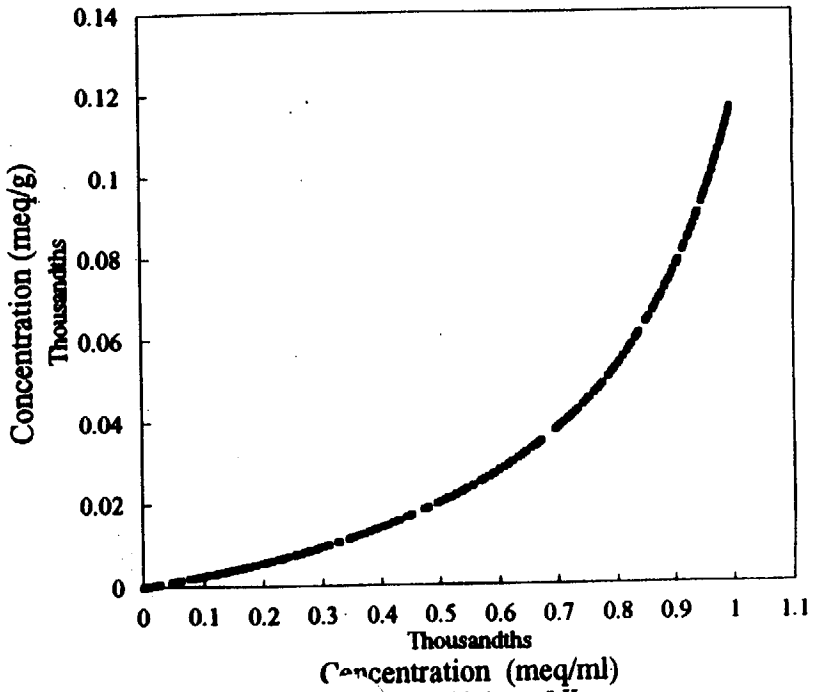
Column: 1 meq/l X- 1 meq/l Na+; liquid, 1meq/l Na+
Flushing n: 2 meq/l K+



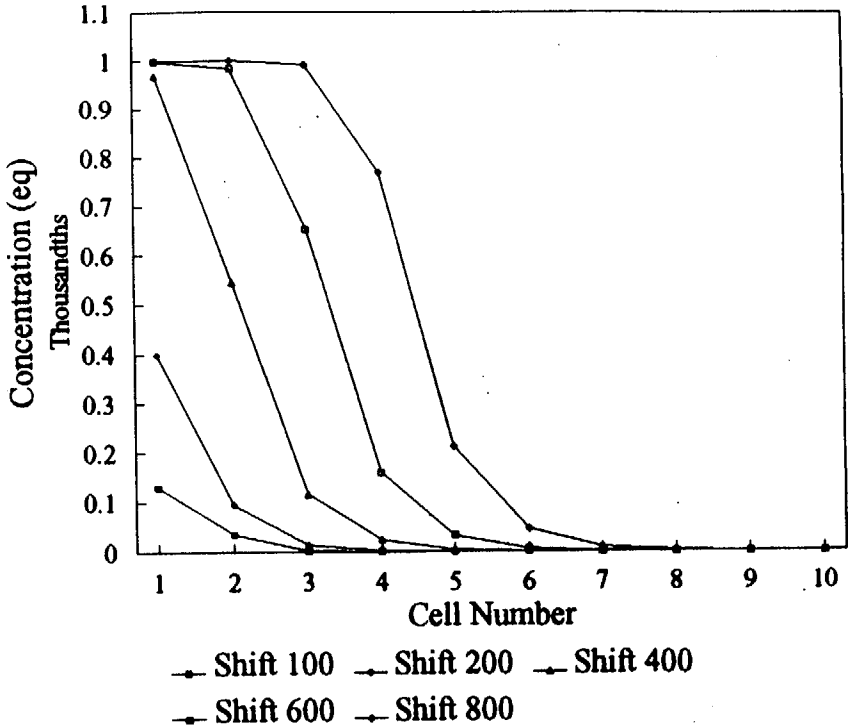
Column: solid, 1 meq/l X- 1meq/l K+; liquid, 1 meq/l K+
Flushing solution: 1 meq/l Na+



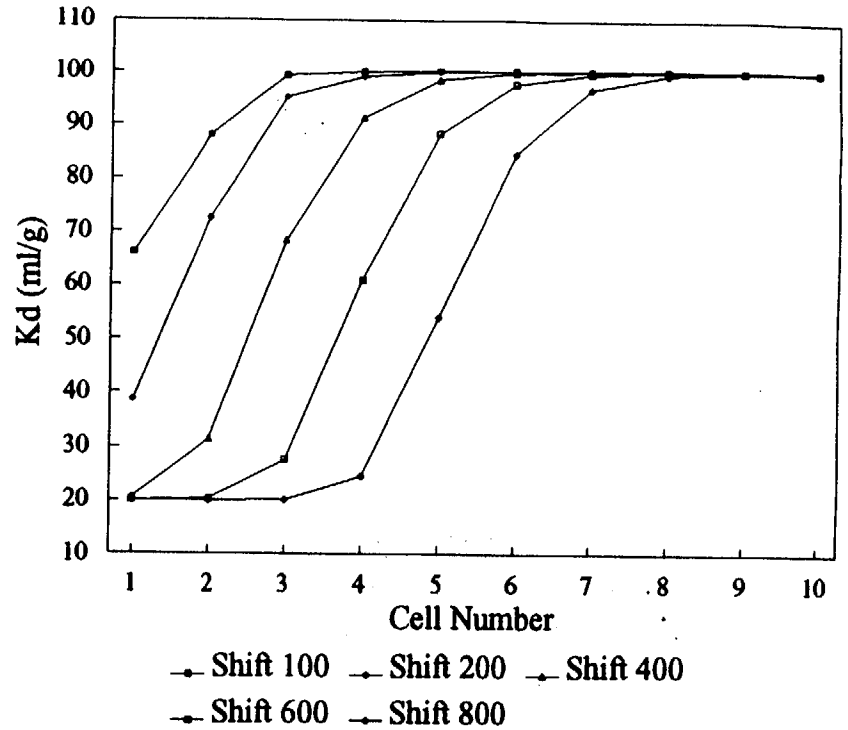
Column: solid, 1 meq/l X- 1meq/l K+; liquid, 1 meq/l K+
Flushing solution: 1 meq/l Na+



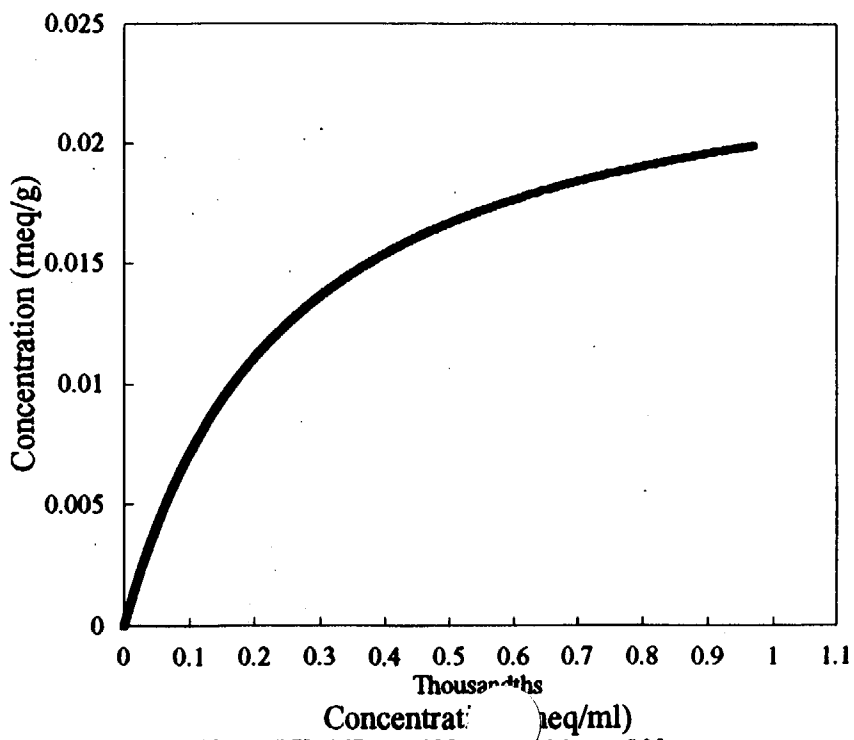
Column: solid, 1 meq/l X- 1 [illegible]+; liquid, 1 meq/l K+
Flushing solution: 1meq/l Na+



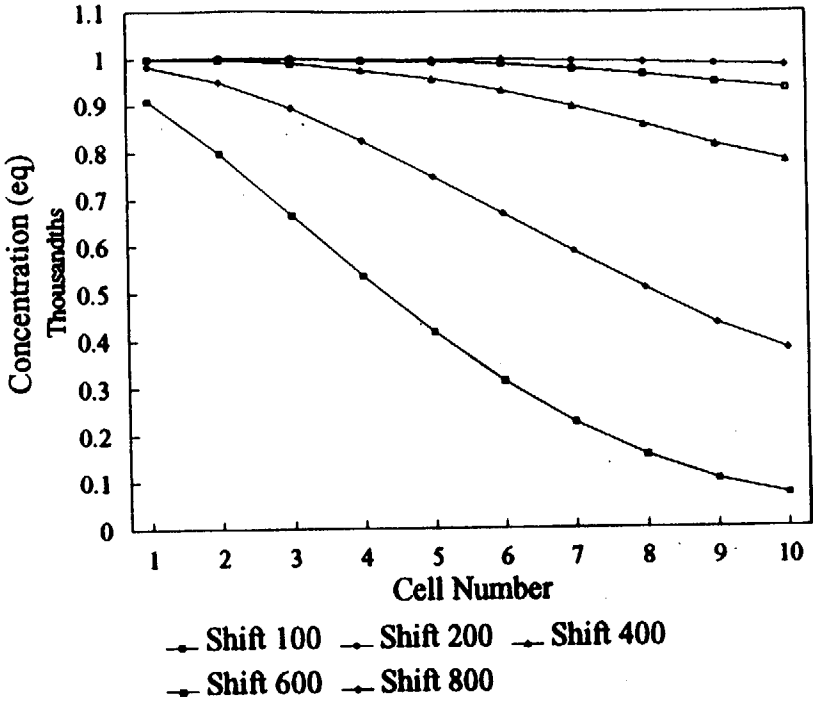
Column: solid, 167 meq/l X- 167 meq/l Na+; liquid, 1 meq/l Na+
Flushing Solution: 1 meq/l K+



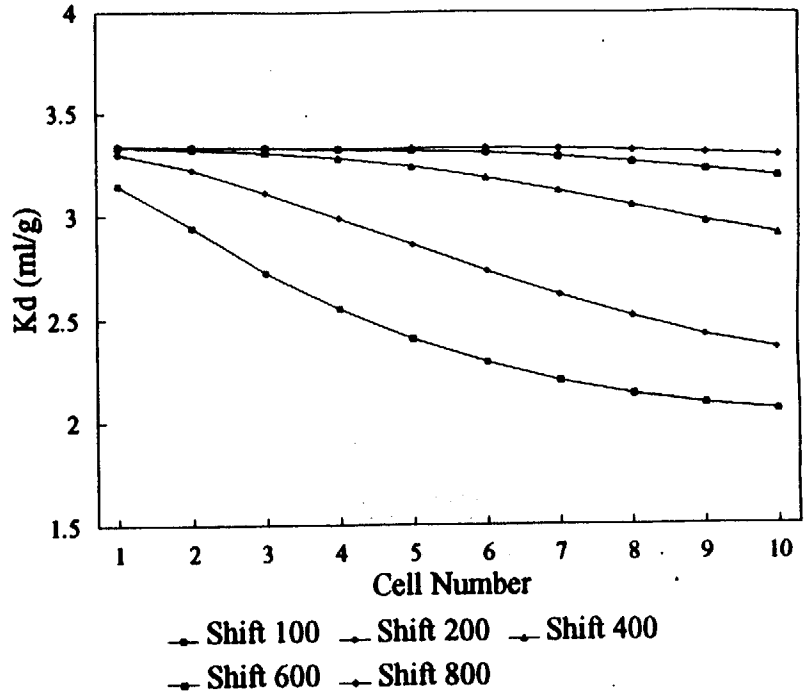
Column: solid, 167 meq/l X- 167 meq/l Na+; liquid, 1 meq/l Na+
Flushing solution: 1 meq/l K+



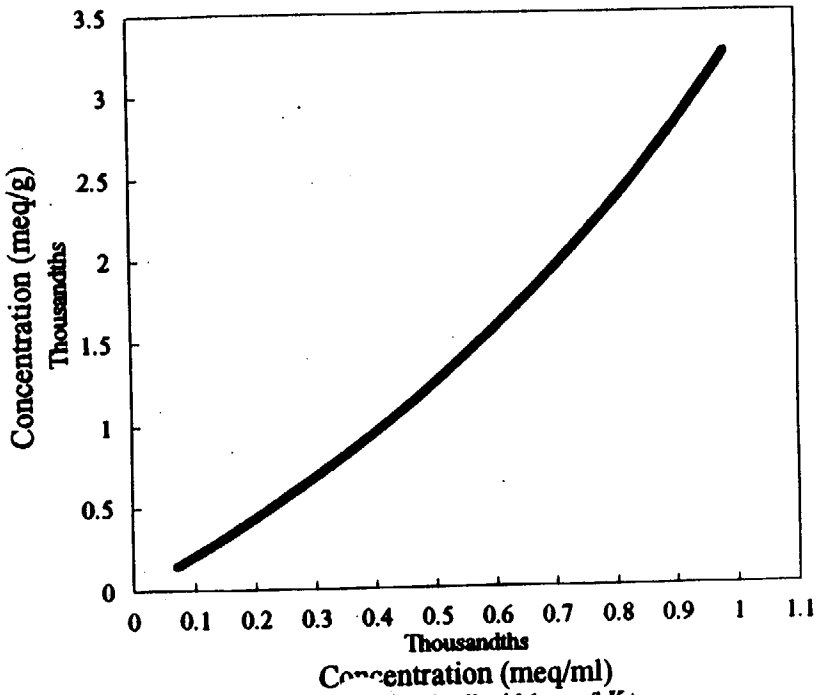
Column: solid, 167 meq/l X- 167 meq/l Na+, id 1 meq/l Na+



