

**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

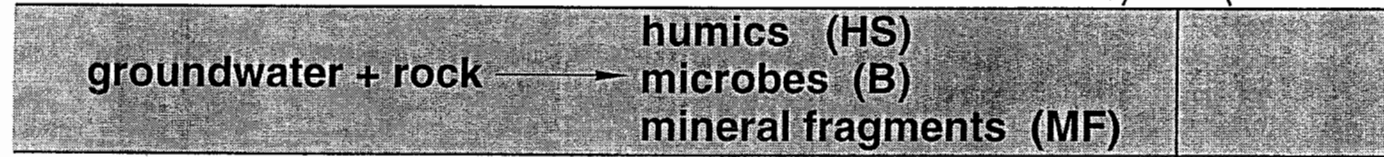
Retardation of Colloidal Actinides in the Culebra

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

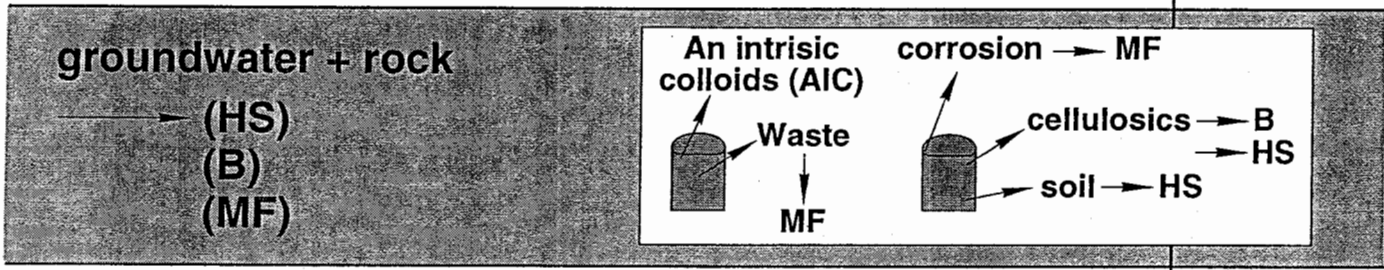
Several Potential Sources of Colloidal Actinides Exist in the WIPP System



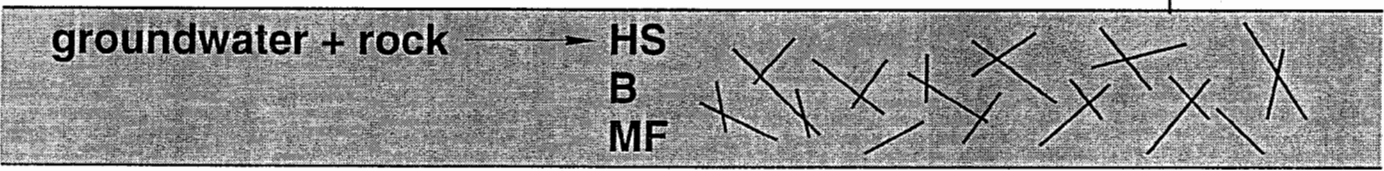
Culebra



Salado



Castile



Colloidal Particle Types Affected Differently by Chemical Conditions

Colloid Type	Stability Behavior in WIPP Brines	Uptake Mechanism for Th, U, Np, Pu, Am
<i>mineral fragments</i>	electrostatically destabilized	sorption
<i>microbes</i>	not affected	passive or active bioaccumulation
<i>actinide intrinsic</i>	solubility reduced; electrostatically destabilized	intrinsic
<i>humic substances</i>	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)]

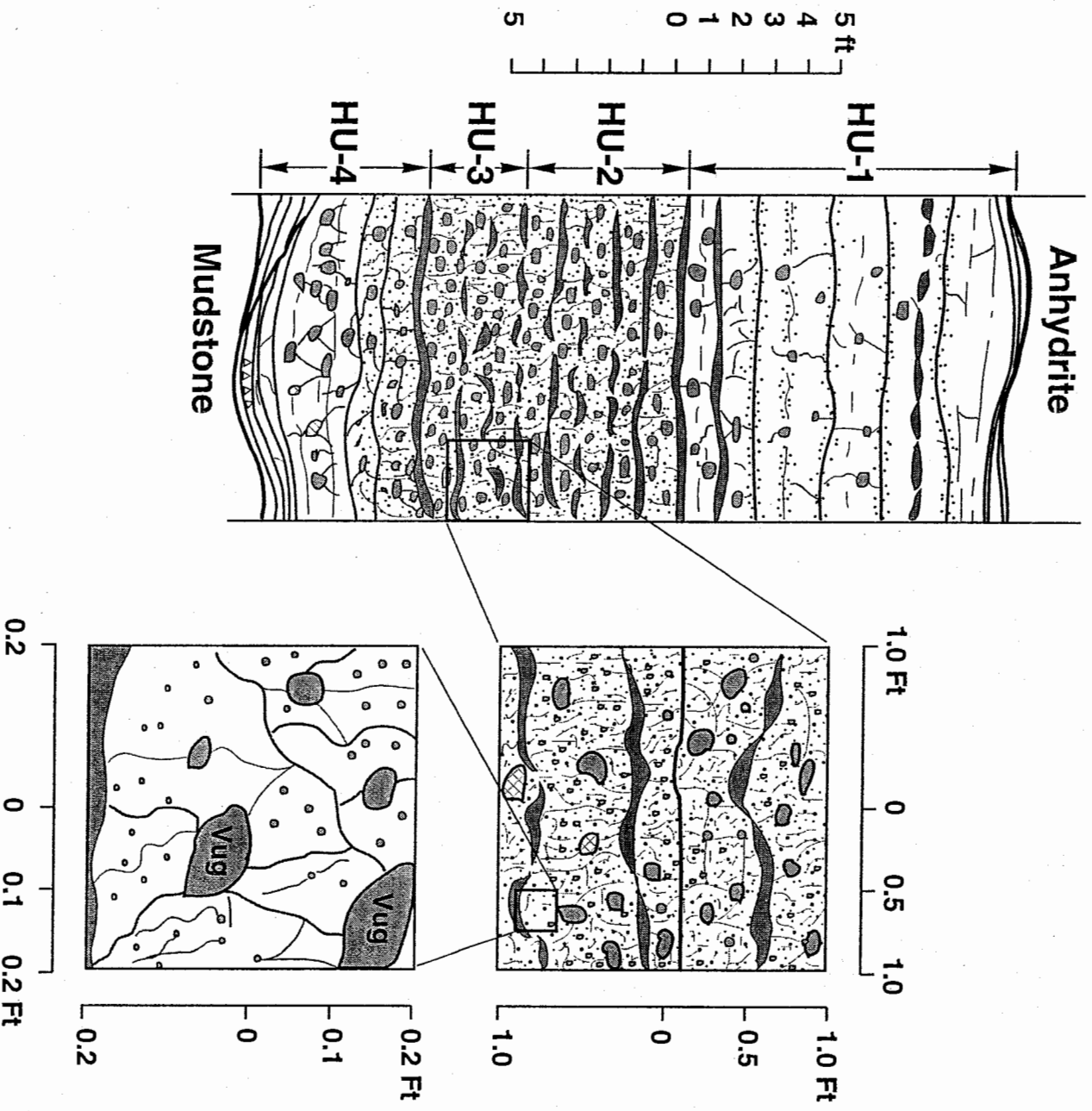
Summary of ranges

(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, γ

- 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)	γ (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 (γ) includes interception and sieving, sedimentation, irreversible sorption

Advection-dispersion equation with adsorption:

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

Filtration equation:

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

Interpretation of Crushed-Rock Column Flow Experiments, cont.

