# WIPP Colloidal Actinide Retardation Research Program

DOE Consultation with the State of New Mexico

21 May 1996

Carlsbad, NM

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# Outline of Presentation

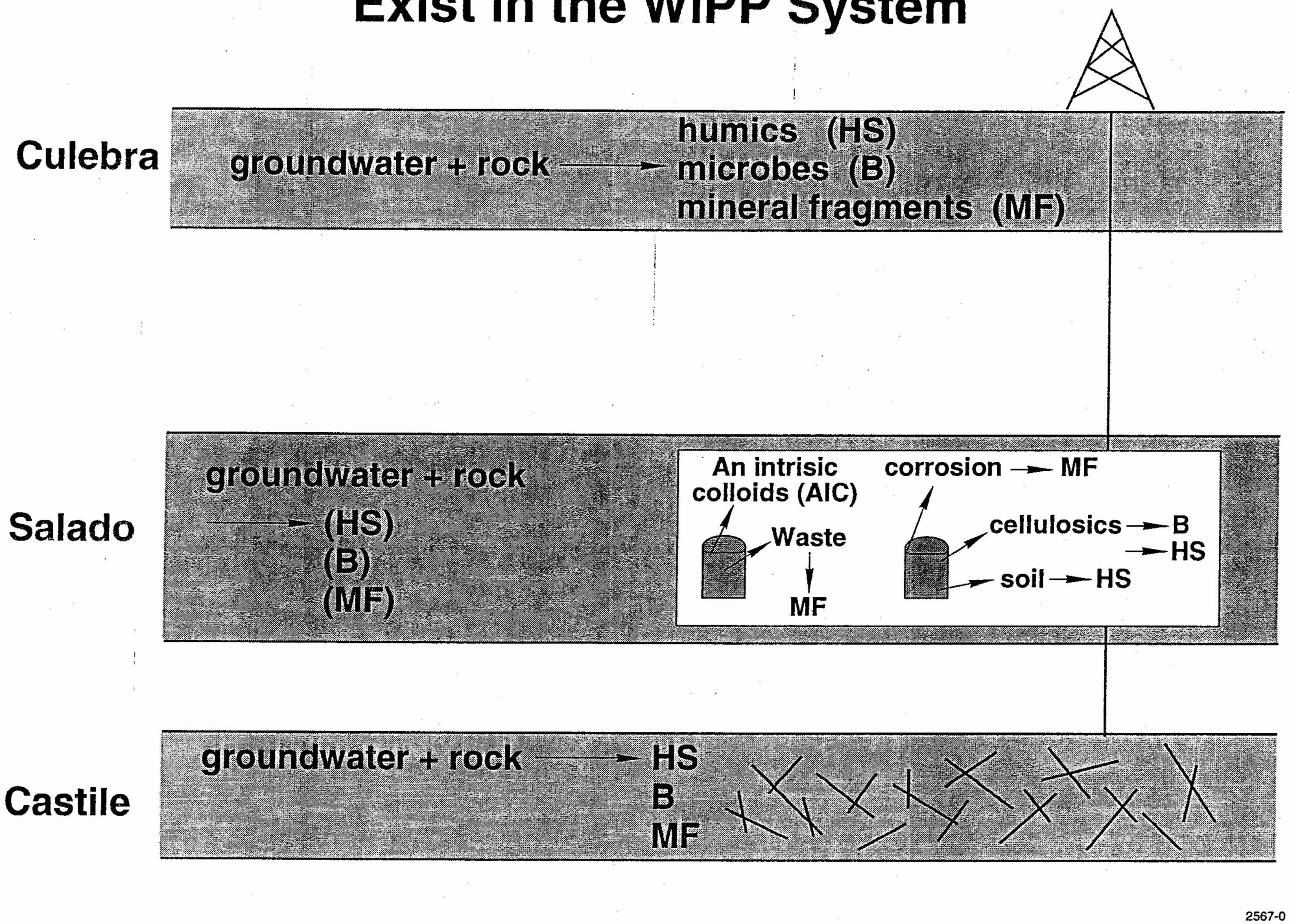
## Mobile Colloidal Actinide Source Term

- Overview
- Results

## Retardation of Colloidal Actinides in the Culebra

- Conceptual models
- Program strategy
- Experiments
- Results by colloidal particle type
- Summary

# Several Potential Sources of Colloidal Actinides Exist in the WIPP System



# Colloidal Particle Types Affected Differently by Chemical Conditions

| Colloid Type | Stability Behavior in WIPP Brines | Uptake Mechanism for Th, U, Np, Pu, Am |
|---|---|---|
| *mineral fragments* | electrostatically destabilized | sorption |
| *microbes* | not affected | passive or active bioaccumulation |
| *actinide intrinsic* | solubility reduced; electrostatically destabilized | intrinsic |
| *humic substances* | solubility reduced | complexation |

# Mobile Colloidal Actinide Source Term

## Concentrations dependent on repository brine scenario

- Salado brine, lower redox [Th(IV), U(IV), Np(IV), Pu(III), Am(III)]
- Salado brine, higher redox [Th(IV), U(VI), Np(V), Pu(IV), Am(III)]

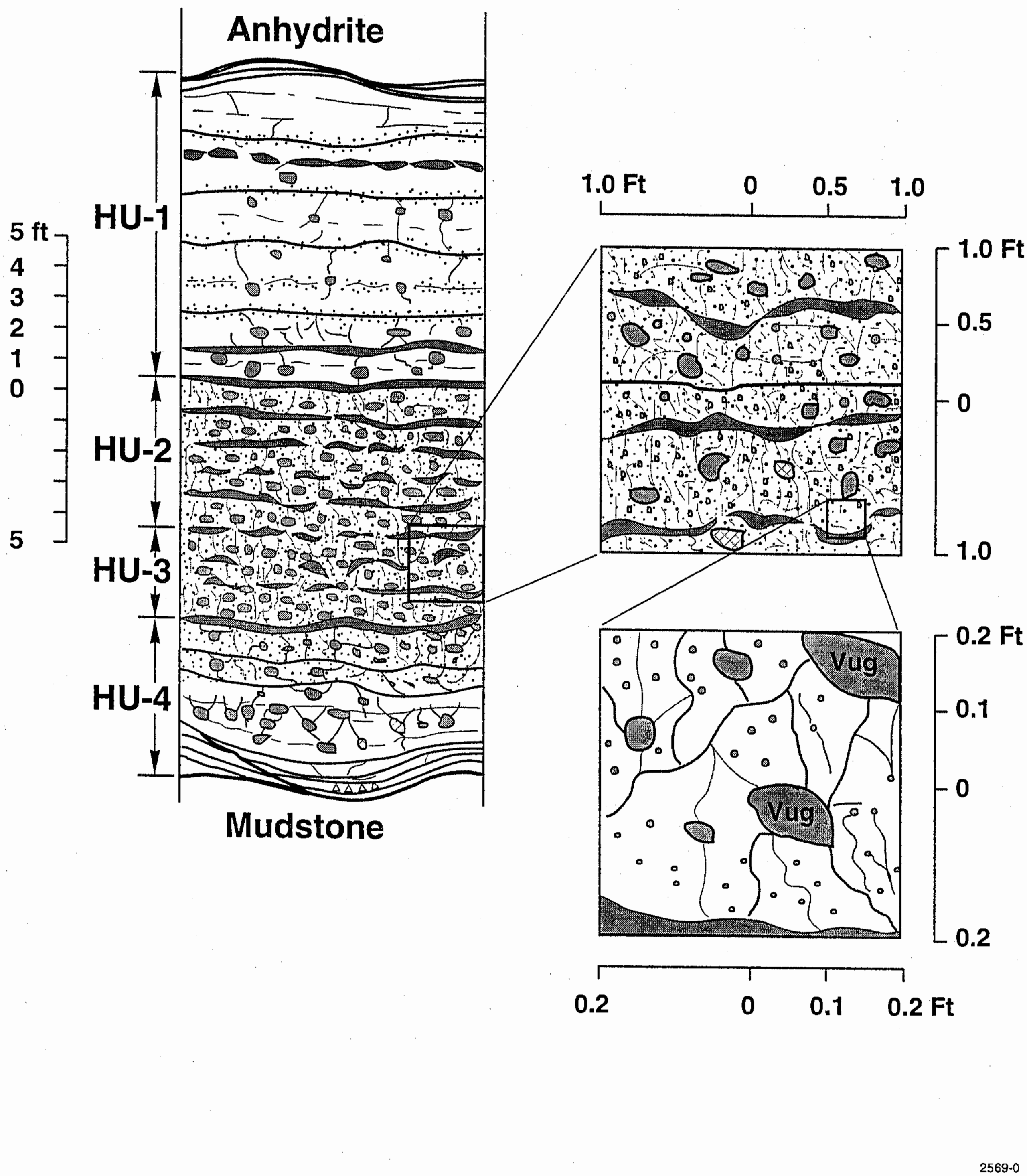
- Castile brine, lower redox [Th(IV), U(IV), Np(IV), Pu(III), Am(III)]
- Castile brine, higher redox [Th(IV), U(VI), Np(V), Pu(IV), Am(III)]