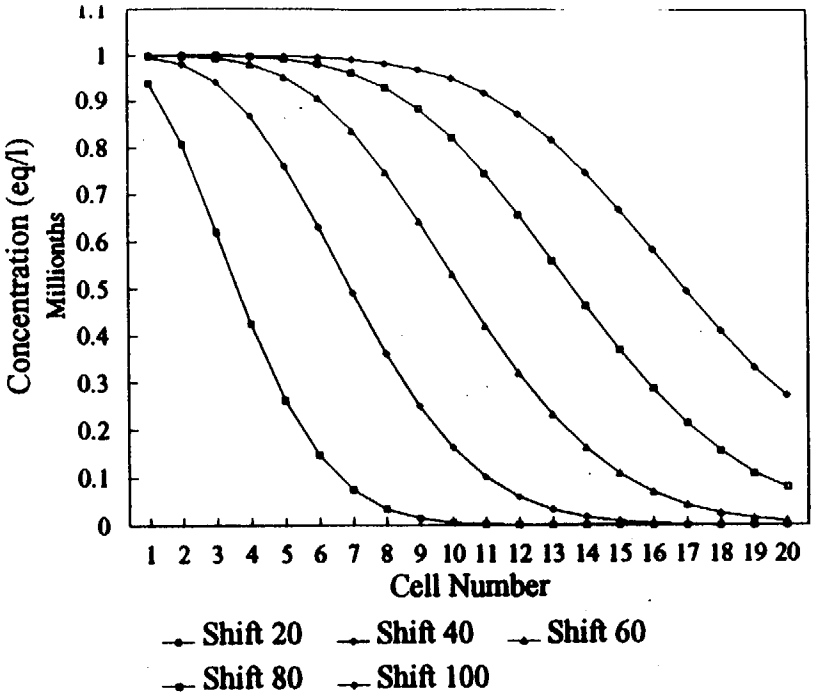
Column: solid, 167 meq/l X- 167 meq/l K+; liquid 1 meq/l K+
Flushing solution: 1 meq/l Na+



Column: solid, 167 meq/l X- 167 meq/l K+; liquid, 1 meq/l K+
Flushing solution: 1 meq/l Na+



Column: solid, 167 meq/l X- 1 /l K+; liquid 1 meq/l K+
Flushing solution: 1 meq/l Na+



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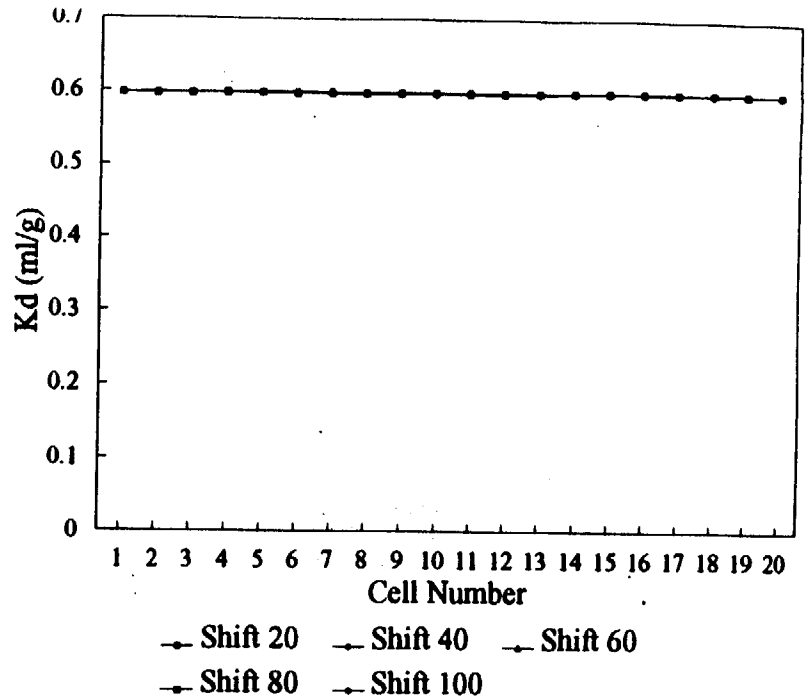
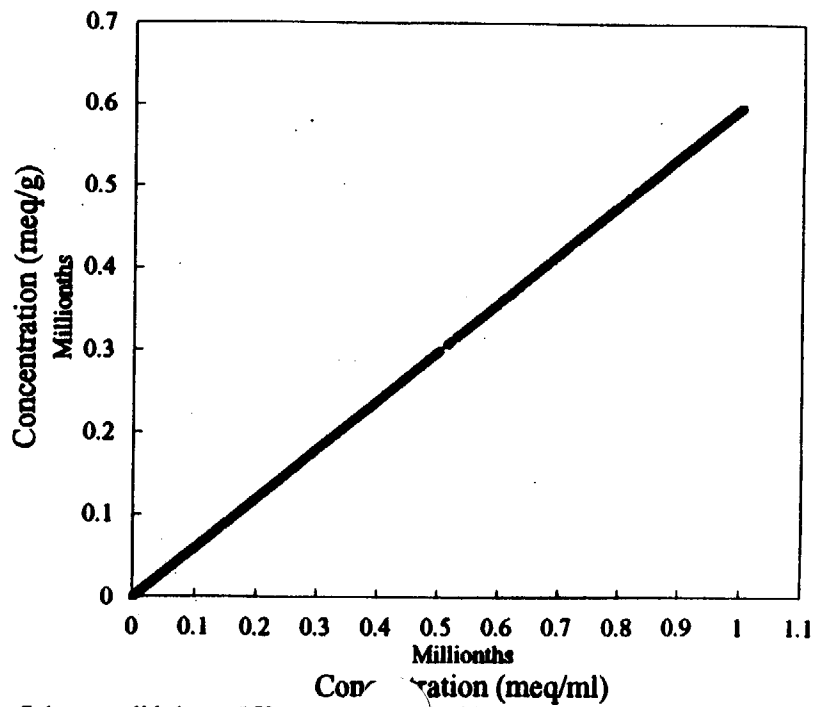
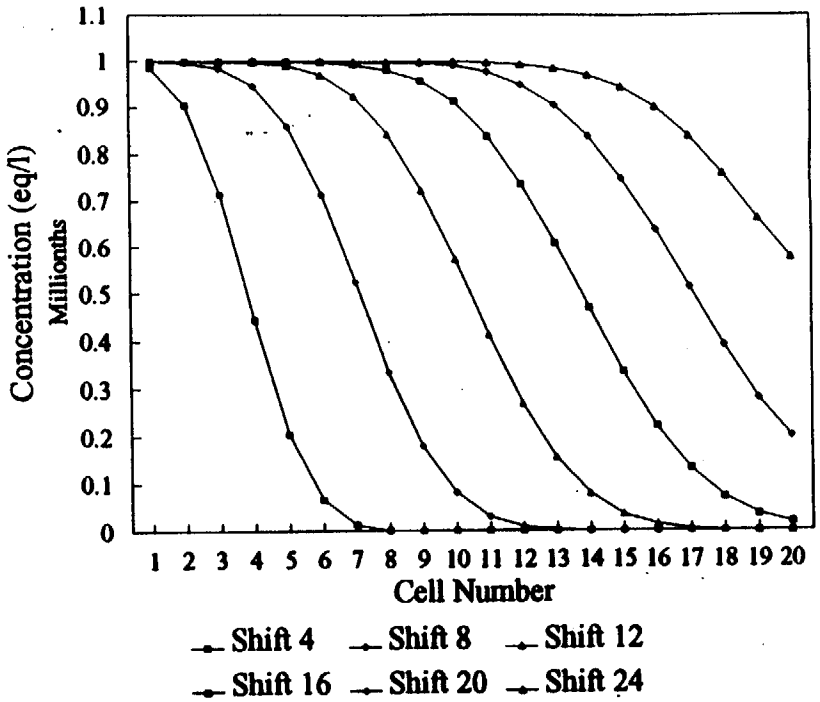
Flushing solution: 0.001 meq/l K+



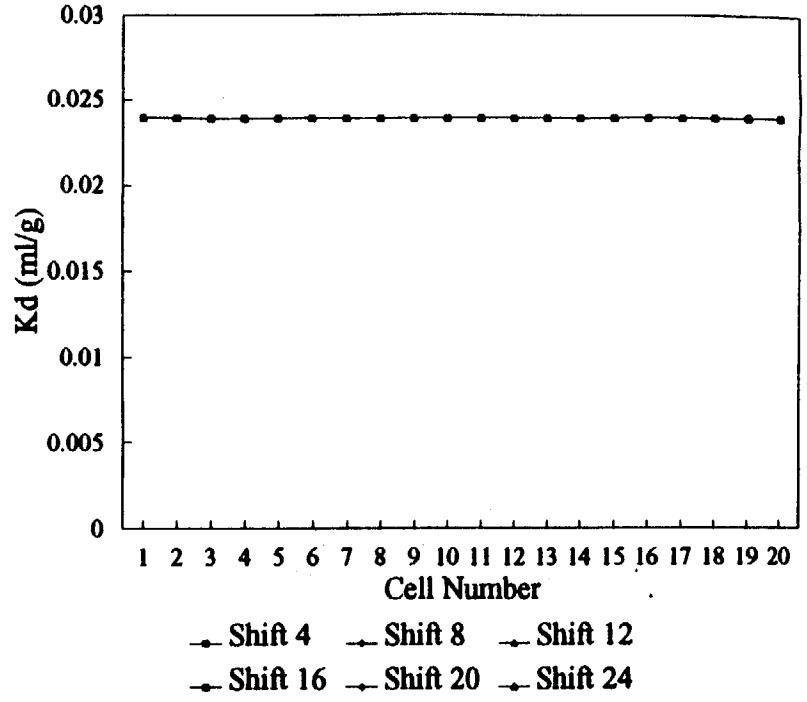
Column: solid, 1 meq/l X- 1 meq/l Na+; liquid, 1 meq/l Na+
Flushing solution:0.001 meq/l K+



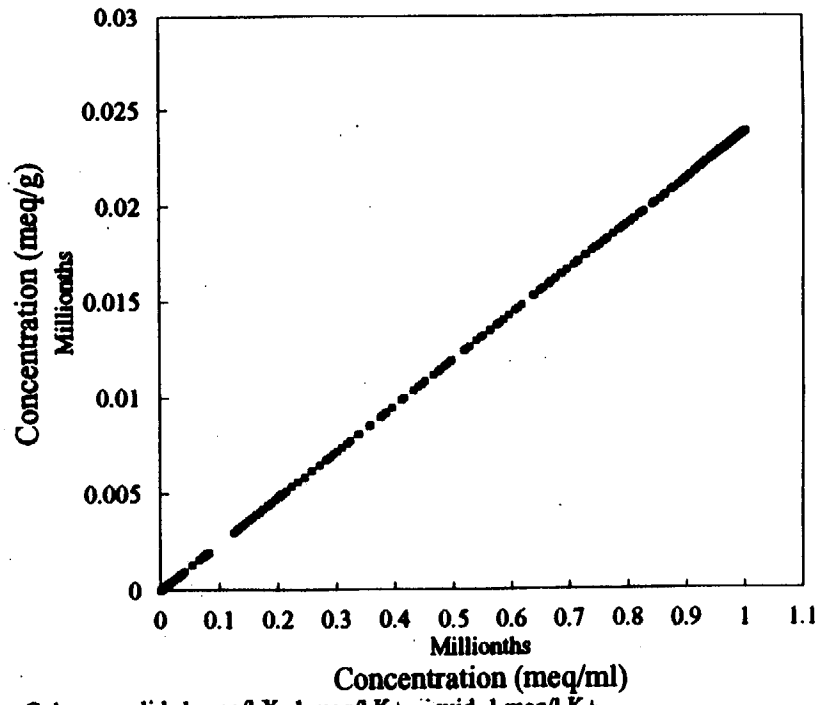
Column: solid, 1 meq/l X- 1 meq/l iquid, 1 meq/l Na+
Flushing solution: 0.001 meq/l K+



Column: solid, 1meq/l X- 1 meq/l K+; liquid, 1 meq/l K+
Flushing solution: 0.001 meq/l Na+



Column: solid, 1 meq/l X- 1 meq/l K+; liquid, 1 meq/l K+
Flushing solution: 0.001 meq/l Na+



Column: solid, 1 meq/l X- 1 meq/l K+; liquid, 1 meq/l K+
Flushing solution: 0.001 meq/l Na+

Conclusions

Isotherm need not be linear to calculate retardation from K_D. If isotherm is convex up, retardation corresponds to K_D at maximum concentration.

Isotherm is linear when radionuclide is trace relative to the competing cation

However, J-13 is a very dilute solution. Therefore, U, Np, Cs, and Tc may not be occur in trace amounts.

