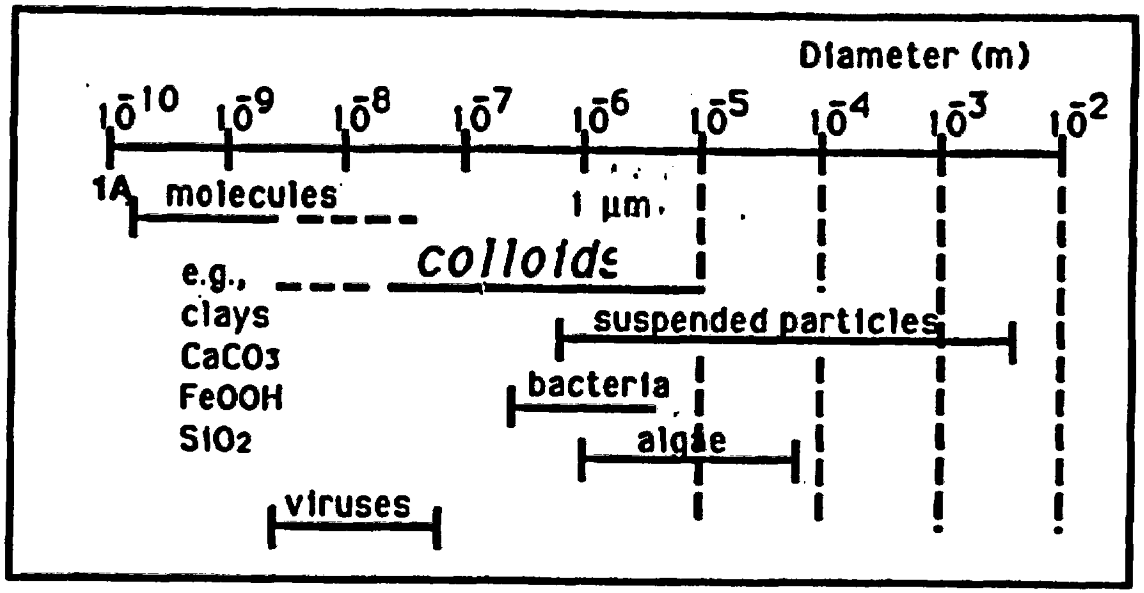
Review of LANL Colloid Investigations

Ines Triay



Diameter (m)
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
1A
molecules
1 µm
colloids
e.g.,
clays
$CaCO_3$
FeOOH
SiO_2
suspended particles
bacteria
algae
viruses

Colloid Nomenclature

Groundwater (or aquatic) colloids: naturally occurring colloids in aquatic systems; consist of inorganic and/or organic molecular constituents (or microorganisms)

Real actinide colloids (Radiocolloids): produced by the agglomeration of hydrolyzed actinide ions

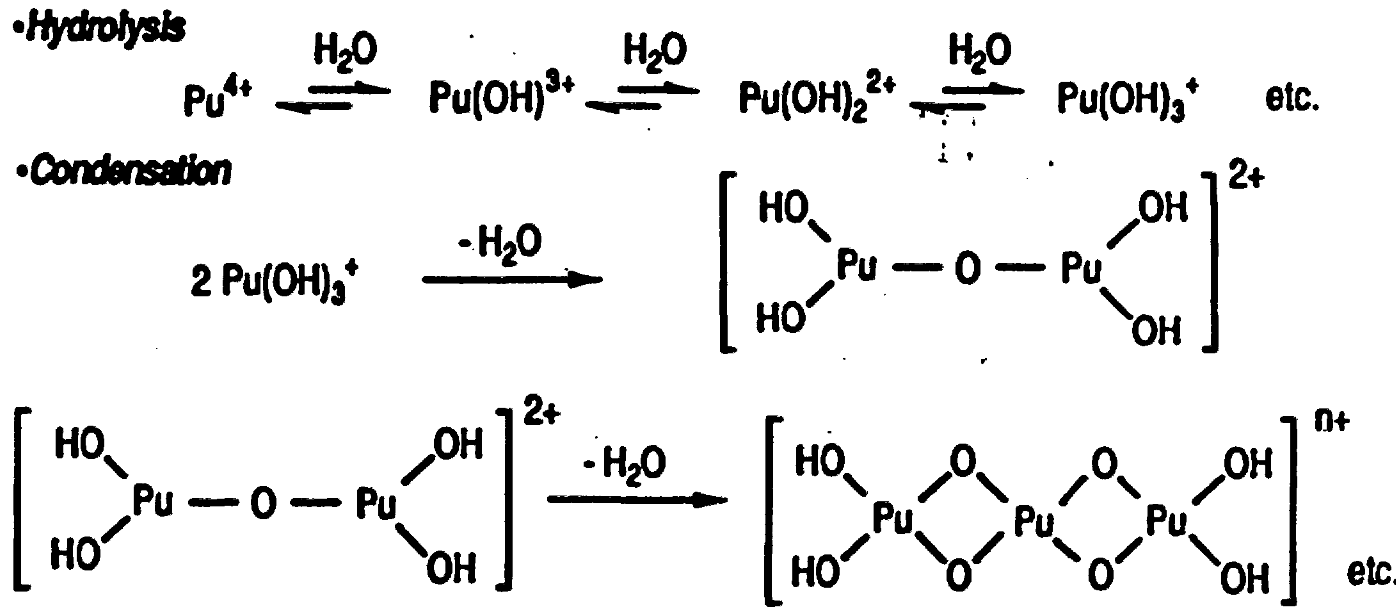
Pseudocolloids: generated by the association of radionuclides (in soluble or colloidal form) with groundwater or repository-generated colloids

Part One:

Column Experiments with Pu(IV) Real Colloids

Real Pu(IV) Colloids

- produced by the agglomeration of hydrolyzed Pu(IV) ions
- electrochemically reactive and structurally similar to plutonium oxide
- stable under acidic conditions; are in the size range from ~1 nm to 0.4 μm



Stepwise formation of plutonium(IV) colloid

Size Determination of Pu Colloids Using APS

Pu(IV) Colloid	Method of Preparation	Molarity[a]	pH	Age[b] days	Diameter(s)[c] nm
A	Pu(IV) in 2M HNO_3 taken to dryness in air stream; distilled water added to form colloid; suspension aged at room temperature for 30 days	0.002	2.4	30	ND
1	Dropwise addition of Pu(IV) stock[d] to distilled water	0.01	1.3	223	3.7
2	Dropwise addition of Pu(IV) stock to distilled water and aging at room temperature	0.003	2	606	2.6
3	Dropwise addition of Pu(IV) stock to distilled water at 70°C	0.003	1.65	45	2.1
4	Dropwise addition of Pu(IV) stock to distilled water; heated at 75-80°C for 4.5 hours	0.01	1.3	20 223	4.0 5.7

Pu Colloids (Continued)

Pu(IV) Colloid	Method of Preparation	Molarity[a]	pH	Age[b] days	Diameter(s)[c] nm
5	Aliquot of Pu(IV) colloid suspension A heated at 90°C for 285 hours; purification by centrifugation and cation exchange followed	0.003	~2	37	6.1
6	Pu(IV) stock taken to near dryness and 0.001 M HCl added to form colloid	0.015	1.6	216	3.0
7	Aliquot of Pu(IV) colloid suspension A evaporated to about 1/2 its initial volume in a stream of air at 40°C; purification by cation exchange followed	0.003	~2	43	0.2 & 7.1
8	Pu(IV) in 0.5 M HNO_3 diluted to 0.08 M acid followed by near neutralization using 1 M NaOH	0.008	1.7	14	1.5
9	Pu(IV) stock added to 0.7 M $NaHCO_3$ with stirring; precipitate washed with water and peptized in 0.02 M HNO_3 at 80°C for 2.5 hr and then centrifuged and suspended in 0.01 M HNO_3	0.05	2	26	14. & 370

Pu Colloids (Continued)

Pu(IV) Colloid	Method of Preparation	Molarity[a]	pH	Age[b] days	Diameter(s)[c] nm
10	Aliquot of Pu(IV) colloid suspension A brought to pH 4 with $NaHCO_3$; precipitate washed with dilute HNO_3 and suspended in 0.01 M HNO_3; solid remaining removed by centrifugation	0.003	~2	49	13. & 150
11	Aliquot of Pu(IV) colloid suspension A brought to pH 5 with $NaHCO_3$; precipitate washed with water and heated 29.5 hours at 93°C; precipitate washed with dilute HNO_3, peptized in 0.05 M HNO_3 at 40°C for 30 minutes, and then centrifuged and suspended in 0.01M HNO_3	0.003	~2	37	41.
12	Slow auto-oxidation[e] of Pu(III) at pH 4	0.006	2.8	227	32.
13	50-50 mixture of #3 and #12 by volume				1.5 & 33.

Notes:

(a) Moles of Pu, as monomer, per liter
(b) Age at the time of the APS determination
(c) Most probable diameter; Analyzed using Regularization
(d) Typical stock was about 1 M in Pu and 3-4 M in HCl
(e) Alpha induced and/or air oxidized

Colloid Transport Experiments through Crushed Tuff with J-13

- investigated the retardation of Pu(IV) real colloid (polymer) through columns made of crushed tuff (in the size range from 75 to 500 μm)

- columns used were 5 cm long and 0.45 cm in diameter with a porosity of 0.5 to 0.6.

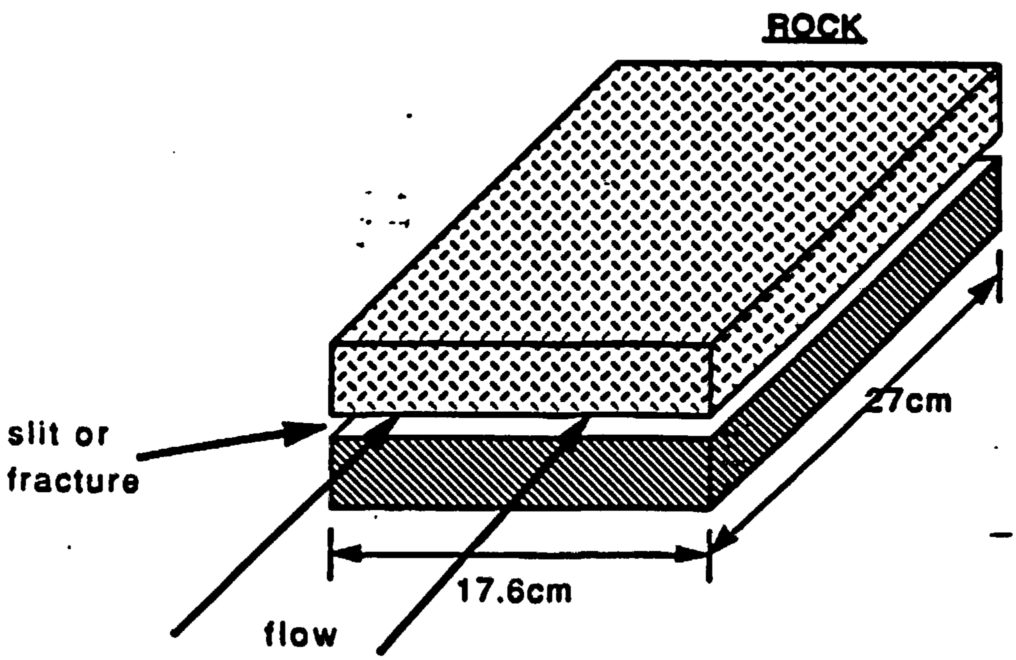
- interstitial velocity was 150 m/y

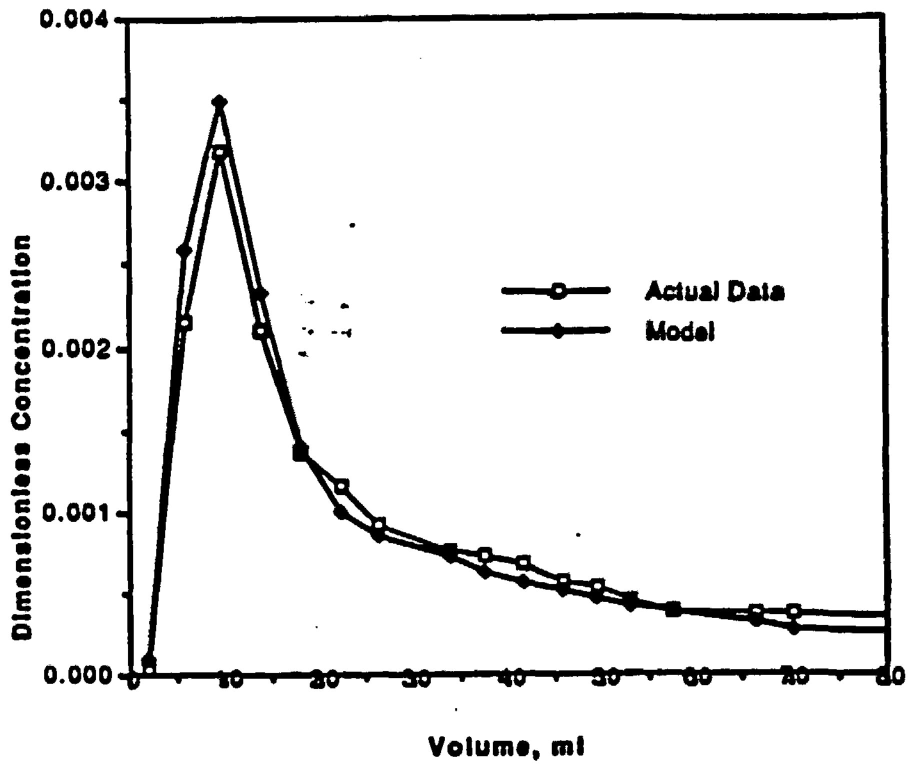
- Pu(IV) real colloid eluted ranged in size from 50 nm to 0.4 μm

- Pu(IV) real colloids are largely retained by the tuff, with a small fraction of the injected material moving through the columns faster than the tritiated water (used as the conservative tracer)

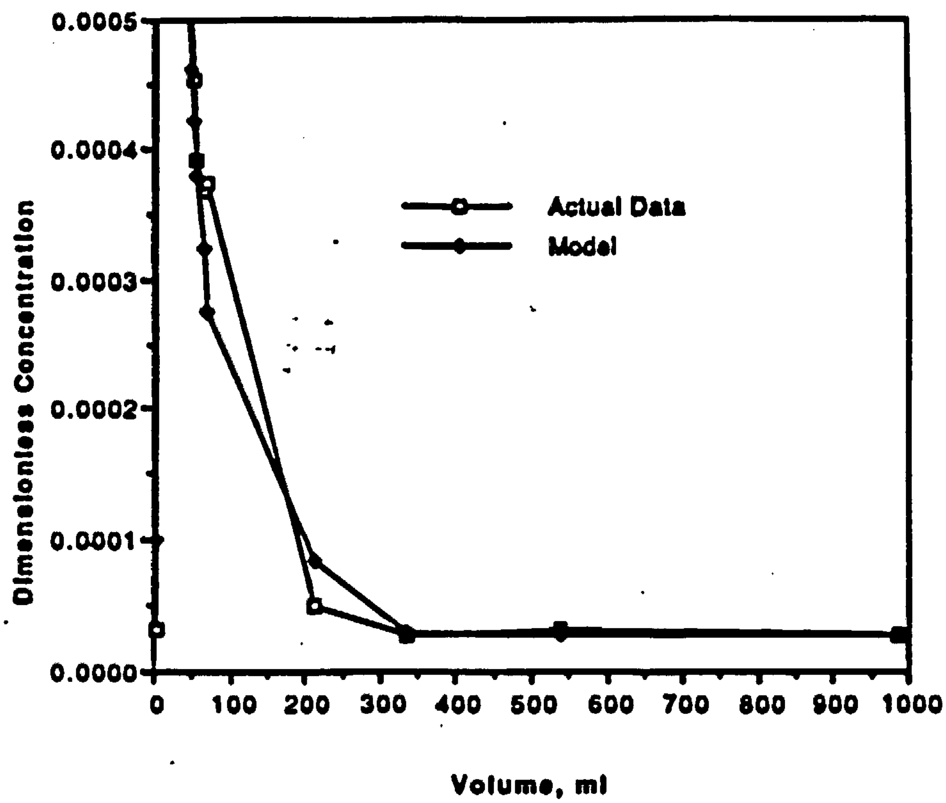
Part Two:

Elution of Colloids Through Fractured Tuff


ROCK
slit or
fracture
27cm
17.6cm
flow



0.004
0.003
0.002
0.001
0.000
0
10
20
30
40
50
60
70
80
Dimensionless Concentration
Volume, ml
Actual Data
Model


0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
Dimensionless Concentration
Actual Data
Model
0
100
200
300
400
500
600
700
800
900
1000
Volume, ml

Conclusions from Experimental and Modeling Studies through Fractured Rock

Colloids readily transported through fractured rock

Colloids not permanently captured by rock matrix but continually released

Experiments modeled (using CTCN code) assuming adsorption/desorption reactions

Part Three:

Colloid Stability

collision frequency

$$\frac{\partial n_k}{\partial t} = \alpha \frac{1}{2} \sum_{i+j=k} \beta(v_i, v_j) n_i n_j - \alpha\, n_k \sum \beta(v_i, v_k) n_i$$

where:

$\frac{\partial n_k}{\partial t}$ = net generation of particles of size k

β = transport mechanism

α = aggregation efficiency

transport mechanism - Brownian motion

$$\beta(v_i,v_j) = \frac{2k_bT}{3\mu}\left(\frac{1}{d_i} + \frac{1}{d_j}\right)(d_i + d_j)$$

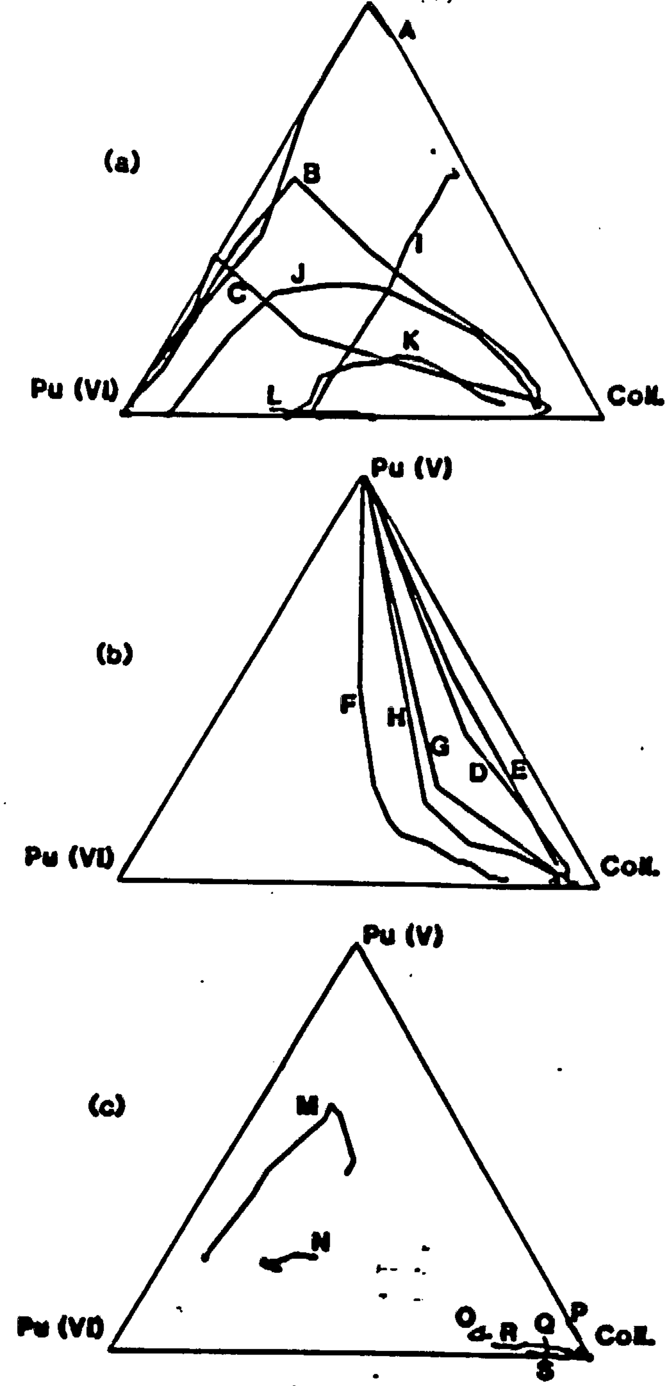
where:

k_b = Boltzman's constant

T = absolute temperature

μ = viscisity of medium

d_i, d_j = diameter of particles i and j



Ternary Composition Diagrams vs Starting Composition
(a) Pu(VI) or Pu(VI) + Pu(IV) Colloid
(b) Pu(V)
(c) Pu(IV) Colloid or all components

Reaction Conditions: 1.3 ≤ pH ≤ ~2.2 / 0.01 M ≤ I.S. ≤ 1.0 M

Newton et al. *Radiochim. Acta* 39, 139 (1986)

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Solubility Results in UE25p#1 Water from Oversaturation

Nitsche et al. YMP Milestone Report 3329 (1993)

	Steady-State Concentration (M)		Oxidation State in Supernatant Solution (%)	
	25°C	60°C	25°C	60°C
pH 6	(8.3 ± 0.4) x 10^{-7}	(8.9 ± 1.4) x 10^{-8}	III + Poly.: (3 ± 1) IV: (9 ± 1) V: (85 ± 7) VI: (3 ± 3)	III + Poly.: (1 ± 1) IV: (1 ± 1) V: (4 ± 1) VI: (94 ± 11)
pH 7	(4.5 ± 0.4) x 10^{-7}	(9.1 ± 1.2) x 10^{-8}	III + Poly.: (2 ± 1) IV: (12 ± 1) V: (78 ± 7) VI: (9 ± 4)	III + Poly.: (2 ± 1) IV: (1 ± 1) V: (5 ± 1) VI: (93 ± 11)
pH 8.5	(1.0 ± 0.1) x 10^{-6}	(9.3 ± 6.0) x 10^{-7}	III + Poly.: (3 ± 1) IV: (31 ± 1) V: (64 ± 6) VI: (2 ± 1)	III + Poly.: (5 ± 2) IV: (10 ± 1) V: (0) VI: (86 ± 12)

	Eh (mV) vs. NHE		Solid Phase	
	25°C	60°C	25°C	60°C
pH 6	(348 ± 15)	(326 ± 15)	Amorphous Pu(IV) polymer	Being Analyzed
pH 7	(282 ± 15)	(334 ± 15)	Amorphous Pu(IV) polymer	Being Analyzed
pH 8.5	(273 ± 15)	(231 ± 15)	PuO_2	Being Analyzed

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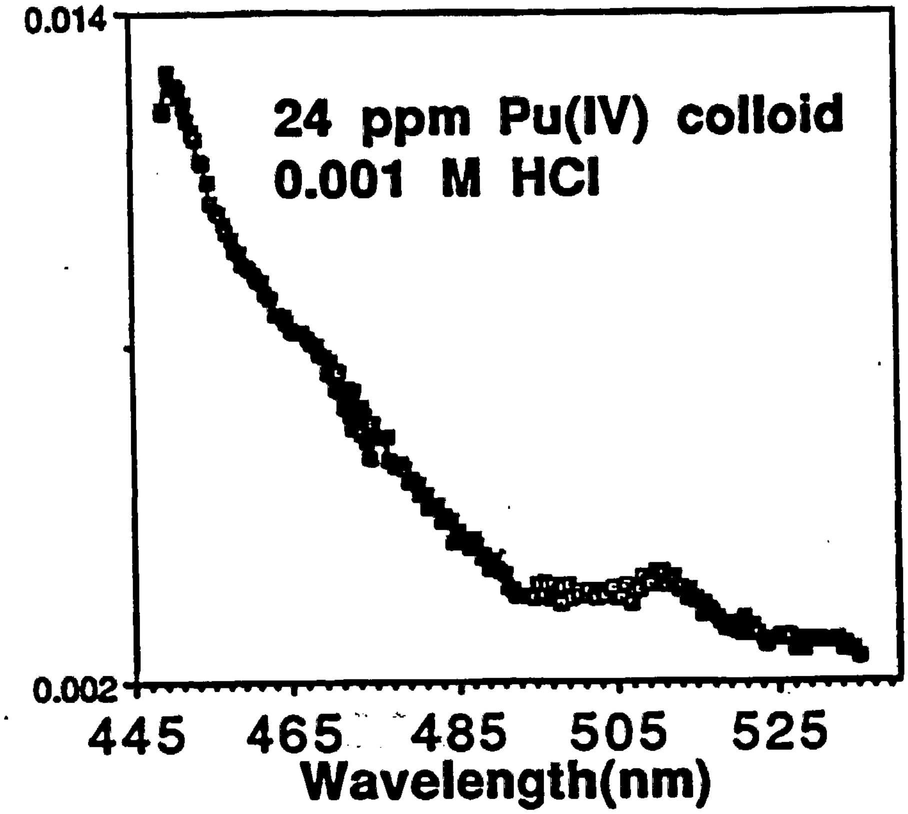
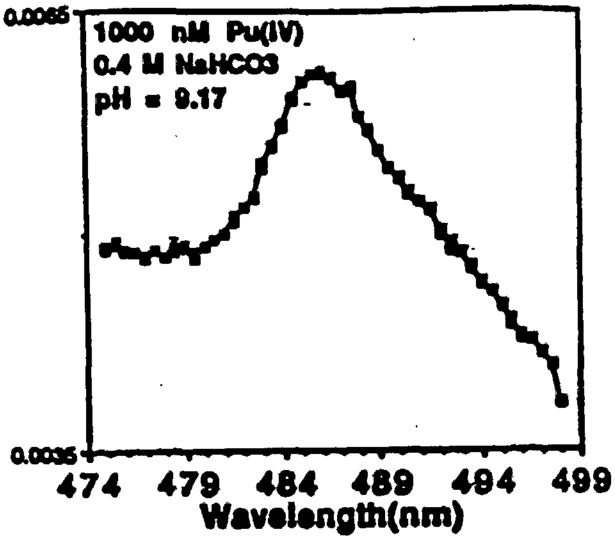
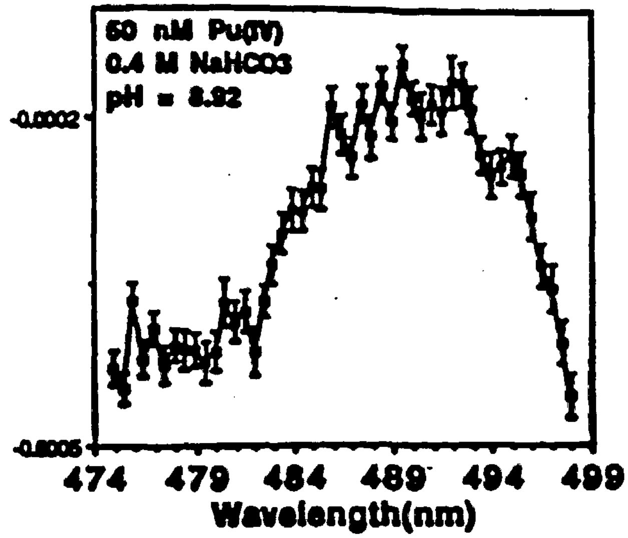
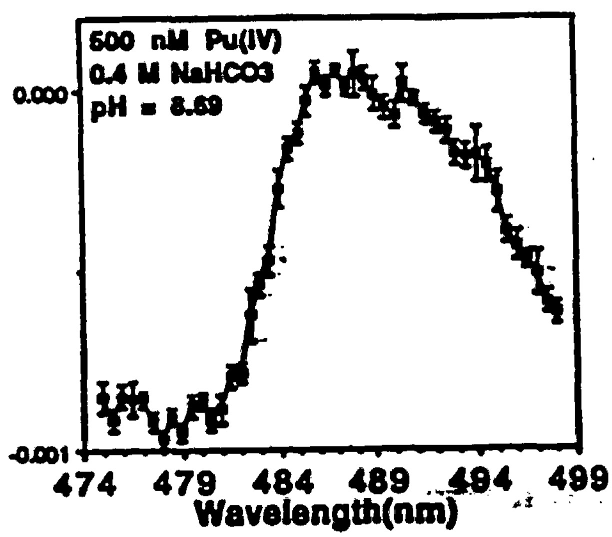
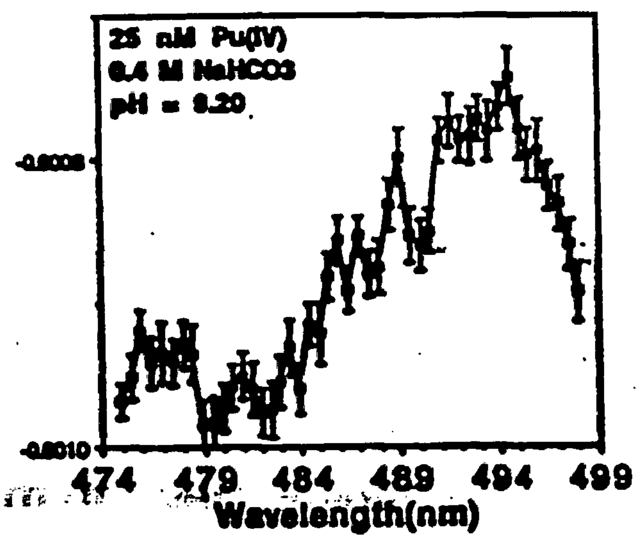