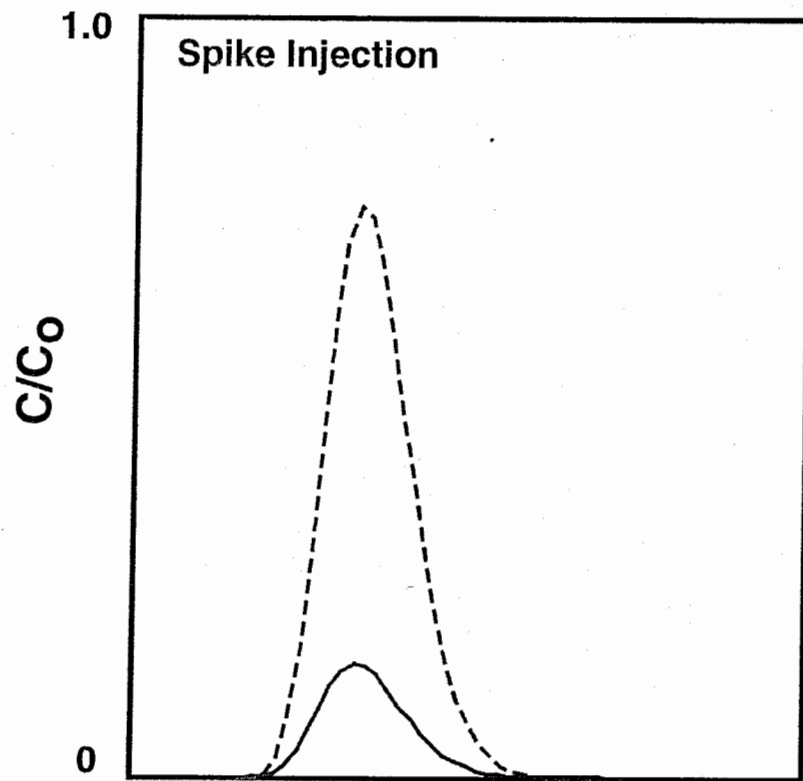
Advection-dispersion equation with adsorption and filtration:

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

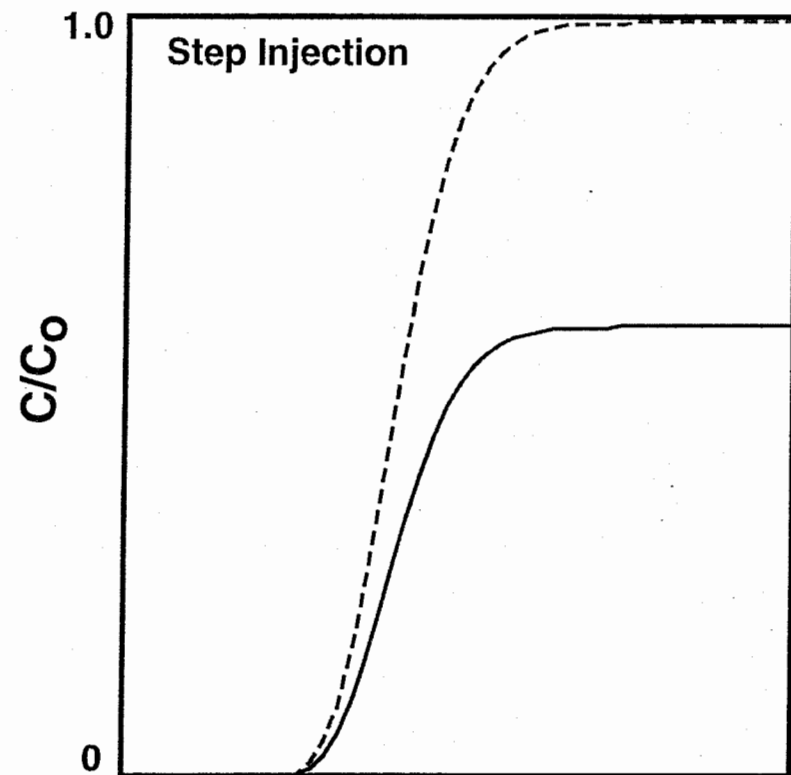
Solution of (3) described in Harvey and Garabedian (1991):

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

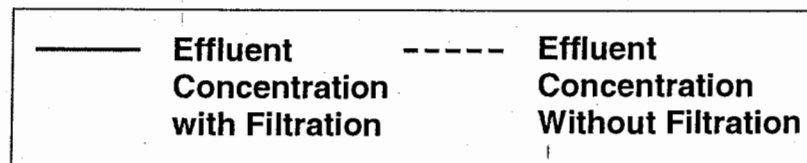
Conceptualization of the Effect of Filtration on Column Breakthrough



Pore Volumes



Pore Volumes



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)
- γ 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)O₂⁺, U(VI)O₂²⁺, 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
- γ 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 γ
- 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 γ
- γ 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