## Summary of ranges
(moles colloidal actinide per Liter of dispersion)

| actinide | mineral | intrinsic | microbe* | humic* |
|---|---|---|---|---|
| Th | $10^{-9}$ | 0 | $10^{-8}$ to $10^{-5}$ | $10^{-8}$ to $10^{-5}$ |
| U | $10^{-9}$ | 0 | $10^{-11}$ to $10^{-8}$ | $10^{-8}$ to $10^{-5}$ |
| Np | $10^{-9}$ | 0 | $10^{-7}$ to $10^{-4}$ | $10^{-9}$ to $10^{-5}$ |
| Pu | $10^{-9}$ | $10^{-9}$ | $10^{-9}$ to $10^{-6}$ | $10^{-8}$ to $10^{-5}$ |
| Am | $10^{-9}$ | 0 | $10^{-7}$ to $10^{-6}$ | $10^{-7}$ |

* based on mean actinide solubilities reported by Novak and Moore (1996)

# Culebra Conceptual Hydrogeological Model



# Transport Behavior Depends on Colloid Type and Culebra Characteristics

Possible interactions between colloidal-actinides and rock:

| Colloid Type | Colloid Size Range; Shape | Diffusion ? | Sorption ? | Filtration ? |
|---|---|---|---|---|
| mineral fragments | 1 to 1000 nm; various shapes | smaller colloids only | yes | yes |
| microbes | 250 to 2000 nm; rod shaped | no | yes | yes |
| actinide intrinsic | 1 to 10 nm; dissolved, compact | yes | yes | no |
| humic substances | 1 to 10 nm; dissolved, compact | yes | yes | no |

*mean pore throat size in Culebra matrix is 630 nm (Kelley and Saulnier, 1990)

# Experimental Approach Tailored to each Colloid Type

Batch sorption experiments (LANL) — $K_d$
- humic substances (Th, U, Np, Pu, Am)
- actinide intrinsic colloids [Pu(IV)-polymer]

Crushed-rock column flow experiments (SNL, BNL) — R, $\gamma$
- humic substances
- preserved microbes
- live microbes
- mineral fragments

Intact-core column flow experiments (SNL, BNL) — R
- humic substances (mixed with U, Pu, Am)
- live microbes (mixed with U, Am)

Diffusion parameter estimation (SNL) — $D_{col}$, M
- all colloid types

# PA Parameter Values for Colloidal Actinide Retardation

| Colloid | Actinide | $K_d$ (mL/g) | $\gamma$ ($cm^{-1}$) |
|---|---|---|---|
| mineral fragments | Th, U, Np, Pu, Am | 0.0[a] | 0.3 |
| microbes | Th, U, Np, Pu, Am | 0.0[a] | 0.5 |
| intrinsic | Pu | 0.0[b] | |
| | Th, U, Np, Am | 0.0[c] | |
| humic substances | Am(III) | 20 to 500[d] | |
| | Th(IV), U(IV), Np(IV) | 900 to 20,000[d] | |
| | Np(V) | 1 to 200[d] | |
| | U(VI) | 0.03 to 30[d] | |

Notes:
a chemical retardation observed, but is not included in PA calculations
b sorption expected but not quantifiable because of analytical detection limitations
c source term is zero for these intrinsic colloids
d from Dissolved Actinide Retardation Research Program

# Crushed-Rock Column Experiments (SNL)

## Packing

- Culebra (AIS; Culebra Bluffs)
- dolomite cleavage rhombohedra (Butte, Montana)
- hand crushed, washed, sieved 125-250 µm; 250-500 µm; 500-1000 µm
- hand crushed, sieved, washed, sieved, dried at low T

## Colloidal particles

- humic substances
- preserved and live microbes
- quartz, goethite, hematite
- latex microspheres (non-functional; carboxylated; sulfonated)

## Eluent

- H-17 brine simulant; Air intake shaft simulants; 0.001 M NaCl
- $CO_2$ partial pressure = $10^{-3.5}$ atm
- flow rate 0.1 to 0.5 mL/min

## Test configuration

- columns 1 cm diameter; 5 to 100 cm length
- spike injections
- step injections

# Crushed-Rock Column Experiments (SNL), cont.

## Analytical methods

- in-line laser particle spectrometry
- scanning fluorometry, fixed wavelength fluorometry
- ICP-AES
- epifluorescence microscopy (BNL)

## Porosity characterization

- equivalence of advective and measured porosity confirmed with "non-sorbing" tracers (fluoroscein, rhodamine WT, rhodamine B, sulforhodamine B, lithium, bromide)
- gravimetric determinations similar to fluoroscein
- porosity typically 45%

## Evaluation of potential artifacts

- varied column lengths
- varied flow rates
- varied injection type
- reversed flow
- varied packing diameter; colloid diameter

# Interpretation of Crushed-Rock Column Experiments

Transport and retardation phenomena

- advection (average linear flow velocity; v)
- dispersion and diffusion (D)
- adsorption (R or $K_d$)
- filtration ($\gamma$) includes interception and sieving, sedimentation, irreversible sorption

Advection-dispersion equation with adsorption:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial x} \qquad (1)$$

Filtration equation:

$$\frac{\partial C}{\partial x} = -\gamma C \qquad (2)$$

# Interpretation of Crushed-Rock Column Flow Experiments, cont.

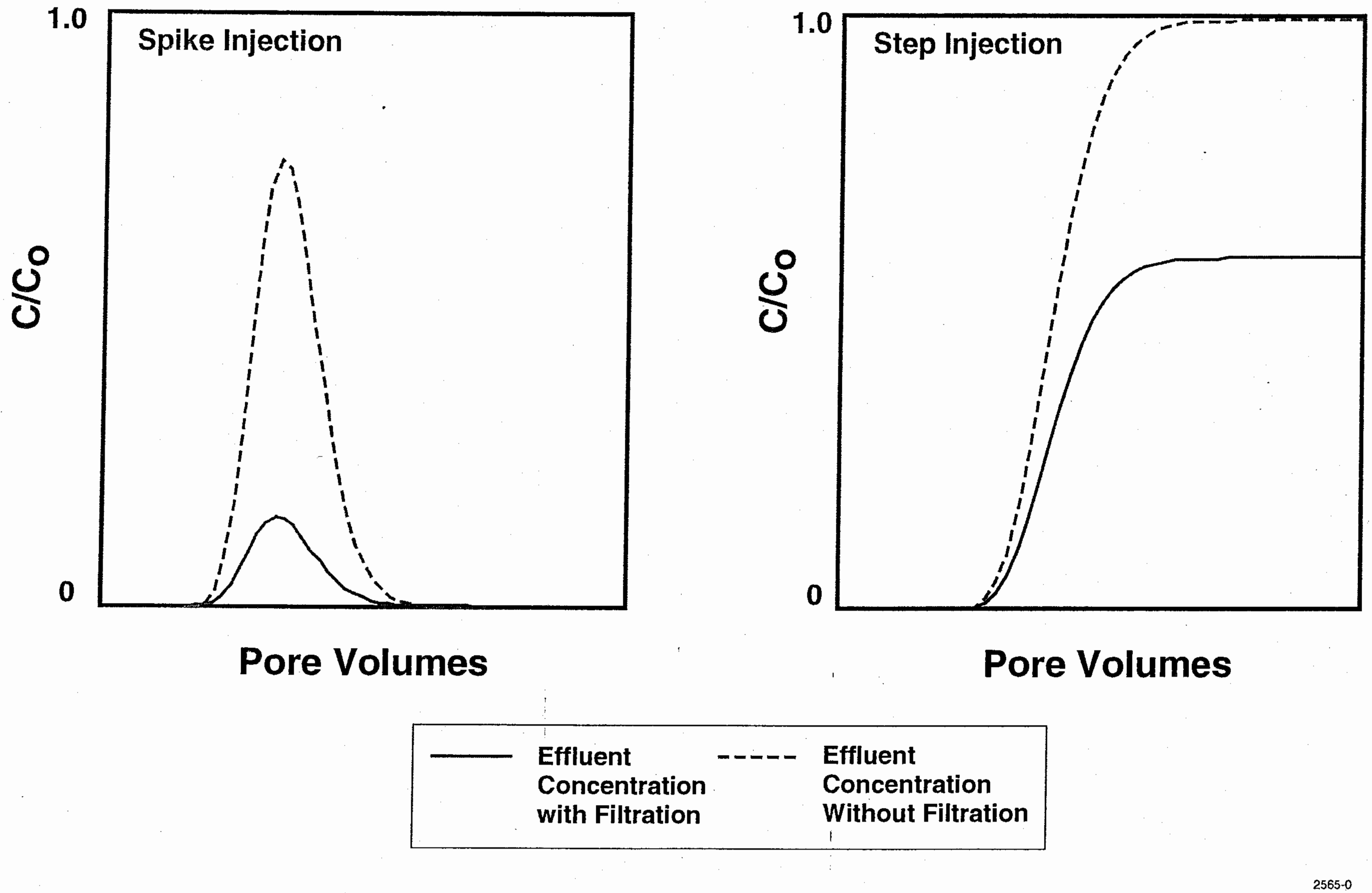
Advection-dispersion equation with adsorption and filtration:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\left(\frac{\partial C}{\partial x} + \gamma C\right) \qquad (3)$$