SORPTION MODELING FOR HIGH-LEVEL WASTE PERFORMANCE ASSESSMENT

PRESENTED

by

David R. Turner

AT THE NRC/DOE TECHNICAL EXCHANGE
Los Alamos National Laboratory
October 13, 1993

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES
SOUTHWEST RESEARCH INSTITUTE
San Antonio, Texas

CNWRA Project Manager: H. Lawrence McKague
NRC Project Manager: G. F. Birchard

Investigators:
Roberto T. Pabalan, David R. Turner, and Paul Bertetti

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

OBJECTIVES:

TASK 2 - SORPTION MODELING:

- DEVELOP SIMPLIFIED SORPTION MODELING APPROACHES AND EVALUATE THEIR ADEQUACY FOR PERFORMANCE ASSESSMENT NEEDS
- INVESTIGATE APPLICATION OF EXISTING COUPLED HYDROGEOCHEMICAL TRANSPORT CODES

TASK 3 - SORPTION EXPERIMENTS:

- DERIVE EXPERIMENTAL DATA ON SORPTION OF URANIUM AND OTHER RADIONUCLIDES
- EVALUATE EFFECTS OF SOLUTION CHEMISTRY AND ROCK/MINERAL PROPERTIES ON RADIONUCLIDE SORPTION
- IDENTIFY SORPTION PROCESSES/MECHANISMS IMPORTANT TO THE YUCCA MOUNTAIN ENVIRONMENT

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

ACCOMPLISHMENTS FROM PROJECT INCEPTION (9/90):

- COMPLETED EXTENSIVE LITERATURE REVIEW OF SORPTION MODELING AND REACTIVE TRANSPORT (TASK 1)

TASK 2:

- IDENTIFIED, ACQUIRED AND INSTALLED SORPTION CODES

  -MINTEQA2 SORPTION/SPECIATION CODE (Allison et al. , 1991)
  -FITEQL PARAMETER OPTIMIZATION CODE (Westall, 1982)

- DEVELOPED RADIONUCLIDE THERMODYNAMIC DATABASE FORMATTED FOR SORPTION MODELING USING MINTEQA2

- ANALYSIS OF POTENTIOMETRIC TITRATION DATA TO DERIVE MODEL-SPECIFIC ACIDITY CONSTANTS FOR SIMPLE (HYDR)OXIDES

- COMPILATION AND ANALYSIS OF AVAILABLE RADIONUCLIDE SORPTION DATA USING SURFACE COMPLEXATION MODELS

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

TASK 3:

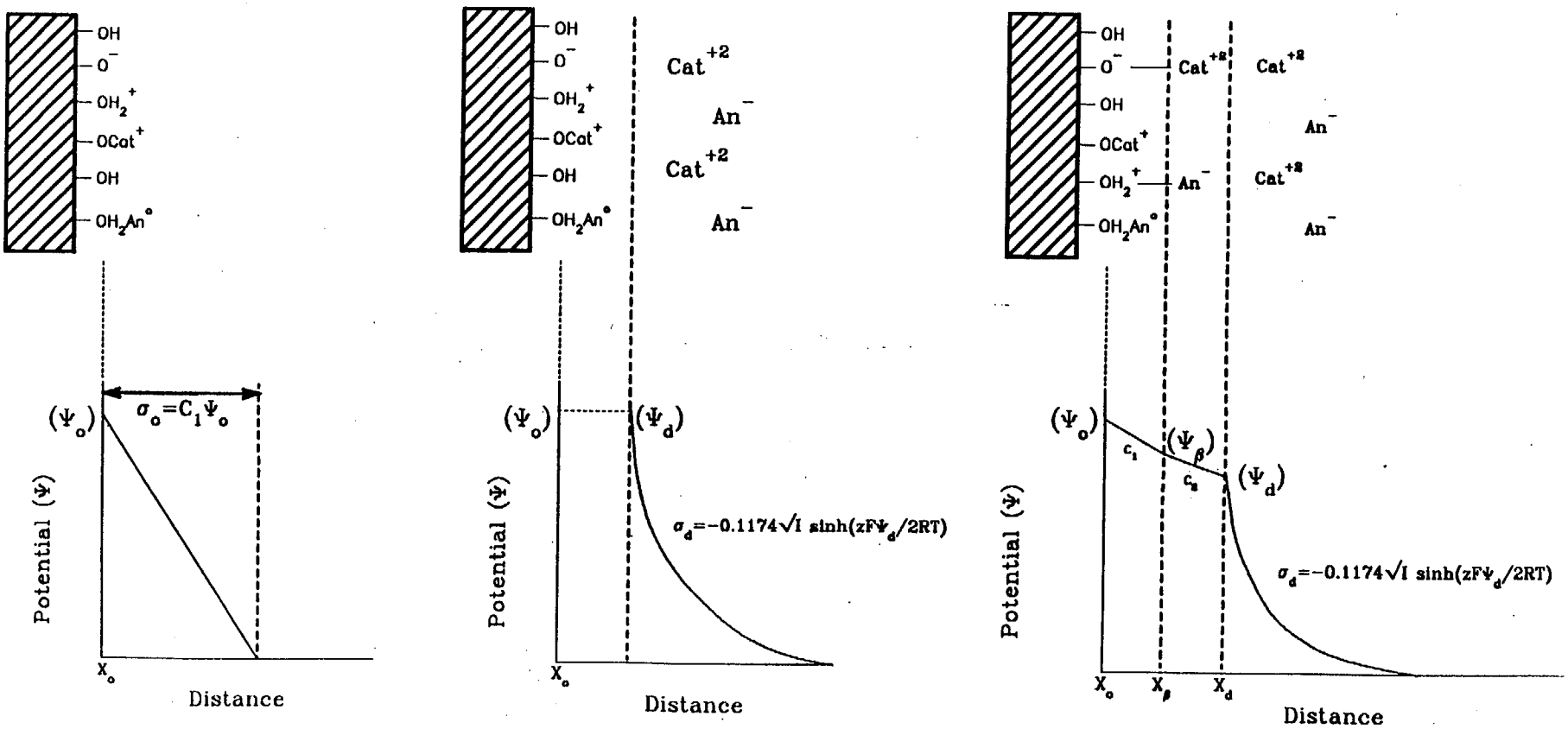
- CONDUCTED EXPERIMENTS ON URANIUM SORPTION ON CLINOPTILOLITE, ALUMINUM-OXIDE, AND MONTMORILLONITE
  - DISTINCT MINERAL STRUCTURE AND SURFACE PROPERTIES
  - VARIABLE SOLUTION CHEMISTRY (E.G., pH AND ΣU), BUT FIXED pCO_2 (ATMOSPHERIC).
  - VARIABLE SURFACE-AREA/SOLUTION-VOLUME RATIO
- CONDUCTED CAREFUL CONTROL EXPERIMENTS TO CHARACTERIZE EXPERIMENTAL LOSS TO CONTAINER, FILTERS, PIPETTES, ETC.

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

SURFACE COMPLEXATION MODELS (SCMs):

- ALL MODELS CORRECT FOR ELECTROSTATIC EFFECTS USING DIFFERENT REPRESENTATIONS OF MINERAL-WATER INTERFACE

CONSTANT CAPACITANCE *DIFFUSE-LAYER* *TRIPLE-LAYER*



SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

GOAL: A UNIFORM APPROACH TO DETERMINE BINDING CONSTANTS FOR SURFACE COMPLEXATION MODELS

NEEDS: MODEL-SPECIFIC PARAMETERS TO DESCRIBE MINERAL ACID-BASE BEHAVIOR BASED ON UNIFORM DATA

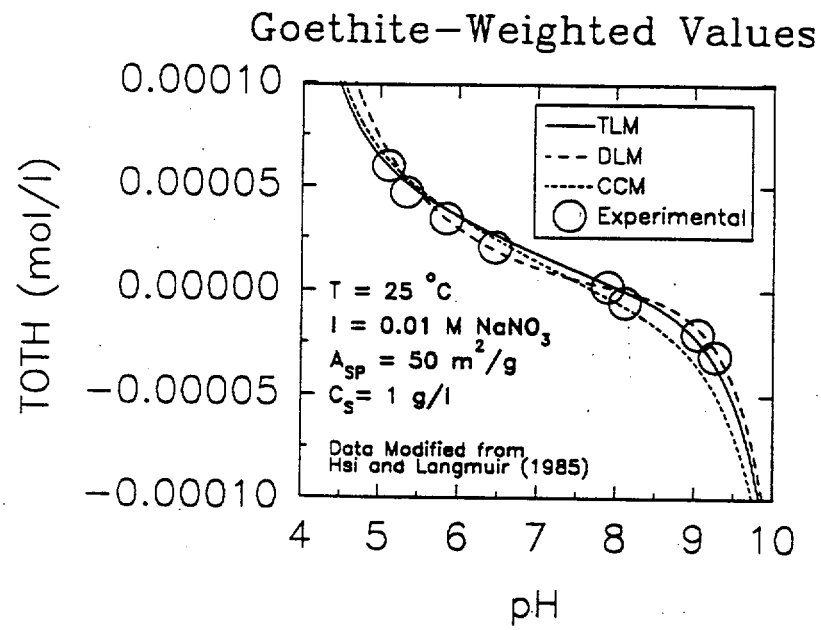
DATA: MINERAL POTENTIOMETRIC TITRATION DATA FROM OPEN LITERATURE

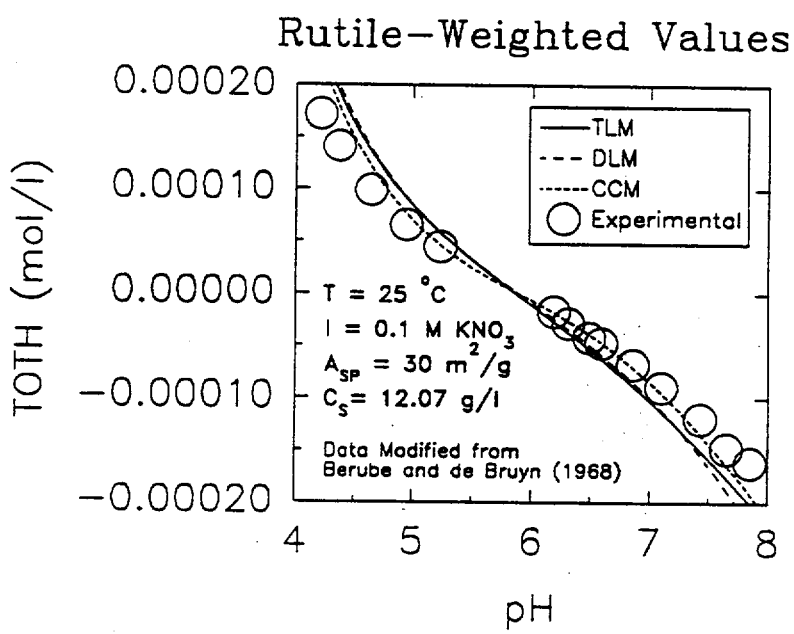
Mineral	Generalized A_{SP} (m^2/g)	pH_{ZPC} ($\pm 1\ \sigma$)	Reference(s)
Goethite	50	8.0±0.8 (n=11)	Hsi and Langmuir (1985); Hayes et al. (1990); Yates and Healy (1975); Balistrieri and Murray (1981); Mesuere (1992)
Ferrihydrite$_{(a)}$	600	8.0±0.1 (n=9)	Hsi and Langmuir (1985); Davis (1977); Swallow (1978); Yates (1975)
Magnetite	5	6.7±0.1 (n=2)	Regazzoni et al. (1983)
Pyrogenic-SiO_2	175	2.8±0.3 (n=3)	Abendroth (1970); Bolt (1957)
α-Al_2O_3	12	8.9±0.4 (n=4)	Hayes et al. (1990)
γ-Al_2O_3	120	8.4±0.3 (n=3)	Huang and Stumm (1972); Sprycha (1989)
δ-MnO_2	270	1.9±0.5 (n=7)	Murray (1974); Catts and Langmuir (1986)
TiO_2(anatase)	(b)	6.1±0.2 (n=2)	Sprycha (1984); Berube and de Bruyn (1968)
TiO_2(rutile)	30	5.9±0.3 (n=4)	Berube and de Bruyn (1968); Yates (1975)

(a)Values recommended in Dzombak and Morel (1990).
(b)The reported value of 16 m^2/g used with data of Sprycha (1984); 125 m^2/g used with data of Berube and de Bruyn (1968).

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

Model Comparison



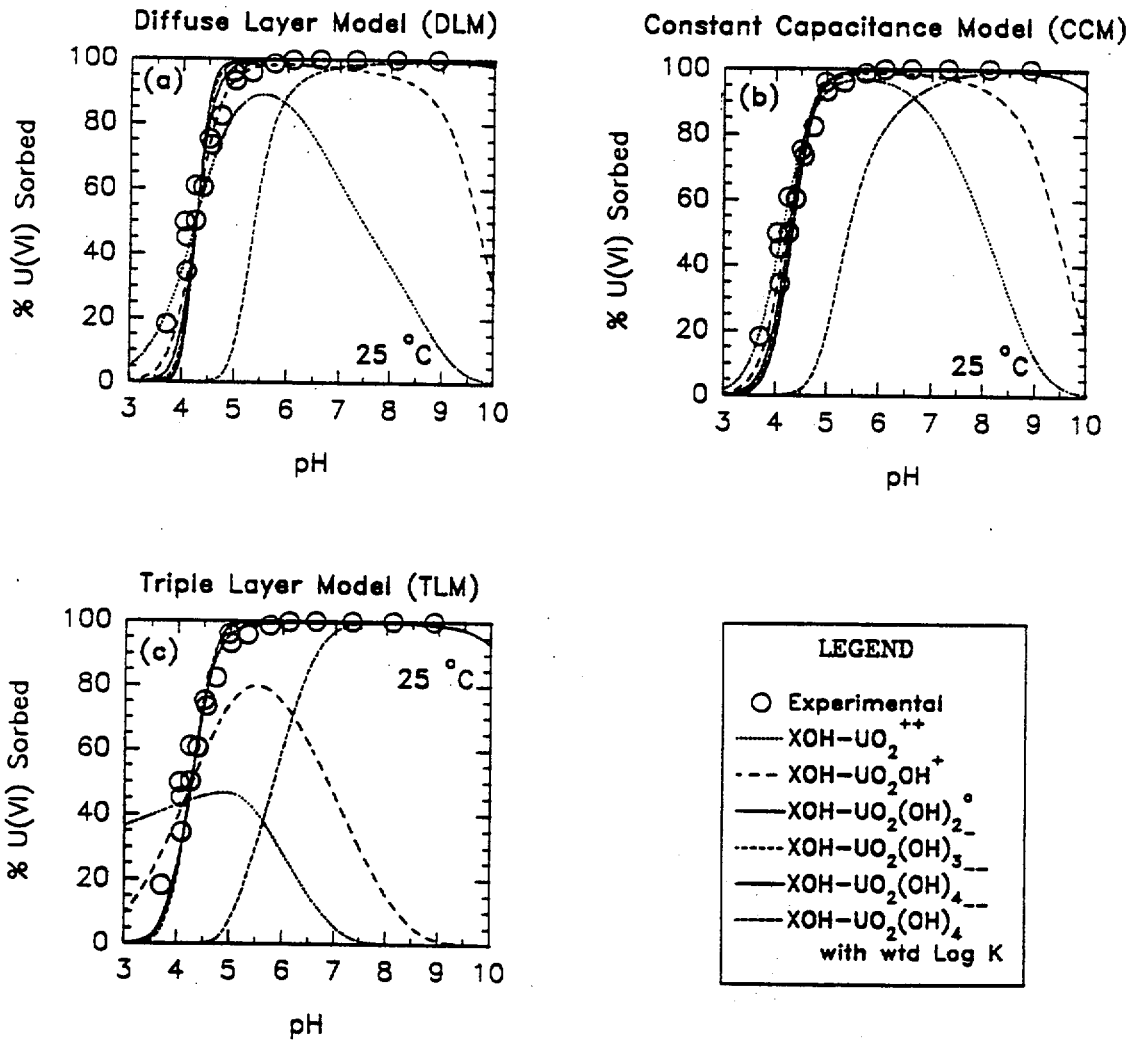


SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

SORPTION OF U(VI) ON GOETHITE

Experimental data from Hsi & Langmuir (1985)