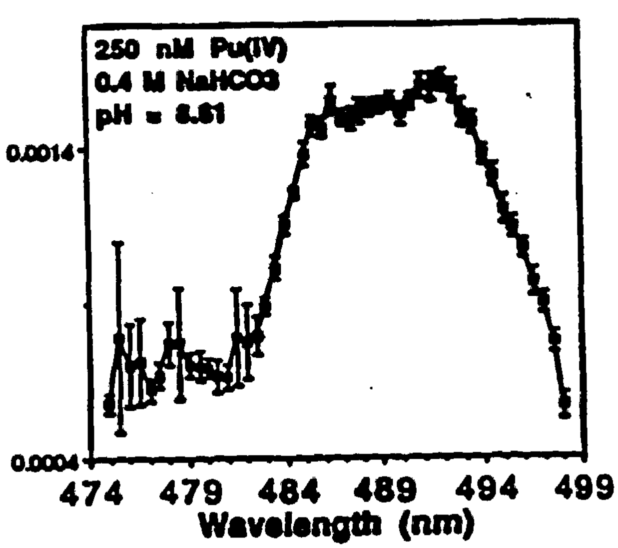
0.014
0.002
24 ppm Pu(IV) colloid
0.001 M HCl
445
465
485
505
525
Wavelength(nm)


1000 nM Pu(IV)
0.4 M NaHCO3
pH = 9.17
0.0065
0.0035
474 479 484 489 494 499
Wavelength(nm)


50 nM Pu(IV)
0.4 M NaHCO3
pH = 8.92
-0.0002
-0.0005
474 479 484 489 494 499
Wavelength(nm)


500 nM Pu(IV)
0.4 M NaHCO3
pH = 8.69
0.000
-0.001
474 479 484 489 494 499
Wavelength(nm)


25 nM Pu(IV)
0.4 M NaHCO3
pH = 8.20
-0.0008
-0.0010
474 479 484 489 494 499
Wavelength(nm)


250 nM Pu(IV)
0.4 M NaHCO3
pH = 8.61
0.0014
0.0004
474 479 484 489 494 499
Wavelength (nm)

Pu(IV) Colloid Particle Size Distribution by Centrifugation

Ichikawa and Sato *J. Radioanal. Nucl. Chem.* 84, 269 (1984)

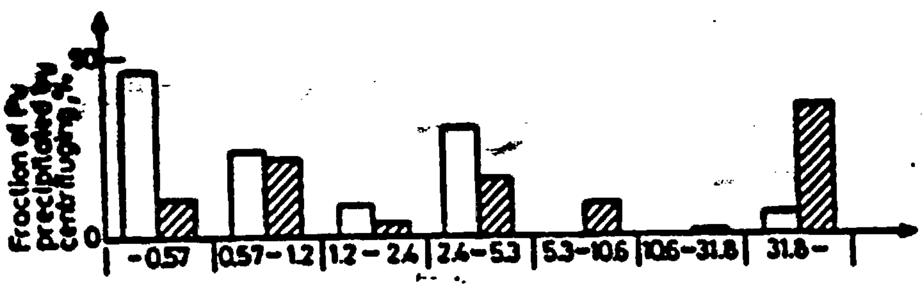


Fig. 4. A histogram of relative particle size of colloidal plutonium. □ – fresh colloid, ■ – ag colloid

Peptization in D.I. H_2O of residue from drying 4 M HNO_3 solution

Pu(IV) Colloid Particle Size Distributions by Dynamic Light Scattering (APS)

Triay et al. Radiochim. Acta 52/53, 127 (1991)

Prep	Conc (N)	pH	Age (days)	Diameter (nm)
Dilution of stock acid solution	0.01	1.3	223	3.7
	0.003	2	606	2.6
Dilution of acid soln + heating	0.01	1.3	20	6.4
			223	5.7
Auto-oxidation of Pu(III)	0.006	2.8	227	32
Neutralization of acid stock in bicarb, peptization in nitric acid	0.05	2	26	14 / 370

Pu(IV) Colloid Density by Ultracentrifugation

Rundberg et al. *Mat. Res. Soc. Symp. Proc.* 112, 243 (1988)

- For ~ 2 nm colloidal particles, $\rho = 9.0 \pm 2.0$ g/cm^3

- For comparison, for PuO_2, $\rho = 11.5$ g/cm^3

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Small-Angle Neutron Scattering Studies of Pu(IV) Colloid

Thiyagarajan et al. *Inorg. Chem.* 29, 1902 (1990)

Sample Prep	Diameter	Length
Water Only	47	>1900
Polymerized with U(VI)	25	84
Polymerized, then reacted with U(VI)	22	120

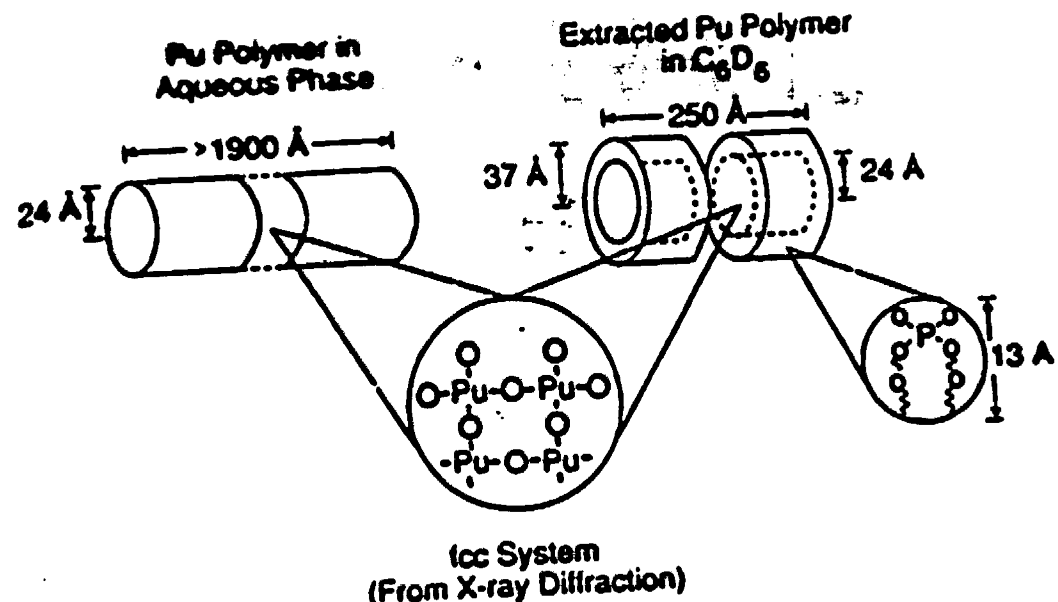

Figure 5. Schematic representation of a model for the observed Pu(IV) polymer.

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Chemical Structure of Pu(IV) Colloid

The Link to PuO_2

- **X-ray diffraction pattern of precipitated colloid is the same as that of PuO_2**

  Ockenden and Welch J. Chem. Soc. 3358 (1956)

- **Electron diffraction pattern of dried colloid is the same as cubic PuO_2**

  Lloyd and Haire Radiochim. Acta 25, 139 (1978)

- **X-ray diffraction pattern of "wet" colloid is the same as that of PuO_2**

  Zeltman, private communication, 1978

- **IR spectrum of dried colloid has Pu-O vibrational band at 360 cm^{-1}, coincident with band of high-fired PuO_2**

  Toth and Friedman J. Inorg. Nucl. Chem. 40, 807 (1978)

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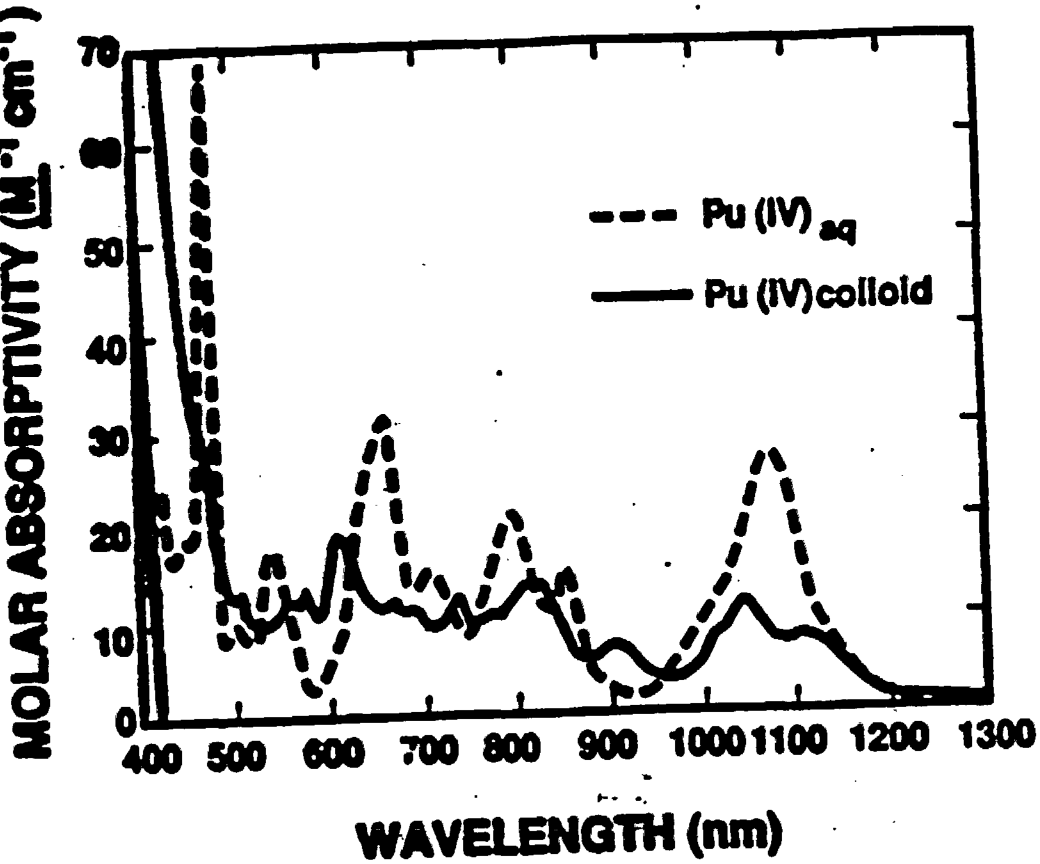
Electronic Absorption Spectra



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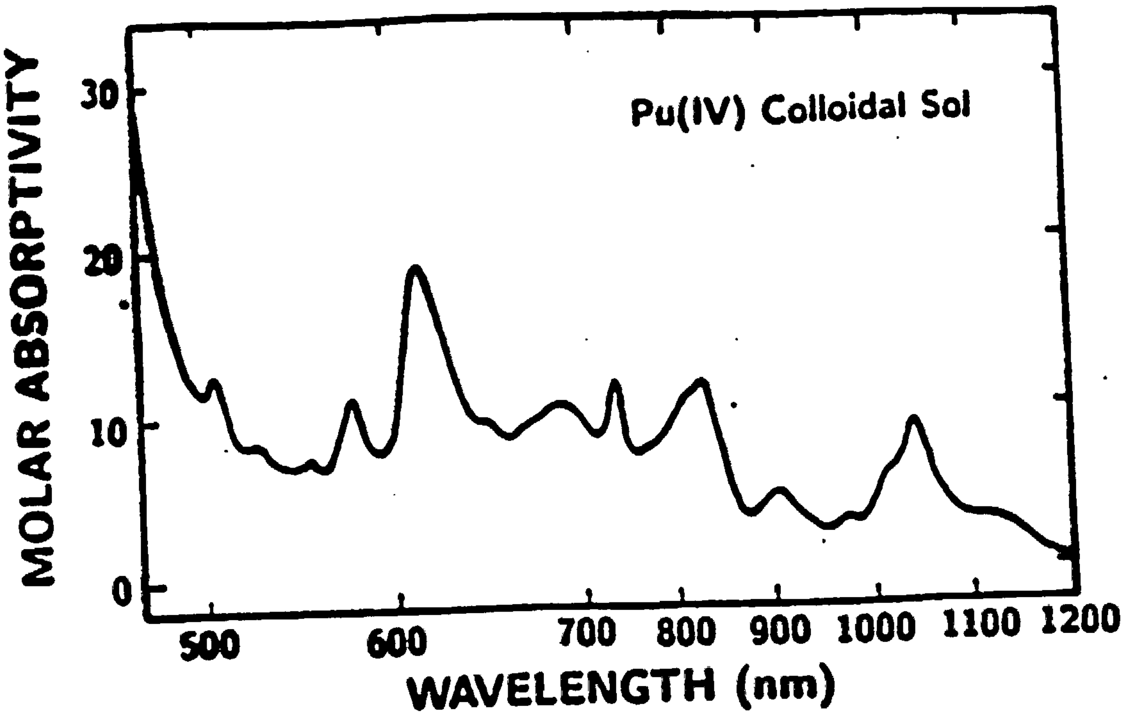
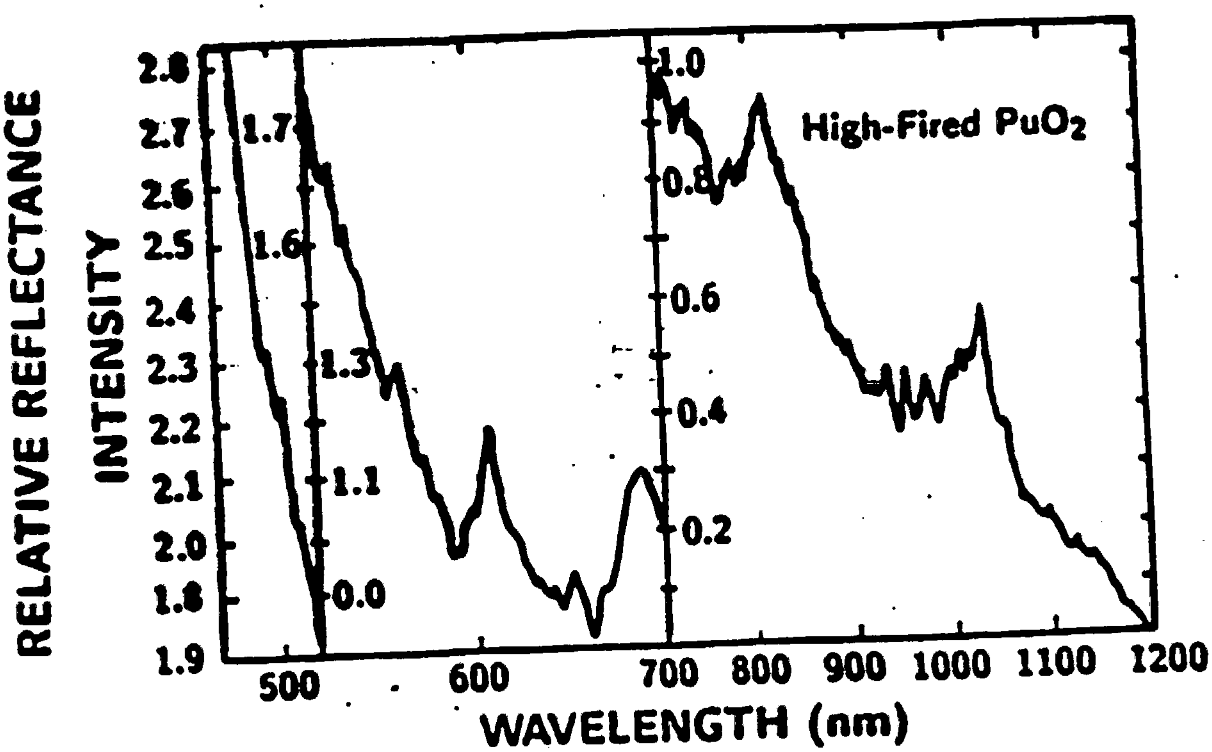
Electronic Absorption Spectra





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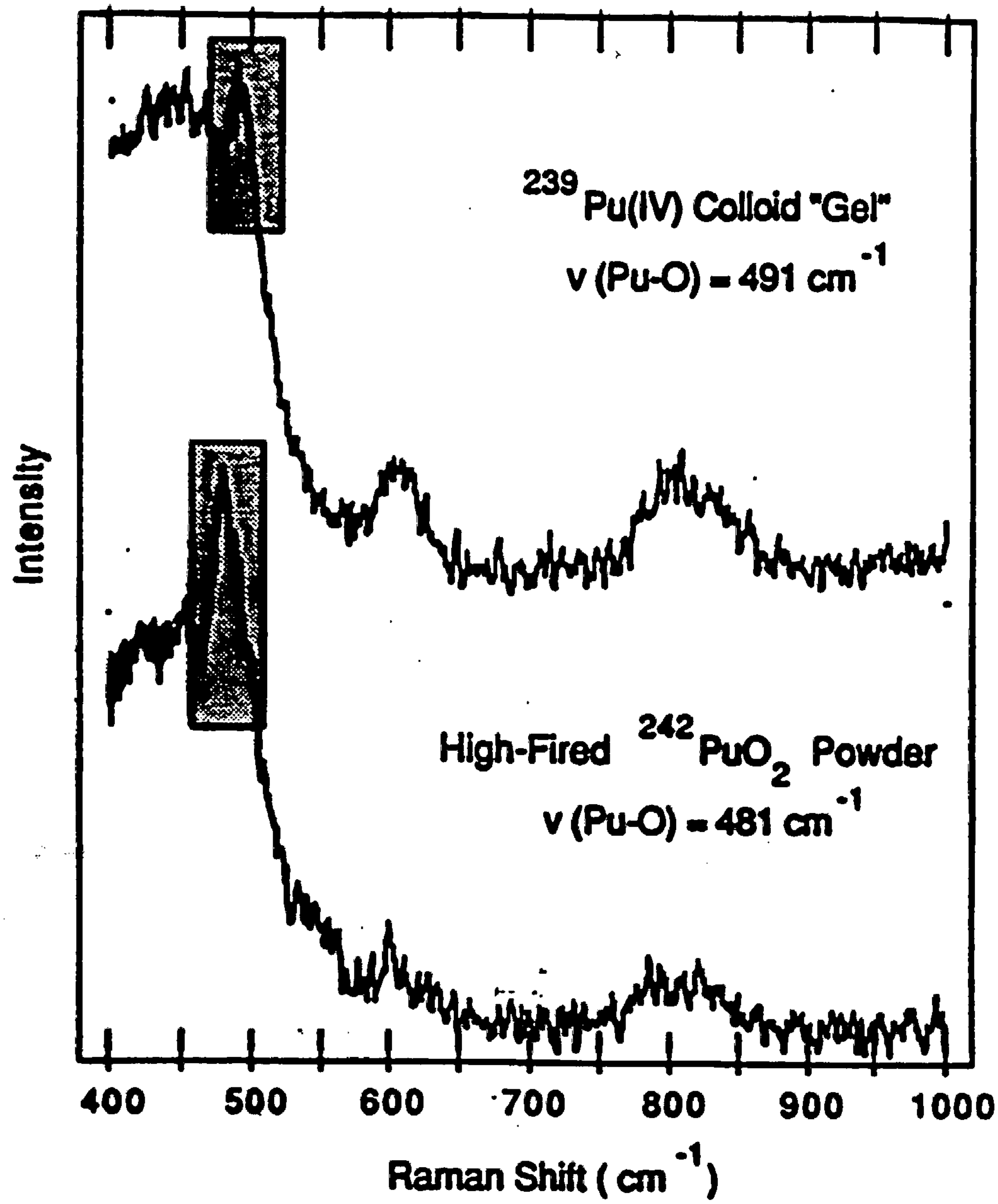
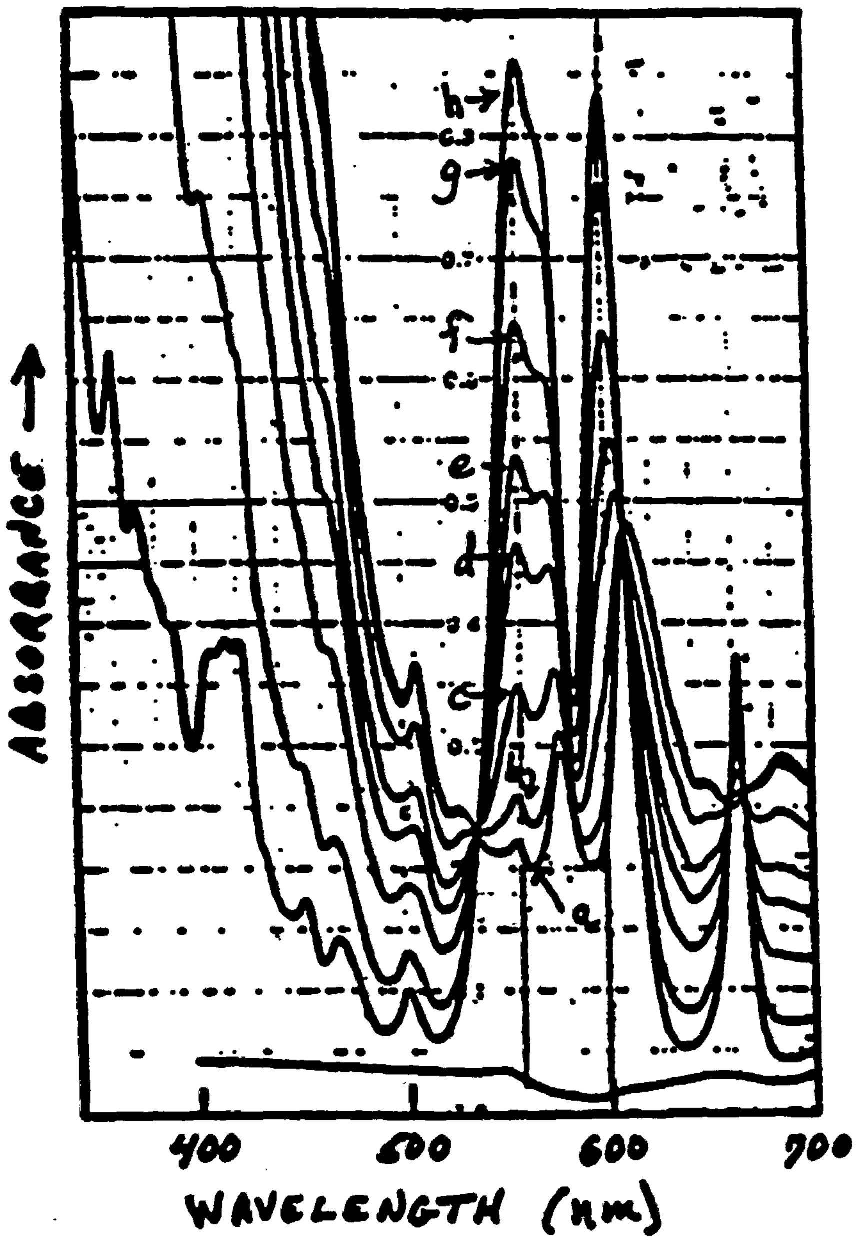
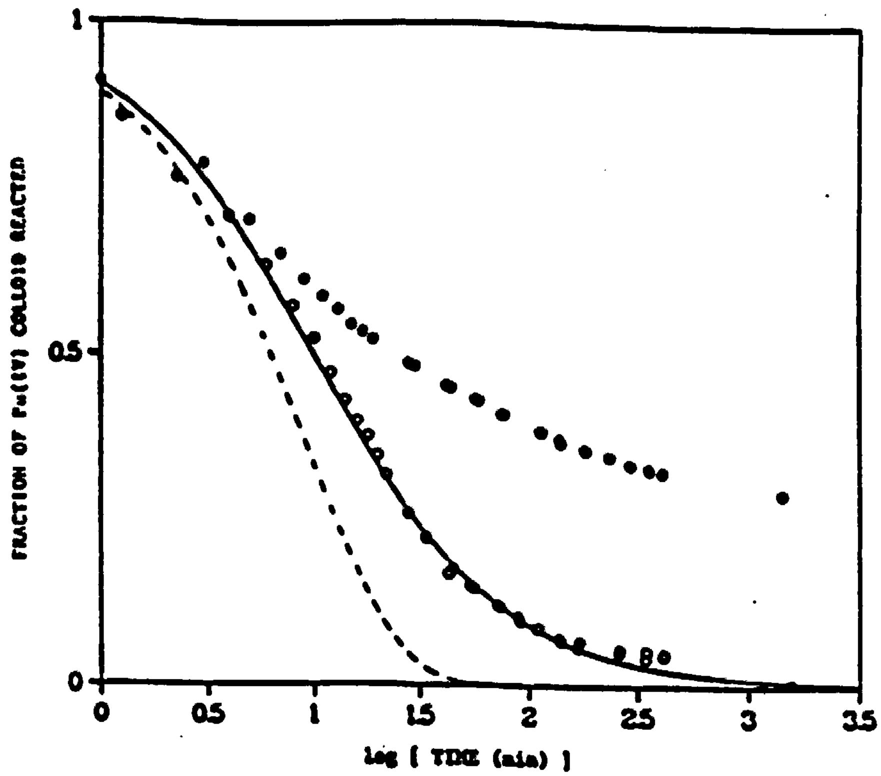
RAMAN SPECTRA OF Pu(IV) Colloid and PuO_2