Solution of (3) described in Harvey and Garabedian (1991):

[peak concentration obtained from (1)] * $\exp(-\gamma x)$ (4)

# Conceptualization of the Effect of Filtration on Column Breakthrough



# Interpretation of Crushed-Rock Column Flow Experiments, cont.

Steps in interpretation of elution curves

- R estimated from peak position
- breakthrough curves are often noisy; not suitable for automated curve-fitting procedures
- conservative value of D is established (literature; test with conservative tracer; sensitivity analyses)
- theoretical peak height without filtration calculated with R and D using CXTFIT (Parker and Genuchten, 1984)
- $\gamma$ calculated (L is column length):

observed peak concentration = theoretical peak concentration * $\exp(-\gamma L)$

$$\gamma = -\ln\left(\frac{\text{observed peak concentration}}{\text{theoretical peak concentration}}\right) * \frac{1}{L}$$

# Batch Sorption Experiments (LANL)

## Test design

- rock crushed and wet sieved; 75 to 500 μm fraction used
- rock washed with dilute HCl; rock pretreated in brine
- 1 g rock and 20 mL brine during pretreatment, sorption and desorption experiments
- brines analyzed with ICP-MS or LSC
- $K_d$ determined from difference between initial and final actinide concentration in brine
- controls used to assess whether experimental artifacts occurred, e.g., loss to vessel or coprecipitation

## Humic substance mixture consisted of equal parts of:

- purified Lake Bradford, Florida, aliphatic humic acid (FSU)
- Suwannee River aromatic humic acid (International Humic Substances Association; IHSA)
- Suwannee River fulvic acid (IHSA)
- two total concentrations used: 0.01 and 1.0 mg/L

# Intact-Core Column Flow Experiments with Colloids (SNL)

## Core used

- four Culebra cores extracted from the air intake shaft (AIS) from two stratigraphic horizons (HU-2 and HU-3)
- cores well preserved, intact, horizontally oriented in direction of the current flow path
- colloid test cores approximately 5.7 inches diameter x 4 inches long
- live microbe test with core VPX-27-7A (HU-3)
- humic test with core VPX-25-8A (HU-2)

## Test design

- test design consisted of sequential comparison tests
  - without and with live microbes, introduced in eluent
  - without and with humic substances, introduced in eluent
- Am(III), Pu(V)$O_2^+$, U(VI)$O_2^{2+}$, tested in AIS brine
- Am and Pu injected as spikes directly on rock to minimize sorption on apparatus
- U injected as step to provide time for colloid-uranium interaction
- flow rate close to upper flow rate in Culebra (0.1 mL/min)

# Microbial Actinide Transport Attenuated by Filtration

## Crushed-rock column transport tests

- WIPP-relevant live and preserved microbes supplied by BNL
- experiments with live microbes conducted with and without nutrient
- packing particle size varied
- H-17 brine with or without nutrients
- step injection tests conducted with $10^6$ to $10^7$ cells/mL; spike injection tests conducted with $10^7$ to $10^8$ cells/mL

## Results

- experiments with 125-250 μm packing resulted in very high filtration
- $\gamma$ quantified in experiments with 250-500 μm particle size
- step injections resulted in column plugging, pressure build-up
- spike injection of low concentration allowed measurement of $\gamma$
- smaller microbes (0.2 to 0.28 μm) less attenuated than larger microbes (0.6 to 1 μm)
- elution curve from smaller microbes used to determine conservative $\gamma$
- $\gamma$ values of about 0.5 $cm^{-1}$ measured for smaller microbes
- R values of about 4 measured

# Microbial Actinide Transport Attenuated by Filtration, cont.

Filtration effects confirmed with intact-core column flow tests

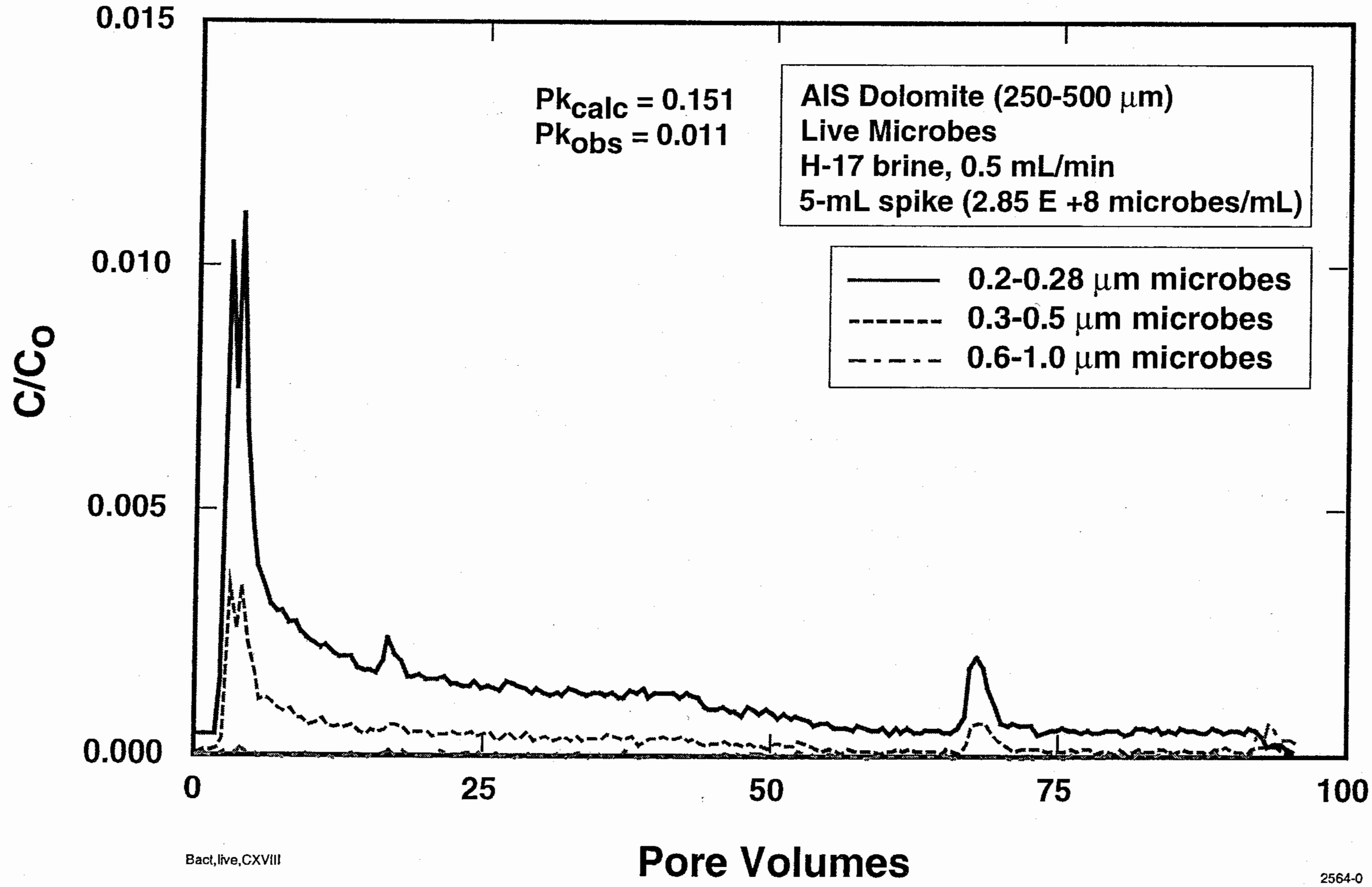
- elution of U matched profile of test without microbes
- Am did not elute during the test, consistent with test without microbes
- direct counts (BNL) of microbes showed background concentrations only