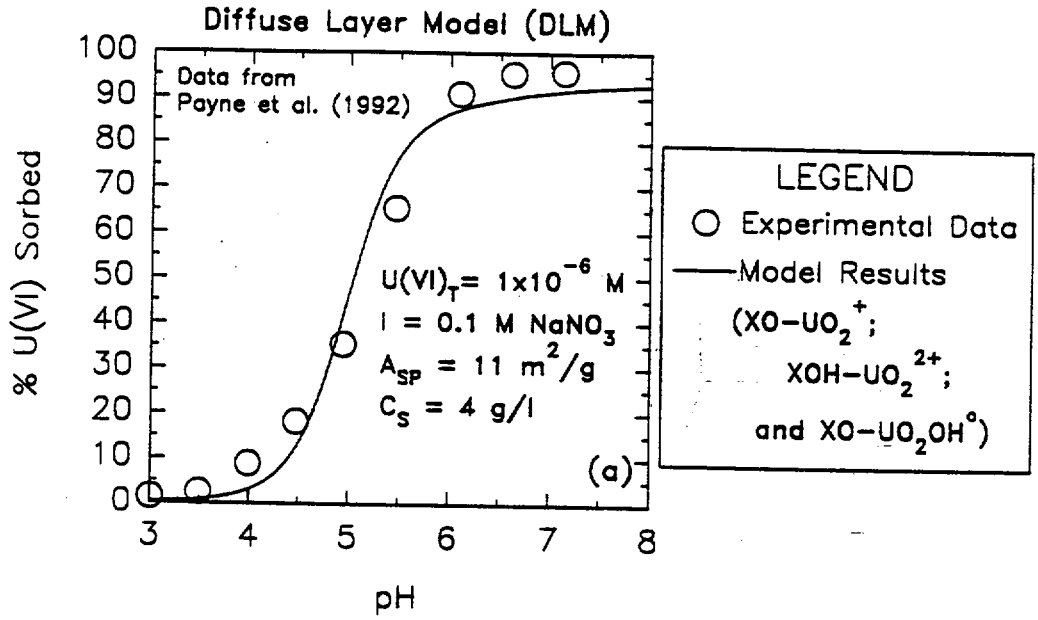
$U(VI)_T = 10^{-5}$ M; 0.1 M $NaNO_3$; No CO_2



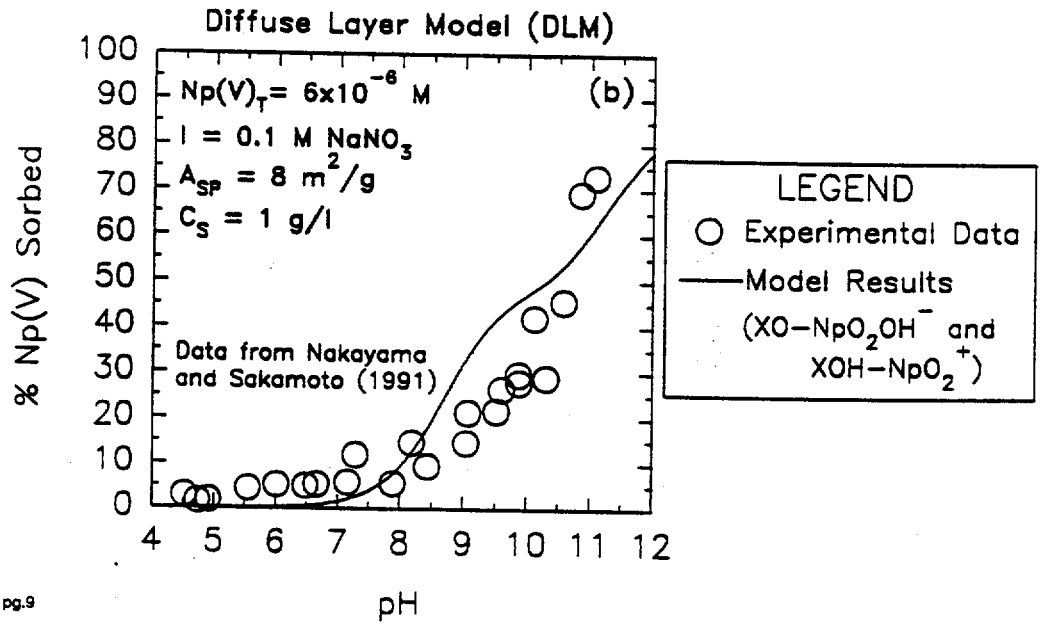
SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

Kaolinite [$Al_2Si_2O_5(OH)_4$] -- SiOH°:AlOH° = 1:1
Biotite [$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$] -- SiOH°:AlOH° = 3:1

SORPTION OF U(VI) ON KAOLINITE

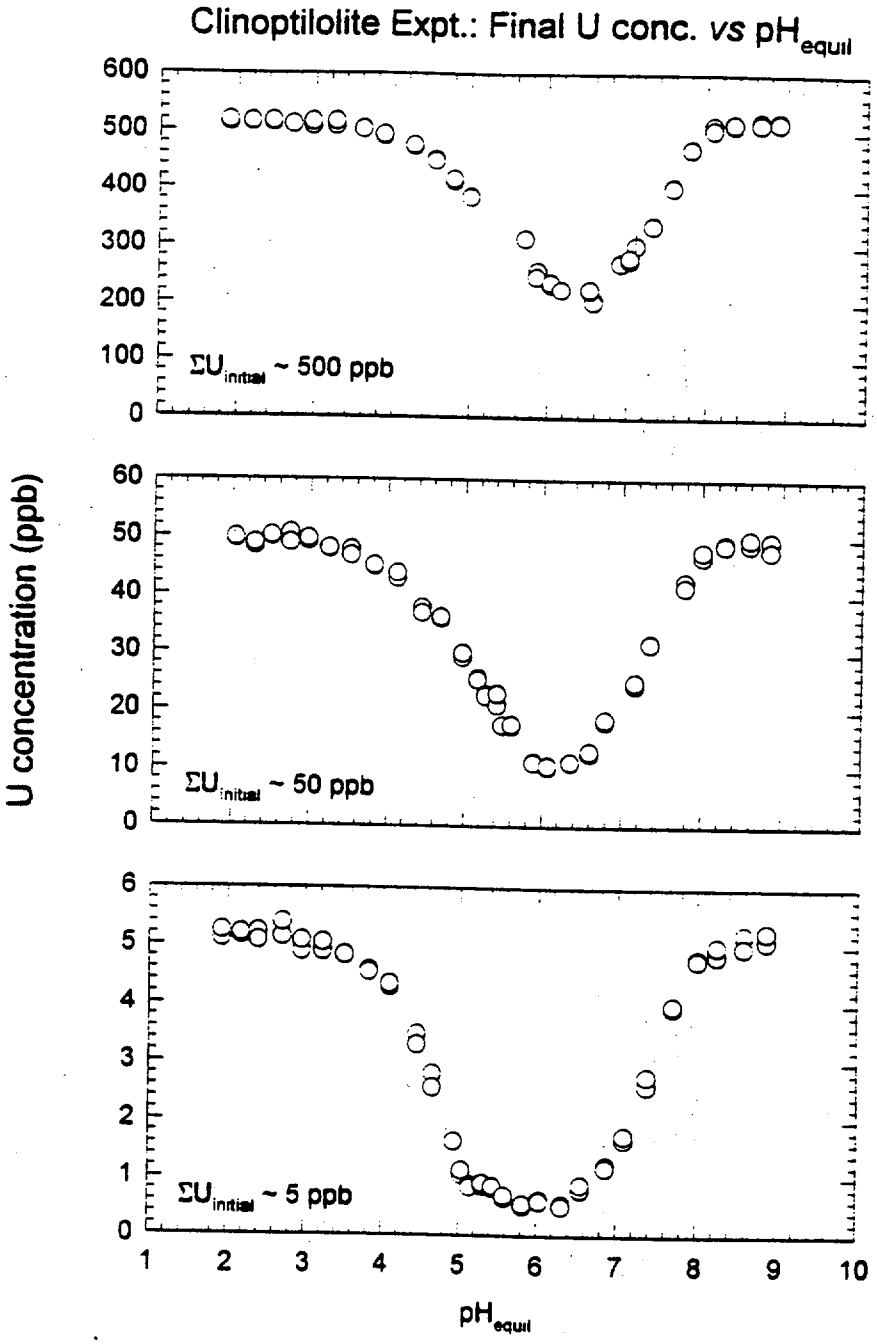


SORPTION OF Np(V) ON BIOTITE



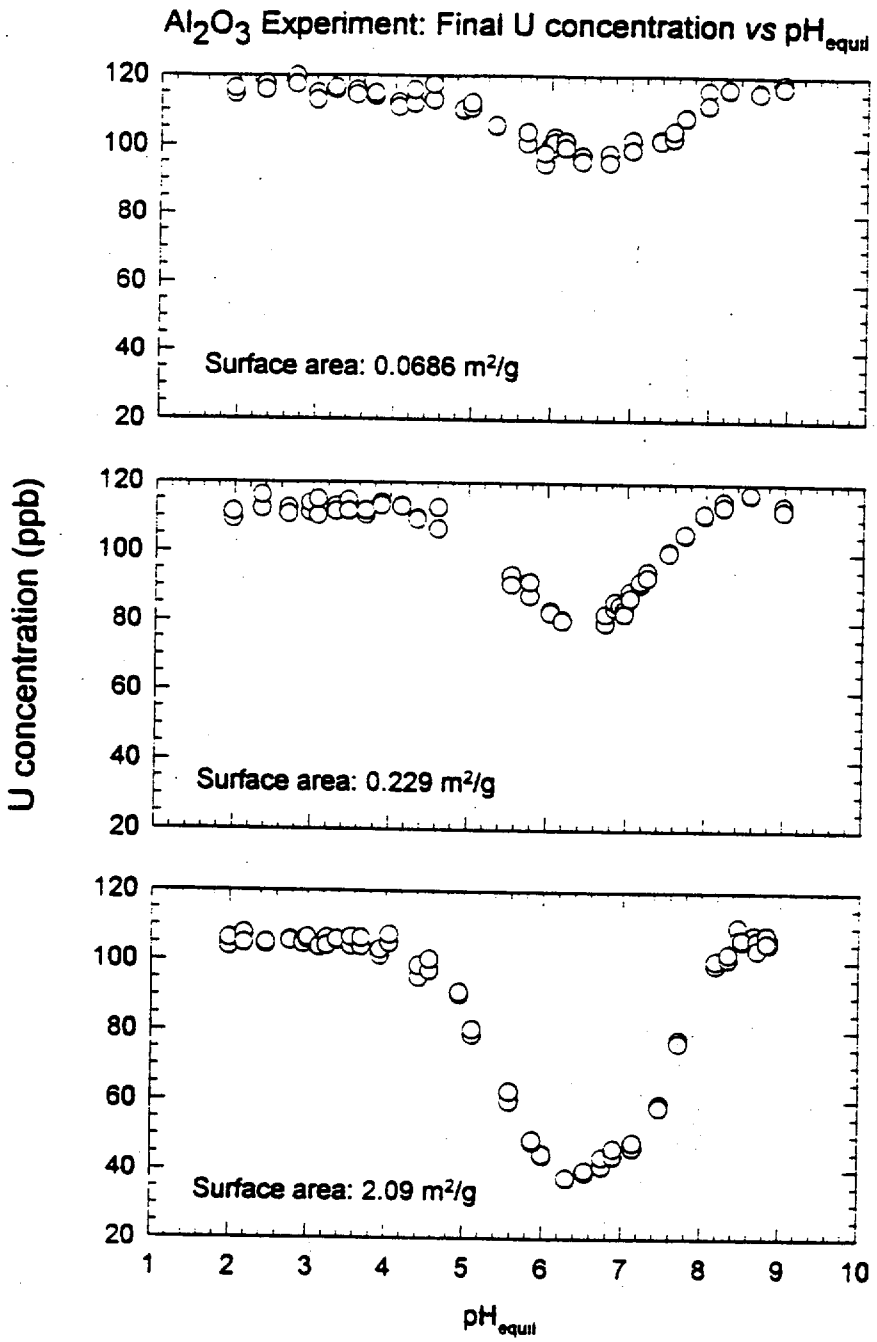
SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

URANIUM CONCENTRATIONS IN CLINOPTILOLITE SORPTION EXPERIMENTS:



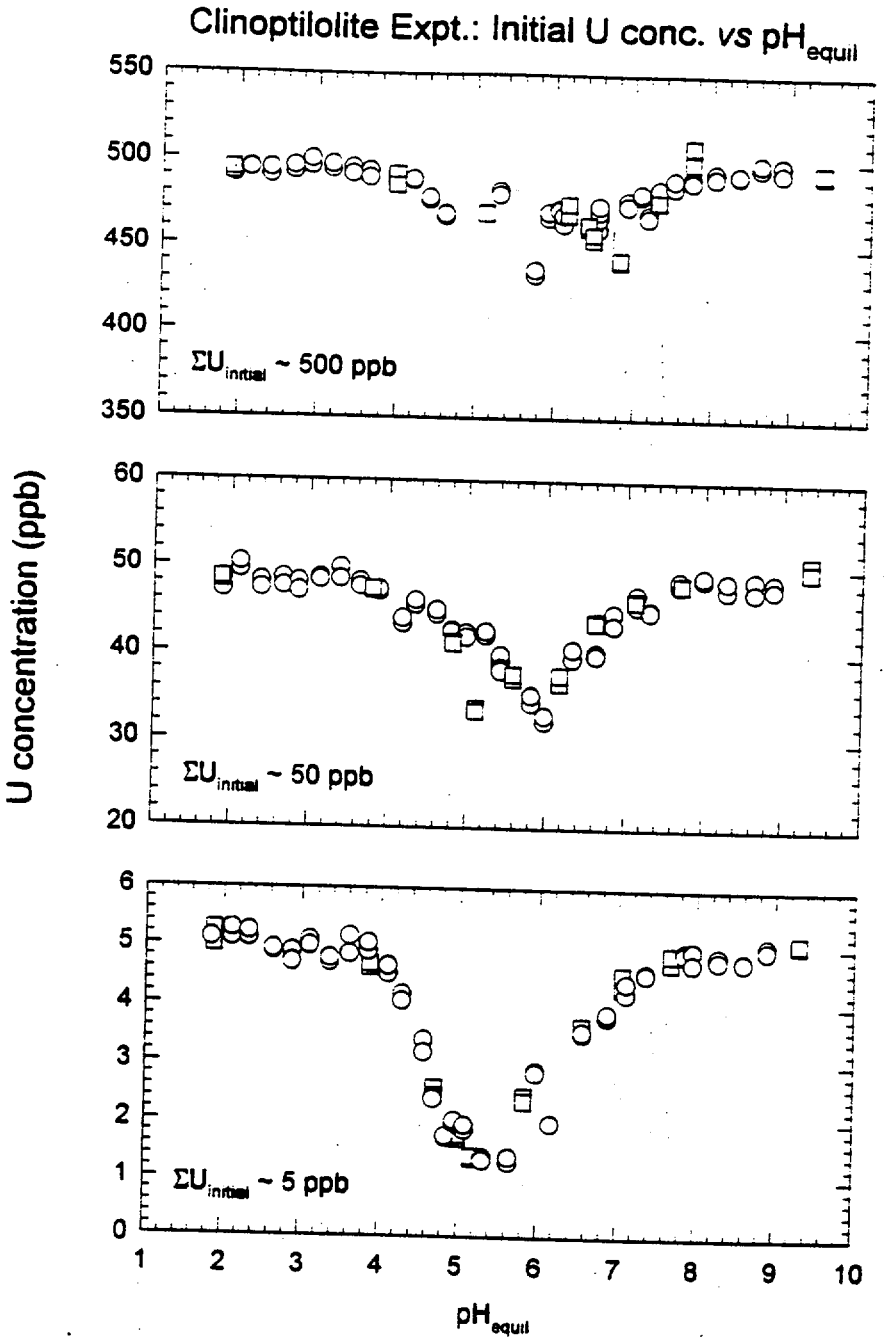
SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

URANIUM CONCENTRATIONS IN α-Al_2O_3 EXPERIMENTS:



SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

URANIUM CONCENTRATIONS IN CONTROL EXPERIMENTS (NO MINERALS PRESENT):



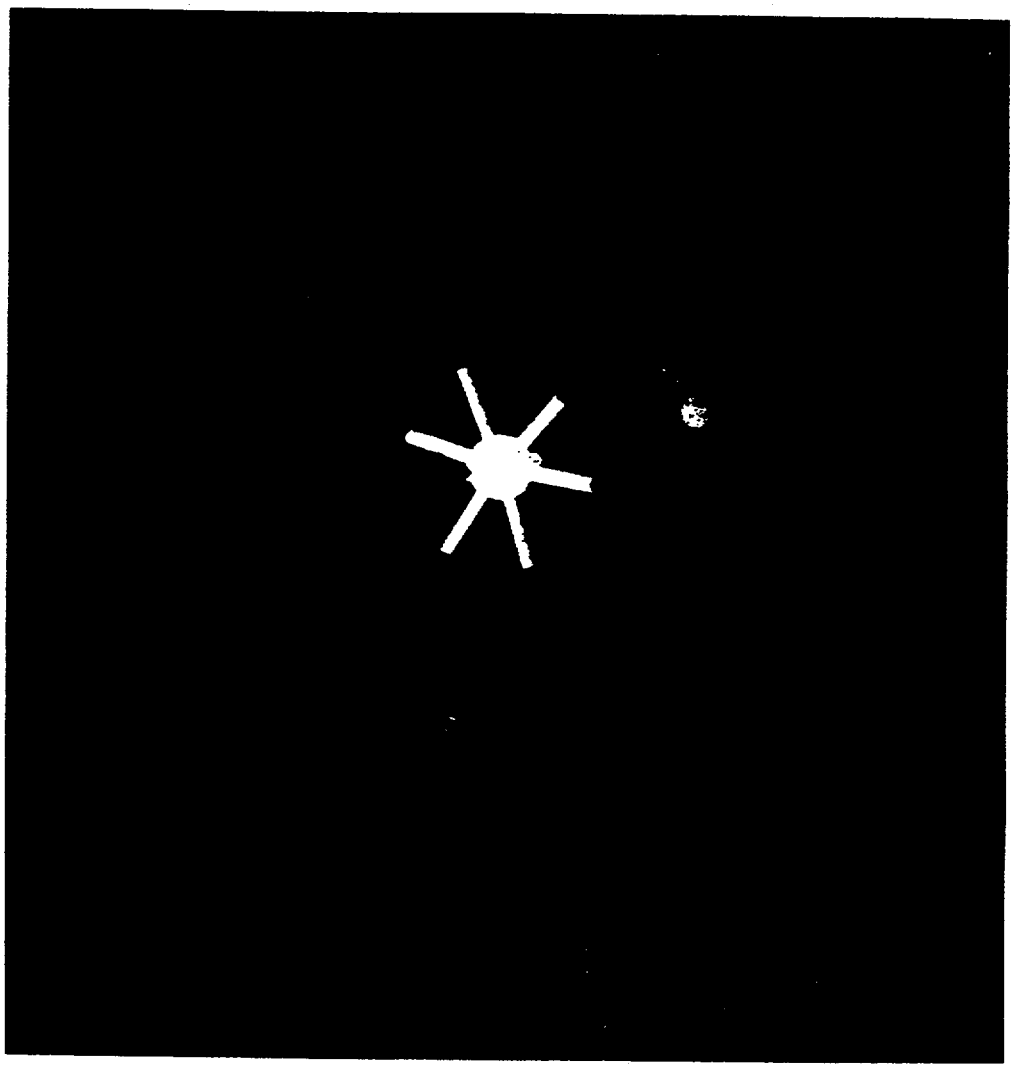
SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

SURFACE CHARACTERIZATION:

- MOLECULAR DYNAMICS SIMULATION OF URANIUM SORPTION (MOLECULAR SIMULATIONS SOFTWARE; M. LUPKOWSKI, SwRI)
  - THEORETICALLY-BASED THROUGH ENERGY MINIMIZATION AND NEWTON'S SECOND LAW ($F = m \cdot a$)
  - SIMULATE EFFECTS OF AQUEOUS SPECIATION AND MINERAL STRUCTURE
  - COMPLEMENTS INFORMATION DERIVED FROM SORPTION EXPERIMENTS AND SPECTROSCOPIC STUDIES (E.G., EXAFS)
- INITIATED CHARACTERIZATION OF MINERAL SURFACES USING ATOMIC FORCE MICROSCOPY

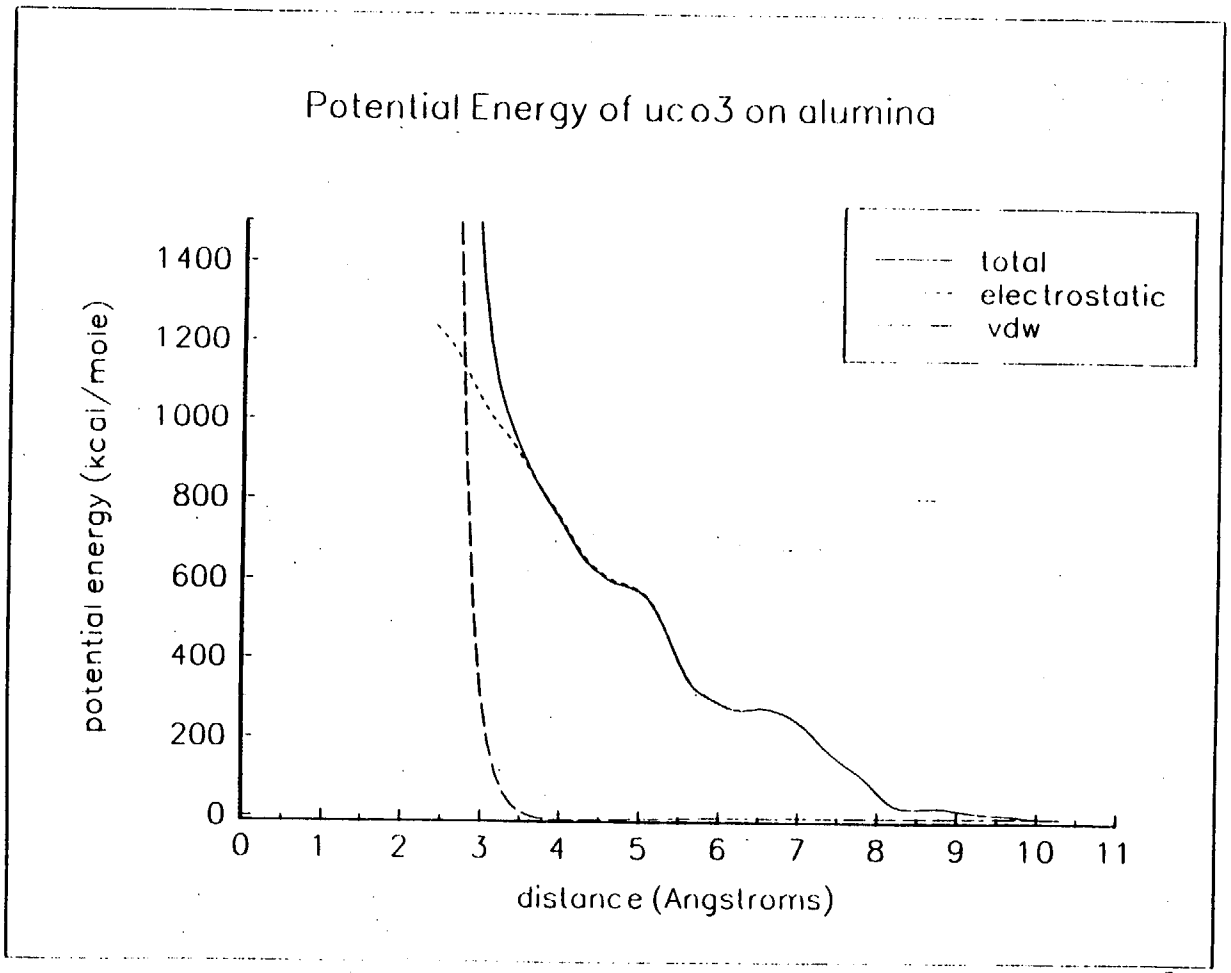
SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

MOLECULAR DYNAMICS: $UO_2(CO_3)_3^{4-}$ -BOND ANGLES AND LENGTHS BASED ON CRYSTALLOGRAPHIC DATA



SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

MOLECULAR DYNAMICS: $UO_2(CO_3)_3^{4-}$ ADSORPTION ON α-Al_2O_3 ENERGY DISTRIBUTION (NEGATIVE SURFACE CHARGE):



<h> ≅ 10.02 Å

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

MOLECULAR DYNAMICS: $UO_2(CO_3)_3^{4-}$ ADSORPTION ON α-Al_2O_3 WITH CO_3^{2-}:

$\langle h \rangle_U$ = [redacted] 10 Å

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

NEXT YEAR'S PROSPECTIVE

TASK 2 -

- EXPAND AND CONTINUE MODEL COMPARISON AND STREAMLINING; EVALUATE PREDICTIVE CAPABILITIES
- HYDROGEOCHEMICAL MODELING OF LABORATORY-SCALE TRANSPORT
- CONTINUE TO MODEL U-SORPTION RESULTS FROM TASK 3 - SORPTION EXPERIMENTS
- MODEL EFFECTS OF $p(CO_2)$, SOLID/LIQUID RATIO, $C_{radionuclide}$, IONIC STRENGTH
- RESULTS TO BE PRESENTED AT MIGRATION '93 (CHARLESTON, SC; DECEMBER, 1993)

SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

NEXT YEAR'S PROSPECTIVE:

TASK 3:

- CONTINUE SORPTION EXPERIMENTS ON CLINOPTILOLITE, MONTMORILLONITE, AND ALUMINUM OXIDE (VARIABLE pCO_2)
- INITIATE BATCH AND FLOW-THROUGH COLUMN EXPERIMENTS ON URANIUM SORPTION AND TRANSPORT USING WEDRON QUARTZ SAND
- INITIATE BATCH SORPTION EXPERIMENTS ON NEPTUNIUM
- INPUT EXPERIMENTAL DATA INTO TASK 2 (SORPTION MODELING)
- CONTINUE MOLECULAR DYNAMICS SIMULATIONS OF URANIUM SORPTION
- CONTINUE CHARACTERIZATION OF MINERAL SURFACES USING ATOMIC FORCE MICROSCOPY (USING FLUID CELL)
- RESULTS TO BE PRESENTED AT MIGRATION '93 (CHARLESTON, SC; DECEMBER, 1993)

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GEOCHEMICAL MECHANISMS AND EFFECTS OF VAPORIZATION IN THE NEAR FIELD OF A PROPOSED REPOSITORY AT YUCCA MOUNTAIN

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Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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GEOCHEMICAL MECHANISMS AND EFFECTS OF VAPORIZATION IN THE NEAR FIELD OF A PROPOSED REPOSITORY AT YUCCA MOUNTAIN