REDOX REACTIVITY OF Pu(IV) COLLOID



SPECTROPHOTOMETRIC DATA FOR THE REDUCTION OF Pu(IV) COLLOID [a] TO Pu(III) [h] BY Zn(Hg)



Powell Plots for the reaction

$$Pu(IV)_{coll} + 2\ Ce(IV) \longrightarrow Pu(VI)O_2^{2+} + 2\ Ce(III)$$

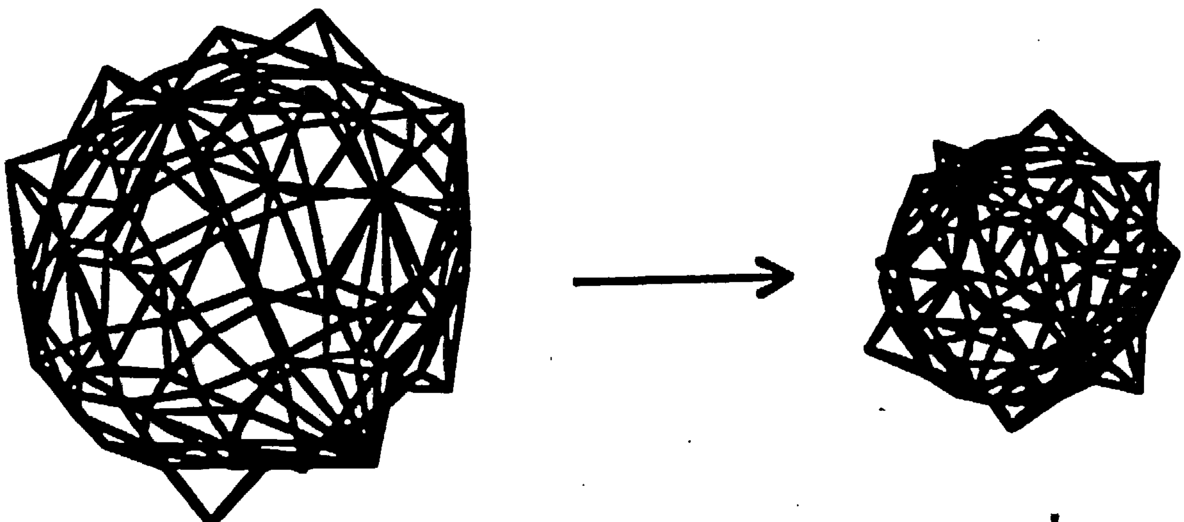
○ exptl data in dilute HNO_3 / colloid particle dia. = 2.1 nm

● exptl data in dilute $HClO_4$ / colloid particle dia. = 25.5 nm

– – – – theoretical first-order reaction

——— theoretical second-order reaction

Shrinking Sphere Model of Pu(IV) Colloid Reactivity



+ Ce(IV) → + Pu(VI) + Ce(III)

If rate is proportional to surface area

$$- dV / dt = k A$$

$$V^{1/3} = V_0^{1/3} - k't$$

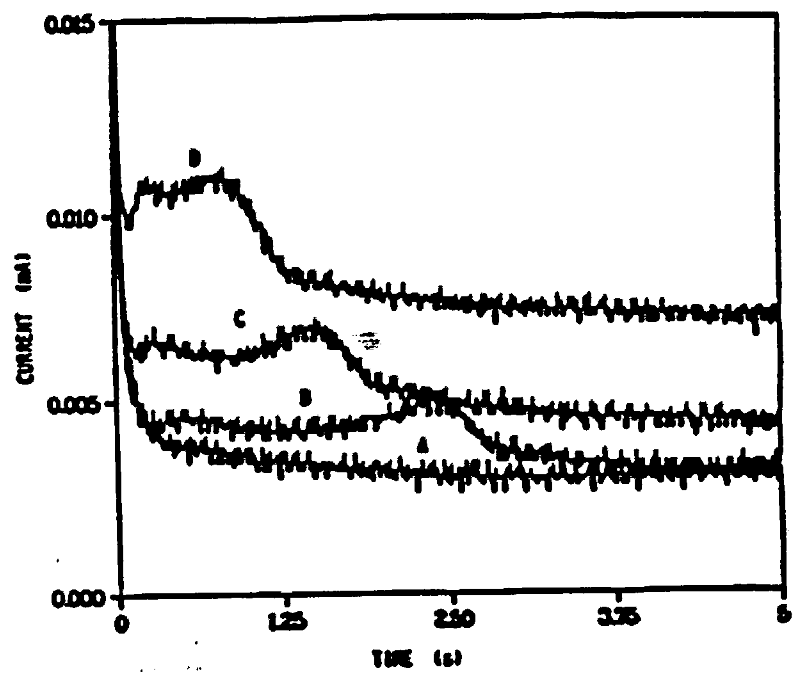
REDUCTIVE CHRONOAMPEROGRAMS
AS A FUNCTION OF POTENTIAL STEP SIZE

Initial Potential = 0.0 V vs Ag/AgCl

2.1 nm Pu(IV) Colloid
in dilute HCl at pH 1.8

Final Potential (V vs Ag/AgCl)

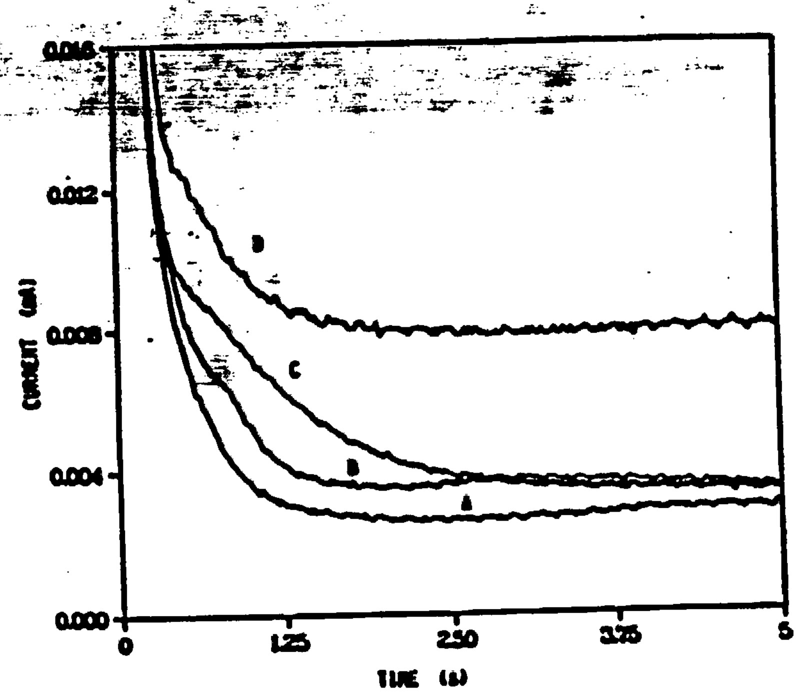
(A)	- 1.20
(B)	- 1.25
(C)	- 1.30
(D)	- 1.35



25.5 nm Pu(IV) Colloid
in dilute HCl at pH 2.6

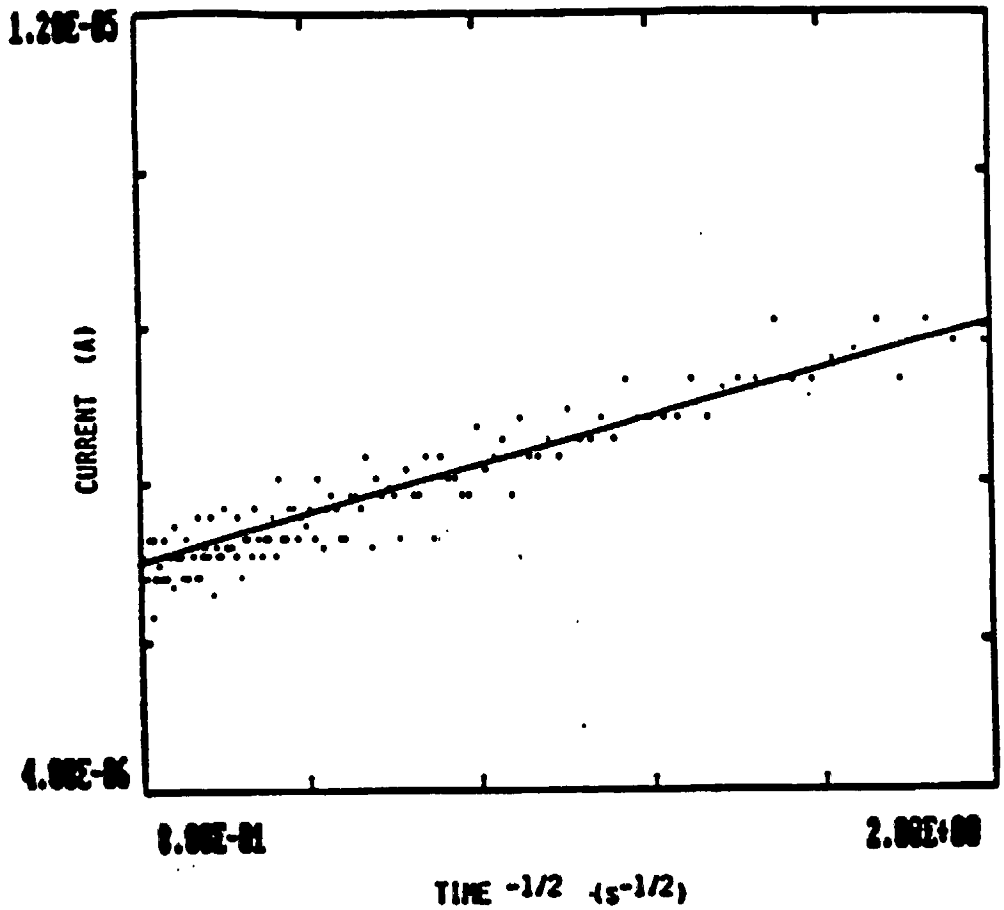
Final Potential (V vs Ag/AgCl)

(A)	- 1.20
(B)	- 1.30
(C)	- 1.40
(D)	- 1.50



COTTRELL - PLOT DETERMINATION OF Pu(IV) Colloid DIFFUSION COEFFICIENTS

2.1 nm Pu(IV) Colloid in 0.1 M KCl at pH 1.8



Slope = 2.2 ± 0.1 uA-s $^{1/2}$

Diff. Coeff. = $1.1 \pm 0.1 \times 10^{-6}$ cm^2 s^{-1}

<u>Hydrodynamic Diameter = 3.8 ± 0.2 nm</u>

SUMMARY
Pu(IV) COLLOID DATA

- Forms under a variety of chemical conditions
  - It is unstable w.r.t. precipitation at pH > ~ 5
  - It does not form from Pu(IV) solutions at dilute concentrations
- Particle size distribution varies widely
  - ~ 2 nm to > 10 µm
- Density for small particles is ~ 9 g / cm^3
- Chemical structure is comparable to PuO_2
- Chemical reactivity varies widely

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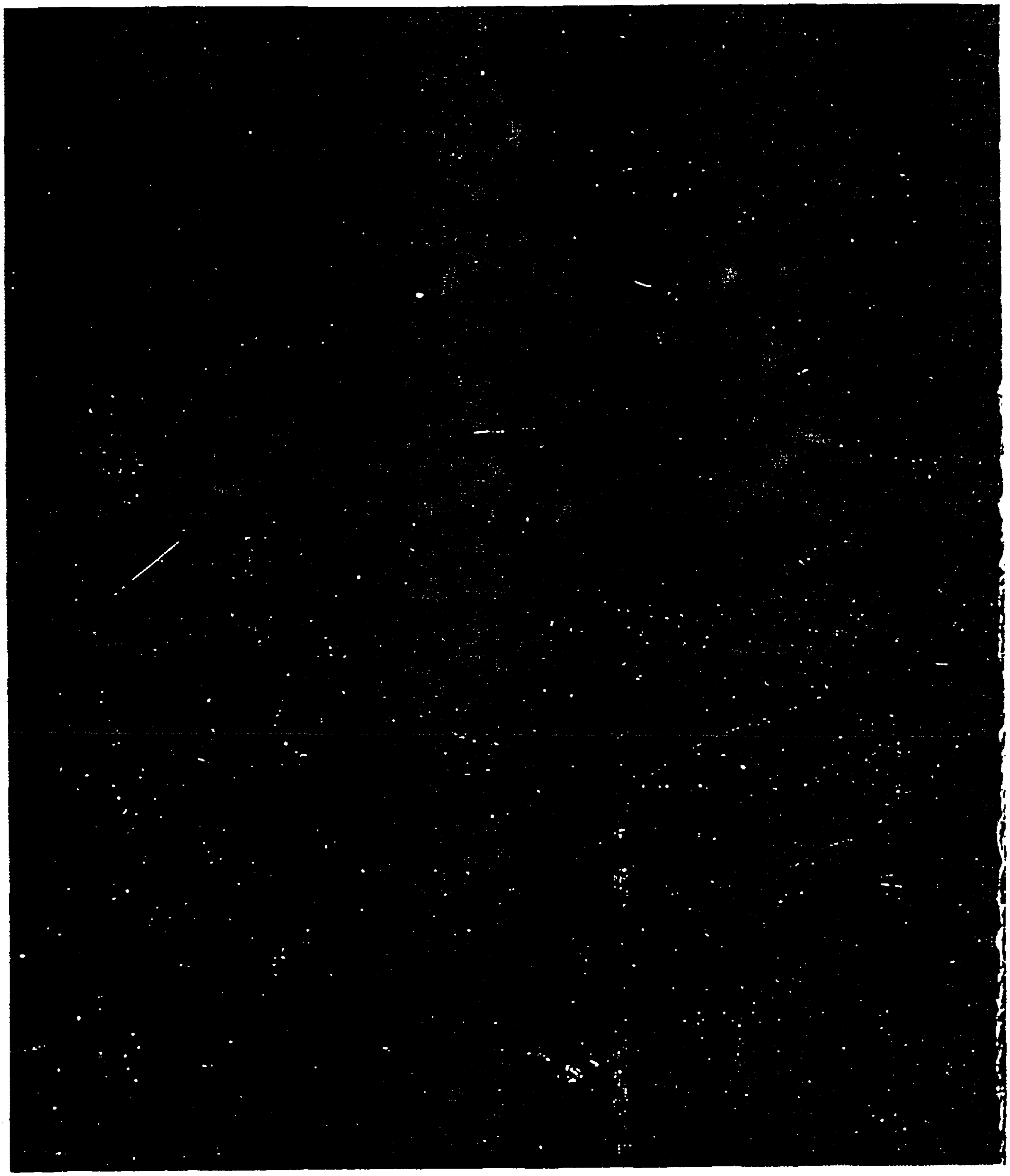
Points to Ponder

- **Is Pu(IV) Colloid (and other radiocolloids) exclusively a near-field issue?**

- **What are the sorptive properties of Pu(IV) Colloid?**

- **Can Pu(IV) Colloid serve as a "secondary" source term for dissolved Pu species in the far field?**

Colloids from Waste Form Reactions - John K. Bates - Edgar C. Buck, ANL



I will discuss colloid formation from glass, UO_2, and spent fuel reaction on the following basis

- general approach (testing)
- methodology
- application

Approach

The approach fits well into the American Society of Testing Methods (ASTM) format for prediction of long-term material performance.

Identify Materials

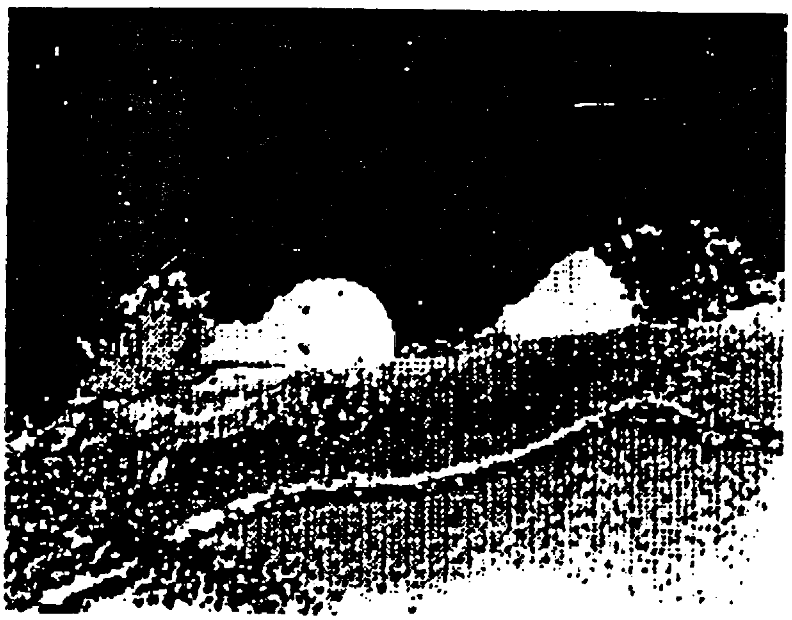
Spent Fuel
Glass

Identify Credible Conditions

Unsaturated

Have to rethink basic premises

The surface of the vapor phase reacted glass is covered with alteration phases of unique structure and composition.

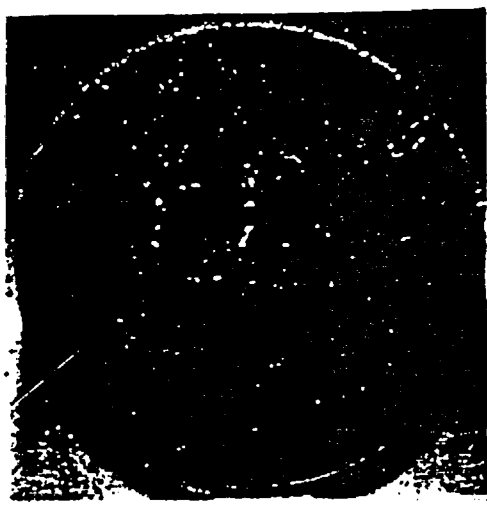


Alteration Products

Reacted Glass

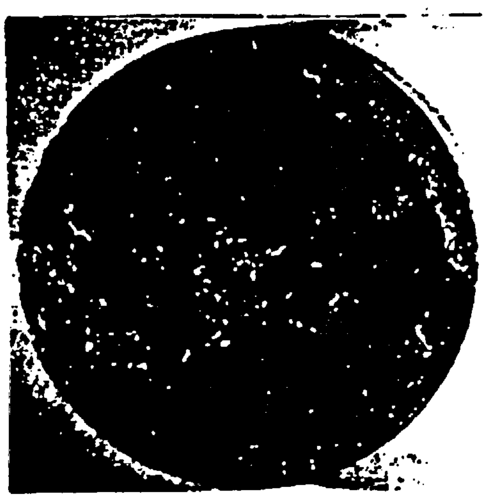
However, under certain circumstances the formation of a stable phase may actually promote reaction.

UO_2 Pellet Exposed to Dripping Repository Water in an Oxidizing Environment



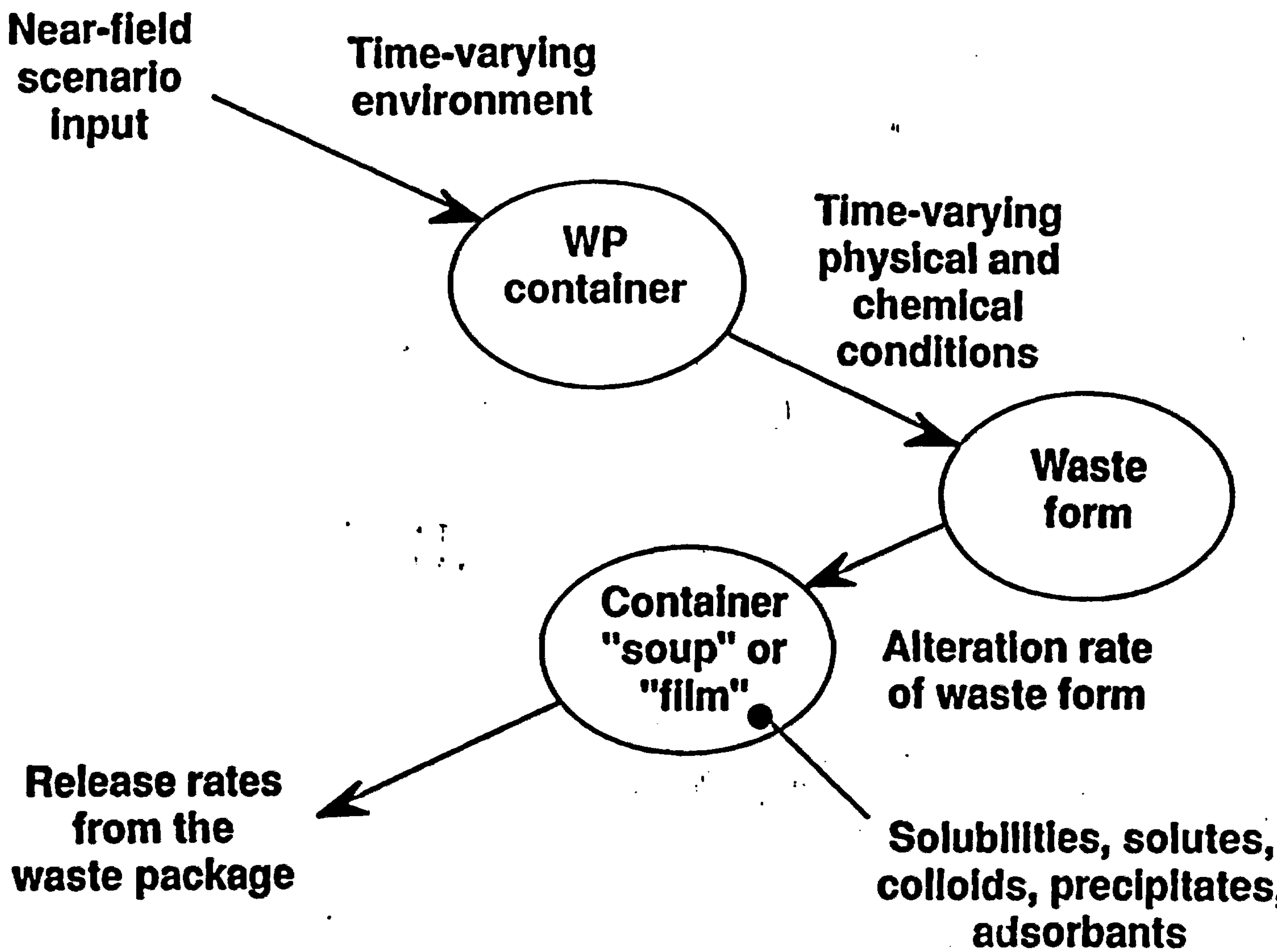
Top, 3x

Bottom, 23x
$U_3O_8 \cdot 8H_2O$



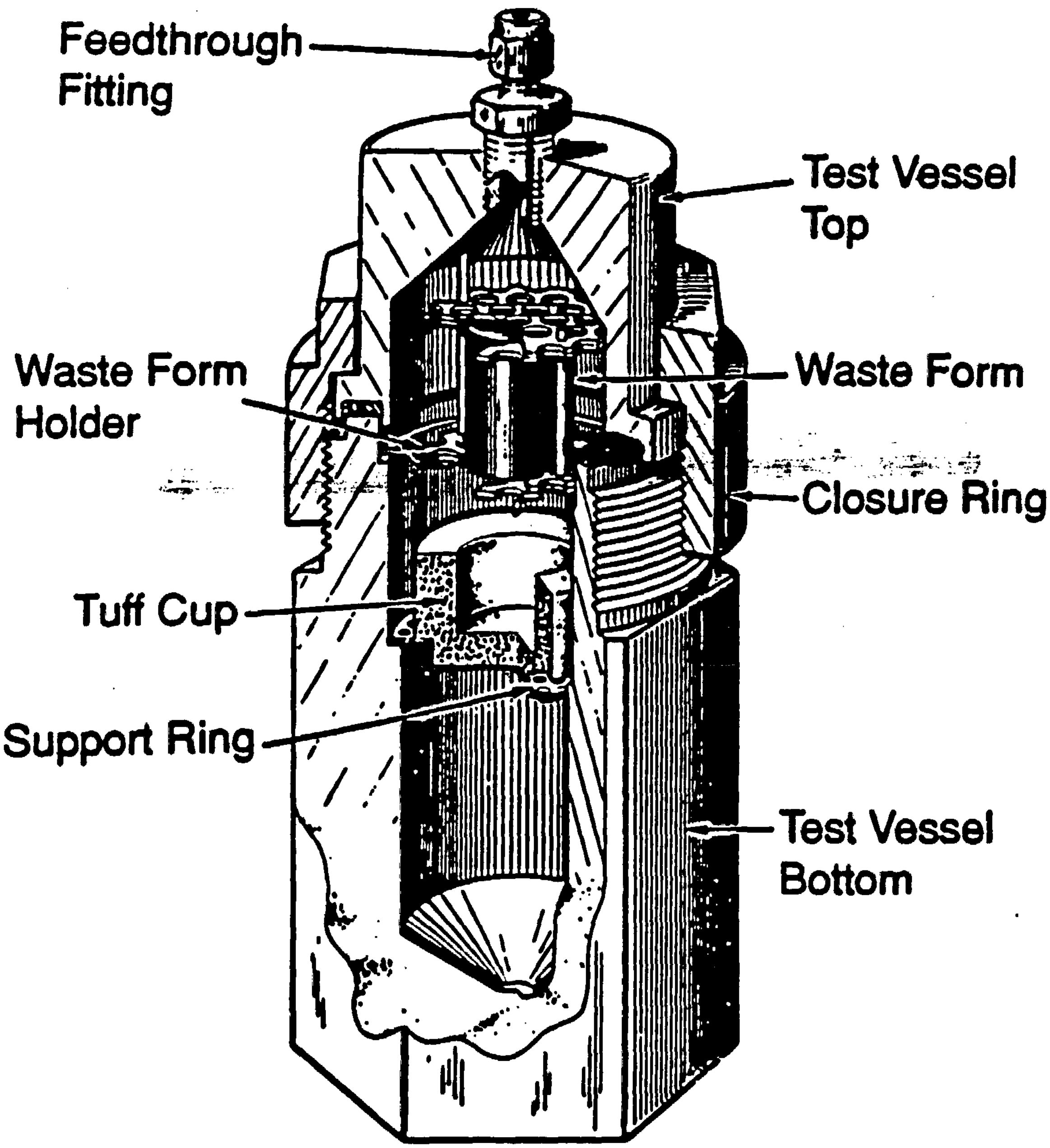
Bottom, 3x

Site-relevant testing identifies parameters that are important to evaluate waste package performance.