Microbe results supported by crushed-rock column flow tests with mineral fragments and latex microspheres

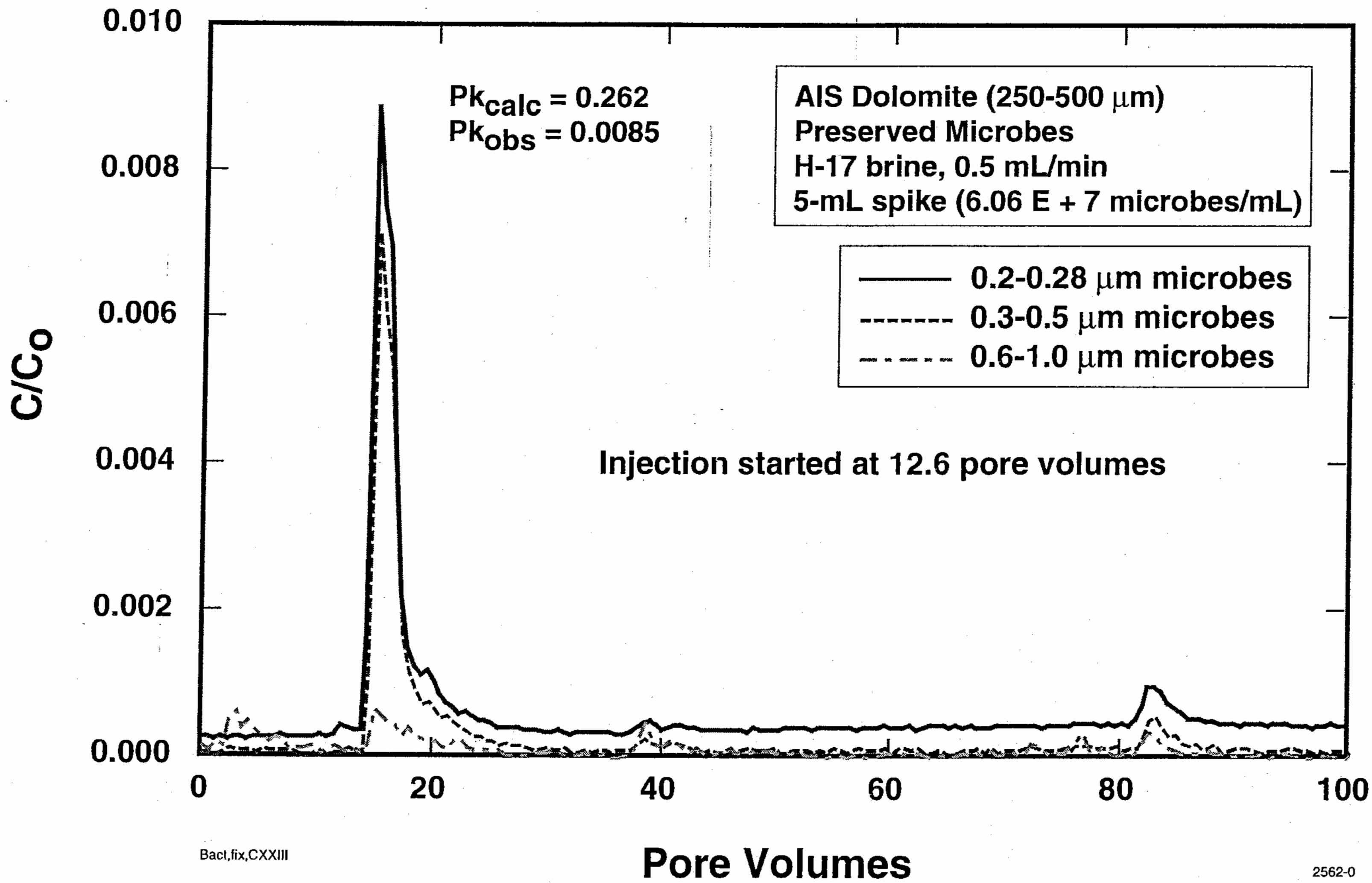
PA Implementation

- represent attenuation with $\gamma$
- set R equal to 1 due to complexities of combining R with $\gamma$ values in SECOTP-2D simulation

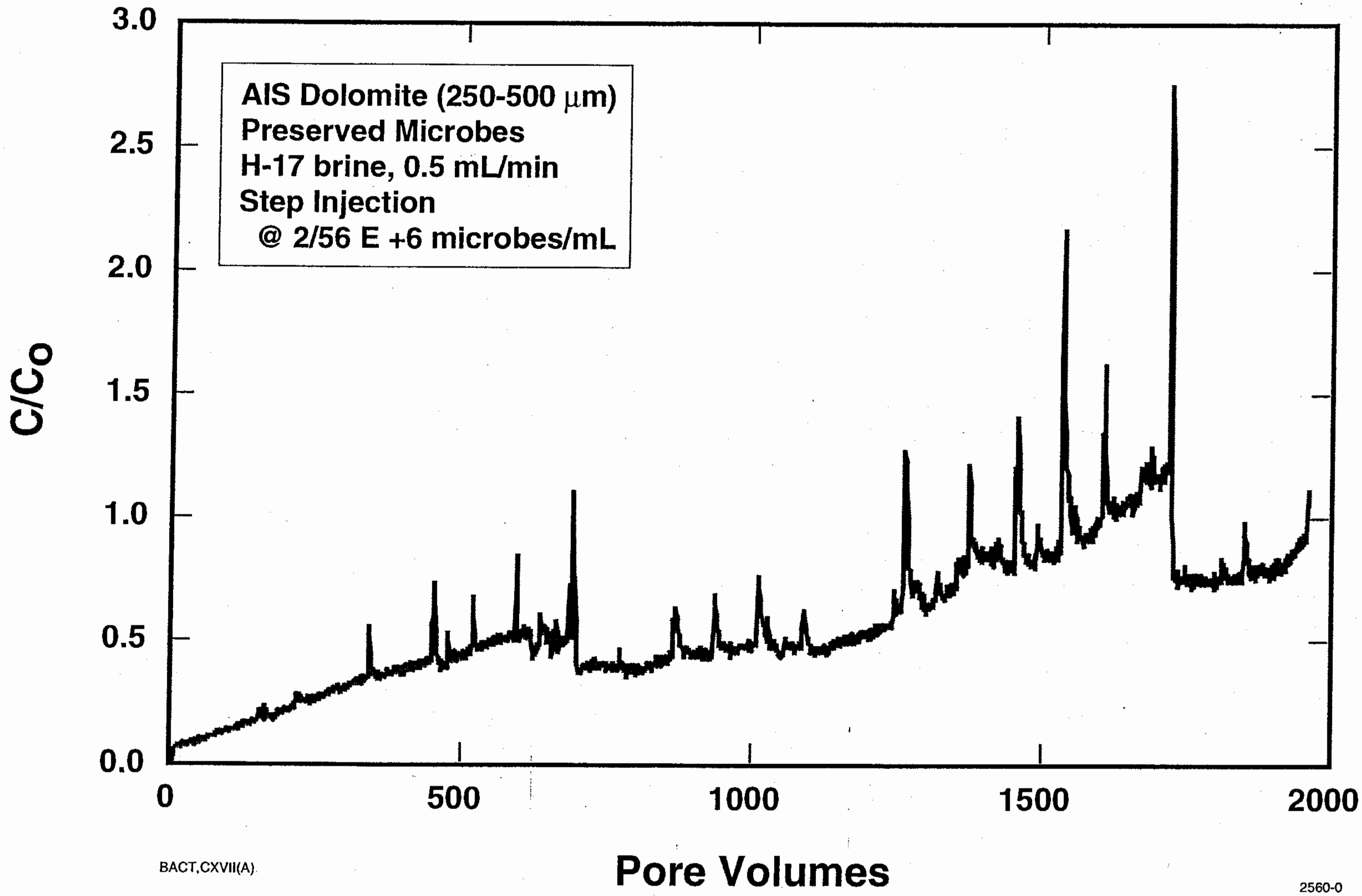
# Microbe Transport Through a Crushed-Rock Column