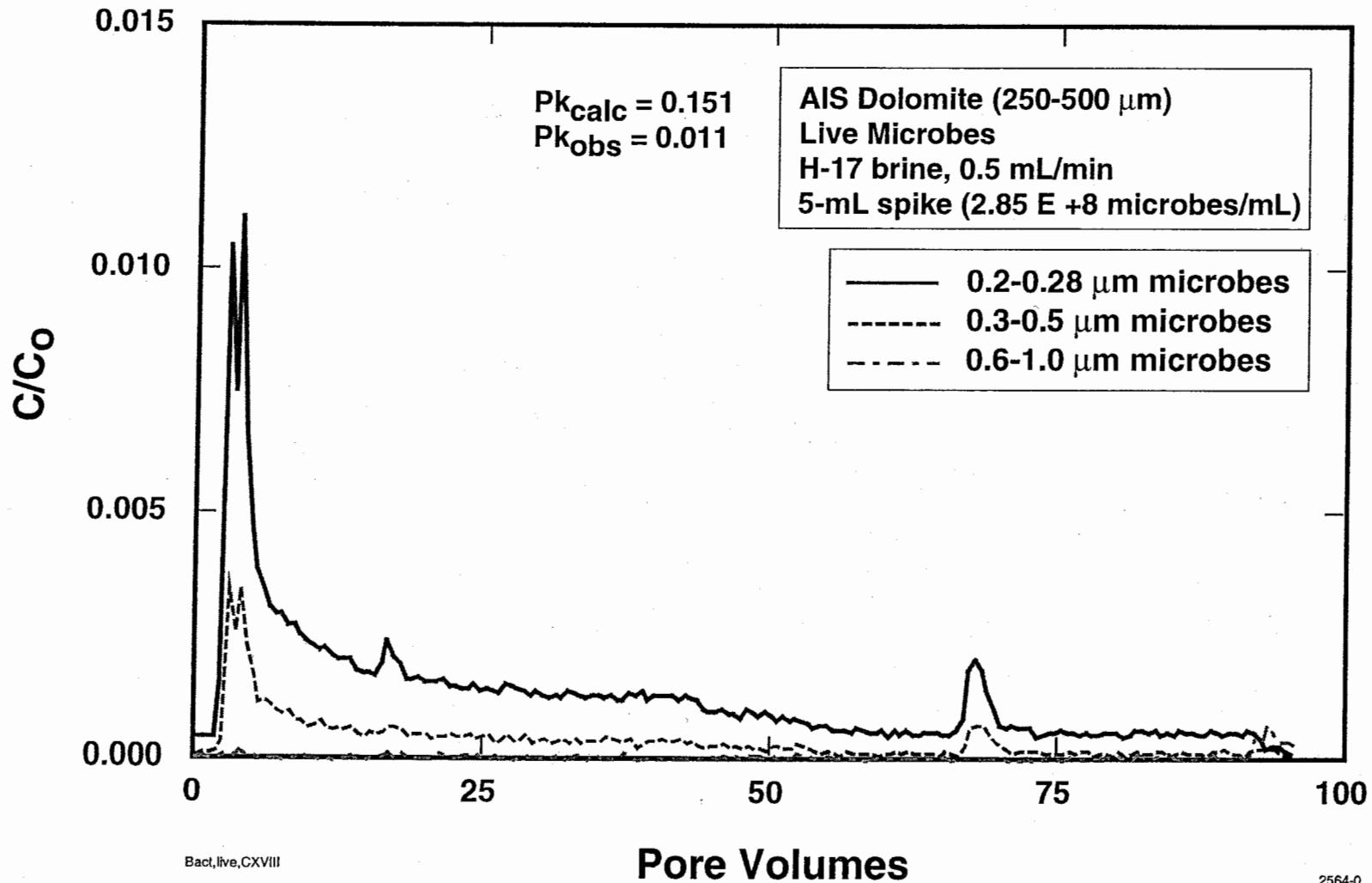
- elution of U matched profile of test without microbes
- Am did not elute during the test, consistent with test without microbes
- direct counts (BNL) of microbes showed background concentrations only