Drip Tests have been Developed to Simulate the Expected Conditions for the Unsaturated Repository

Test Vessel



Methods

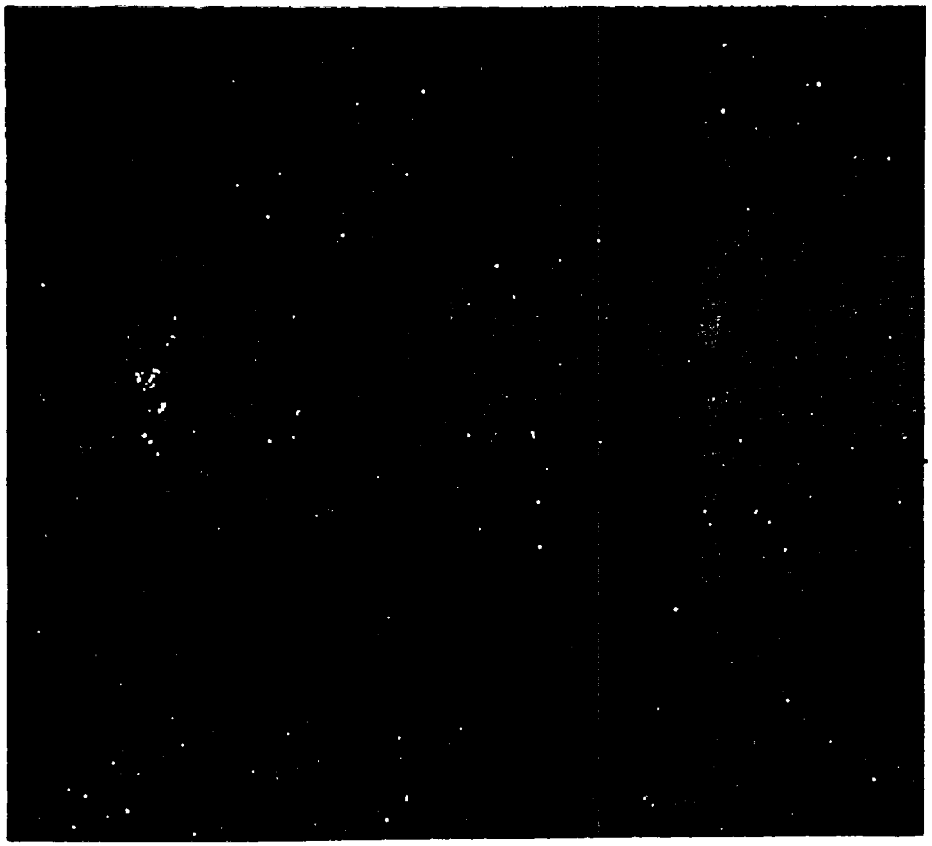
Objectives:

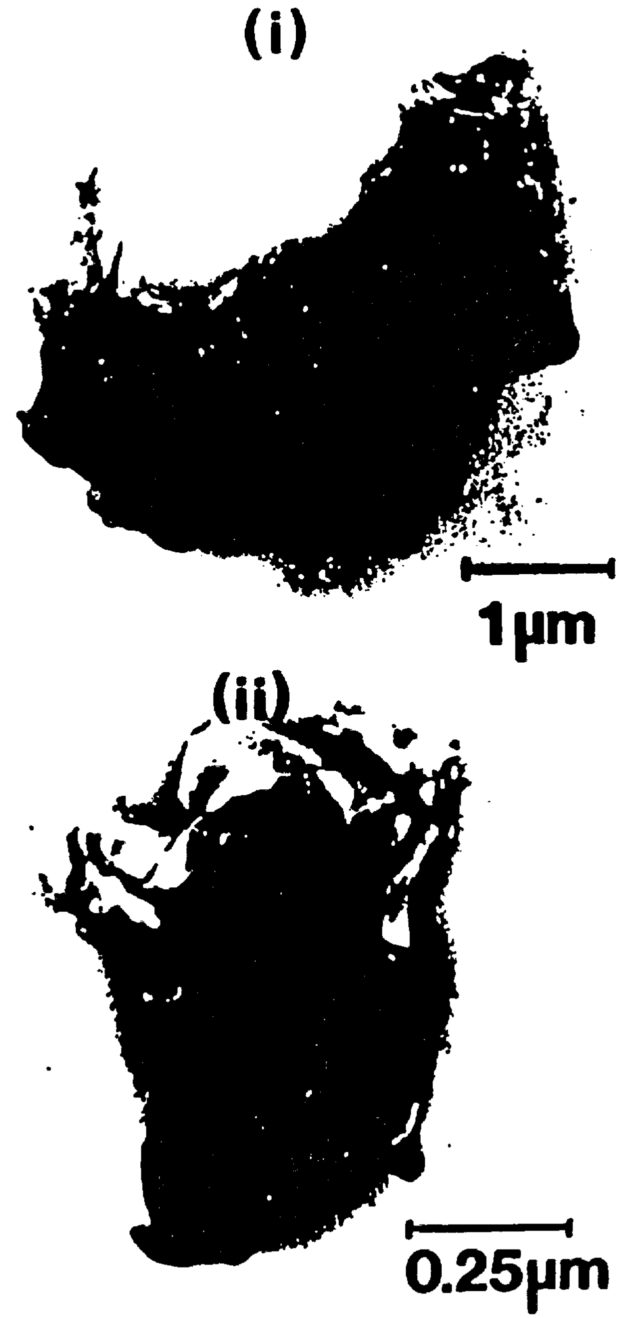
- Determine whether radionuclide colloids are formed in waste form reactions.
- Characterize any colloids material observed.
- Provide input to help predict transport behavior.

Methods

- Sequential filtering
- Small particle handling - isolation of 200 nm phases
- Autoradiography of individual phases
- Analytical electron microscopy with EDS/EELS
- Particle size analysis light scattering
- Zeta potential
- Direct observation

The isolation and identification of actinide-bearing phases in solution is essential.



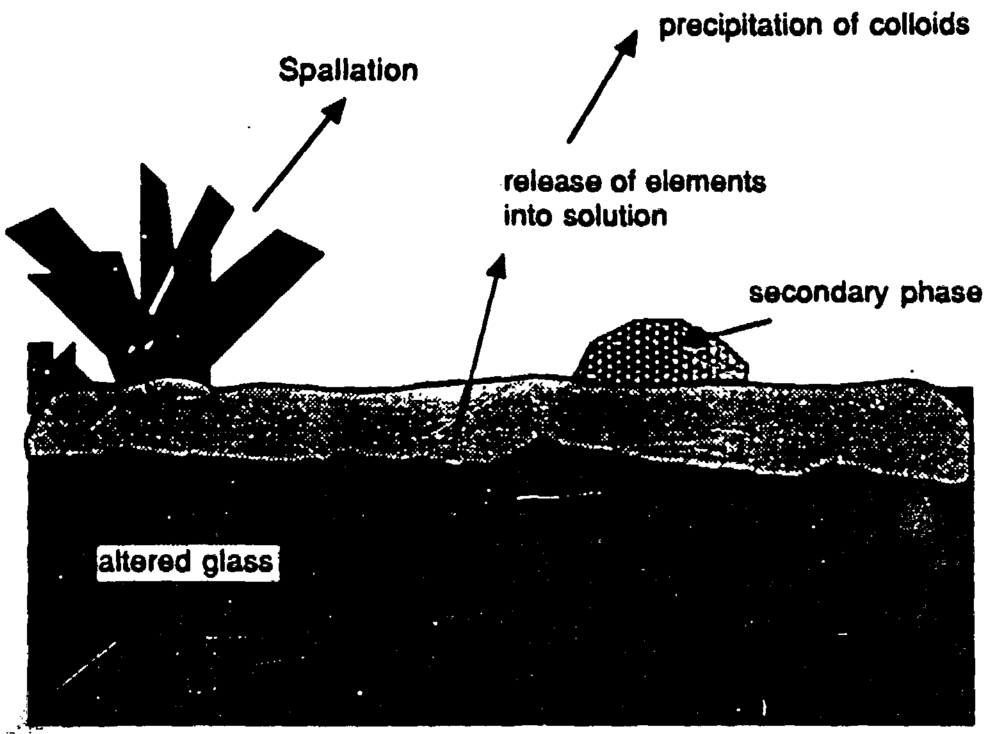


Application

Glass

UO_2

Spent Fuel



<u>Sources of Colloids</u>:

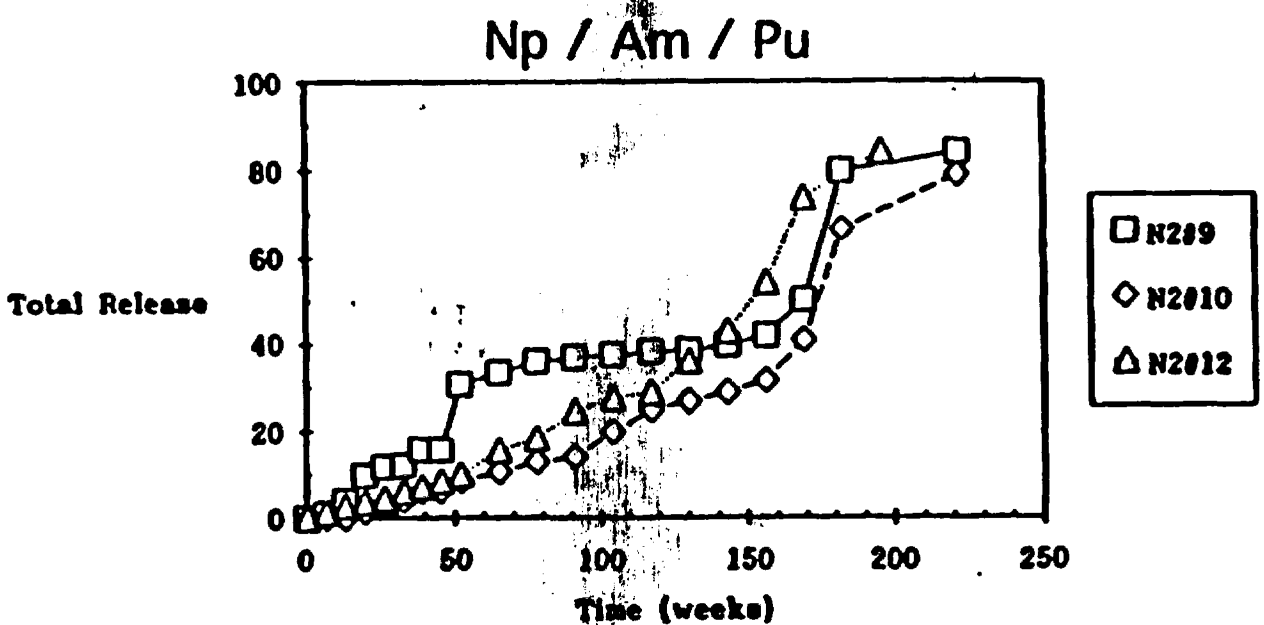
1. Primary
   - spallation (alteration phases fall into solution)
   - precipitation (clay smectite colloids)

2. Secondary
   - pseudocolloid (groundwater)
   - real colloid (actinide hydrolysis)

Results

Intermittent or Dripping Water

For as-cast, actinide-doped glass, the actinide release over long-time periods proceeds at a fairly continuous rate.

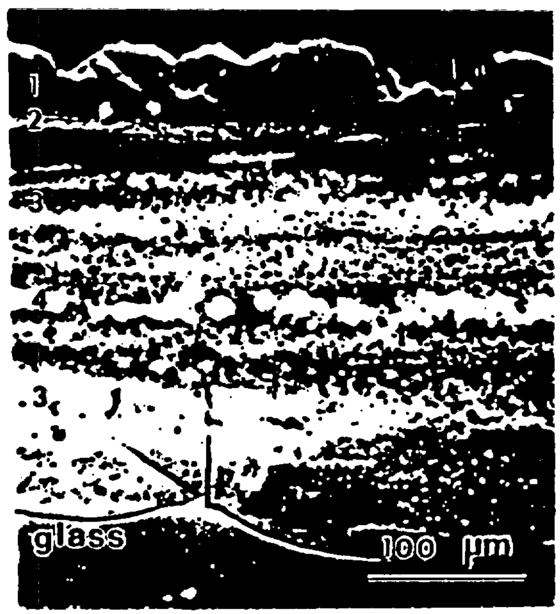


- Pu/Am - suspended in solution
- Np - dissolved in solution

During reaction under exposure to water vapor, the glass reacts and Pu and Am are concentrated in discrete mineral phases.

secondary phases
original surface

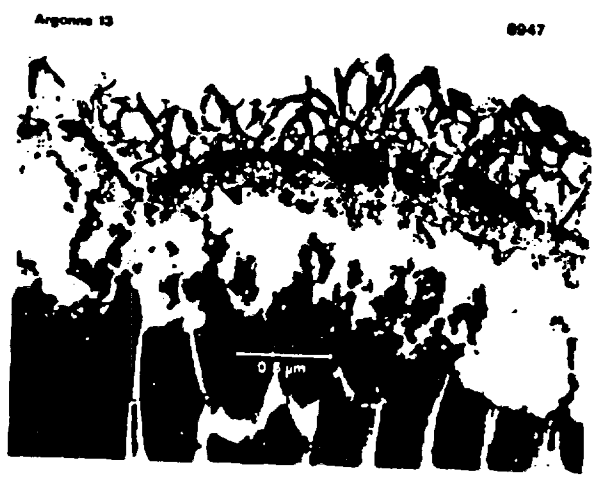
brockite
hydrated layer



165 Glass

- Temporal trends in layer growth indicate a different alteration layer structure than for 131 glass.
- The hydrolysis and <u>in situ</u> restructuring now result in a layer not attached to the glass surface.

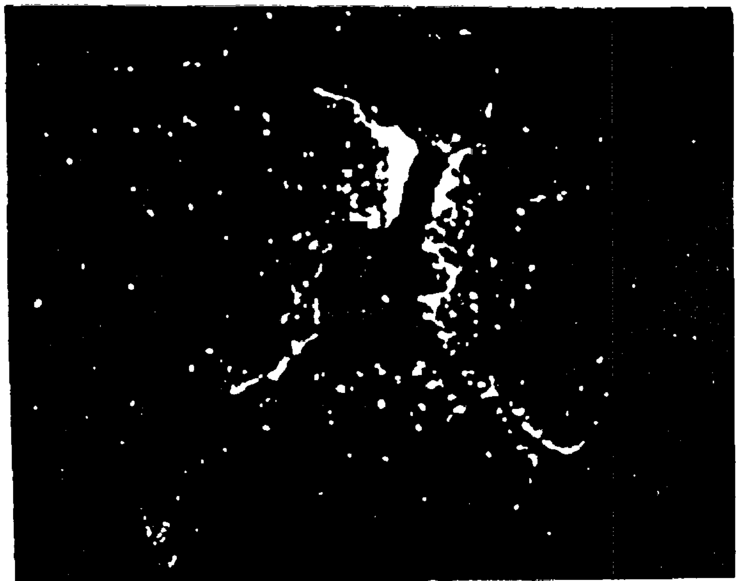
56 days

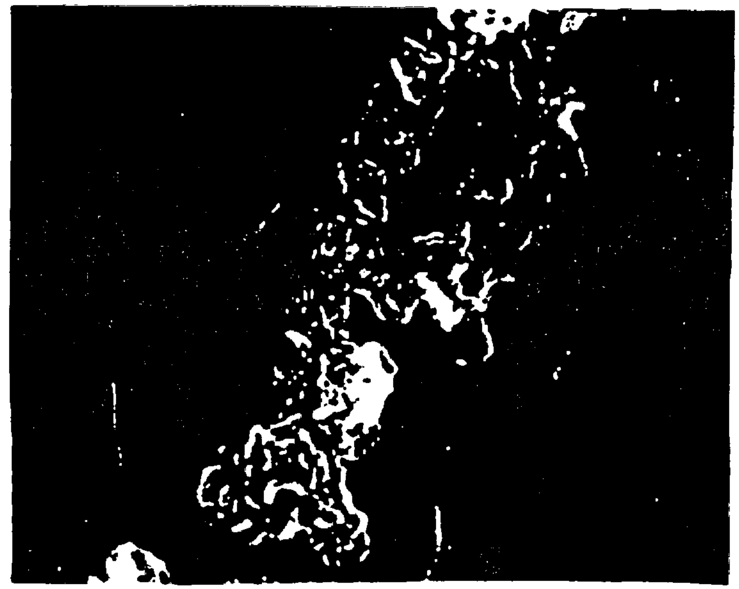


91 days

280 days

Spallation of glass during the drip test results in increased release.





—— = 80 μm

Mag = 400X

Spallation of reacted layer exposing base glass.

—— = 1 μm

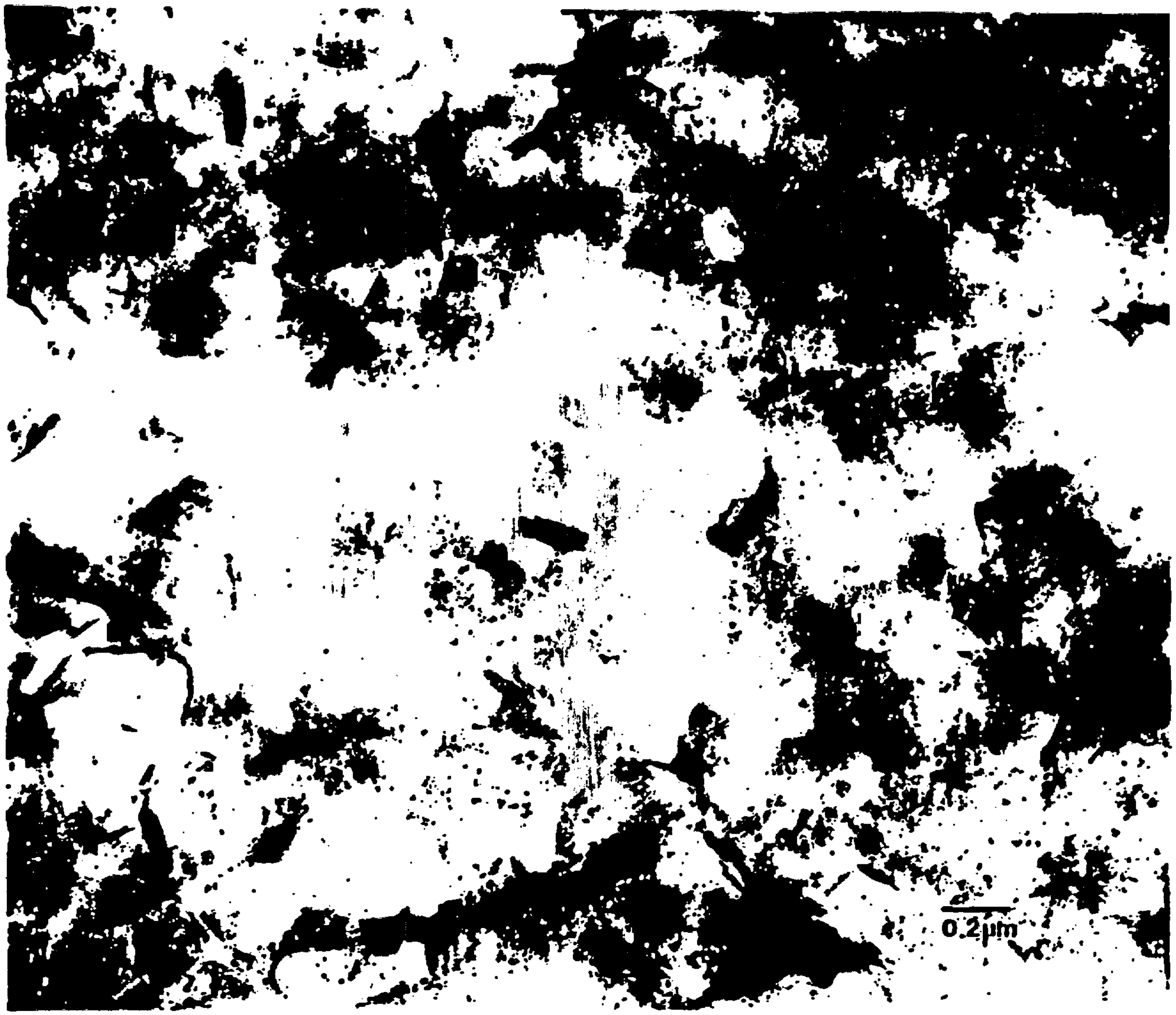
Mag = 10,000X

Precipitation of clay onto newly exposed base glass.

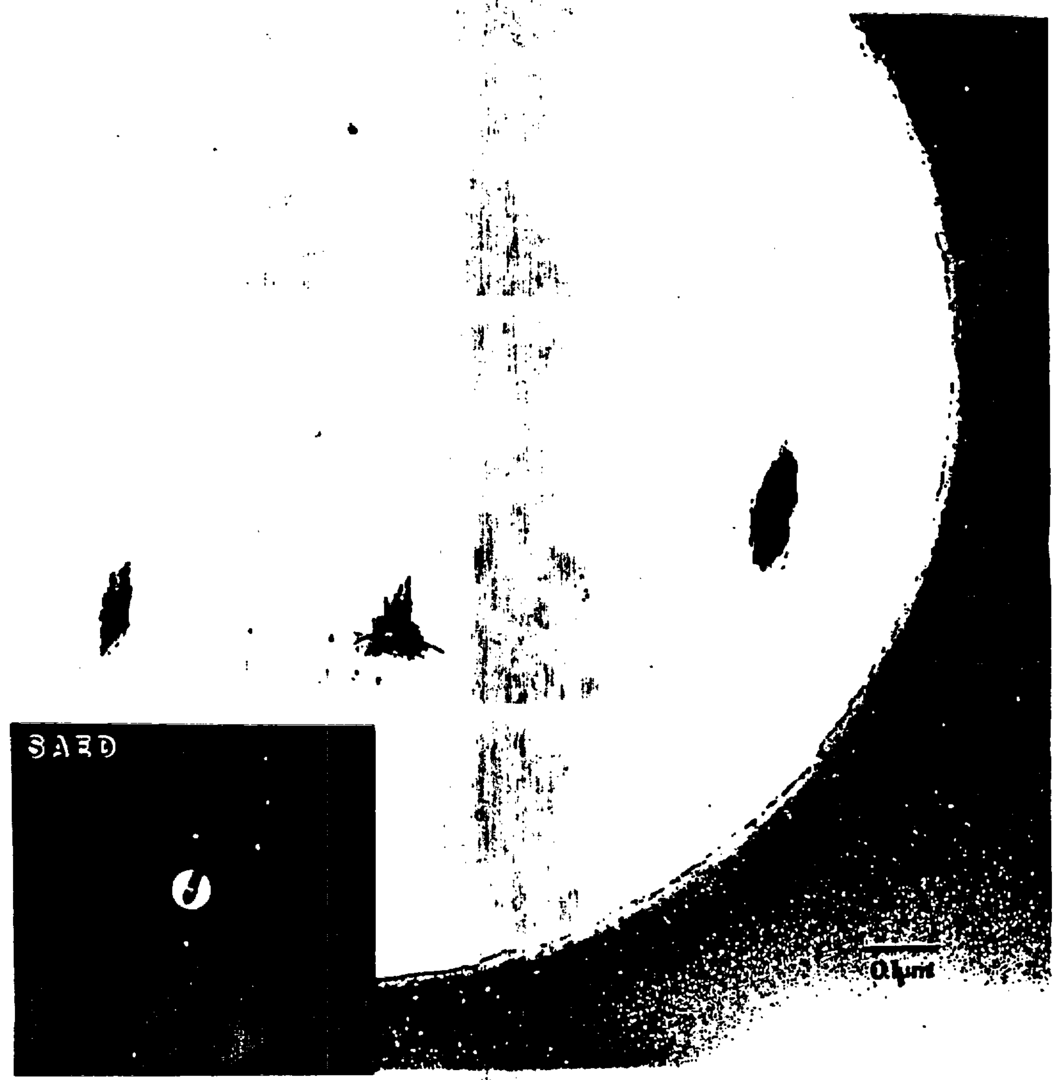
Smectite clay colloids found agglomerated around a hole in the 'holey' carbon film in a N4#6 test.