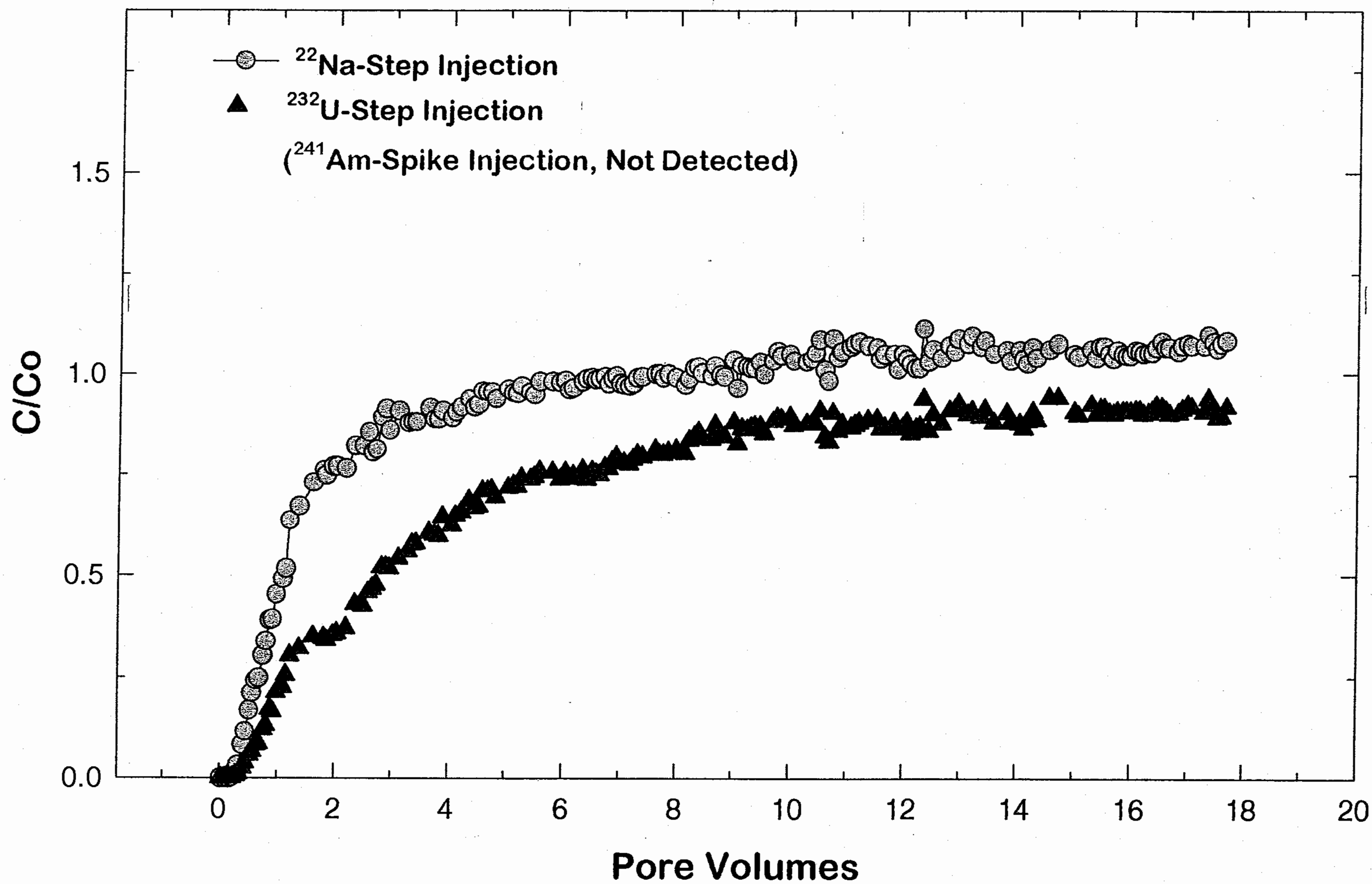
# Microbe Transport Through a Crushed-Rock Column



# Microbe Transport Through a Crushed-Rock Column



# Microbial-Actinide Transport through an Intact Core




Test E-3
VPX27-7A

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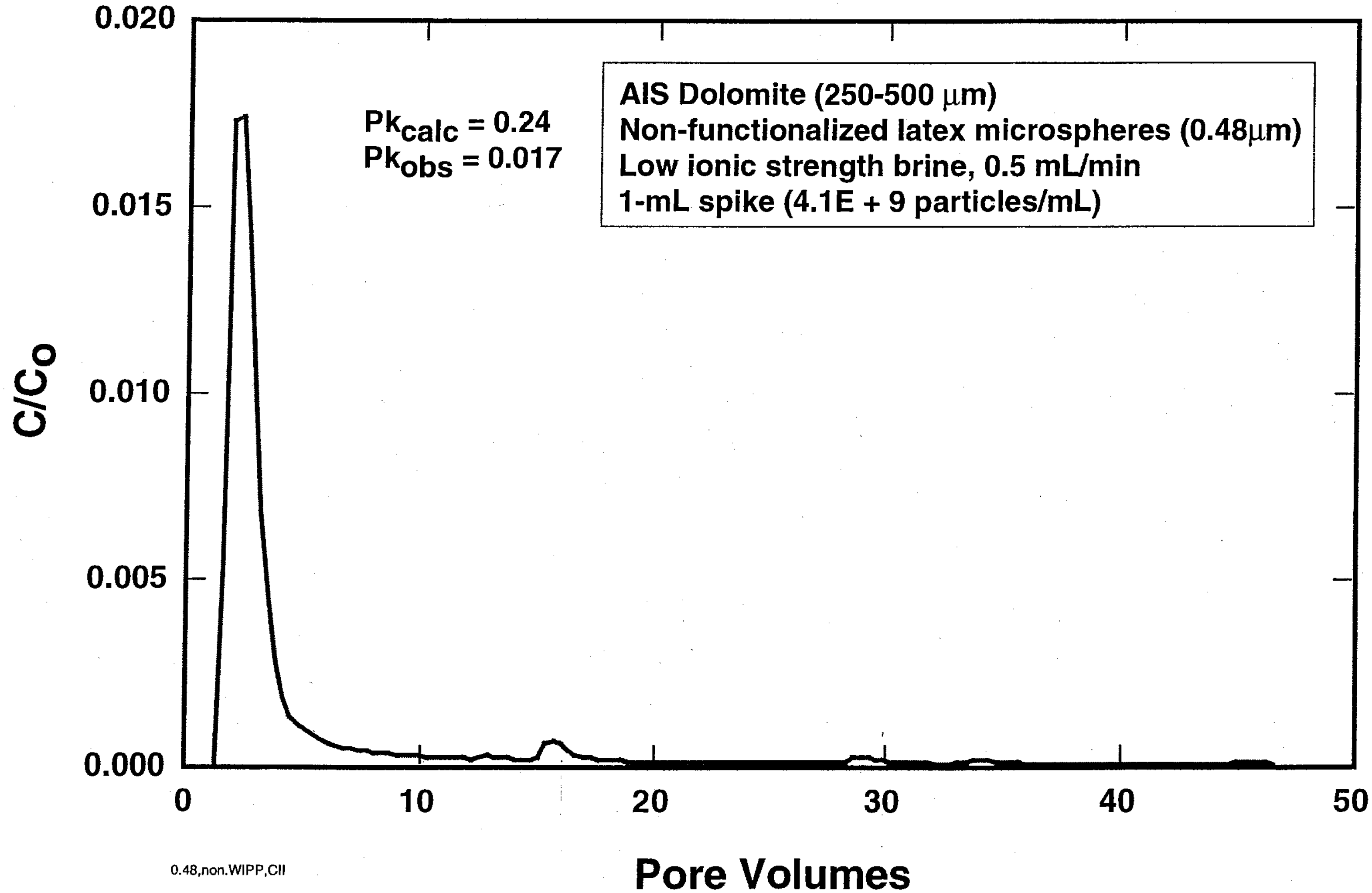
# Latex Microsphere Transport Through a Crushed-Rock Column

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# Mineral Fragment Transport Attenuated by Filtration

## Crushed-rock column transport tests

- dispersions of mineral fragments prepared by chemical precipitation or mechanical milling
- colloids in spike allowed to coagulate and settle to reach a steady-state population before injection; spike filtered with 1.2 μm filter
- low ionic strength eluent used to isolate filtration effects from kinetic destabilization
- results consistent with microbe tests and latex microsphere tests