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

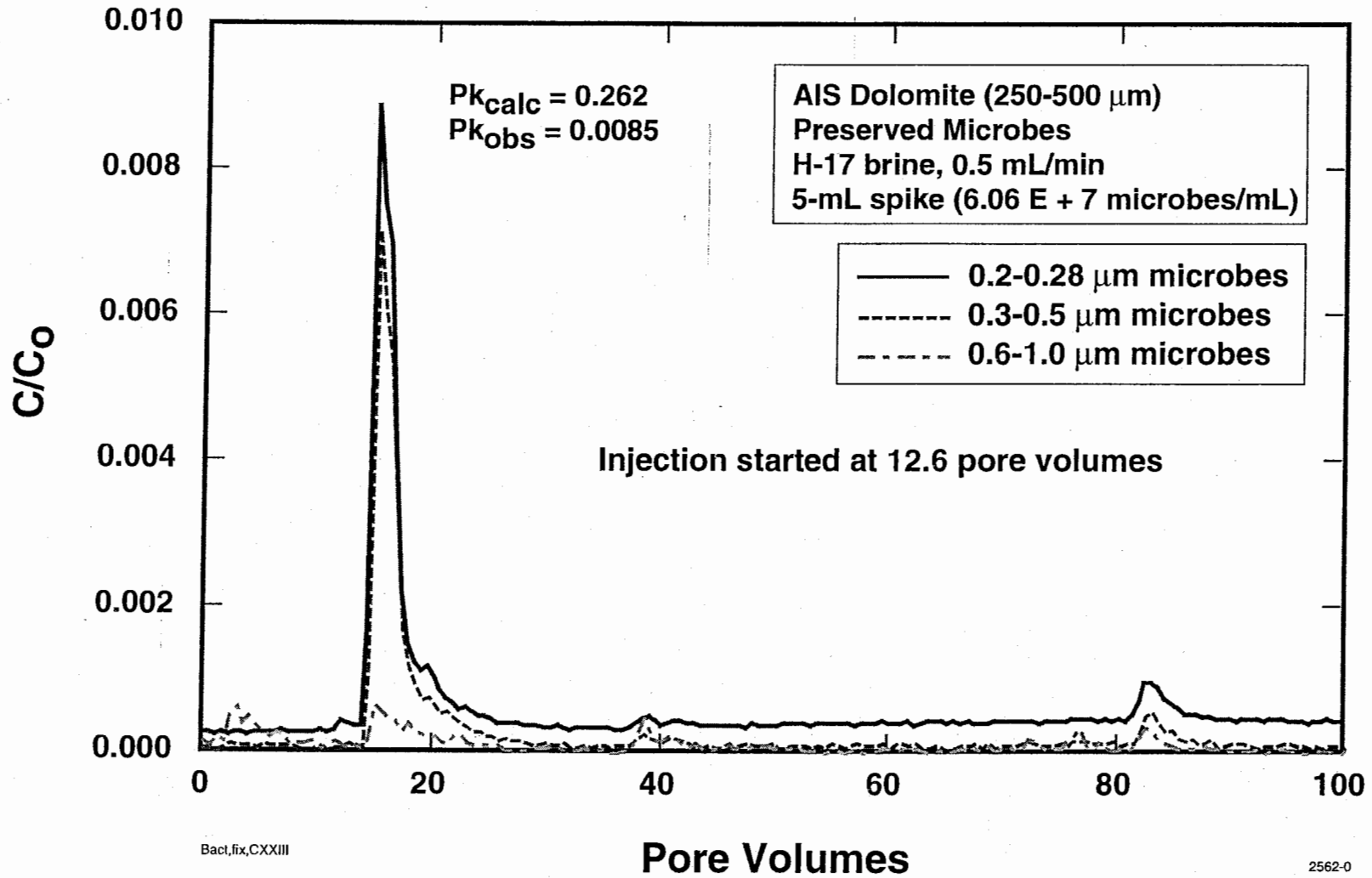
PA Implementation

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

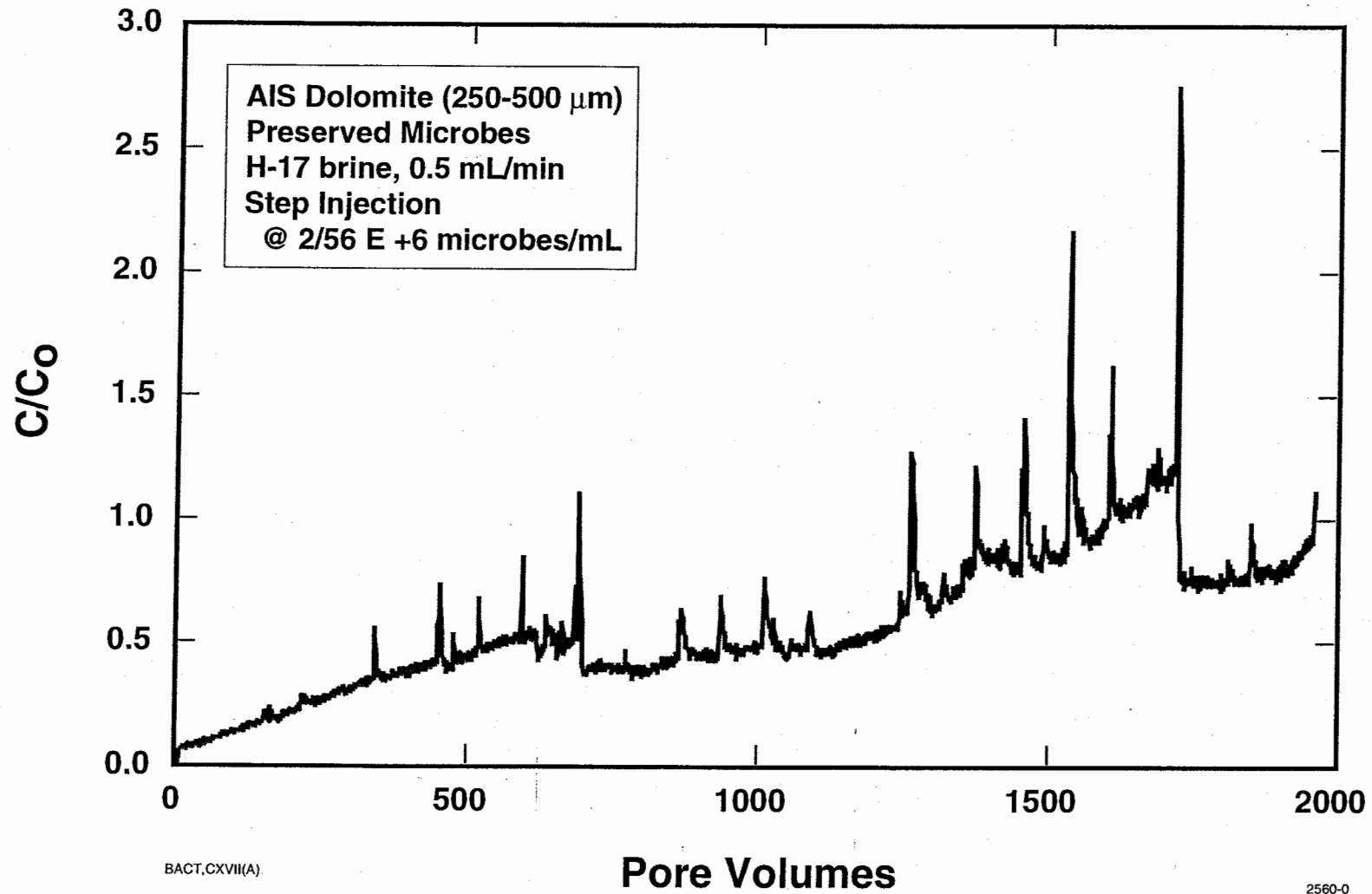
Microbe Transport Through a Crushed-Rock Column



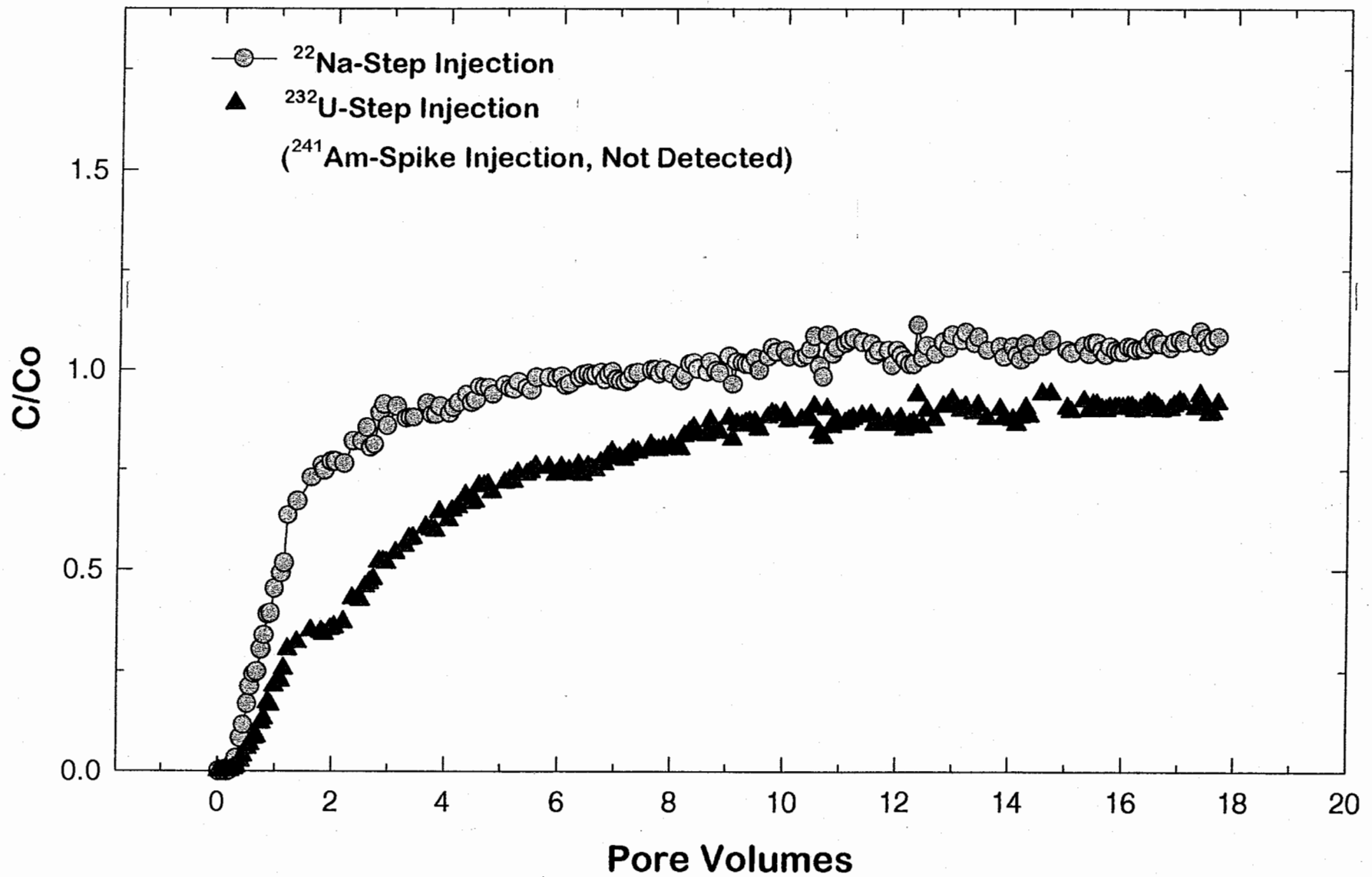
Microbe Transport Through a Crushed-Rock Column