Typical colloidal morphology of the manganese oxide mineral **birnessite** within smecite clay colloids, which was confirmed by SAED analysis, from a N4#9 test.

Colloids from a SRL202U glass reacted at 340/m for 560 days. The dark regions are uranium-titanium-oxide phases.



100 nm uranium-rich colloids found in the leachate of a SRL202A glass test reacted at 2000/m for 980 days.



Identification of other Colloidal Phases

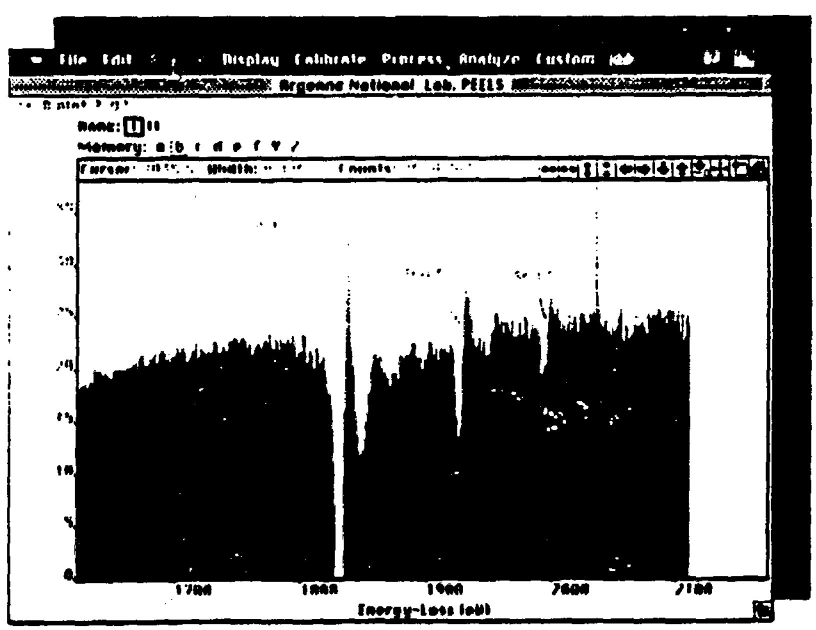
Phase identified as the zeolite, heulandite, ideally, ($M^{2+}Al_2Si_7O_{18}.6H_2O$).

Table I. Composition of zeolite phase from the leachate of a 131A glass test.

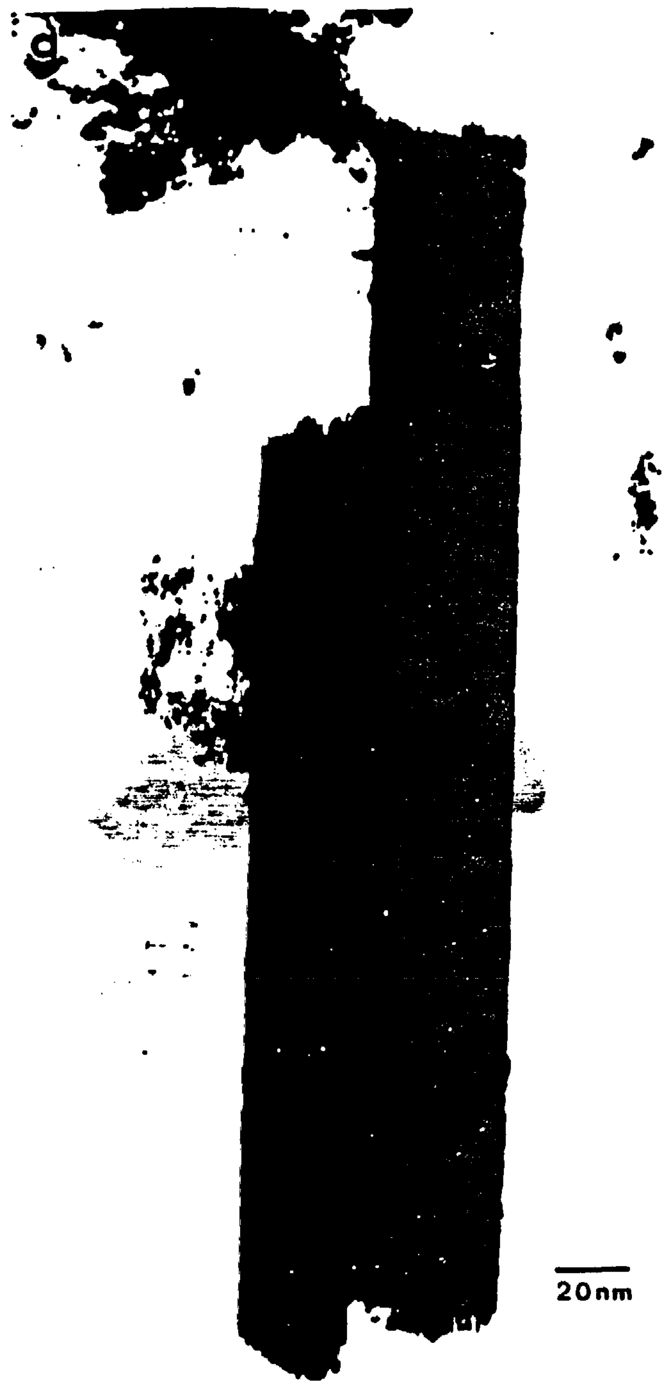
El	Atom%	wt%
Si	53.5	50.5
Al	31.2	29.0
Ca	13.1	17.6
Fe	1.5	2.8

Table II. Electron diffraction data on zeolite phase (including errors).

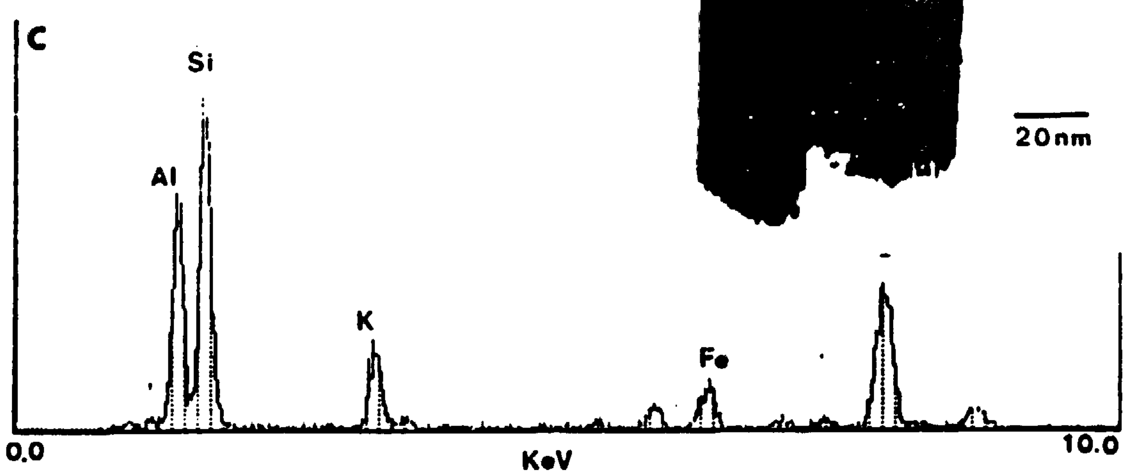
d/A	±A	JCPDS - 21-131
4.37	0.08	4.36
3.79	0.06	3.72
3.26	0.05	3.19
2.44	0.04	2.43
2.15	0.03	2.12



High magnification micrograph (a) of **colloidal mica phase** found in in test N4#6. Convergent beam electron diffraction (**b**) of the phase down the c* axis shows the pseudohexagonal symmetry. EDS composition is shown in (**c**).

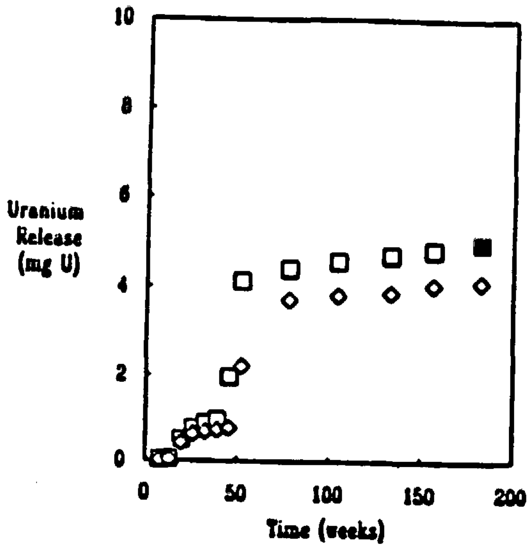


b

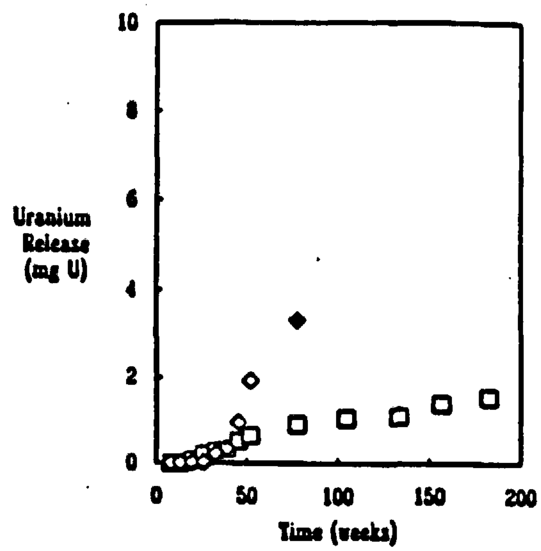


Reaction occurs resulting in release of uranium, plus the formation of secondary phases.

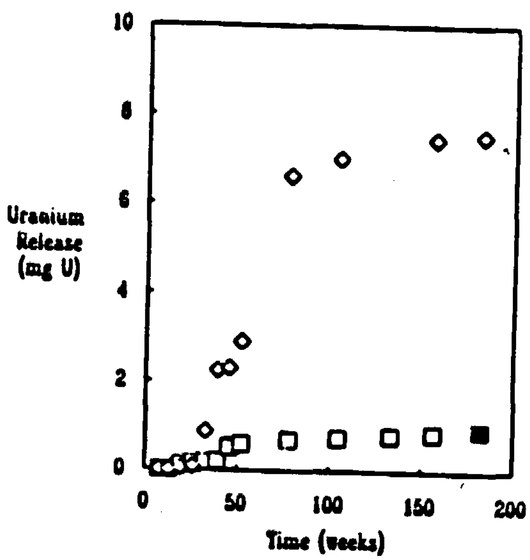
Solid symbol = test terminated



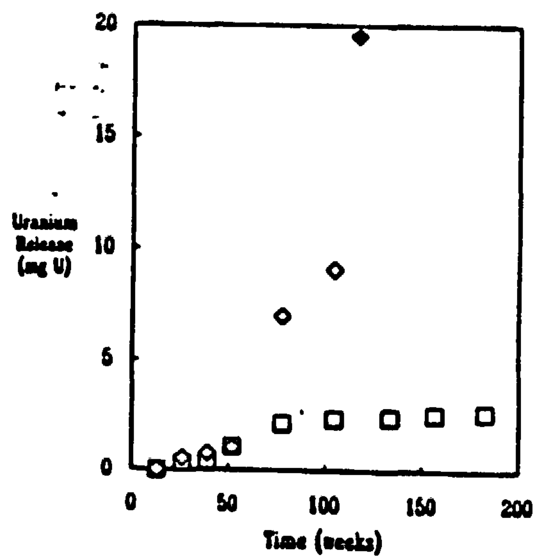
11 Disks



2 Disks + Crushed

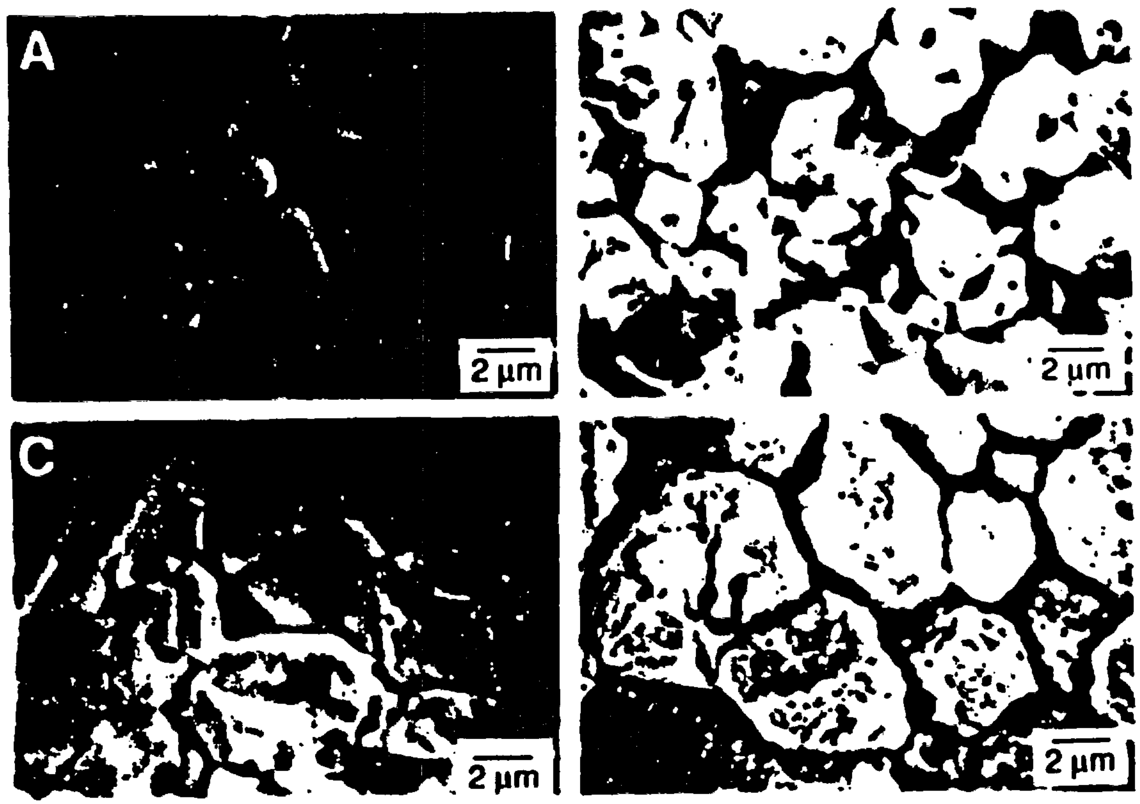


3 Pellets



3 Pellets, Low Flow

The main release pulse can be associated with etching of the grain boundaries and release of partially dissolved grains.



The aggregation efficiency factor, α, is incorporated in the collision frequency equation to reflect the chemical and hydrodynamic aspects of the aggregation process.

$$\alpha = \frac{\text{rate of particle attachment}}{\text{rate of particle collision}}$$

hydrodynamic interactions

van der Waals forces

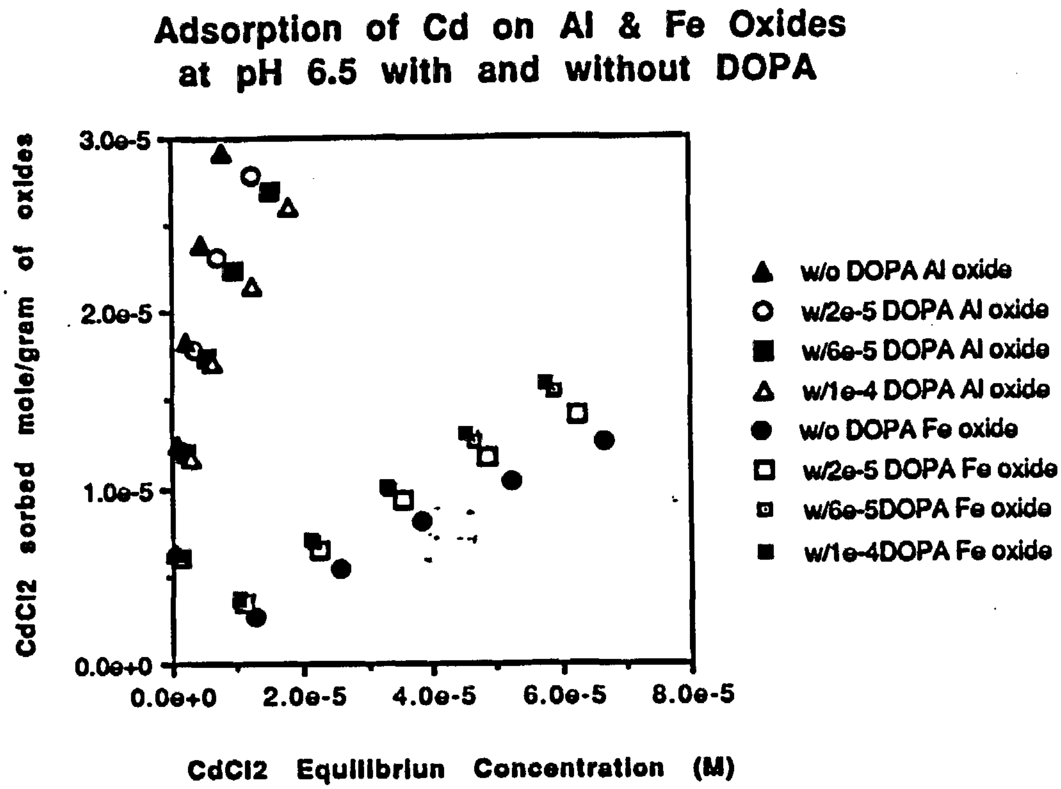
electrostatic repulsion

Stability Experiments

- utilize a light scattering technique
- use colloidal silica sol (obtained by dispersing negatively charged amorphous silica particles in water)
- silica concentration is approximately 0.06 g/l
- size of silica colloids is 50-80 nm
- silica colloids remain in suspension for 90 hours in a Ca^{+2} solution of 2.5 mmoles/l

Part Four:

Effect of Organic Coatings on Sorption


Adsorption of Cd on Al & Fe Oxides
at pH 6.5 with and without DOPA
CdCl2 sorbed mole/gram of oxides
3.0e-5
2.0e-5
1.0e-5
0.0e+0
0.0e+0
2.0e-5
4.0e-5
6.0e-5
8.0e-5
CdCl2 Equilibriun Concentration (M)
w/o DOPA Al oxide
w/2e-5 DOPA Al oxide
w/6e-5 DOPA Al oxide
w/1e-4 DOPA Al oxide
w/o DOPA Fe oxide
w/2e-5 DOPA Fe oxide
w/6e-5DOPA Fe oxide
w/1e-4DOPA Fe oxide

Gels and Colloids Around Yucca Mountain

Schön Levy
EES-1, Geology - Geochemistry
Los Alamos National Laboratory

Life history of colloids

- Generation
- Transport
- Deposition
- Crystallization

Natural Analog Studies at Yucca Mountain

Life history of colloids under hydrothermal and diagenetic conditions

RELEVANCE OF NATURAL GELS TO NUCLEAR WASTE ISOLATION

- Radionuclide sorption and transport

- Natural analogue to repository-induced alteration

YUCCA MOUNTAIN: Solidified and crystallized remains of former gels

RAINIER MESA: Fluid gels

ELECTRON MICROPROBE ANALYSES OF GELS AND RELATED MATERIALS

	Rainier Mesa, U12t			Drill Hole UE25a#1, Yucca Mountain			
	Silica-rich gels		Smectite	Glass	Smectite	Gel product	Heul.-clino.
Weight %							
SiO_2	20.8	85.8	57.5	72.0	53.6	58.7	64.6
TiO_2	0.00	0.08	0.22	0.09	0.18	0.00	0.00
Al_2O_3	3.18	2.27	24.2	11.7	26.9	10.1	12.3
FeO	0.13	0.14	3.4	0.70	1.4	0.32	0.00
MnO	0.00	0.00	0.23	0.00	0.00	0.00	0.00
MgO	0.00	0.00	1.15	<0.03	0.74	0.35	0.58
CaO	0.36	0.18	0.63	0.40	3.18	3.45	4.60
Na_2O	0.42	0.47	0.54	3.44	0.34	0.44	0.37
K_2O	0.45	0.66	3.00	4.69	0.24	0.51	0.92
TOTAL	25.3	89.6	90.9	93.0	86.6	73.9	83.4

GEL PRODUCTS

Zeolites -- heulandite-clinoptilolite, others
Smectite
Saponite
Silica--opal, chalcedony, cristobalite
Manganese minerals
Iron oxides/hydroxides
Copper, iron sulfates

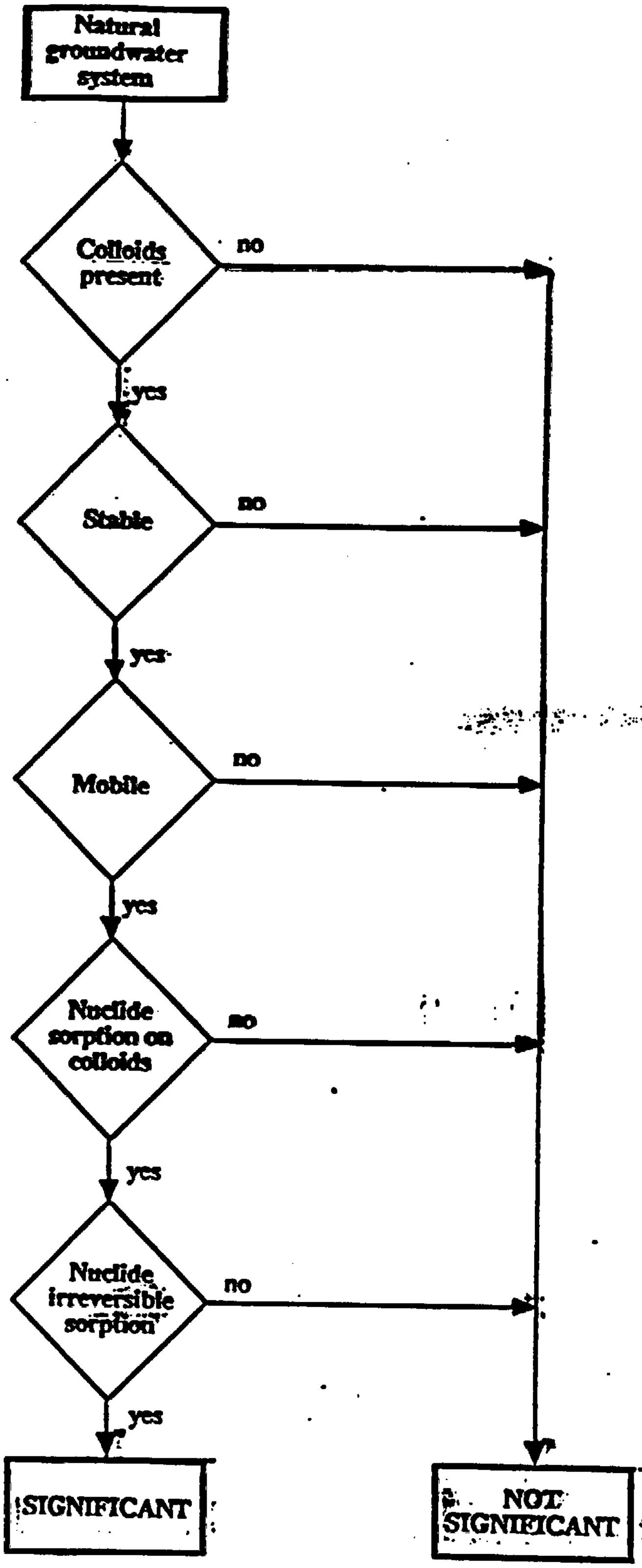
PRODUCTION AND ACCUMULATION OF ABUNDANT GEL ASSOCIATED WITH

- Glass available for alteration
- Free water
- Pores for accumulation

NAGRA AND SKB

Review of Colloid Research Programs

Robert S. Rundberg, Los Alamos



Methodological scheme followed to evaluate the role of colloids for contaminant transport in deep granitic system.

Source	Colloid Phase [coll]	size	Composition	Water Phase T	pH	Remarks artefact
Bad Säckingen	10	10-1000	SiO_2, clay	27	6.0	$CaCO_3$
Grimsel MI	100	10-1000	SiO_2, Illite	12	9.6	$CaCO_3$
Grimsel Gran.	<10^3	10-1000	SiO_2	12	8.0	oxidat.
Leuggern 5	20	10-1000	SiO_2, Illite	66	7.9	$Fe(OH)_3$
Menzenschwand	400	10-1000	Clay	13	6.5	oxic
TGT zone 1	<2 10^3	10-1000	Clay, SiO_2	7	8.8	high Eh
TGT zone 2	<2 10^4	10-1000	Illite	25	9.2	oxid
TGT zone 3	<10^3	10-1000	clay, SiO_2, Fe	5	9.0	oxic
Zurzach 1/2	10	10-1000	SiO_2, Illite	40	8.0	$Fe(OH)_3$

Source	Colloid Phase [coll]	size	Composition	Water Phase T	pH	Remarks artefact
Sweden	100*	50-500-	SiO_2, clay	11	6.0 -	$CaCO_3$
Canada	350*	1-1000	SiO_2, Illite	-	-	$CaCO_3$
France	<100	100-1000	SiO_2, organics	16 -	6.0 -	Oxic GW
Spain	<100	1-1000	not identify	20	7.9	$Fe(OH)_3$

Table 5: comparison of the colloid concentration, size and composition

Conditions: [coll]/ppb, * Sweden ± 100, * Canada ± 1000, size: $Ø$-$Ø_{(M)}$/nm, average temperature T/°C, potential artefact generation is noted.