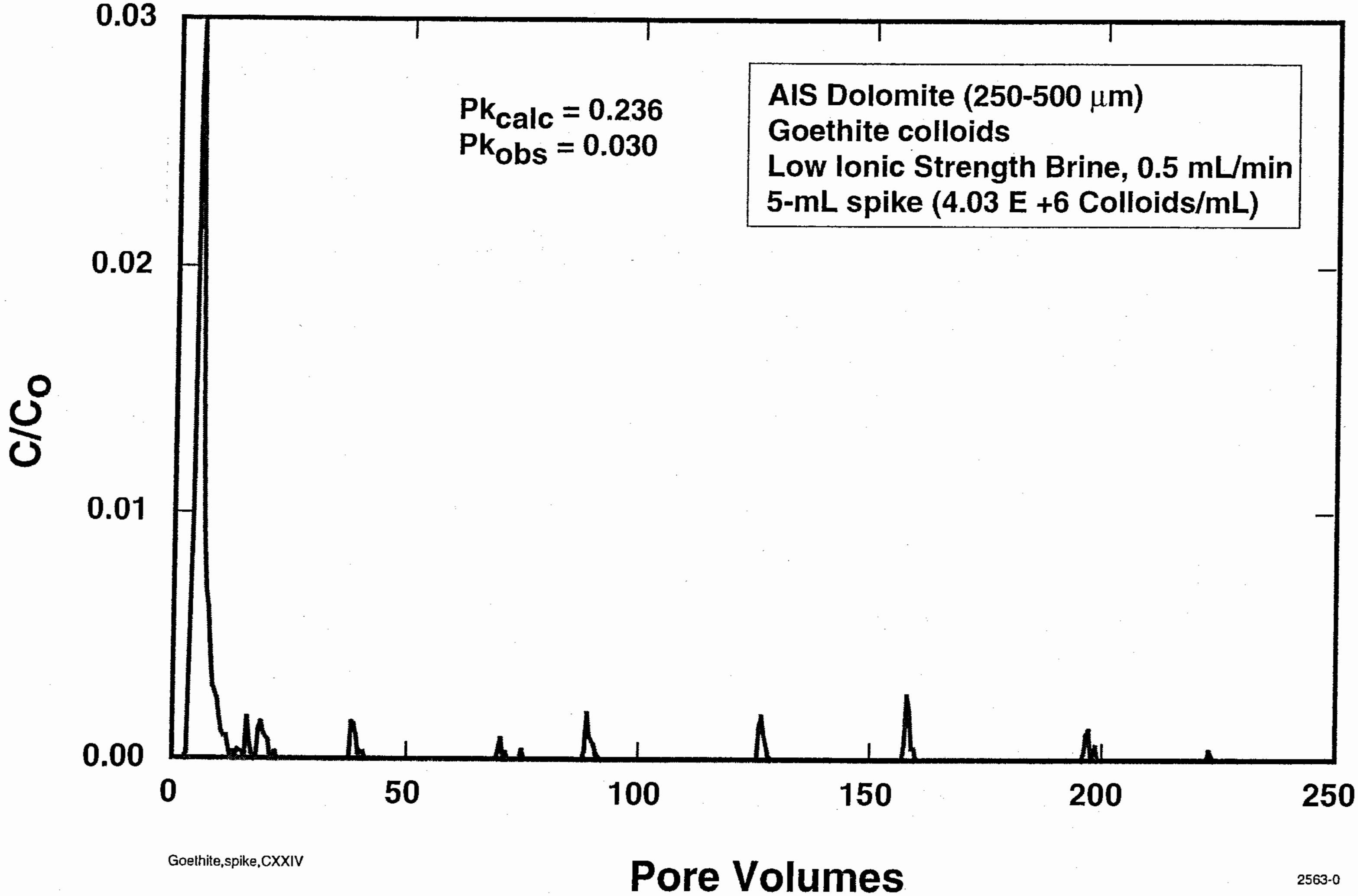
## Results

- measured R values of 4 to 6 in H-17 brine
- measured $\gamma$ value of 0.3 to 0.4 $cm^{-1}$

## PA Implementation

- represent attenuation with $\gamma$
- set R equal to 1 due to complexities of combining R with $\gamma$ values in SECOTP-2D simulation
- measured R values may not represent possible range for other colloids

# Mineral Fragment Transport Through a Crushed-Rock Column



# Attenuation of Humic-Actinides Similar to that of Dissolved Actinides

Crushed-rock column flow tests demonstrate no enhanced transport of humic substances (SNL)

- aliphatic humic acid (purified Aldrich; Aldrich Chemical Co.; FSU)
- aliphatic humic acid (Lake Bradford, Florida; FSU)
- aromatic humic acid (Suwannee River; IHSA)
- fulvic acid (Suwannee River; IHSA)

Batch sorption experiments with and without humic substances nearly identical (LANL)

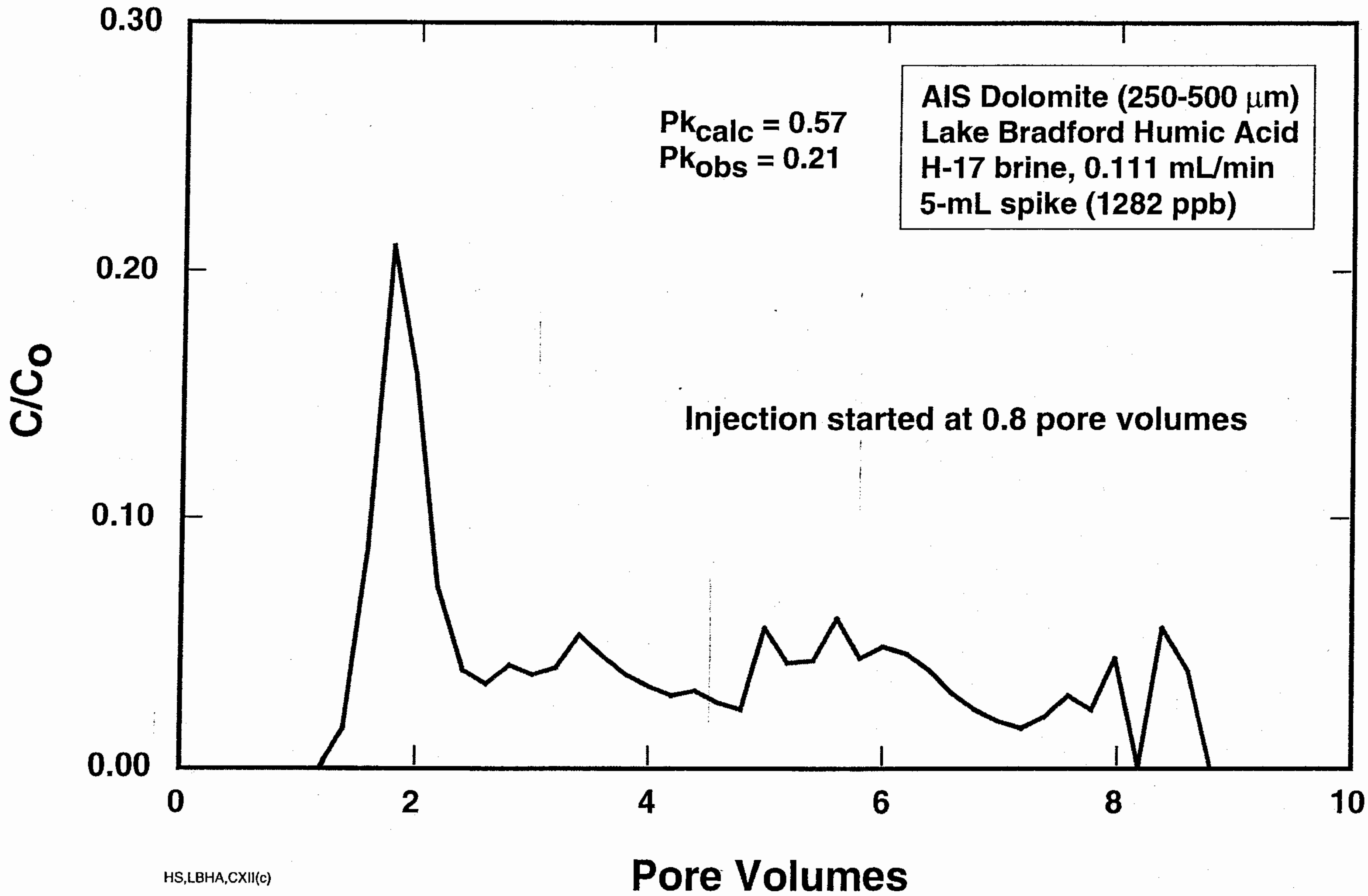
- 1:1:1 mixture of aliphatic + aromatic humic acid + fulvic acid

Intact-core column flow tests demonstrate no difference in elution of U, Pu, Am with and without humics (SNL)