OUTLINE

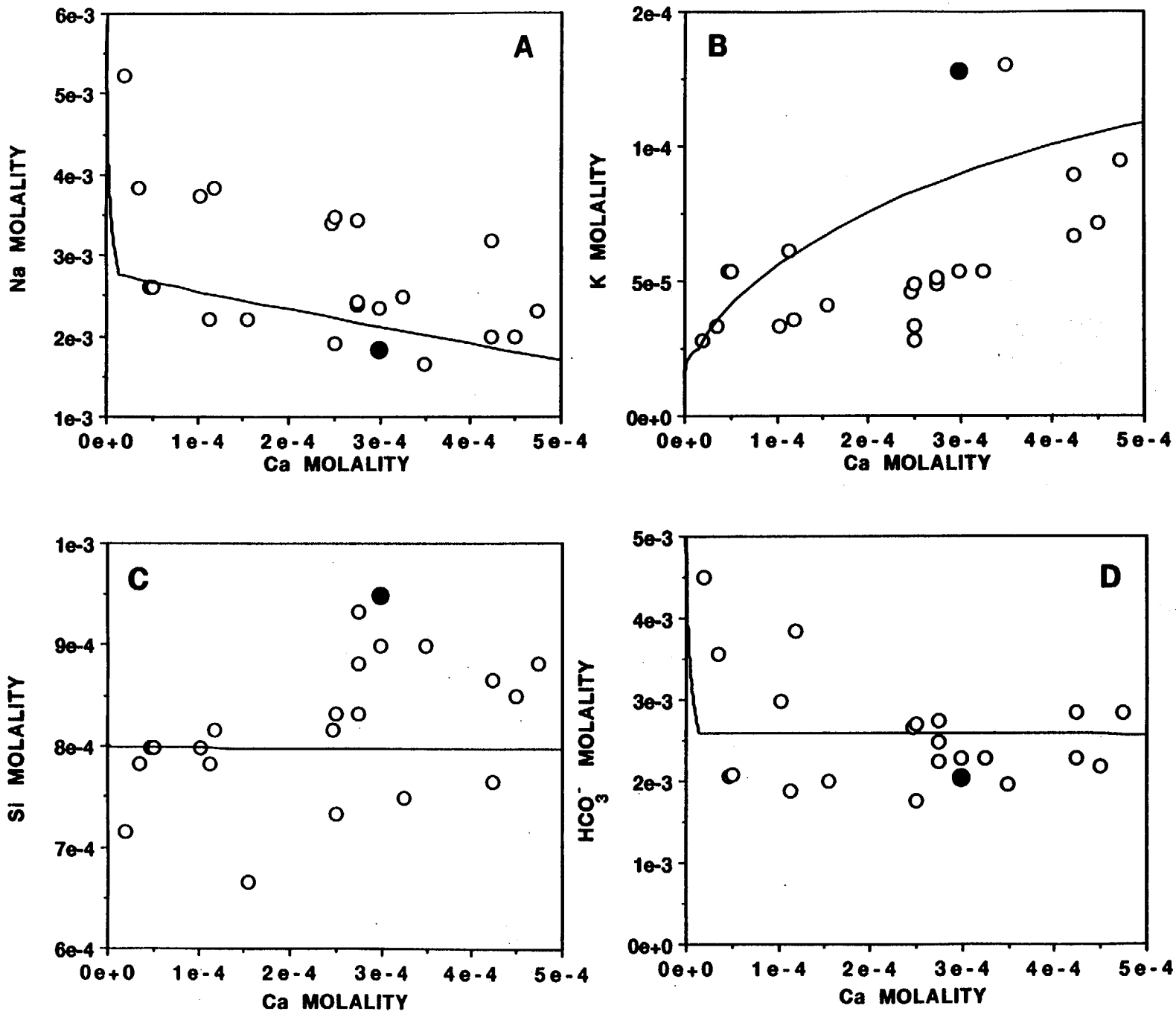
I. Partial equilibrium, multicomponent, reaction path model for natural conditions

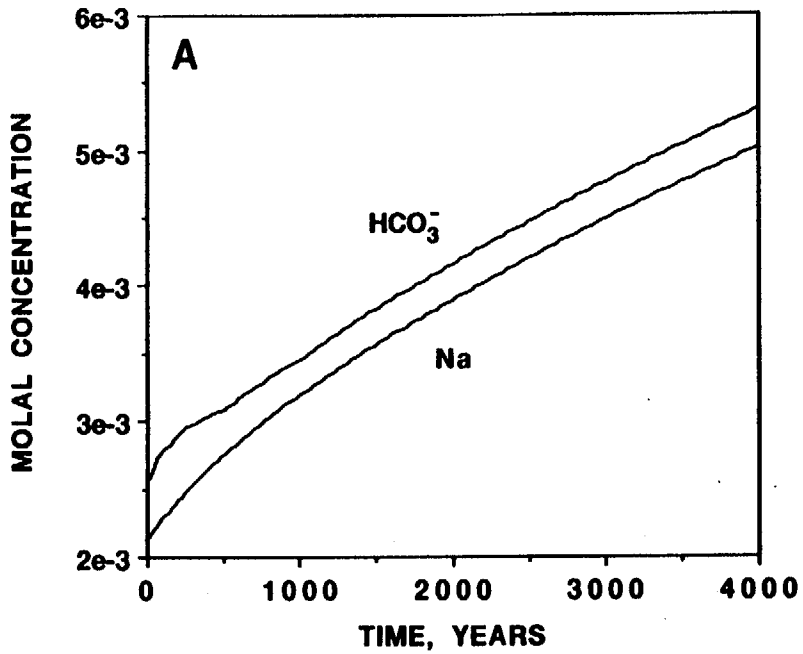
II. Nonisothermal, kinetic, multicomponent, partial equilibrium, reaction path model for heated repository conditions

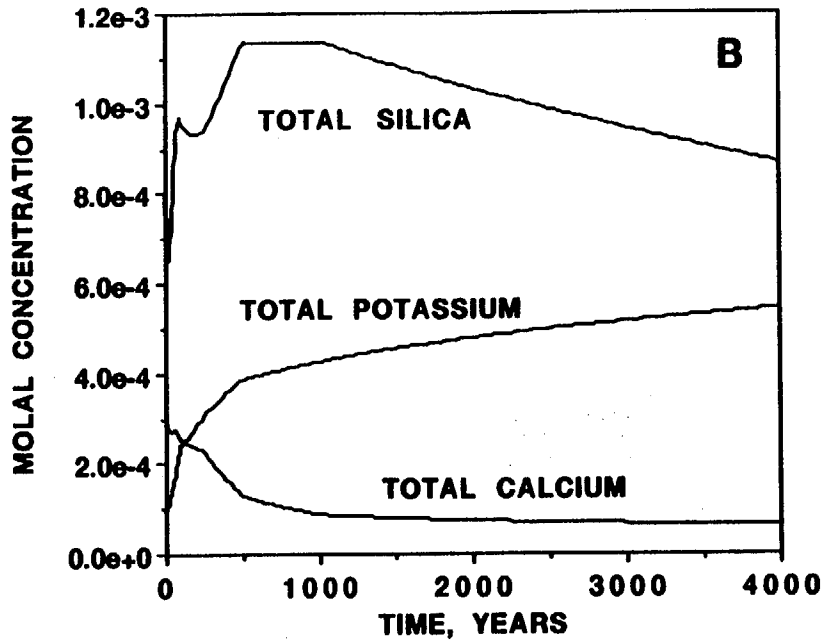
III. Local equlibrium, multicomponent, 100°C, reaction path model for boiling to 99.6% dry, assuming CO_2 buffering, using extended Debye Huckel equation

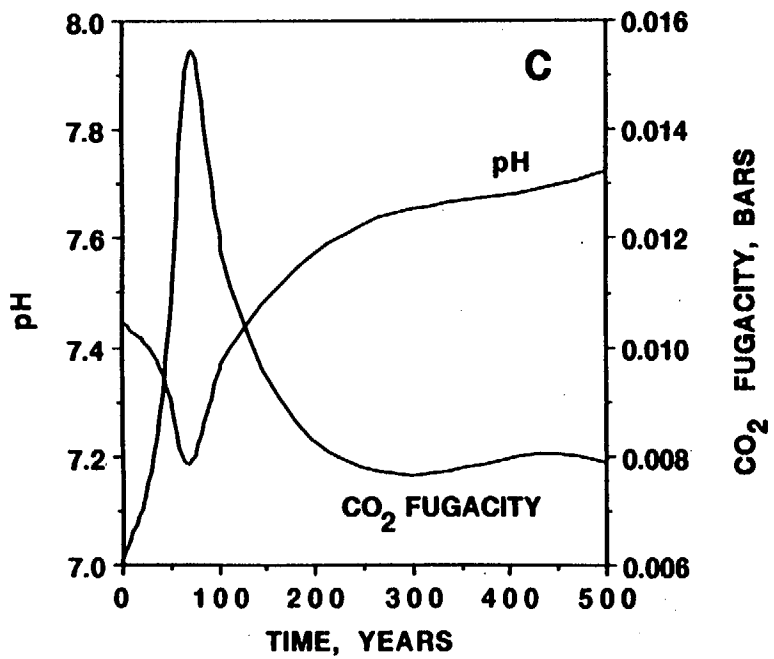
IV. Rayleigh fractionation model for CO_2 and H_2O volatilization for the carbonate system at 100°C

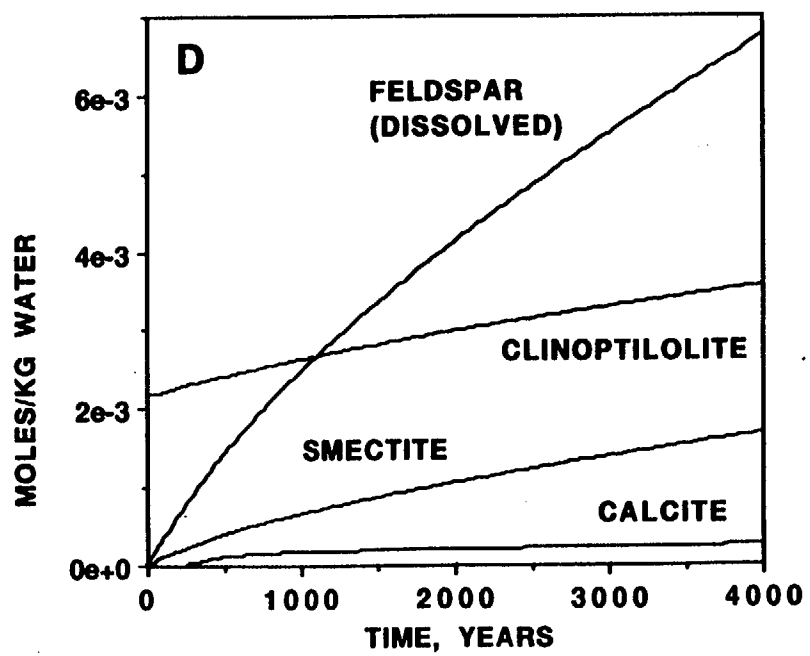
V. Local equilibrium, multicomponent (with no silica), 25°C, reaction path model for evaporation to 99.997% dry, assuming alternate buffered CO_2 pressures, using Pitzer equations

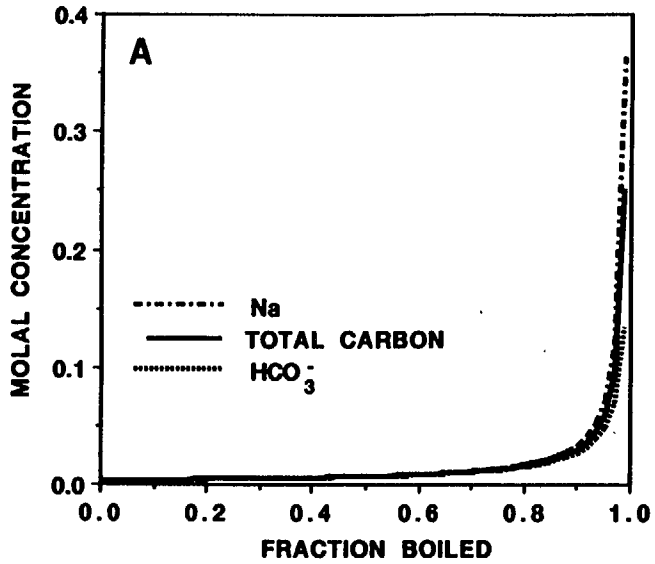

A
Na MOLALITY
6e-3
5e-3
4e-3
3e-3
2e-3
1e-3
0e+0
1e-4
2e-4
3e-4
4e-4
5e-4
Ca MOLALITY
B
K MOLALITY
2e-4
1e-4
5e-5
0e+0
Ca MOLALITY
C
Si MOLALITY
1e-3
9e-4
8e-4
7e-4
6e-4
Ca MOLALITY
D
HCO_3^- MOLALITY
5e-3
4e-3
3e-3
2e-3
1e-3
0e+0
Ca MOLALITY

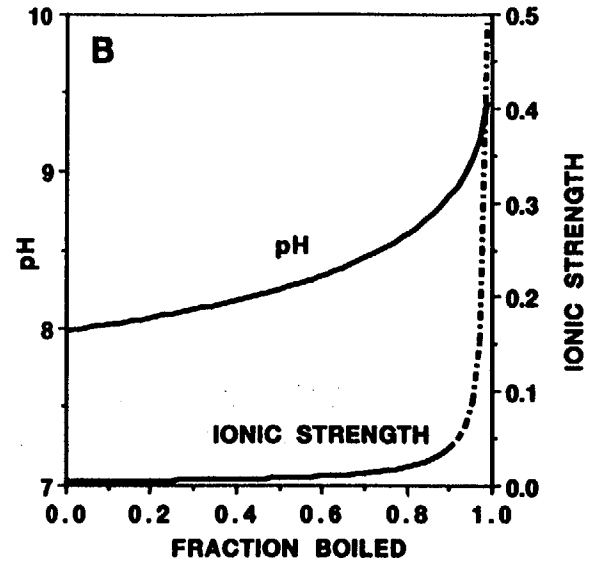

A
MOLAL CONCENTRATION
6e-3
5e-3
4e-3
3e-3
2e-3
HCO_3^-
Na
0
1000
2000
3000
4000
TIME, YEARS

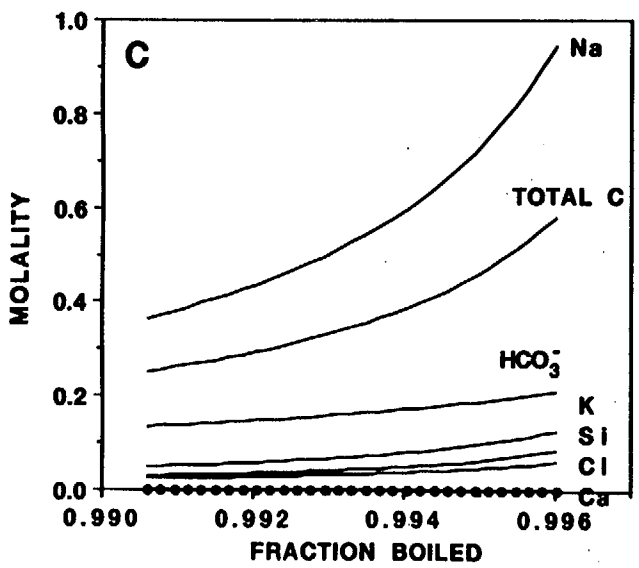

B
MOLAL CONCENTRATION
1.2e-3
1.0e-3
8.0e-4
6.0e-4
4.0e-4
2.0e-4
0.0e+0
TOTAL SILICA
TOTAL POTASSIUM
TOTAL CALCIUM
0
1000
2000
3000
4000
TIME, YEARS