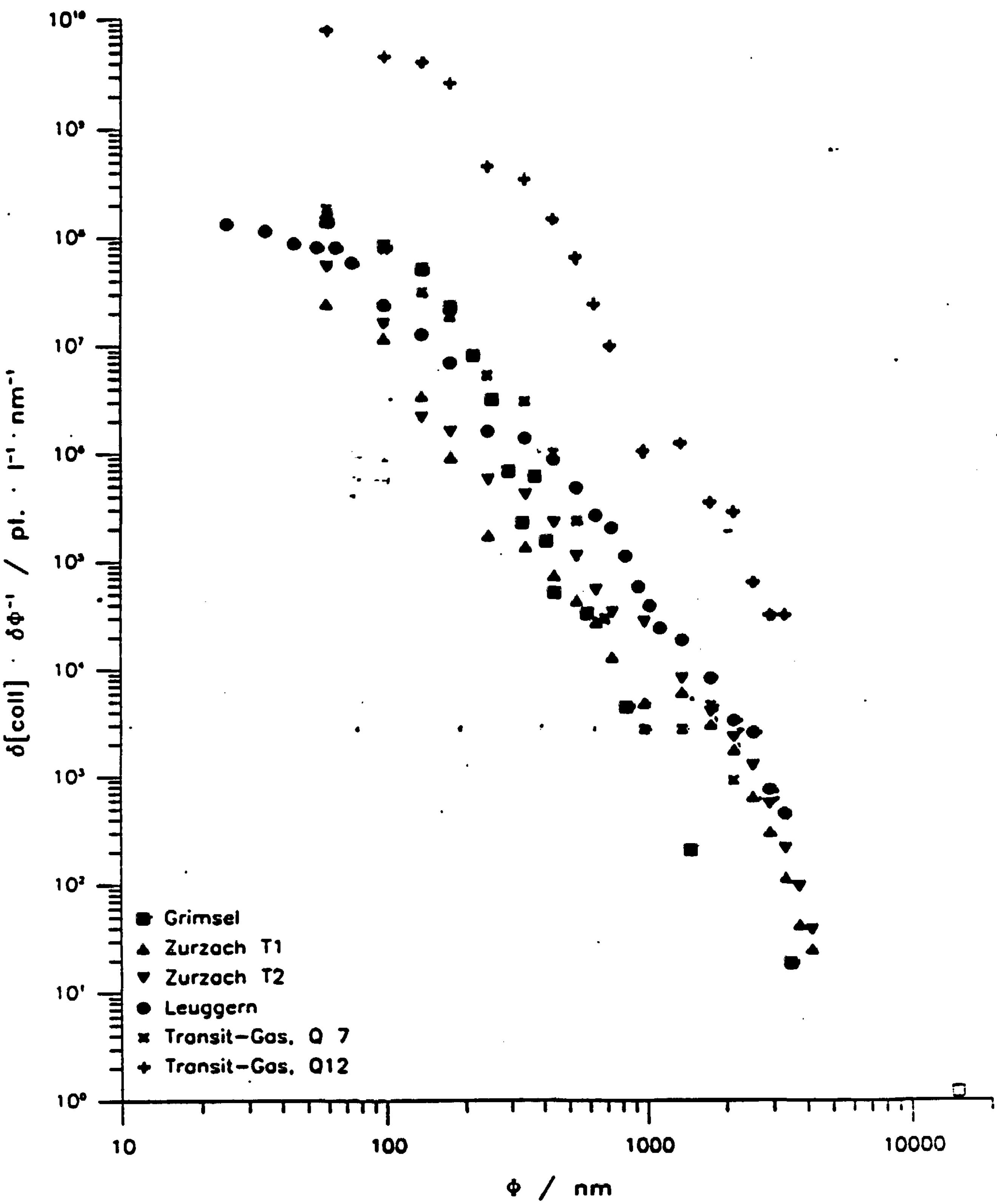
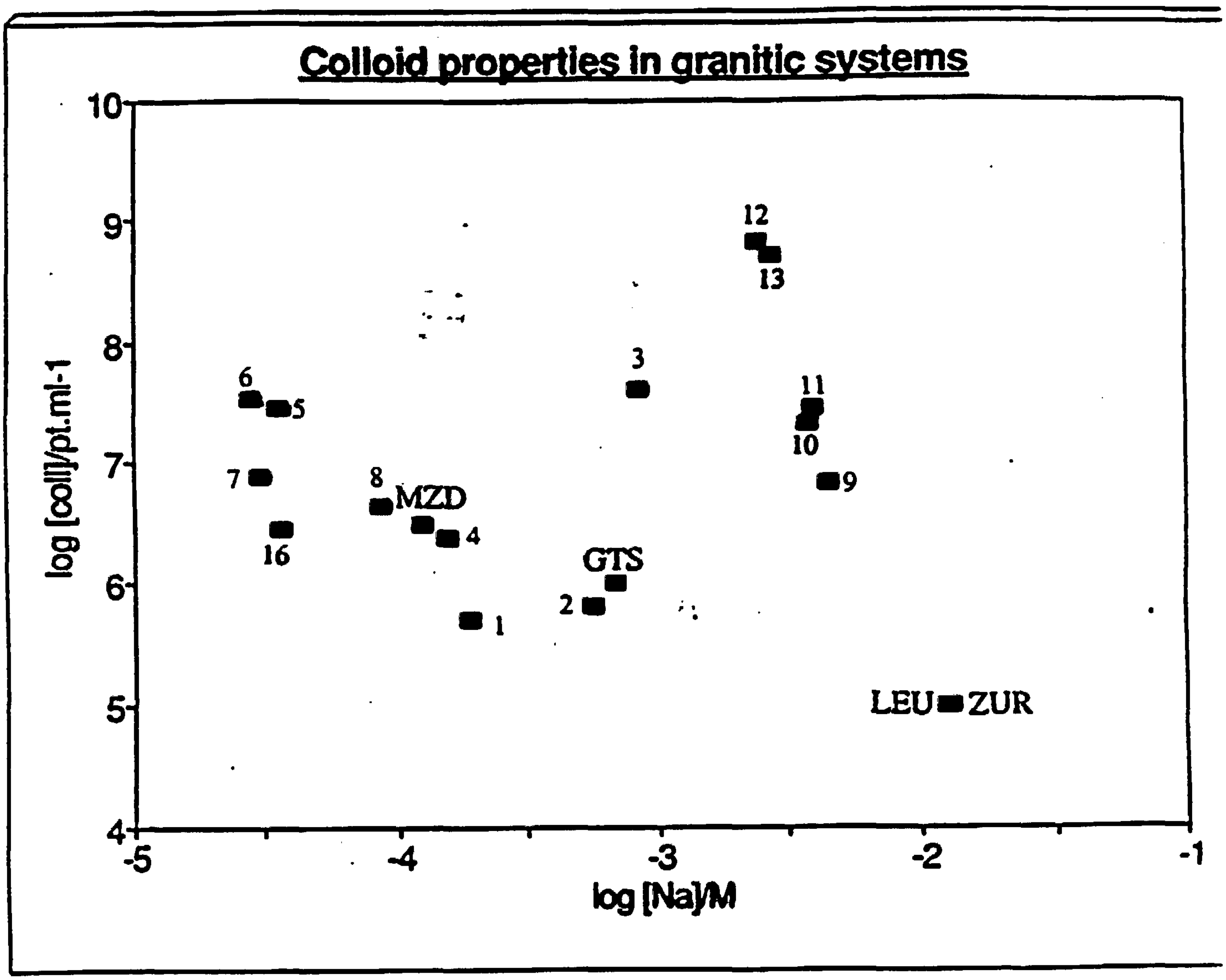
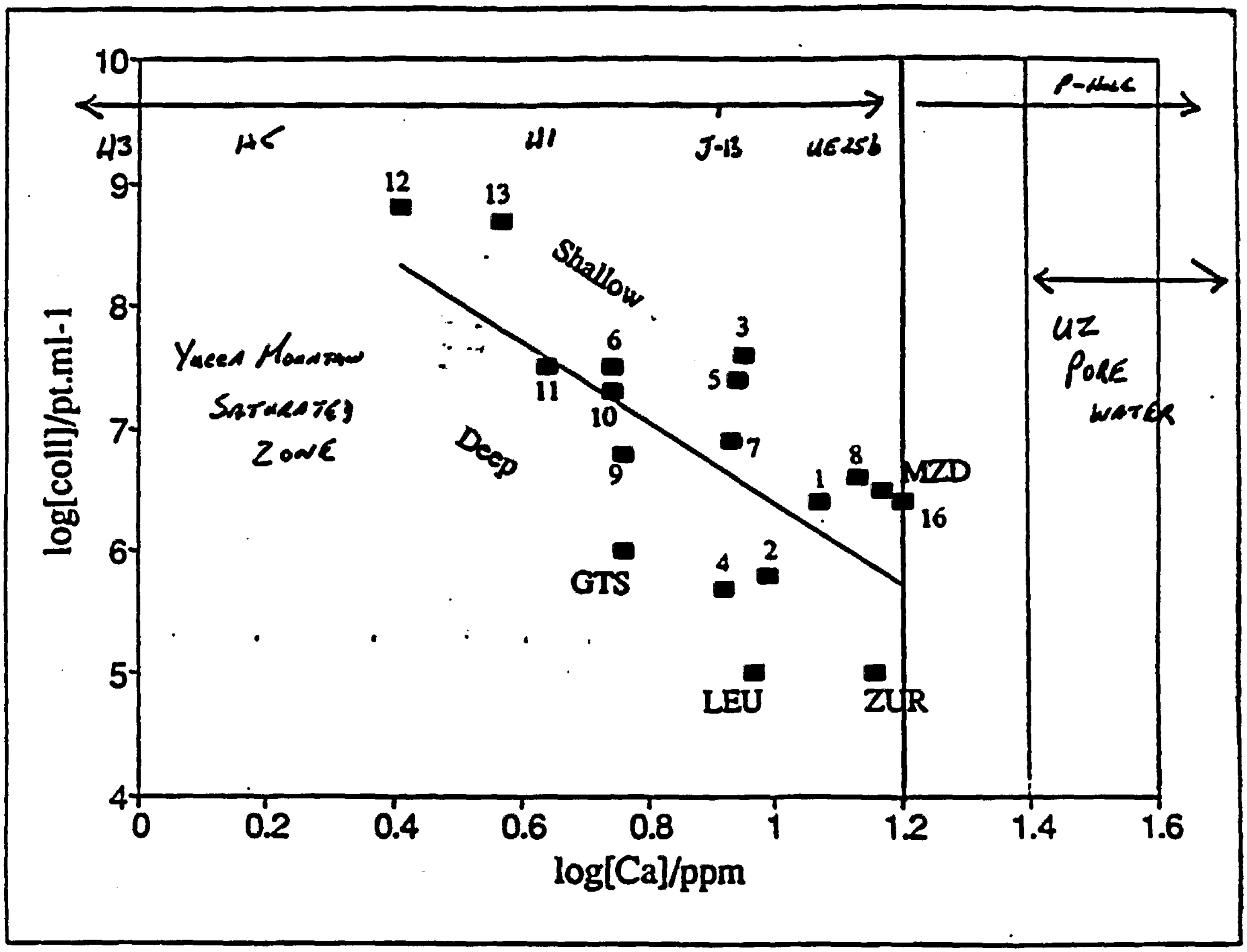


Figure 7 : Colloid size distribution comparison
Conditions: from on-site filtration with 3 nm membrane, SEM analysis, average [coll] precision 20%.



Colloid properties in granitic systems
log [coll]/pt.ml-1
log [Na]/M
10
9
8
7
6
5
4
-5
-4
-3
-2
-1
1
2
3
4
5
6
7
8
9
10
11
12
13
16
MZD
GTS
LEU
ZUR

PSI/WASTE MANAGEMENT PROGRAM/COLLOID SUBPROGRAM



Correlation between colloid and Ca concentration in granitic groundwaters.

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

Transitgas tunnel (N° label), Menzenschwand (MZD)

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

NAGRA

Results of current Strategy:

- Natural concentration low
- Not stable
- Sorption on colloids not sufficient to compete with surrounding rock matrix

NAGRA

Pertinence to Yucca Mountain

Sampling techniques - avoid artifacts

Groundwater similar in composition Na, Ca

Major minerals in mylonite are K-feldspar,
quartz, albite, biotite, and muscovite.

Natural Colloid level same as J-13

SKB

Program

Field measurements of Colloids

Transport of iron oxides in quartz columns with and without sorbed radionuclides

Sorption of radionuclides by groundwater bacteria

SKB

Studying Colloid Transport

Present Status:

Studies of Iron oxide transport in silica columns

High filtration at pH below PZC

Some release if pH is raised above PZC

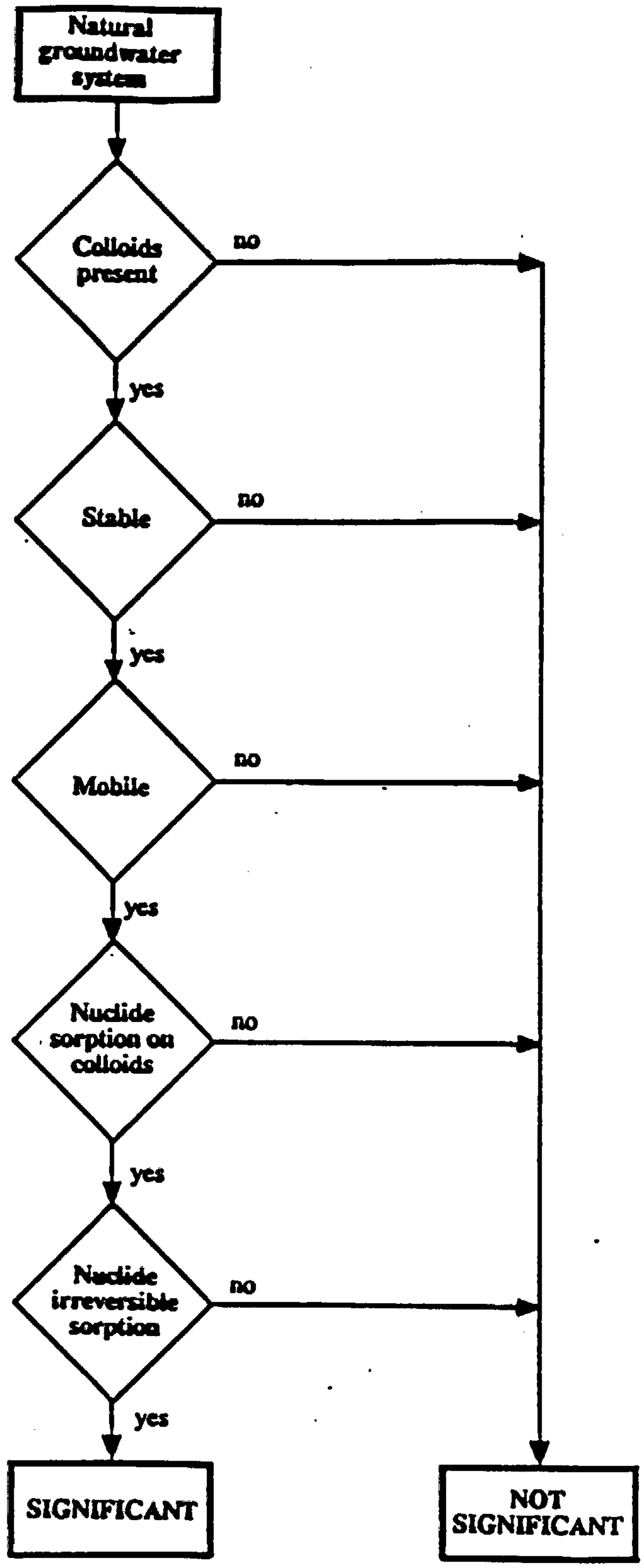
SKB

Pertinence

Columns experiments are of a generic nature

Might expect Pu colloid (PZC ~6) to behave as other metal oxides

Qualitatively the results of column experiments are predictable



Methodological scheme followed to evaluate the role of colloids for contaminant transport in deep granitic system.

REVIEW OF AECL

COLLOID TRANSPORT EXPERIMENTS

By

Peter Vilks and Don Bachinski

AECL Research
Whiteshell Laboratories
Pinawa, Manitoba

YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT
COLLOID WORKSHOP

1993 MAY 03 - 05

OBJECTIVE OF MIGRATION STUDIES

To Determine the Mobility of Colloid-Sized Particles and Suspended Particles in Fractures, and Their Role in Radionuclide Migration.

1. Evaluate particle generation from fracture surfaces caused by groundwater flow

2. Characterize the filtration and remobilization of particles introduced into fractures

   - latex spheres, silica, clay, natural colloids

   - effect of water velocity

   - effect of particle size

   - effects of channelling and fracture orientation

LABORATORY LARGE BLOCK (LB4) COLLOID MIGRATION EXPERIMENTS

- Quarried granite block with dimensions of 83 x 90 x 60 cm
- Flow fields within horizontal fracture are controlled through a set of 9 boreholes
- With this experimental configuration, it is possible to achieve a level of control over particle migration in a natural fracture that is not possible in field-scale experiments

EXPERIMENTS IN LB4

1) HYDRAULIC CHARACTERIZATION

   - Identified sets of boreholes suitable for migration experiments

   - Hydraulic transmissivities between some boreholes depended upon flow direction

   - Low transmissivity around one borehole decreased with continued pumping

2) PARTICLE GENERATION FROM FRACTURE

   - By flushing with particle-free groundwater from fracture zone 2 of the URL

3) MIGRATION TESTS WITH NON-SORBING TRACERS

   - Uranine and bromine

4) FILTRATION AND REMOBILIZATION OF PARTICLES INTRODUCED INTO THE FRACTURE (LATEX SPHERES, SILICA PARTICLES, NATURAL CLAY PARTICLES FROM THE URL)

METHODS OF PARTICLE CHARACTERIZATION

1) Microtrac Ultrafine Particle Size Analyser (UPA)

- laser-based instrument for determining the size of particles from 6 nm to 2.5 μm

- determines the Doppler shift in the frequency of light scattered from moving particles to calculate particle Brownian motion and size distribution

- particle concentrations can be related to a concentration index or a loading index

- small enough to be easily transported to a filed laboratory

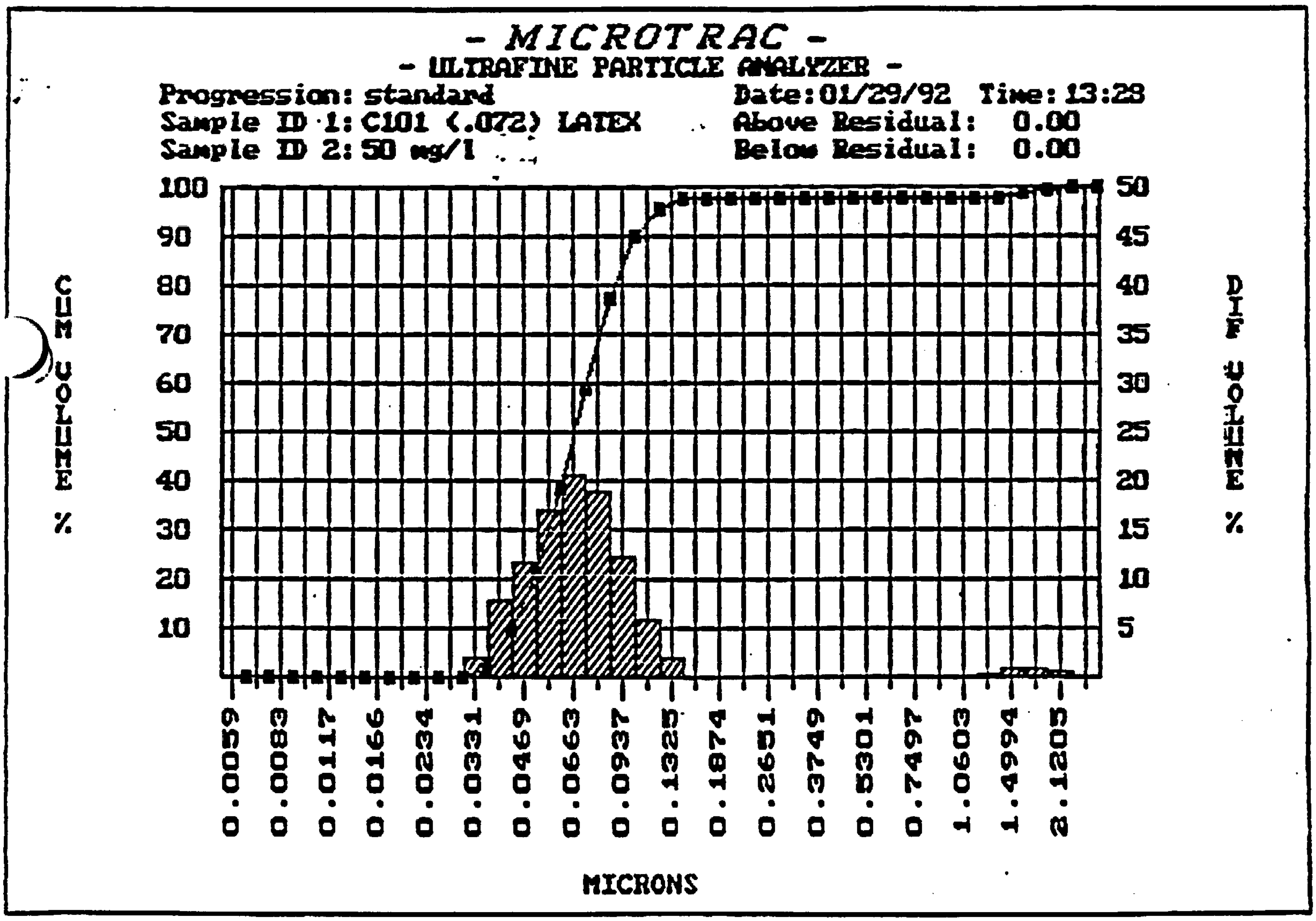
2) CLIMET Particle Counter

- determines the size and concentration of particles from 0.4 μm to 100 μm

- uses a Russel sensor to count particles (1 to 100 μm) by light obscuration. A second sensor counts particles from 0.4 to 20 μm by forward light scattering

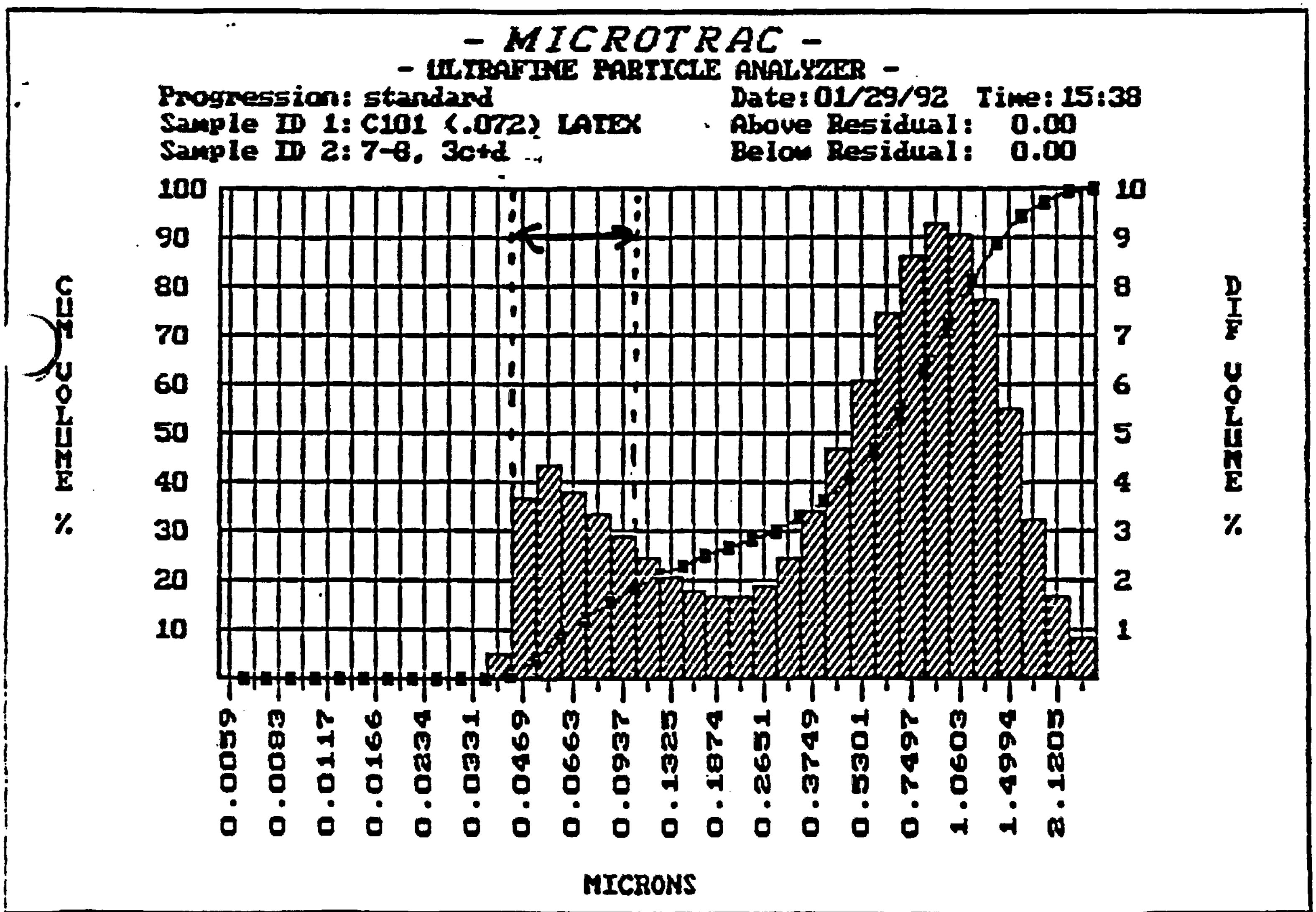
- sensitive to extremely low particle concentrations

Particle Size of Latex Spheres Used in Migration Studies



Peak Concentration of Latex Spheres

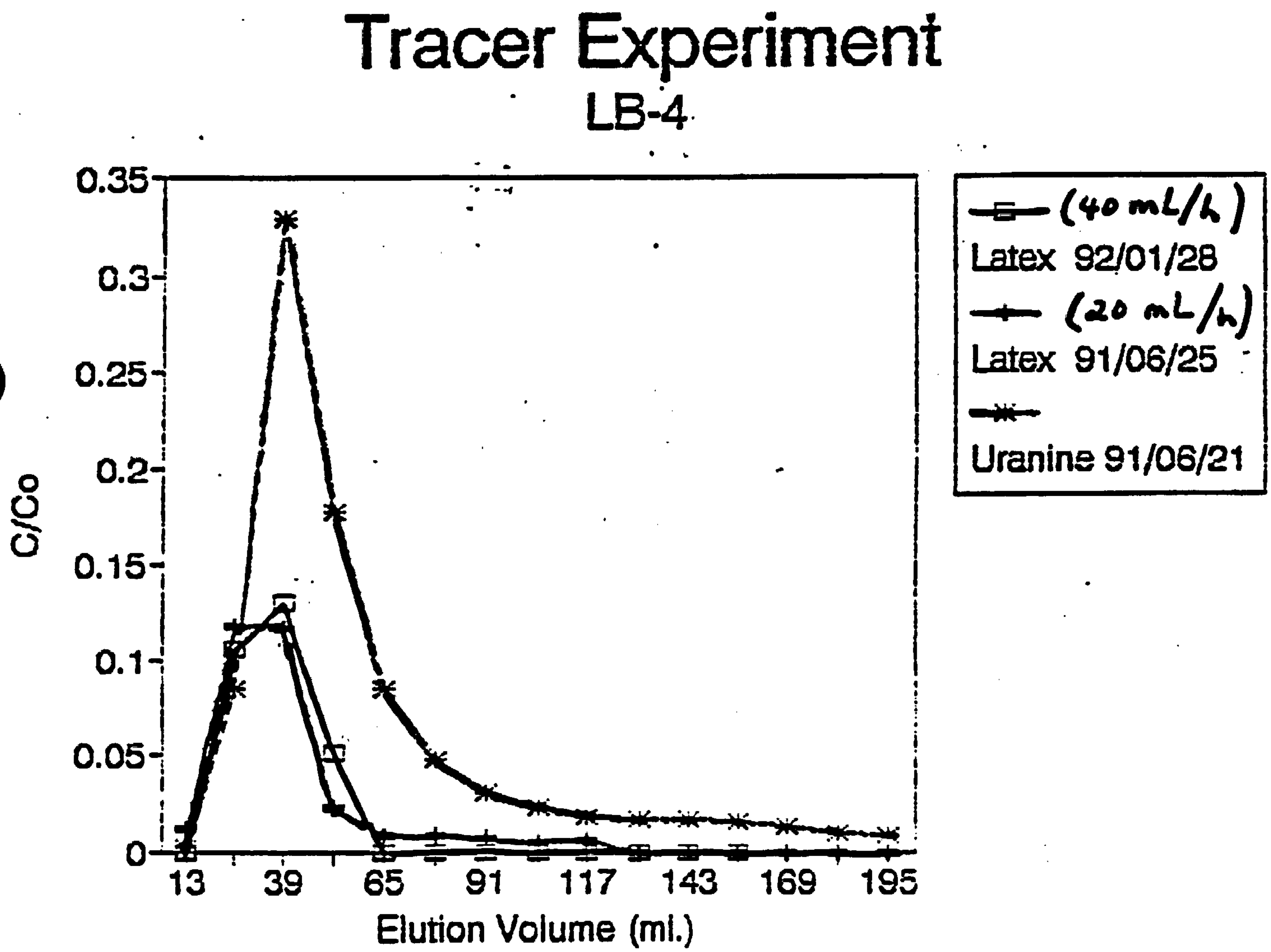
- The 10-20 nm colloids are swamped by the concentration of latex spheres.
- The 72 nm latex spheres appear to have coagulated.