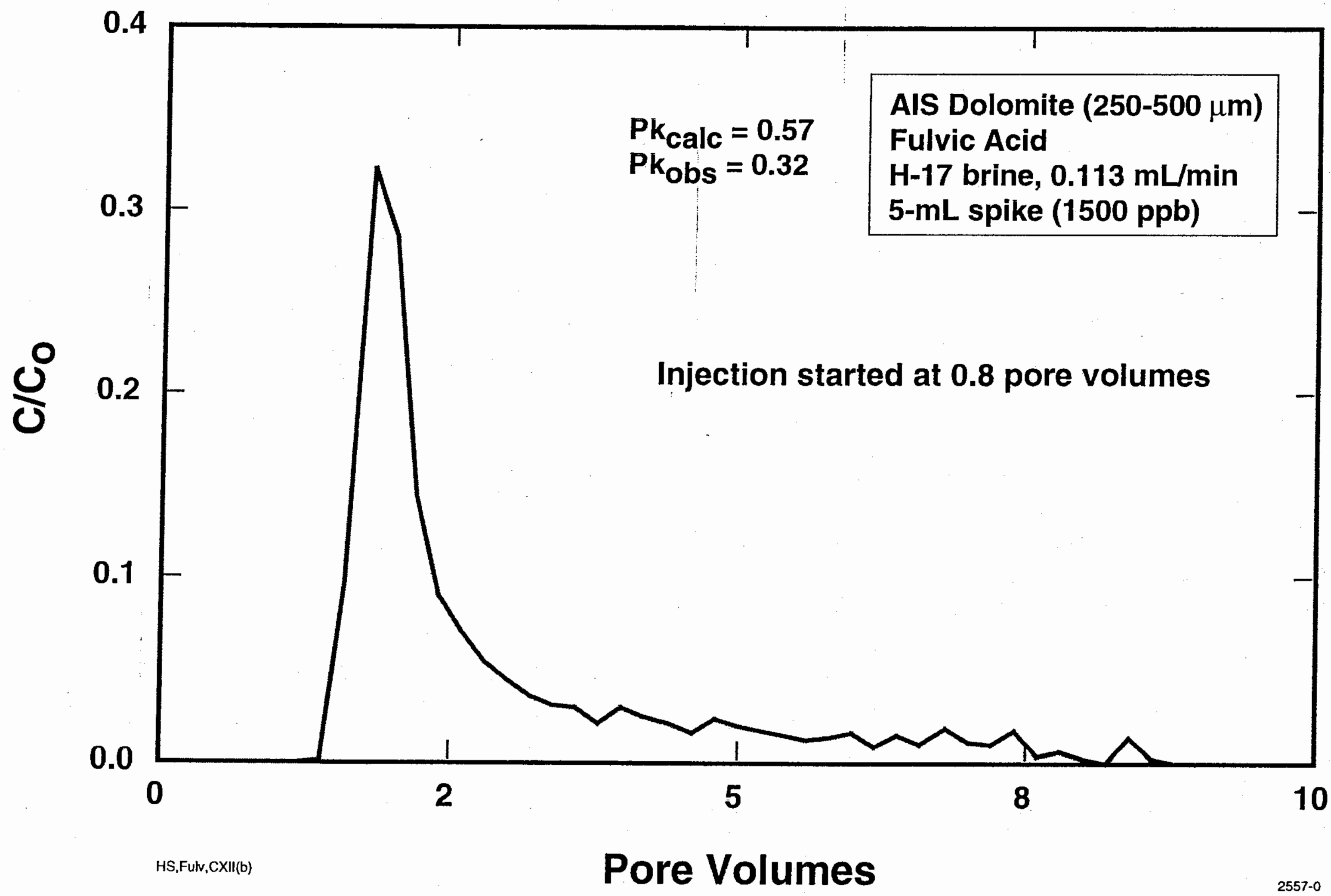
- 1:1:1 mixture of aliphatic + aromatic humic acid + fulvic acid

Retardation can by simulated using values from Dissolved Actinide Retardation Research Program

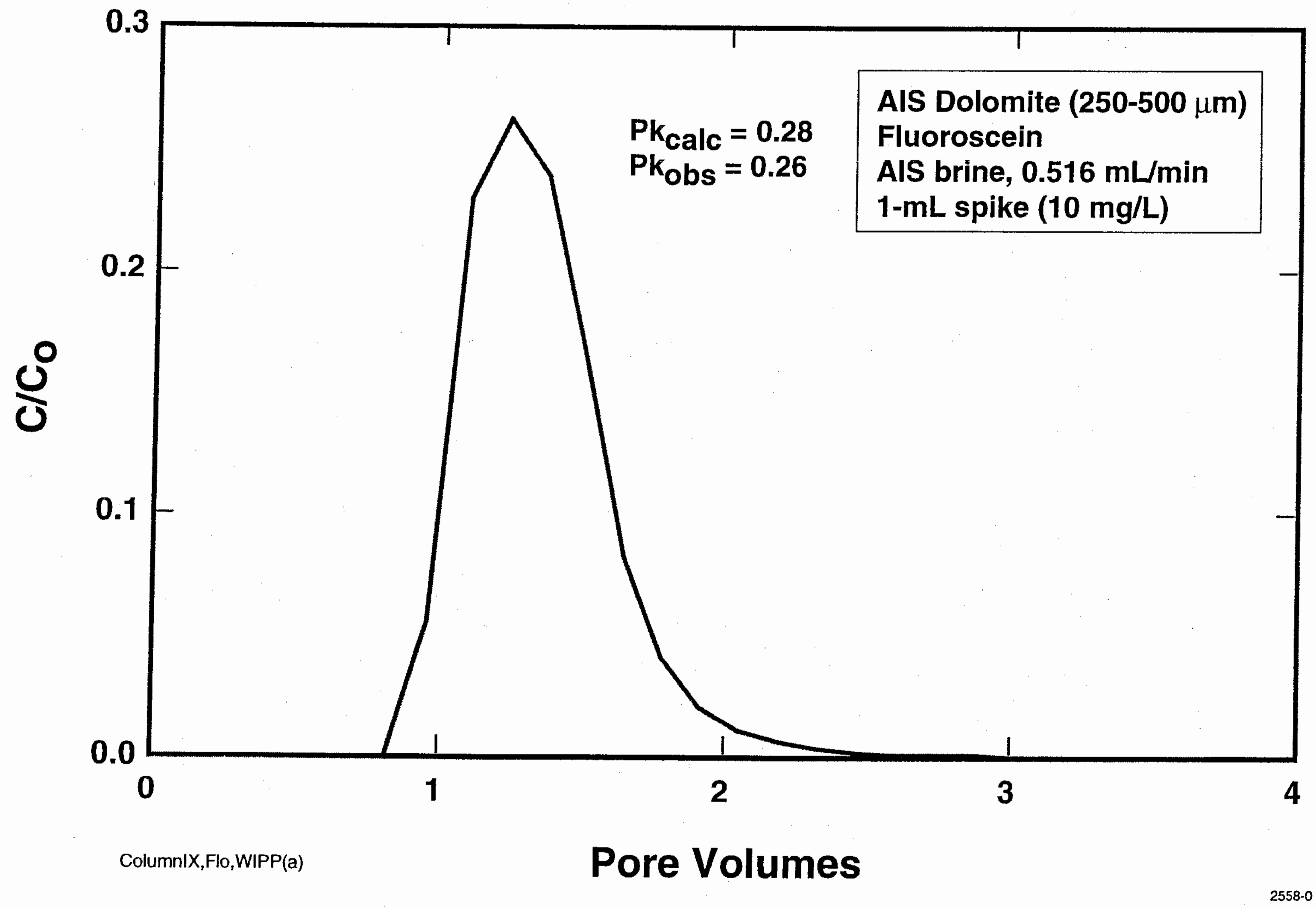
# Humic Acid Transport Through a Crushed-Rock Column