Microbe Transport Through a Crushed-Rock Column



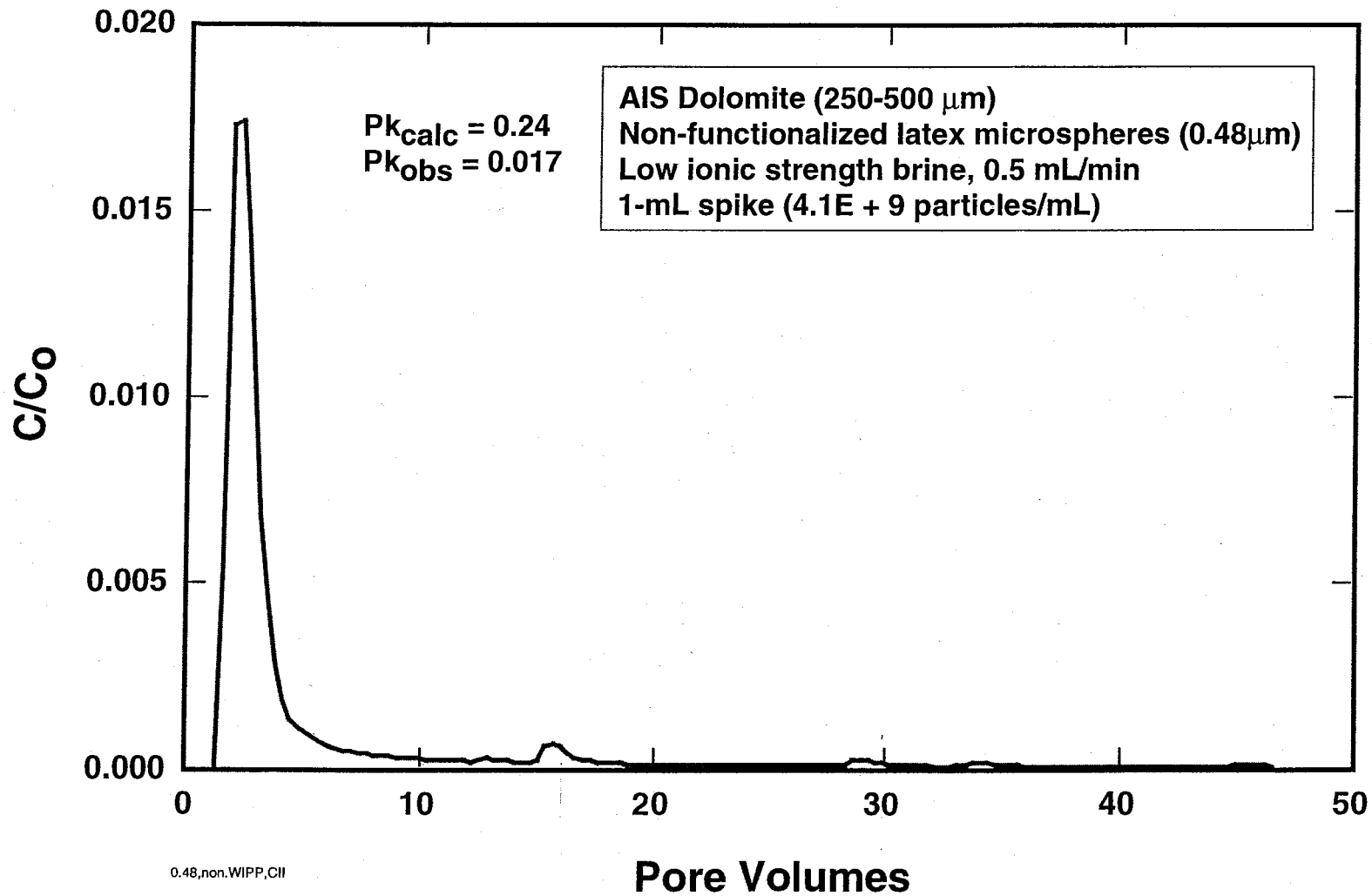
Microbial-Actinide Transport through an Intact Core