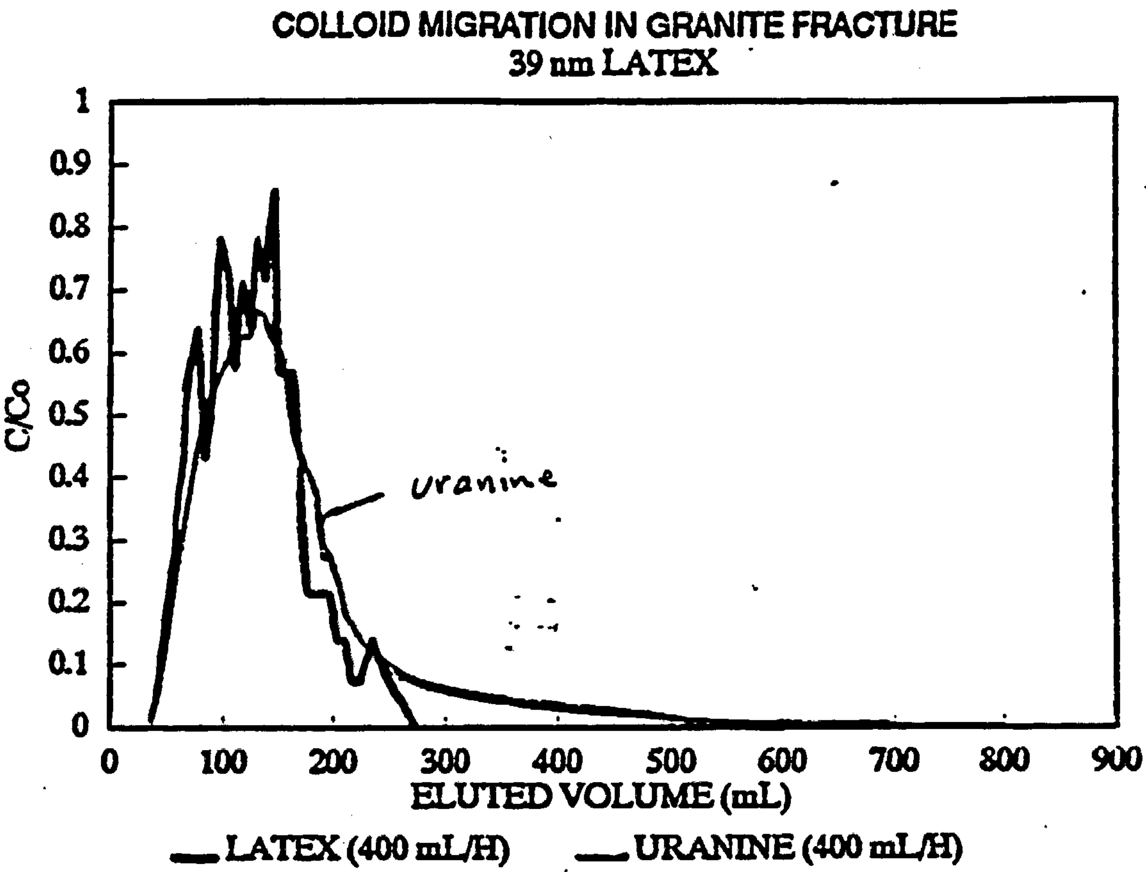


PARTICLE GENERATION FROM FRACTURE

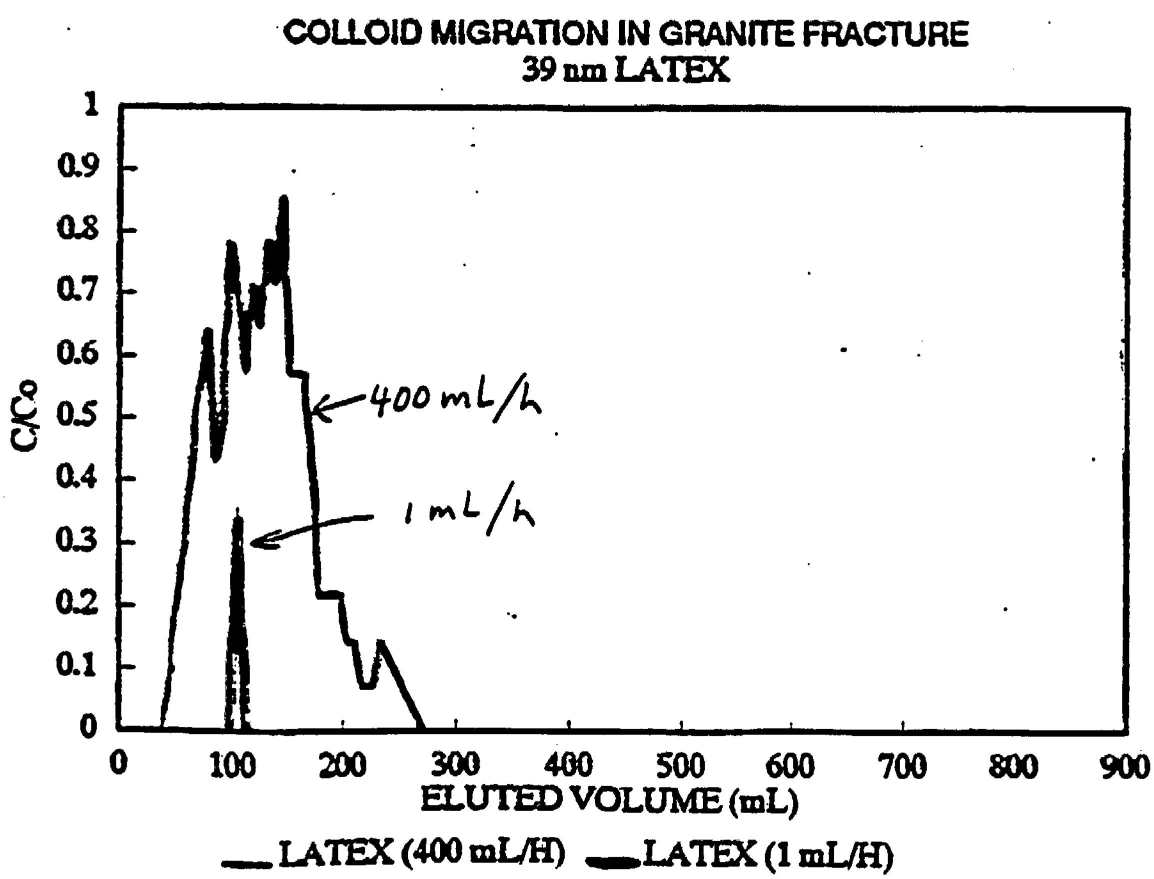
- Clay Minerals, Quartz, Feldspar, Calcite, Bacteria
- Groundwater From Fracture Zone 2 of the URL, Na-Cl-HCO_3-SO_4 Water With an Ionic Strength of 0.013
- Flow Rates 4 mL/h (215 m/a) to 400 mL/h
- Particles as Large as 40 μm were Mobilized by the Low Flow Rate
- An Increase in Flow Rate to 400 mL/h Increased the Release of 5 μm and Larger Particles by 200 Percent, but Did Not Affect Smaller Particles

72 nm latex spheres



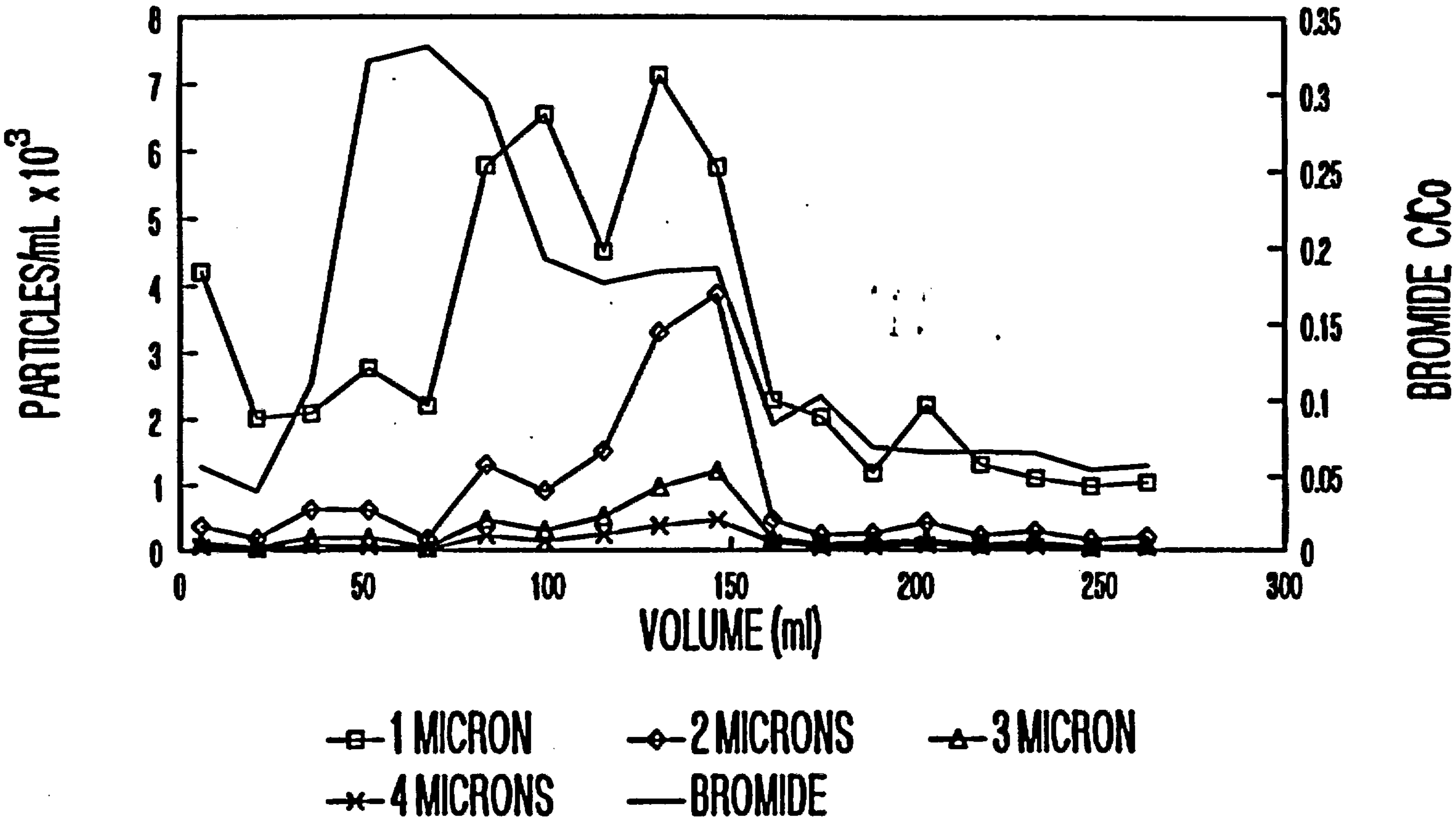


COLLOID MIGRATION IN GRANITE FRACTURE
39 nm LATEX
C/Co
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
uranine
0
100
200
300
400
500
600
700
800
900
ELUTED VOLUME (mL)
LATEX (400 mL/H)
URANINE (400 mL/H)

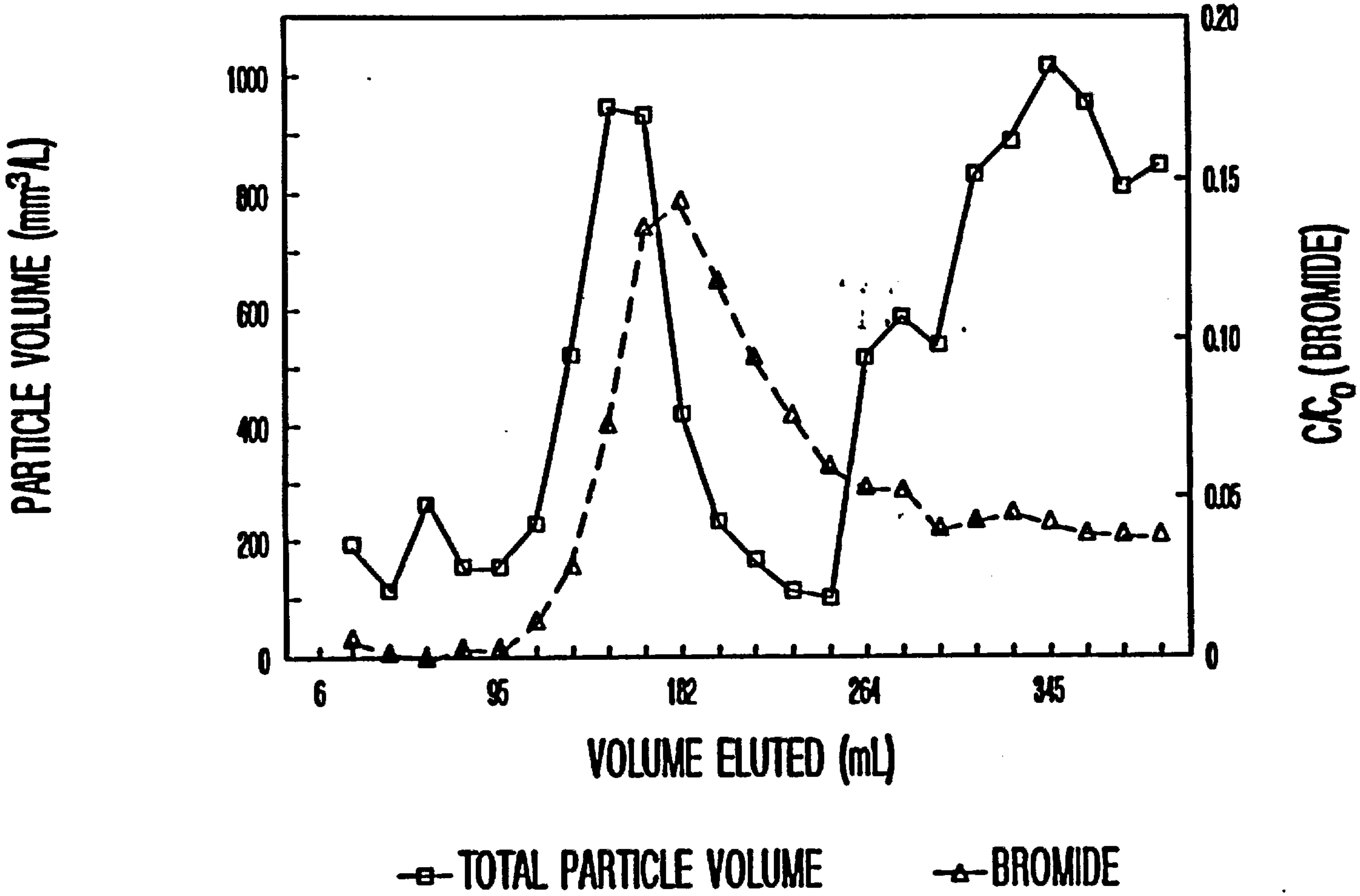


COLLOID MIGRATION IN GRANITE FRACTURE
39 nm LATEX
C/Co
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
400 mL/h
1 mL/h
0
100
200
300
400
500
600
700
800
900
ELUTED VOLUME (mL)
LATEX (400 mL/H)
LATEX (1 mL/H)

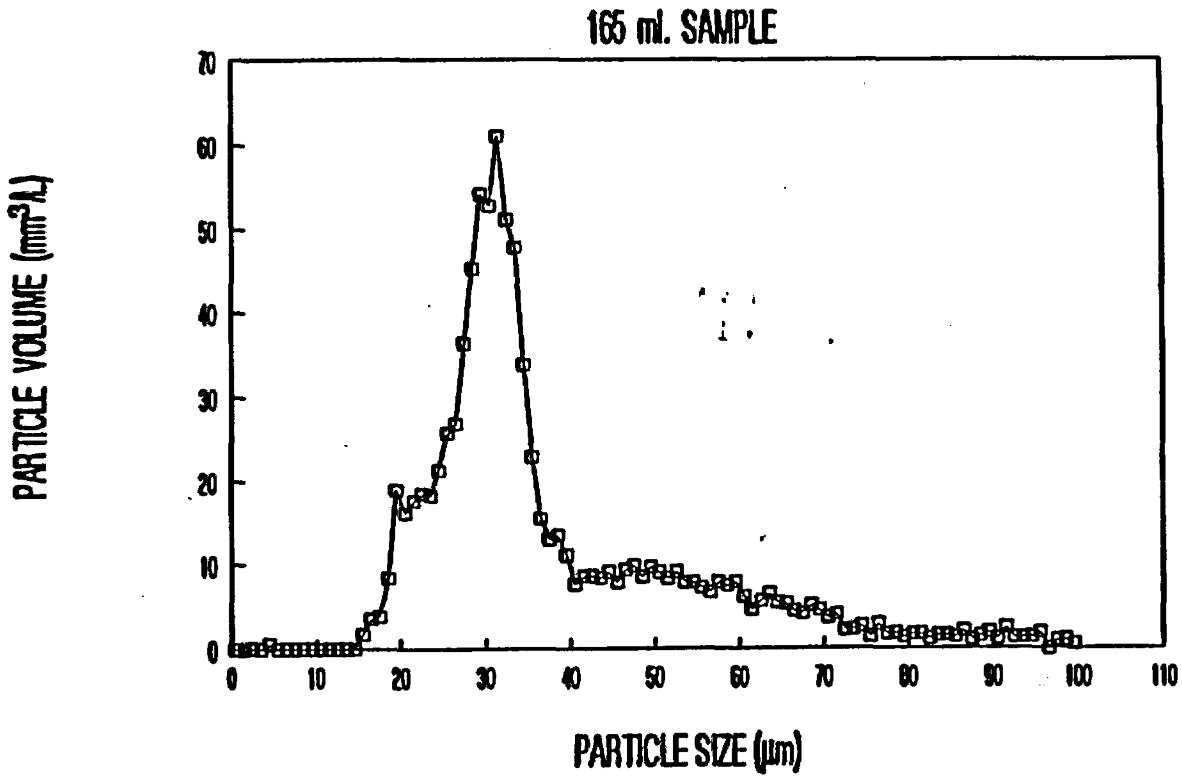
LATEX MIGRATION EXPERIMENT
1 mL/ h



MIGRATION OF COAGULATED LATEX SPHERES
IN GRANITE FRACTURE

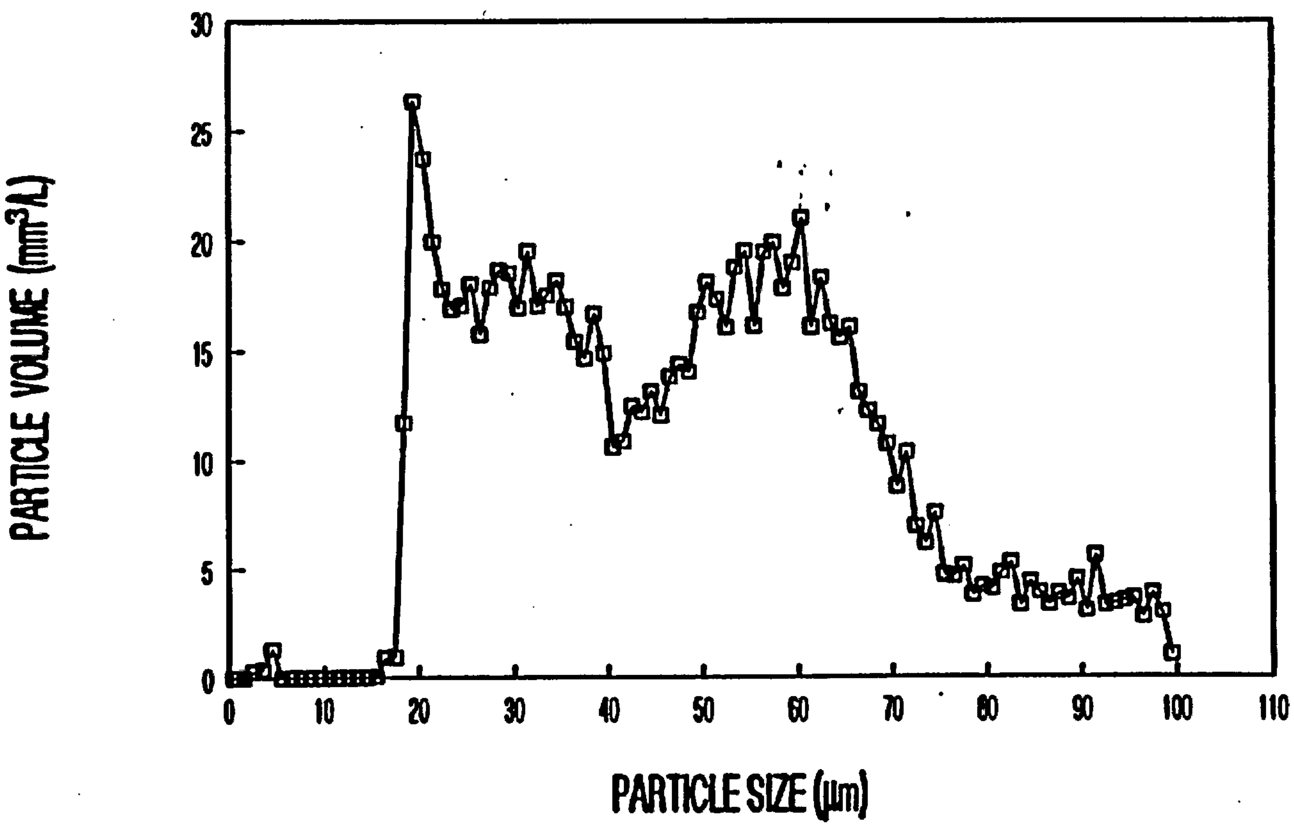


SIZE DISTRIBUTION OF COAGULATED LATEX



SIZE DISTRIBUTION OF COAGULATED LATEX

345 ml. SAMPLE



FIELD SCALE MIGRATION EXPERIMENTS AT THE URL

- Part of AECL's Transport Properties in Highly Fractured Rock Experiment.

- Two-well recirculating test between pairs of boreholes (HC33 and HC27) intersecting Fracture Zone 2 at the Underground Research Laboratory (URL). Flow rate of 5 and 10 L/m, giving average velocities of several m/h.