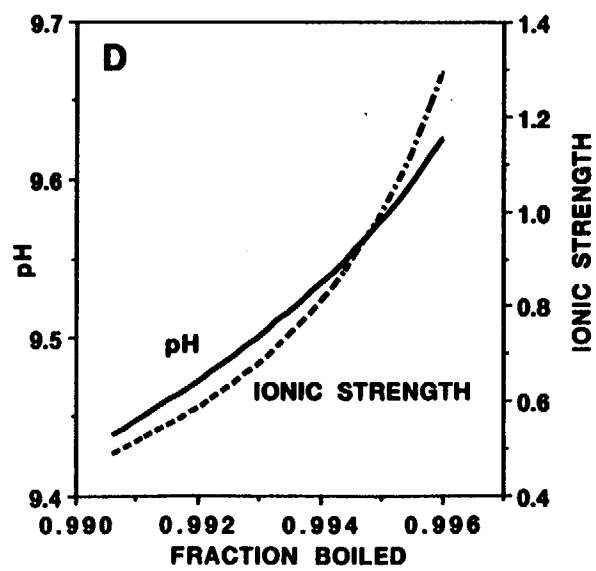

C
pH
8.0
7.8
7.6
7.4
7.2
7.0
0.016
0.014
0.012
0.010
0.008
0.006
CO_2 FUGACITY, BARS
pH
CO_2 FUGACITY
0
100
200
300
400
500
TIME, YEARS

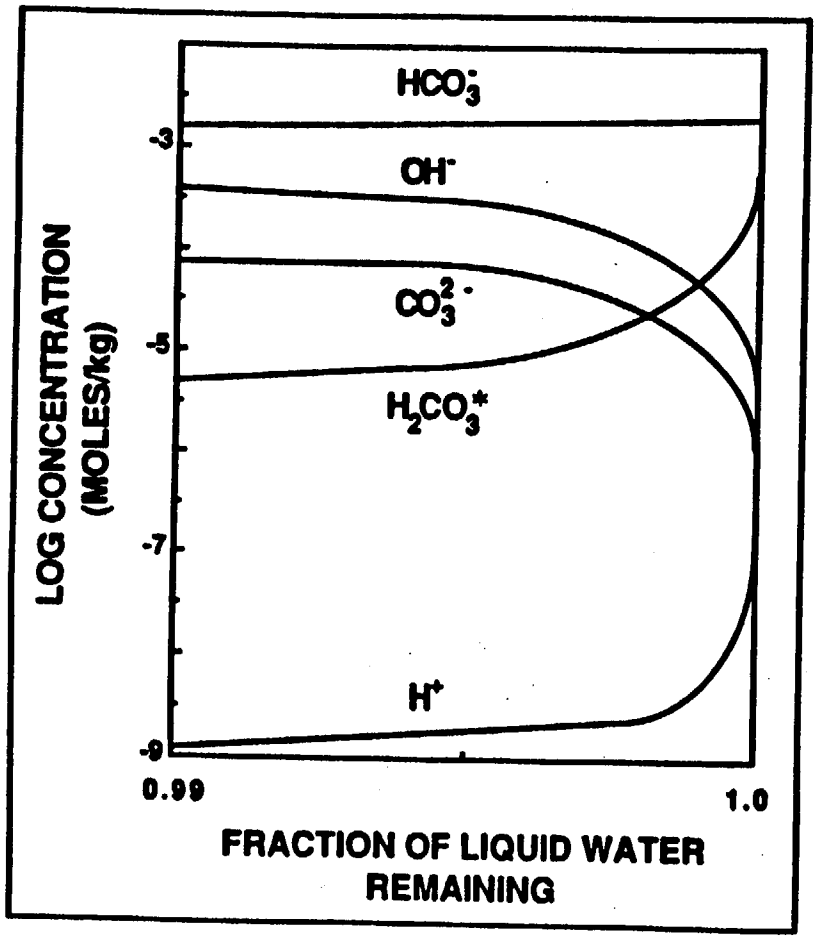

D
MOLES/KG WATER
6e-3
4e-3
2e-3
0e+0
FELDSPAR
(DISSOLVED)
CLINOPTILOLITE
SMECTITE
CALCITE
0
1000
2000
3000
4000
TIME, YEARS


A
MOLAL CONCENTRATION
0.0
0.1
0.2
0.3
0.4
Na
TOTAL CARBON
HCO3-
0.0
0.2
0.4
0.6
0.8
1.0
FRACTION BOILED


B
pH
7
8
9
10
IONIC STRENGTH
0.0
0.1
0.2
0.3
0.4
0.5
pH
IONIC STRENGTH
0.0
0.2
0.4
0.6
0.8
1.0
FRACTION BOILED


C
MOLALITY
0.0
0.2
0.4
0.6
0.8
1.0
Na
TOTAL C
HCO3-
K
Si
Cl
Ca
0.990
0.992
0.994
0.996
FRACTION BOILED


D
pH
9.4
9.5
9.6
9.7
IONIC STRENGTH
0.4
0.6
0.8
1.0
1.2
1.4
pH
IONIC STRENGTH
0.990
0.992
0.994
0.996
FRACTION BOILED



Sci. Géol., Bull., 42, 4, p. 313 - 327, Strasbourg, 1989

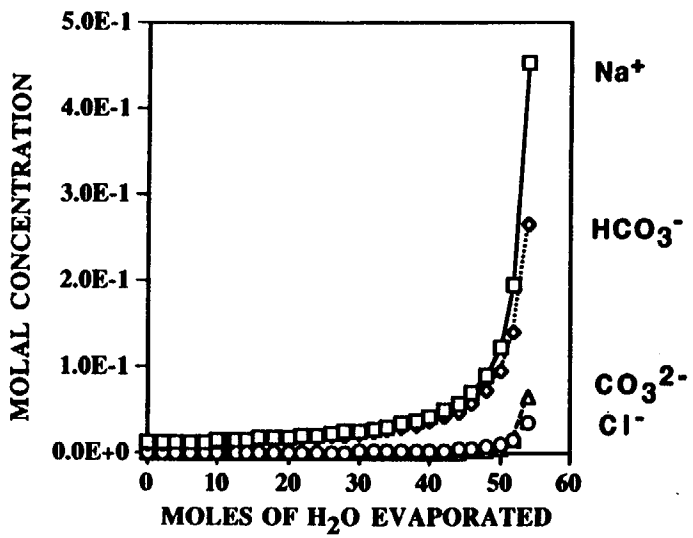
AN ANALYSIS OF GAS-WATER-ROCK INTERACTIONS DURING BOILING IN PARTIALLY SATURATED TUFF

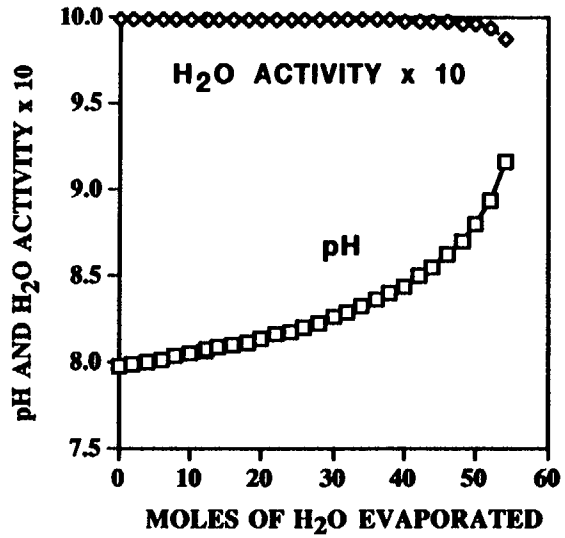
Randolph C. ARTHUR* and William M. MURPHY**

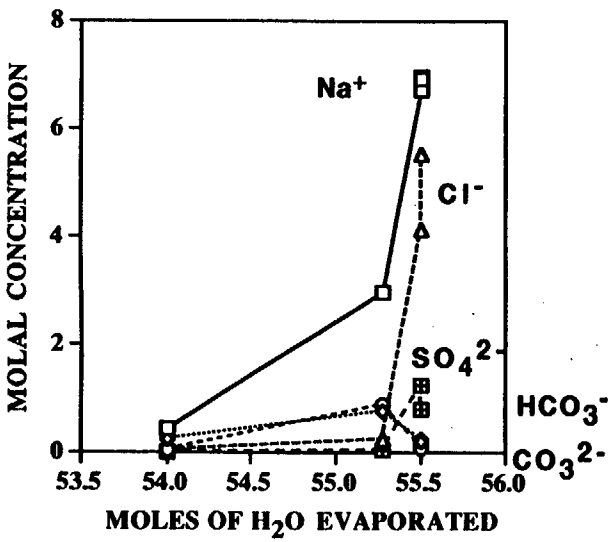
— Figure 2 —

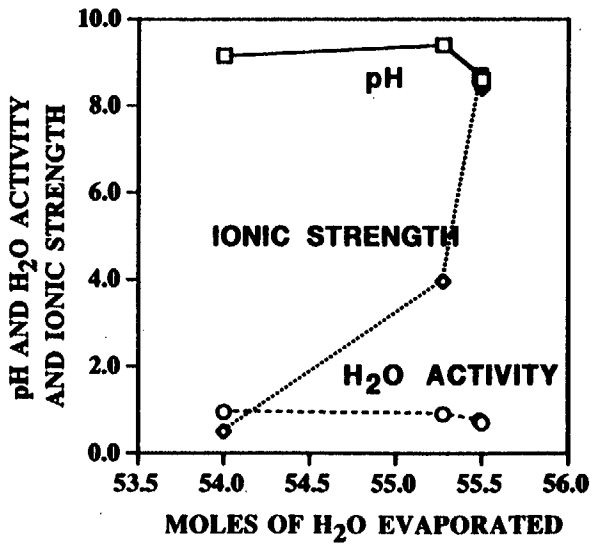
Speciation of dissolved carbonate and H_2O relative to the fraction of H_2O remaining in the liquid phase, ψ, during open-system boiling. The initial system is represented by values at $\psi = 1$, and the system evolves to the left.

Distribution des espèces aqueuses dans le système CO_2-H_2O en fonction de la fraction de la masse d'eau présente dans la phase liquide, ψ, durant l'ébullition en système ouvert. Le système initial correspond à $\psi = 1$, et l'évolution du système s'effectue de la droite vers la gauche.


MOLAL CONCENTRATION
5.0E-1
4.0E-1
3.0E-1
2.0E-1
1.0E-1
0.0E+0
0
10
20
30
40
50
60
MOLES OF H_2O EVAPORATED
Na^+
HCO_3^-
CO_3^{2-}
Cl^-


pH AND H_2O ACTIVITY x 10
10.0
9.5
9.0
8.5
8.0
7.5
0
10
20
30
40
50
60
MOLES OF H_2O EVAPORATED
H_2O ACTIVITY x 10
pH


MOLAL CONCENTRATION
8
6
4
2
0
53.5
54.0
54.5
55.0
55.5
56.0
MOLES OF H_2O EVAPORATED
Na^+
Cl^-
SO_4^{2-}
HCO_3^-
CO_3^{2-}


pH AND H_2O ACTIVITY AND IONIC STRENGTH
10.0
8.0
6.0
4.0
2.0
0.0
53.5
54.0
54.5
55.0
55.5
56.0
MOLES OF H_2O EVAPORATED
pH
IONIC STRENGTH
H_2O ACTIVITY

EVAPORATION MODEL
25°C, NO SILICA, DOLOMITE SUPPRESSED, HIGHER p CO_2
PITZER EQUATIONS (HMW)

Percent Boiled	Mineral Assemblage	Dominant Water Chemistry	pH NBS/rational	Ionic Strength
0.0	Calcite ($CaCO_3$)	Na^+,HCO_3^-	8.0/7.9	0.014
22.6	+Magnesite ($MgCO_3$)	Na^+,HCO_3^-	8.1/8.0	0.018
99.59	+Nahcolite ($NaHCO_3$)	Na^+,CO_3^{2-},HCO_3^-	9.4/9.1	4.0
99.973	+Thenardite (Na_2SO_4)	Na^+,Cl^-,(SO_4^{2-})	8.7/9.4	8.5
99.979	+Halite (NaCl)	Na^+,Cl^-,(SO_4^{2-})	8.6/9.6	8.4
99.988	+Aphthitalite ($NaK_3(SO_4)_2$)	Na^+,Cl^-,(K^+, SO_4^{2-})	8.6/9.6	8.9
99.997		Na^+,Cl^-,(K^+, SO_4^{2-})	8.6/9.6	8.9

EVAPORATION MODEL
25°C, NO SILICA, DOLOMITE SUPPRESSED, LOWER p CO_2
PITZER EQUATIONS (HMW)

Percent Boiled	Mineral Assemblage	Dominant Water Chemistry	pH NBS/rational	Ionic Strength
0.0	none	Na^+, HCO_3^-, Cl^-	8.0/8.0	0.005
7.1	Calcite ($CaCO_3$)	Na^+,HCO_3^-,Cl^-	8.0/8.0	0.0055
57.4	+Magnesite ($MgCO_3$)	Na^+,Cl^-,HCO_3^-	8.2/8.1	0.009
99.965	+Halite (NaCl)	Na^+,Cl^-,K^+,(CO_3^{2-})	9.0/10.0	6.5
99.983	+Pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$)	Na^+,Cl^-,(K^+,CO_3^{2-})	9.3/10.1	7.1
99.993	+Sylvite (KCl)	Cl^-,Na^+,(K^+)	9.3/10.2	7.8
99.997	+Aphthitalite ($NaK_3(SO_4)_2$)	Cl^-,Na^+,(K^+, SO_4^{2-})	9.3/10.3	8.4