Test E-3
VPX27-7A

FILE:TESTE3VU.SPW

Latex Microsphere Transport Through a Crushed-Rock Column



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

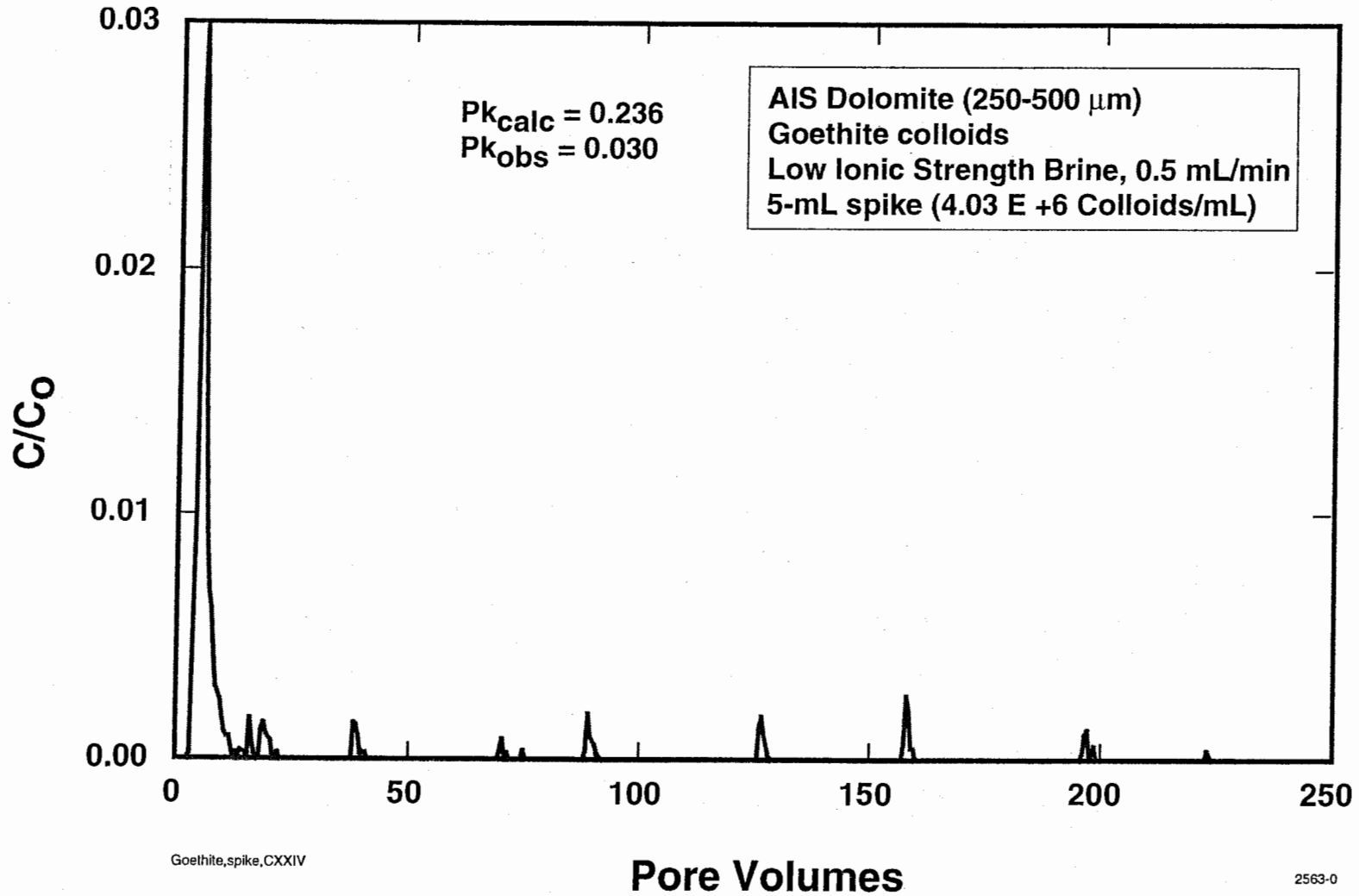
Results

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

PA Implementation

- represent attenuation with γ
- set R equal to 1 due to complexities of combining R with γ 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)

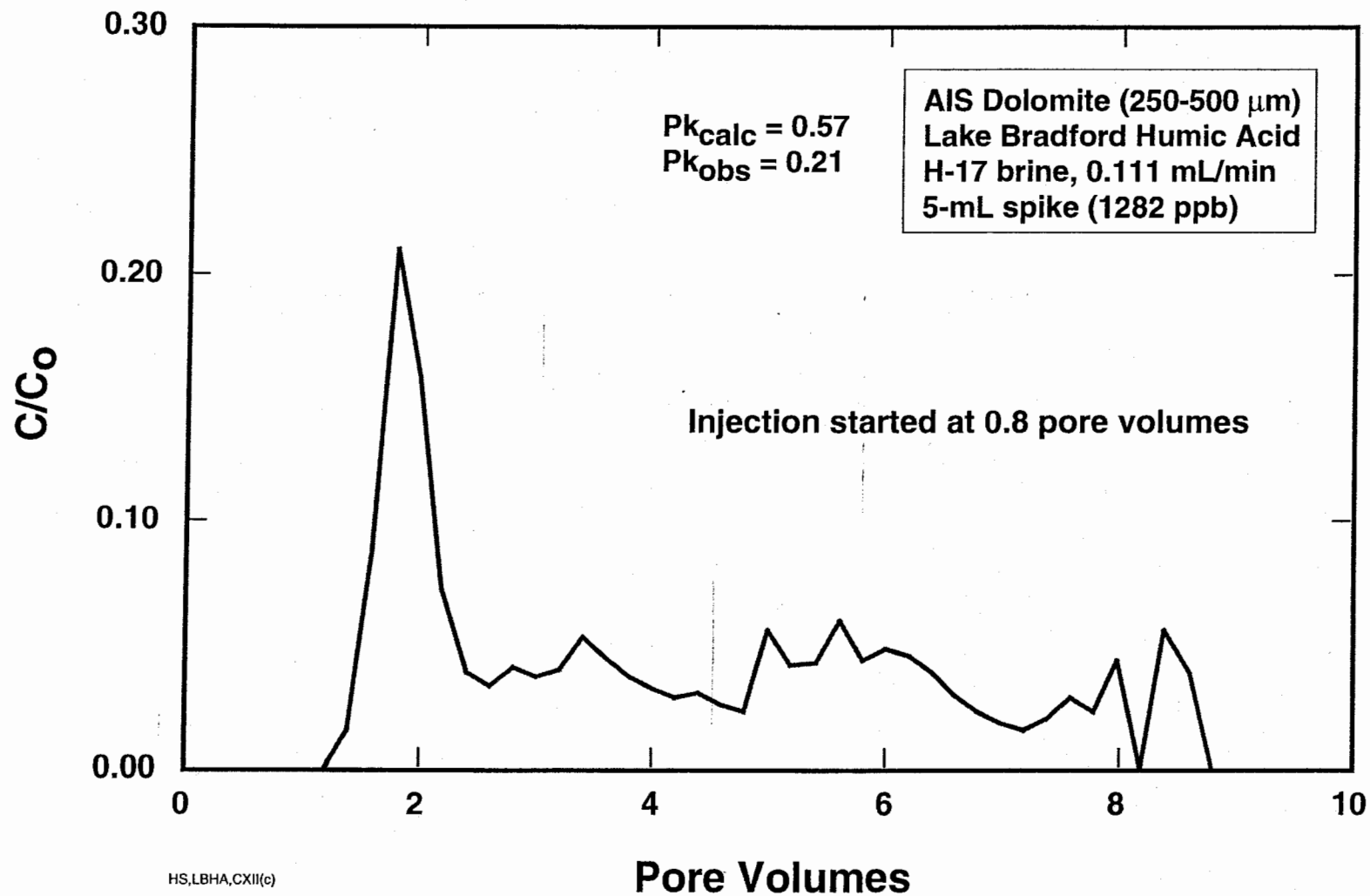
- 1:1:1 mixture of aliphatic + aromatic humic acid + fulvic acid