- Well separation distance: 20 m

- Particle tracers will include latex spheres and silicon particles (20 nm, 2 μm, 44 μm)

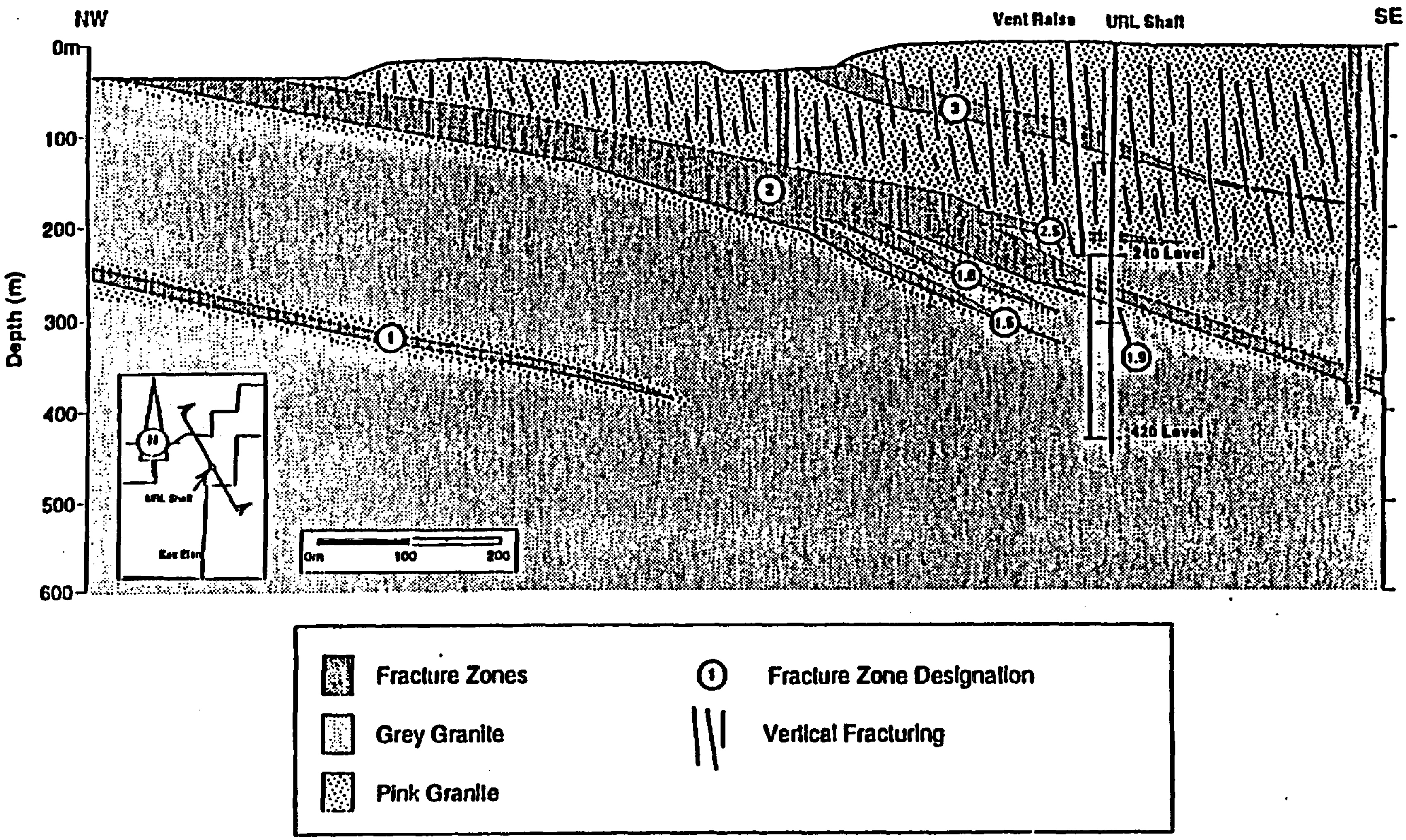


FIGURE 1: Cross Section of Structural Geology of the URL Site

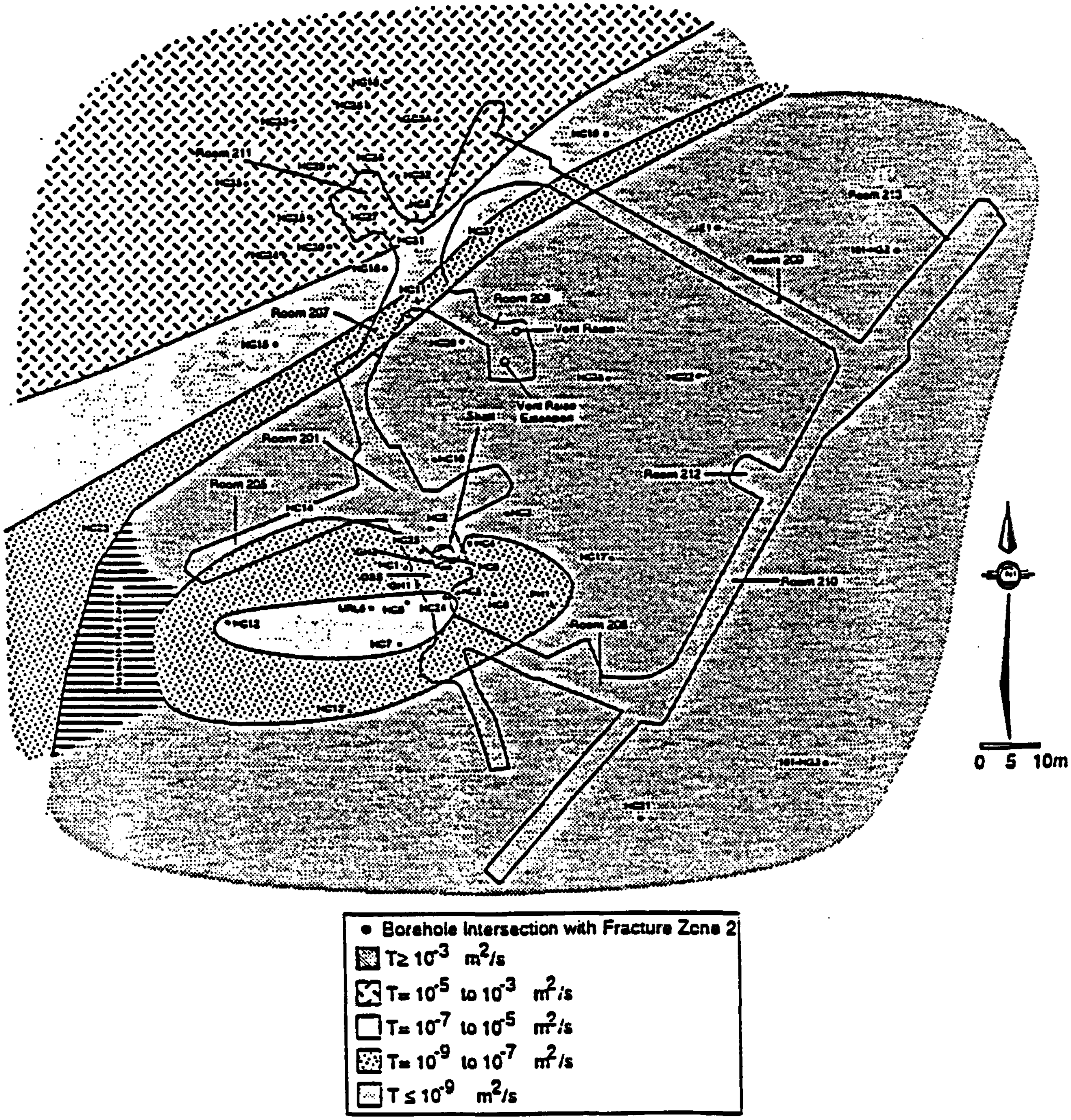


FIGURE 3: Transmissivity Distribution in Fracture Zone 2 Beneath the 240 Level

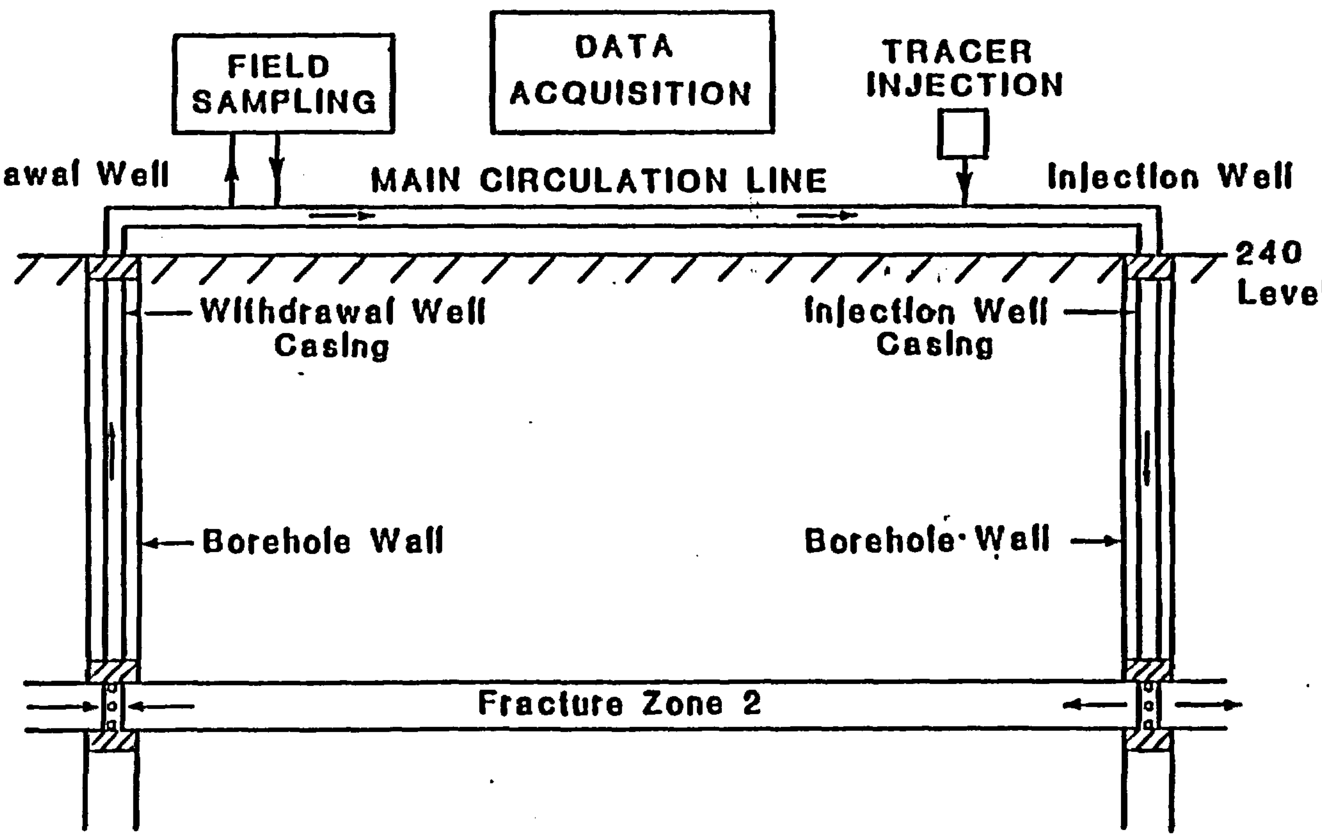
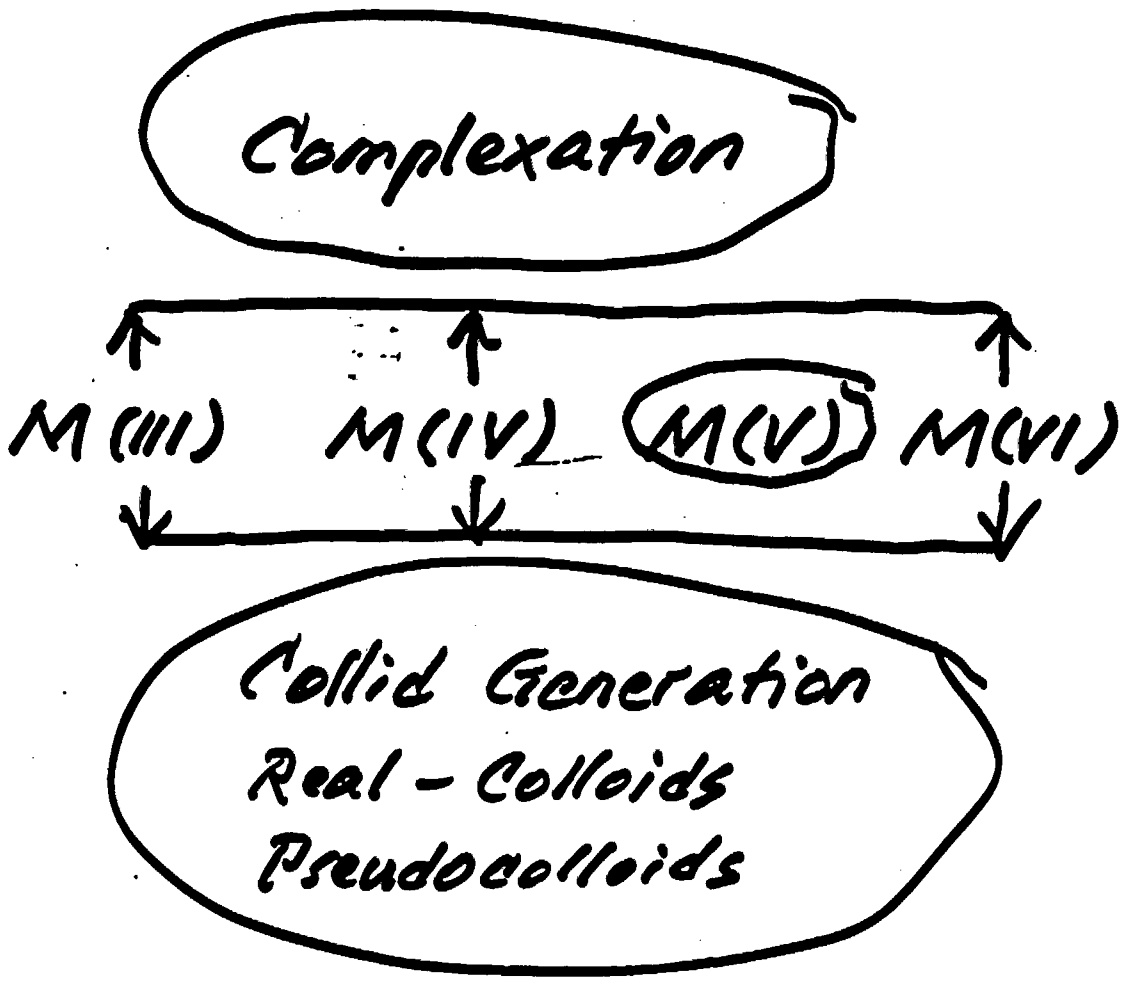


FIGURE 5: Schematic of Two-Well Recirculating Tracer Test

JI Kim

<Mobile RN Species>

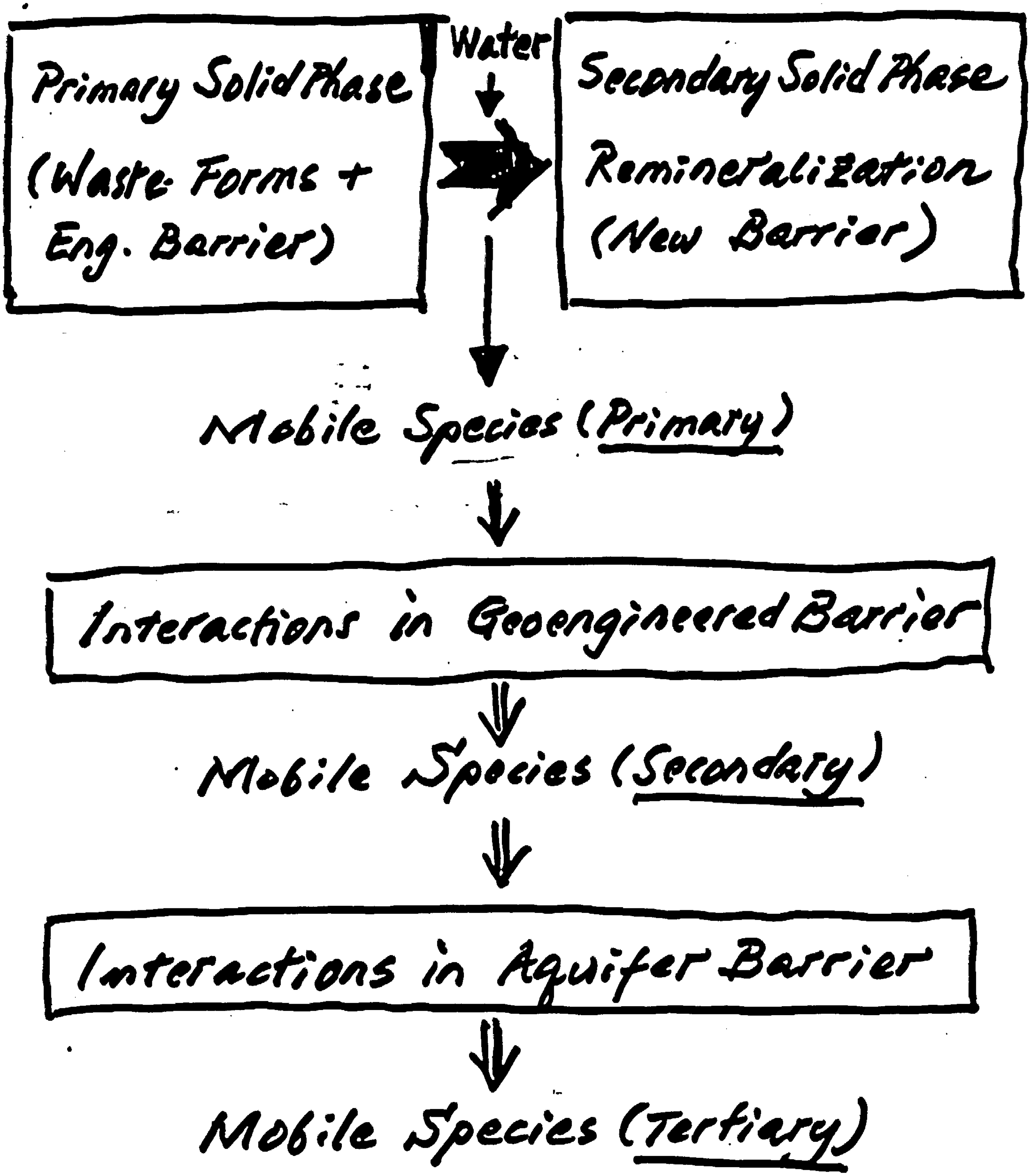


M(V)/M(VI) ⇒ Reduction → Complexation

→ Colloid Generati

in deep aquifer systems

Immobilization by Multibarrier Functions



CONCLUSIONS

Mobile Chem. Species of RN vs. Immobilization of RN

Mobile Species / Migration

- Inorganic Complexes, Organic Complexes of RN
- Pseudocolloids of RN

How to Speciate, Quantify and Parameterize for Modeling?

COLLOID MIGRATION EXPERIMENT

Aquifer System : Aquatic Colloids

↓

Sampling : Groundwater, Colloids, Sediments

↓

Preservation in Lab : Groundwater // Sediment

↓

Characterization, Quantification, Parameterizatio[illegible]

↓

Experiment : Pseudocolloid Generation // Migrat[illegible]

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Geochemical Transport Modeling

↓

Transferability // Validation

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Aquifer System // RN-Migration

"PSEUDOCOLLOIDS" of Actinides

- M^{3+}, M^{4+}, MO_2^{2+} are unstable in natural aquatic system and undergo sorption on the surface

- $M(OH)_n^{m-n}$, $M_x(OH)_y^{mx-y}$ are also unstable in aquatic system

- Actinide ions can be stabilized in natural aquatic systems as
  * Anionic carbonate or organic complexes
  * Pseudocolloids

- Generation of Pseudocolloids

"GROUNDWATER COLLOIDS"
(AQUATIC COLLOIDS)
IN
Gorleben Aquifer Systems

- Particle Size: $\phi \not< 30\,nm$
- Chem. Composition: Organometallics
- Chem. Homologs on Colloids (Actinides):

M(II): Ca^{2+}, Mg^{2+}, Sr^{2+} (Ra^{2+}) 1–20 %

M(III): REE, Fe^{3+}, Cr^{3+}, Sc^{3+} > 95 %

M(IV): Th^{4+}, Zr^{4+}, Hf^{4+}, U^{4+} > 95 %

M(VI): UO_2^{2+} > 95 %

"REAL-COLLOIDS" (RADIOCOLLOIDS)

- Generation by Hydrolysis process

  M(IV) > M(VI) > M(III) > M(V)

- Real-colloids are immobile in natural aquifer systems because of the oxygen bridge building on the surface.

- Real-colloids ⇒ Pseudocolloids in Groundwater

- Tendency of the real-colloid generation:

  $M^{4+} > MO_2^{2+} > M^{3+} \; (MO_2^{+})$

Wednesday, May 5, 1993.
Afternoon Session

Future Direction of Colloid Studies in the Yucca Mountain Project

Panel Discussion:

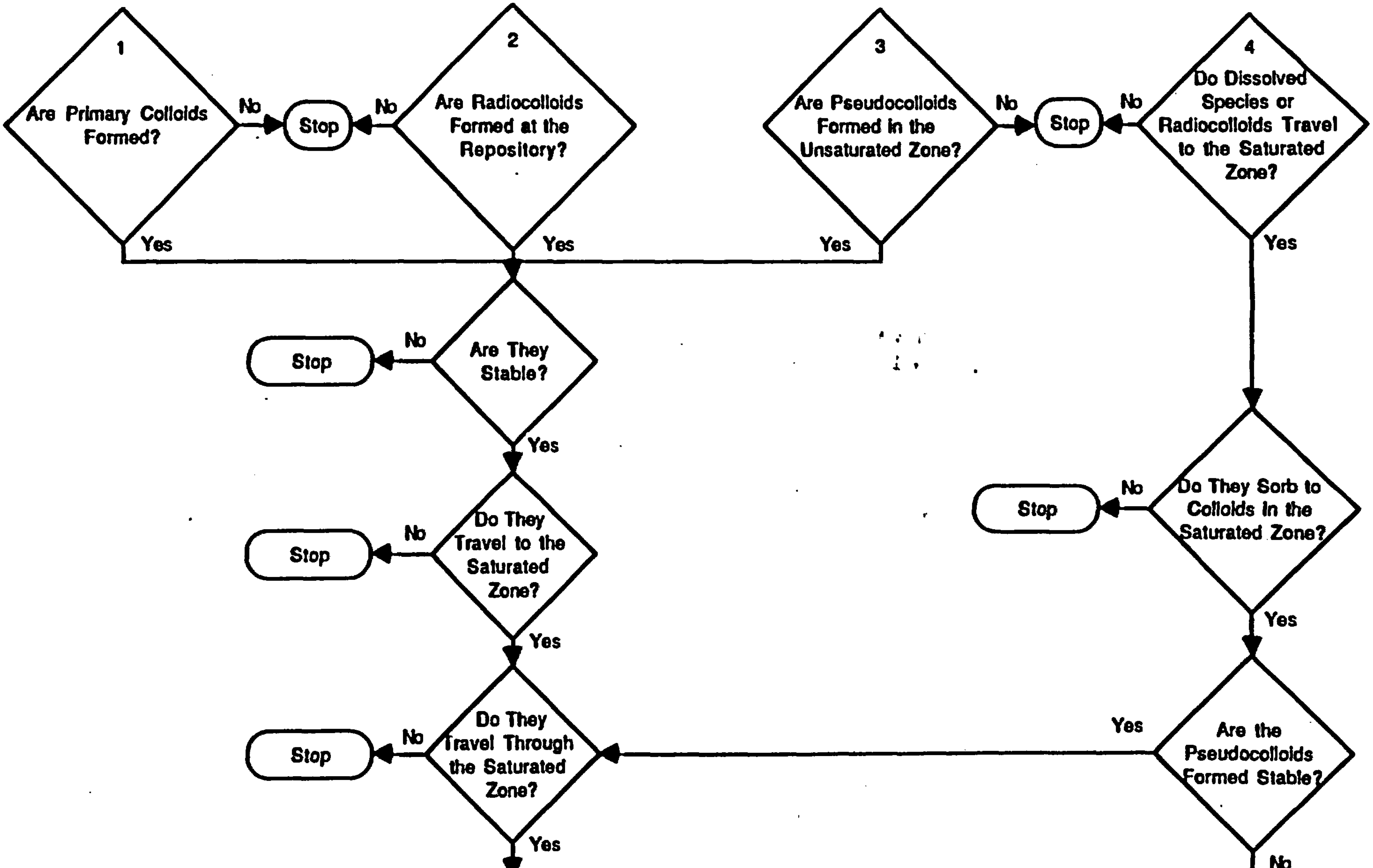
Relative to the objectives of the workshop, what are the priorities for future colloid studies in the Yucca Mountain Project?

Objective: to evaluate whether colloids will significantly increase radionuclide release to the accessible environment

Information needed in the areas of:

- colloid sampling
- colloid generation
- colloid stability
- sorption/desorption of radionuclides onto colloids
- colloid transport

YMP Colloid Strategy



Provide PA with:
1. Colloid Concentration
2. Radionuclide Content
3. Attachment/Detachment Parameters

All Four Major Questions Must Be Answered

What colloids are present?

- sample to measure concentrations and perform characterization of inorganic colloids, organics, and microorganisms in waters from the saturated zone

- perform laboratory experiments to address formation of primary colloids, radiocolloids, and pseudocolloids as the result of the degradation of the waste form and potential canister materials

- perform natural analog studies at Yucca Mountain to address the formation of colloids by natural glass alteration in a repository hydrothermal environment

Life History of Colloids Under Hydrothermal Conditions

- **Generation**
- **Transport**
- **Deposition**
- **Crystallization**

Colloid Stability

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

Pseudocolloid Formation

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

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

Colloid Transport Experiments and Calculations

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

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

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

- validate colloid transport code

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