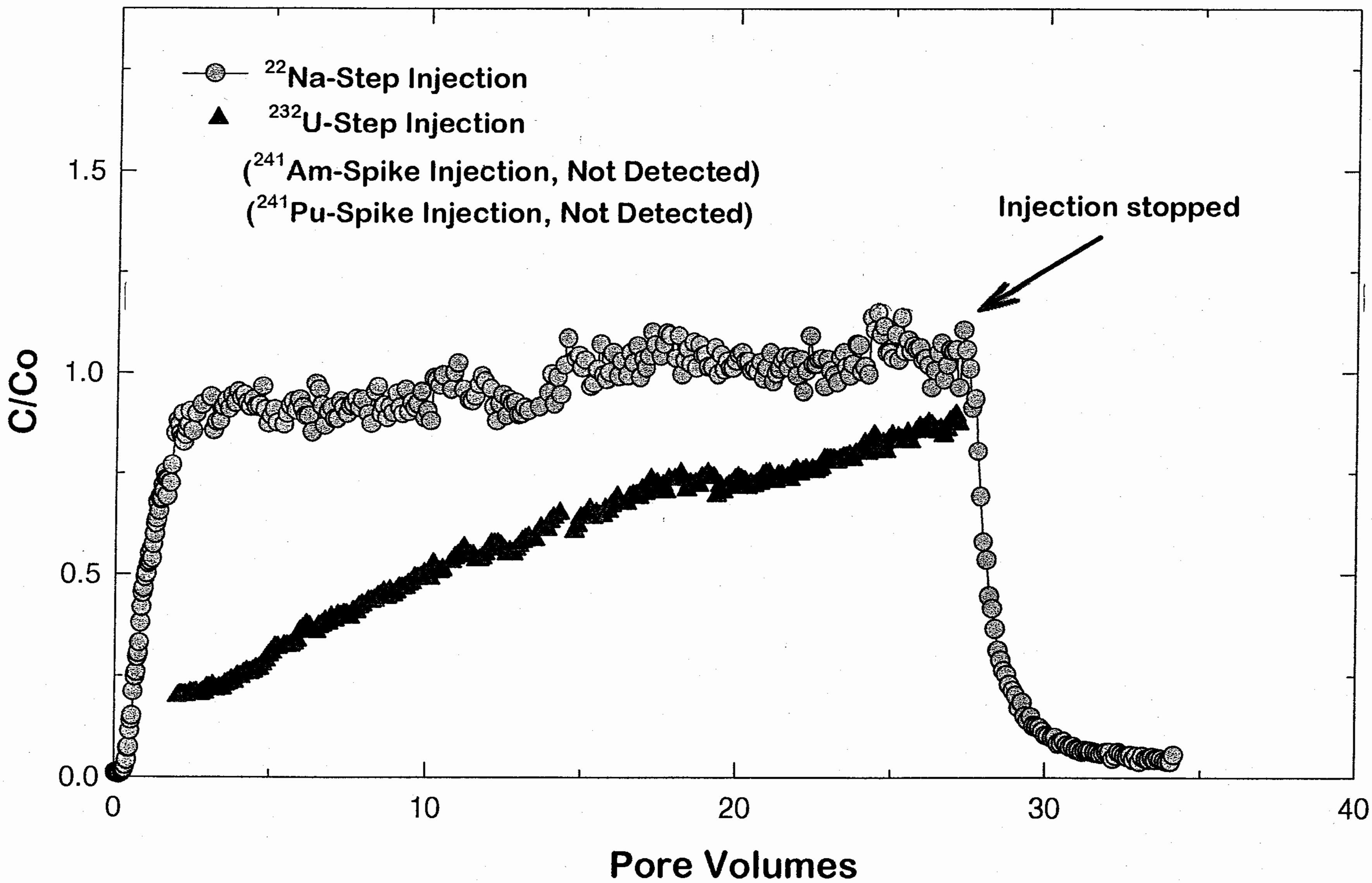
# Fulvic Acid Transport Through a Crushed-Rock Column



# Fluoroscein (Conservative Tracer) Transport Through a Crushed-Rock Column



# Humic-Actinide Transport through an Intact Core




Test D-7
VPX25-8A

FILE:TESTD7VU.SPW

# Humic-Actinide Batch-Sorption Results

($K_d$ values in mL/g)

| actinide | [humic] (mg/L) | Culebra H-17; $pCO_2=10^{-3.5}$ atm | | Culebra H-17; $pCO_2=10^{-1.5}$ atm | | Castile ERDA-6; $pCO_2=10^{-3.5}$ atm | | Castile ERDA-6; $pCO_2=10^{-1.5}$ atm | |
|---|---|---|---|---|---|---|---|---|---|
| Th(IV) | none | 20 | c | 10 | c | 100 | c | 20 | c |
| | 0.01 | 10 | c | 10 | c | 100 | c | 20 | c |
| | 1 | 20 | c | 10 | c | 80 | c | 20 | c |
| U(VI) | none | -2 | b | -1 | b | 0.04 | a | -0.01 | a |
| | 0.01 | -1 | b | -0.8 | b | -0.3 | a | -0.4 | a |
| | 1 | -1 | b | -0.7 | b | 0.4 | a | -0.03 | a |
| Np(V) | none | 5 | b | 1 | b | 90 | a | 100 | a |
| | 0.01 | 5 | b | 1 | b | 80 | a | 100 | a |
| | 1 | 5 | b | 1 | b | 70 | a | 100 | a |
| Pu(V) | none | 20 | b | 9 | b | 200 | a | 200 | a |
| | 0.01 | 20 | b | 7 | b | 200 | a | 200 | a |
| | 1 | 20 | b | 10 | b | 200 | a | 200 | a |
| Am(III) | none | 500 | c | 400 | c | 700 | c | 3000 | c |
| | 0.01 | 600 | c | 400 | c | 1000 | c | 2000 | c |
| | 1 | 600 | c | 400 | c | 2000 | c | 2000 | c |

Notes:
reported values are averages of two replicates
LSC analytical error: "a" indicates $\leq 3\sigma$; "b" indicates 3 to $4\sigma$; "c" indicates $> 4\sigma$

# Colloid Diffusion Coefficients Required to Simulate Diffusion and Dispersion

Free-solution tracer diffusion coefficients for colloidal particles are required for SECOTP-2D

Estimates made with Einstein's equation for spherical particles (Hiemenz, 1986, p. 83):

$$D_{col} = \frac{k\,T}{3\pi\,\mu\,d_p}$$

where:

| | | |
|---|---|---|
| $D_{col}$ | = | free-solution tracer diffusion coefficient for colloidal particles ($cm^2\ sec^{-1}$) |
| $k$ | = | Boltzman constant |
| $T$ | = | temperature in Kelvin |
| $\mu$ | = | brine viscosity |
| $d_p$ | = | colloidal particle diameter |

# Estimates for $D_{col}$ as much as 1000-times less than Values for Dissolved Actinides

| Colloid Type | Colloid Diameter (nm) | $D_{col}$ ($cm^2 sec^{-1}$) |
|---|---|---|
| mineral fragments | 1000 | 2.1e-9 |
| microbes | 1000 | 2.1e-9 |
| humics | 100 | 2.1e-8 |
| Pu(IV)-polymer | 100 | 2.1e-8 |

Notes:

- laboratory measurements of Brine A (Salado-like brine simulant) used as conservative viscosity value ($2.13e10^{-2}$ g $cm^{-1} sec^{-1}$; Gelbard 1993)
- k = 1.38e-16 g $cm^2$ $sec^{-2}$ $°K^{-1}$
- T = 300 °K
- $D_{sol}$ values reported for dissolved actinides range from 1.53e-6 to 4.26e-6 cm $sec^{-1}$ (Brush, 1996)

## Results consistent with published estimations for colloids

- see, e.g., Hiemenz (1986)

# Colloid Mass Concentrations Required to Simulate Diffusion

## Humic substances
- measured concentration (solubility) = $2 \times 10^{-3}$ g/L

## Actinide intrinsic colloids [Pu(IV)-polymer]
- measured solubility limited to minimum analytical detection limit of LSC
- measured concentration (detection limit) = $1 \times 10^{-9}$ moles/L = $2.4 \times 10^{-7}$ g/L

## Microbes
- estimate biomass using laboratory measurements and geometry
  - rod shaped with mean dimensions of 0.9 μm diameter x 1.7 μm length
  - density equal to Brine A (1.2 $g/cm^3$)
  - measured steady-state population of $5 \times 10^6$ cells/mL
- estimated concentration = $5 \times 10^{-3}$ g/L

## Mineral fragments
- estimate concentration using laboratory measurements and geometry
  - residual concentration and mean size measured in stability experiments
  - spherical shapes, specific gravity of 3, monodisperse population
- estimated concentration = $1 \times 10^{-3}$ g/L

# PA Parameter Values for Colloidal Actinide Retardation

| Colloid | Actinide | $K_d$ (mL/g) | $\gamma$ ($cm^{-1}$) |
|---|---|---|---|
| mineral fragments | Th, U, Np, Pu, Am | 0.0[a] | 0.3 |
| microbes | Th, U, Np, Pu, Am | 0.0[a] | 0.5 |
| intrinsic | Pu | 0.0[b] | |
| | Th, U, Np, Am | 0.0[c] | |
| humic substances | Am(III) | 20 to 500[d] | |
| | Th(IV), U(IV), Np(IV) | 900 to 20,000[d] | |
| | Np(V) | 1 to 200[d] | |
| | U(VI) | 0.03 to 30[d] | |

Notes:
[a] chemical retardation observed, but is not included in PA calculations
[b] sorption expected but not quantifiable because of analytical detection limitations
[c] source term is zero for these intrinsic colloids
[d] from Dissolved Actinide Retardation Research Program

# References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