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 be simulated using values from Dissolved Actinide Retardation Research Program

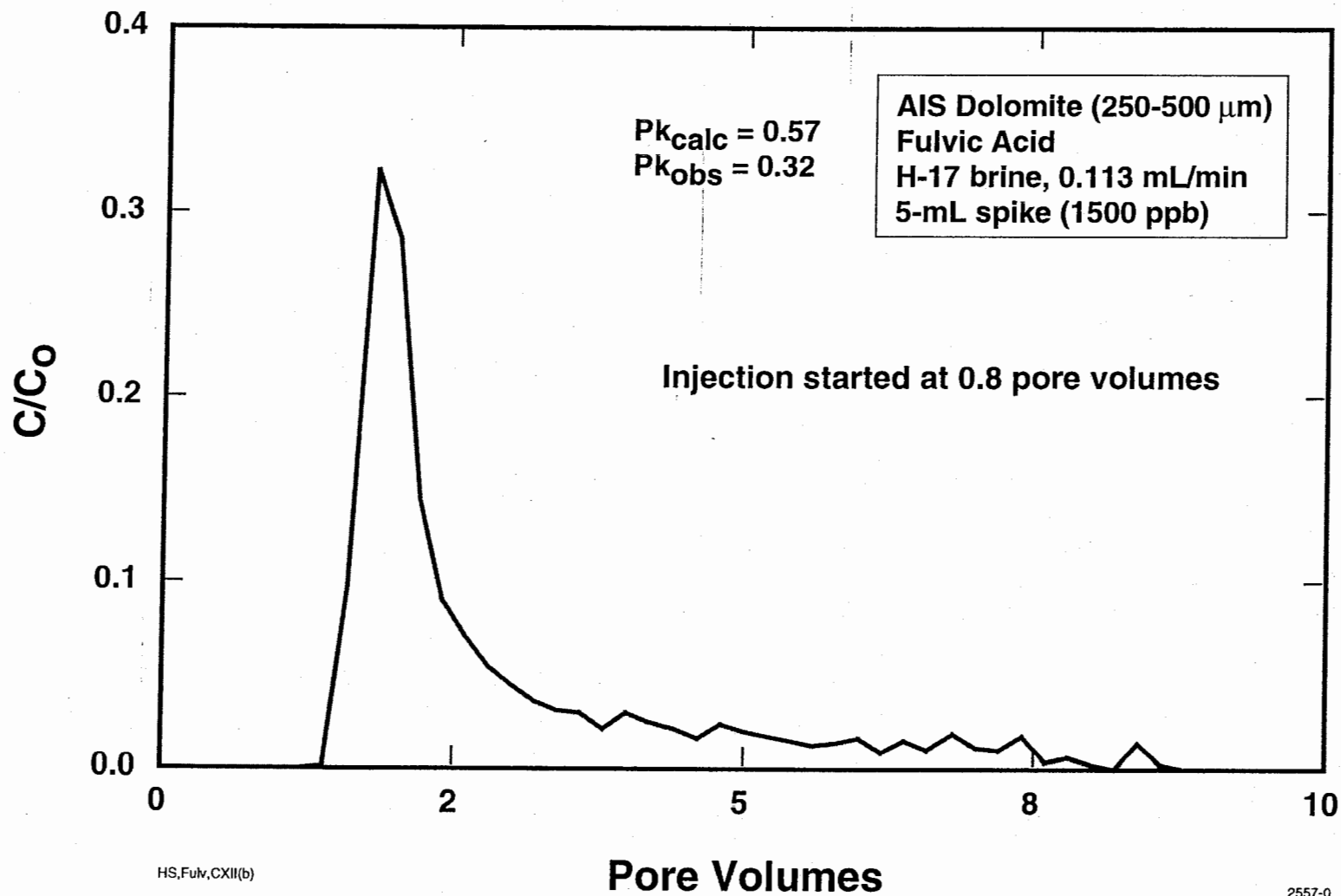
Humic Acid Transport Through a Crushed-Rock Column



HS, LBHA, CXII(c)

2556-0

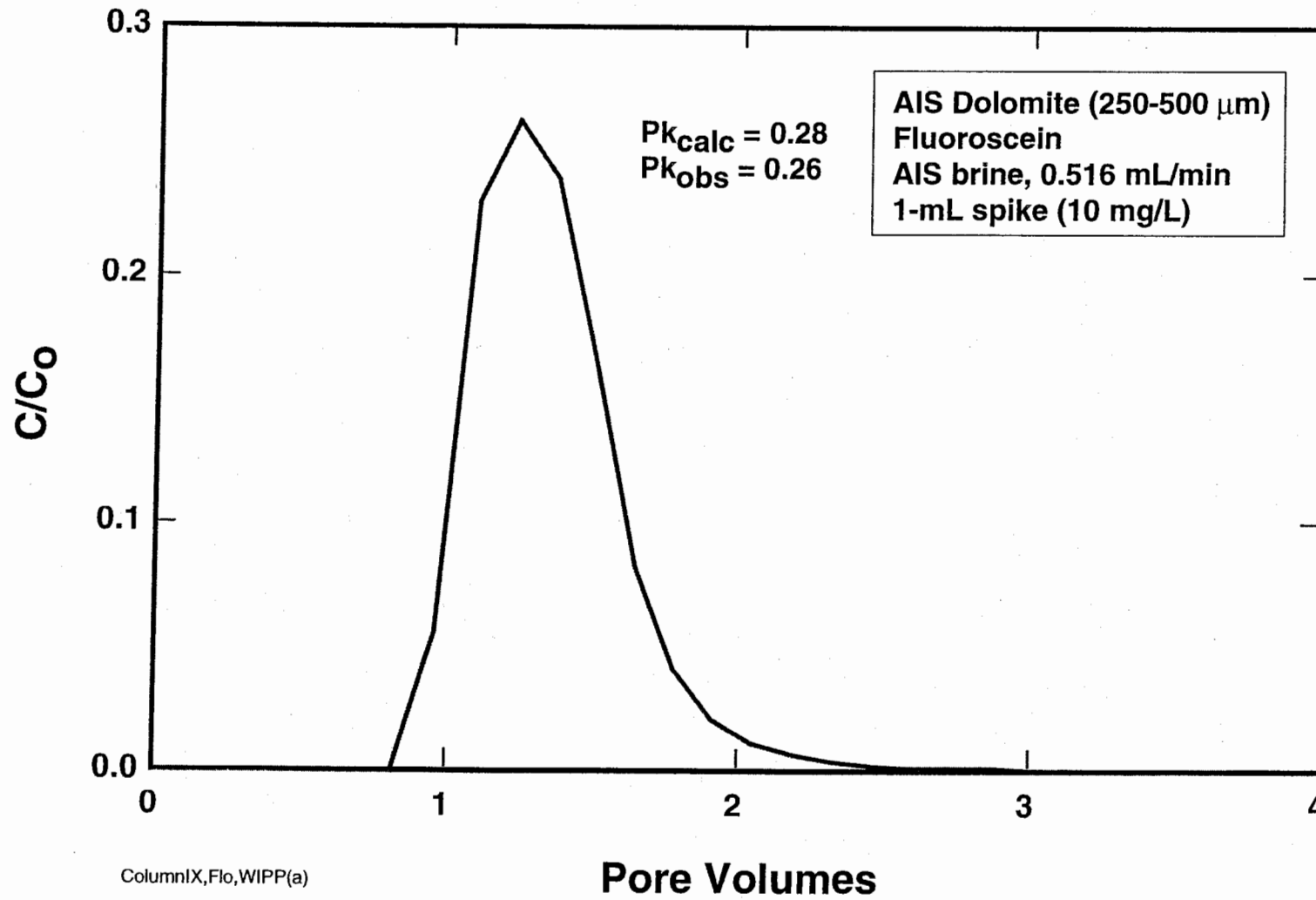
Fulvic Acid Transport Through a Crushed-Rock Column