CONCLUDING REMARKS: SPECULATIVE GEOCHEMICAL CONSEQUENCES OF VAPORIZATION RELEVANT TO REPOSITORY PERFORMANCE

SOLUTIONS AT A REWETTING FRONT WOULD DISSOLVE PRECIPITATED SALTS AND BECOME CONCENTRATED IN SODIUM, CHLORIDE, AND SULFATE

SOLUTIONS THAT DRIP ON CONTAINERS AND EVAPORATE WOULD EVOLVE TOWARD HIGHER pH, AND HIGHER SODIUM (BI-)CARBONATE AND CHLORIDE CONCENTRATIONS

WATER CHEMISTRY CHANGES WOULD AFFECT CONTAINER AND WASTE FORM ALTERATION PROCESSES AND RADIONUCLIDE SPECIATION

VAPOR PRESSURE LOWERING AT EQUILIBRIUM WITH SALTS COULD AFFECT MOISTURE DISTRIBUTION

MINERAL DISSOLUTION AND GROWTH COULD AFFECT HYDROLOGIC PROPERTIES OR FLOW PATHS

FLUID REFLUXING COULD AUGMENT EFFECTS OF VAPORIZATION

U.S. DEPARTMENT OF ENERGY

OCRWM

YUCCA MOUNTAIN

YUCCA MOUNTAIN
SITE CHARACTERIZATION
PROJECT

INTEGRATION WITH TOTAL SYSTEM PERFORMANCE ASSESSMENT (TSPA)

PRESENTED TO

DOE/NRC TECHNICAL EXCHANGE

PRESENTED BY

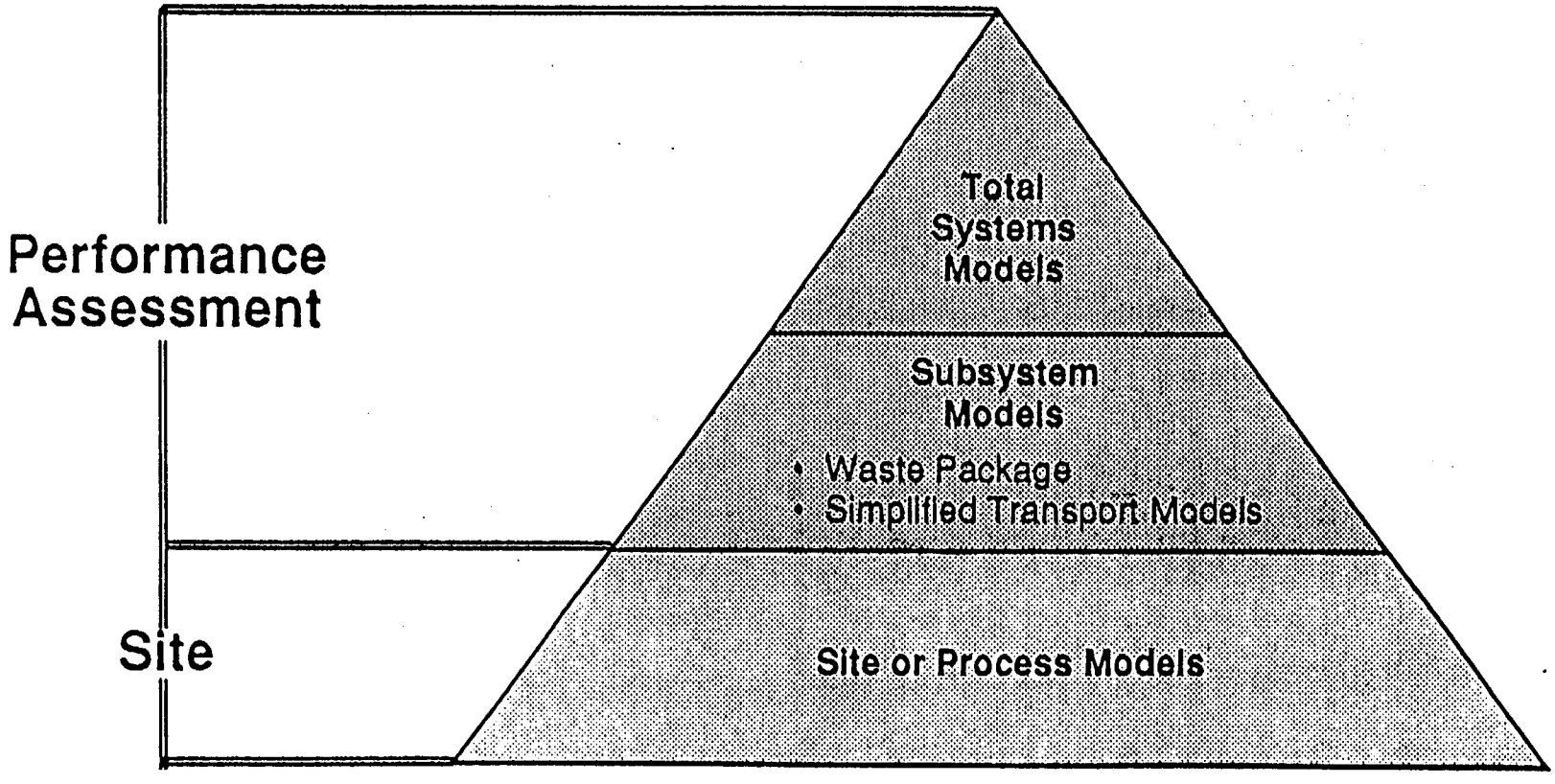
ARDYTH SIMMONS

OCTOBER 13, 1993

INTEGRATION WITH TOTAL SYSTEM PERFORMANCE ASSESSMENT (TSPA)

- December 1991 workshop. "Integration of Geochemistry with Performance Assessment"
- Elicitation of Kd's for TSPA 1
- March 1993 exchange on data needs for TSPA
  - TSPA defined needed parameters
  - Refined values of Rn solubilities; data using J-13
  - Effect of temperature on solubility
- May 1993 attempted to incorporate colloid transport into TSPA 2
- Input to retardation sensitivity analysis - maintain iterative approach
- Hypothesis testing by PA to determine what information is needed with greater confidence

PERFORMANCE ASSESSMENT STRATEGY



INTPALA5.125/10-12-93

SolWOG Consensus Values for the Potential Range of Actinide Solubilities at Yucca Mountain and Environs

Radionuclide	Minimum Value	Maximum Value	Expected Value	Coefficient of Variation	Distribution
Uranium	10^{-8}	10^{-2}	$10^{-4.5}$	0.20	log beta
Neptunium	5×10^{-6} (10^{-8})	10^{-2}	10^{-4}	? (0.20)	log beta
Plutonium	10^{-8} (10^{-10})	10^{-6}	-	-	uniform
Americium	10^{-10}	10^{-6}	-	-	uniform

All concentration values are in molarity units.

Probability Distributions for Kd

Element (rock type)	Distribution Type*	Mean value (ml/g)	Illustrated in Figure Number
Carbon, Iodine, Technetium	constant	0	—
Tin, Plutonium, Americium	constant	100	—
Uranium, Selenium (devitrified)	uniform	2.5	3-11
Uranium, Selenium (zeolitic)	beta	10	3-12
Uranium, Selenium (vitric)	uniform	2	3-13
Neptunium (devitrified)	beta	2	3-14
Neptunium (zeolitic)	beta	4	3-15
Neptunium (vitric)	beta	0.5	3-16
Cesium (devitrified)	beta	50	3-17
Cesium (zeolitic)	beta	2000	3-18
Cesium (vitric)	beta	50	3-17

from TSPA (SNL, 1992)

INTPALA23.125/10-12-93

SUMMARY OF U.S. NUCLEAR REGULATORY COMMISSION AND
U.S. DEPARTMENT OF ENERGY TECHNICAL EXCHANGE ON
NEAR-FIELD RADIONUCLIDE RELEASES FROM THE ENGINEERED BARRIER SYSTEM
October 14, 1993, Los Alamos, NM

On October 14, 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 near-field radionuclide releases from the engineered barrier system. The purpose of the technical exchange was to hold discussions on previous and on-going experiments and computer simulations of near-field phenomena for the Yucca Mountain candidate repository. 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) and Lawrence Livermore National Laboratory. Discussions focused on the effects of heat on the engineered barrier system (EBS) and the saturation of the rock, circulation of air and water vapor, effects of fractures, post-waste emplacement changes in water chemistry, and conceptual models of releases of radionuclides from the EBS. The agenda also included a presentation by an NRC consultant from the Center for Nuclear Waste Regulatory Analyses on analyses of thermally driven vaporization, condensation, and flow around waste packages.

All participants and attendees were provided opportunities for questions and discussion during the technical exchange. At the conclusion of technical exchange presentations, Ms. Ardyth Simmons (DOE YMP) provided a brief synopsis of the status of DOE activities to address unresolved NRC Site Characterization Analysis concerns related to the technical exchange topic.

In the closing remarks, all parties agreed that the presentations had been beneficial and that appropriate time had been allowed for discussion. NRC participants commented that key information related to spent fuel degradation should be integrated into experiments and noted the importance of the field heater tests. The State of Nevada representative observed that DOE activities and presentations appeared to emphasize matrix effects, and that future interactions should focus more on discussions of fracture and rock properties and fracture flow. The representative from Nye County stressed the importance of tests and modeling of the Calico Hills tuff because of that unit's importance to radionuclide migration. He also noted the importance of examining bounding scenarios in determining whether or not the hot and dry repository concept will be used. The Inyo, California, representative stressed the need for site data as input to models and the importance of examining mass transport in alternative ways to strengthen hydrochemical

modeling efforts. He also stated that, because the technical content of performance assessment discussions is limited by the data available at this time, he believed that a discussion on experiments related to radionuclide releases from the waste form should have been substituted for this agenda item.

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
NEAR-FIELD PHENOMENA RELATED TO RADIONUCLIDE RELEASES FROM THE ENGINEERED BARRIER SYSTEM

October 14, 1993 at Los Alamos, NM

8:00	Welcome/Protocol	DOE, NRC, State, Counties
8:15	Overview of radionuclide release studies	DOE (Simmons)
8:45	Modeling effects of heat on the saturation of rock and on the circulation of air and water vapor and modeling of dripping in fractures in the heated zone	DOE (Buscheck)
10:00	BREAK	
10:15	Modeling of coupled processes in the altered zone	DOE (Glassley)
11:00	Testing geochemical modeling codes using New Zealand hydrothermal systems	DOE (Bruton)
11:30	Radiation effects on environmental conditions	DOE (Van Konynenburg)
12:00	LUNCH	
1:15	Experiments on the interactions of steam and water with the components of the EBS	DOE (McCright)
2:00	Integrated testing	DOE (Viani)
2:45	BREAK	
3:00	Conceptual models for releases of radionuclides from the EBS in realistic near- field environments (source term)	DOE (Halsey)
3:45	Thermally driven vaporization, condensation, and flow around waste package	NRC
4:30	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 (PLEASE PRINT)	COMPANY	TITLE
1	Homi Minwalla	WESTON	Task Leader, Nuclear Licensing
2	Steven E. LeRoy	M&O/Duke	Senior Scientist
3	Arend Meijer	Jacobs	Geochemist
4	Raymond H. Wallace Jr.	USGS/HQ	Hydrologist/Liaison to DOE
5	Alan Mitchell	LANL	TCO
6	Rich Van Konynenburg	LLNL	Engineer
7	Robert W. Luce	NWTRB	Sr. Prof. Staff
8	Chris Einberg	DOE/HQ	Engineer
9	Dave Clark	LANL	Staff Member
10	Paul Bertetti	CNWRA	Research Scientist
11	STEVE KUNG	LANL	STAFF MEMBER
12	Randall D. Manteufel	CNWRA	Research Engineer
13	David Turner	CNWRA	Sr. Research Scientist
14	ANDERS WISTROM	LANL	Res Ac.
15	MARVA Johnson	State	Tech Coordin.
16	Edw. C. TAYLOR	M&O/TRW	Sr Scientist
17	Charlotte Abrams	NRC	Sr Proj Mgr
18	Bill HALSEY	LLNL	ENGINEER/TAL-P.A.
19	[illegible]	NYE County	Reg. + Licensing Advisor
20	Donald E. [illegible]	TRAC	Geoscientist
21	John W Bradbury	NRC	Geochemist
22	CARL JOHNSON	NEVADA	TECH. MGR
23	Ginny Colten-Bradley	NRC	Geochemist
24	David Stahl	M&O/BWFC	Mgr, WP Math & Perf Analysis

DOE-NRC Technical Exchange Oct 14, 1993
Near-field Phenomena Related to Radionuclide Releases from the EBS

	NAME (PLEASE PRINT)	COMPANY	TITLE
25	R William Nelson	M&O/INTERA	Sr Staff Consultant
26	Bruce Robinson	LANL	PI Reactive Tracer Study
27	Tom Buscheck	LLNL	Hydrologist
28	Steve Nelson	M&O/WCFS	Geoscientist
29	Daniel McCright	LLL	Metallurgical Engineer
30	Don Langmuir	NWTRB	Geochemist
31	Don Shettel	GMII	Geochemist
32	Marvin Morgenstern	GMII	Geochem, Mineralogy
33	R Daniel Dresser	Weston	Task Leader Regulatory Compliance
34	Andy H Simmons	DOE	Phys-Sci.
35	Barbara Carlos	LANL	PI Fracture Mineralogy
36	[illegible]	NEI	Sr Systems Analyst
37	Brian Viani	LLNL	Chemist
38	Bill Glassley	LLNL	Geochemist
39	William Murphy	CNWRA	Principal Scientist
40	Steven Saterlie	M&O/TRW	Thermal Loading Study Mgr.
41	George Zyvoloski	LANL	Geoscientist
42	APRIL V. GIL	DOE/YMP	Geologist
43	Stephen Bolivar	Los Alamos	Geologist/QA Manager
44	Peter Lichtner	CNWRA	Principal Scientist
45	Lynn Deering	ACNW	Sr Staff Scientist
46	Bill Steinkampf	USGS	Geochemist
47	Carol J. Bruton	LLNL	Geochemist
48			