HS,FuIV,CXII(b)

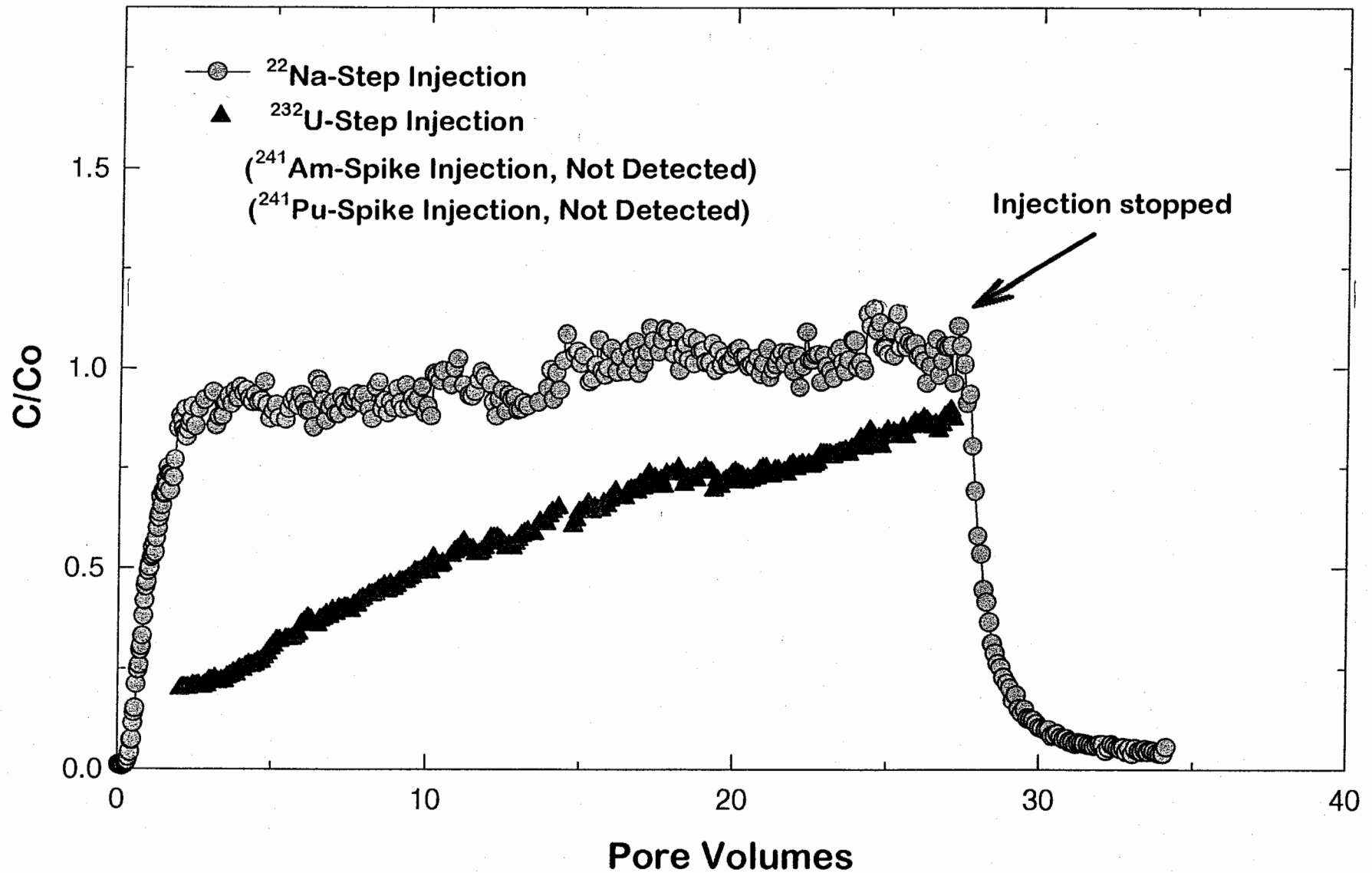
2557-0

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



2558-0

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 4σ ; "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):

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

where: D_{col} = free-solution tracer diffusion coefficient for colloidal particles ($\text{cm}^2 \text{sec}^{-1}$)
 k = Boltzman constant
 T = temperature in Kelvin
 μ = 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 (2.13×10^{-2} g cm⁻¹sec⁻¹; Gelbard 1993)
- $k = 1.38 \times 10^{-16}$ g cm² sec⁻² °K⁻¹
- $T = 300$ °K
- D_{sol} values reported for dissolved actinides range from 1.53×10^{-6} to 4.26×10^{-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) = 2×10^{-3} g/L

Actinide intrinsic colloids [Pu(IV)-polymer]

- measured solubility limited to minimum analytical detection limit of LSC
- measured concentration (detection limit) = 1×10^{-9} moles/L = 2.4×10^{-7} g/L

Microbes

- estimate biomass using laboratory measurements and geometry
 - rod shaped with mean dimensions of $0.9 \mu\text{m}$ diameter x $1.7 \mu\text{m}$ length
 - density equal to Brine A (1.2 g/cm^3)
 - measured steady-state population of 5×10^6 cells/mL
- estimated concentration = 5×10^{-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 = 1×10^{-3} g/L

PA Parameter Values for Colloidal Actinide Retardation

Colloid	Actinide	K_d (mL/g)	γ (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	
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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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