U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: APPLICABILITY OF LABORATORY EXPERIMENTS

PRESENTERS: DR. AREND MEIJER AND
DR. ROBERT S. RUNDBERG

PRESENTER'S TITLE AND ORGANIZATION: GEOCHEMISTS,
LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NEW MEXICO

PRESENTER'S TELEPHONE NUMBER: (505) 667-0675/(505) 667-4559

DECEMBER 11-12, 1989

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APPLICABILITY OF LABORATORY EXPERIMENTS

OVERVIEW

- PHYSICAL AND CHEMICAL PROCESSES THAT DETERMINE RADIONUCLIDE (RN) MOBILITY
- MAIN FACTORS THAT CONTROL SORPTION BEHAVIOR FOR EACH RN
- EXPERIMENTAL R_d DETERMINATIONS
- EXPERIMENTAL DETERMINATION OF OTHER TRANSPORT PARAMETERS
- APPLICABILITY OF LABORATORY EXPERIMENTS TO UNSATURATED-ZONE MOBILITY OF RN AT YUCCA MOUNTAIN

PHYSICAL AND CHEMICAL PROCESSES THAT DETERMINE RN MOBILITY IN GROUND WATER SYSTEMS

- GROUND-WATER FLOW PARAMETERS
  - VELOCITY, DISPERSION, MATRIX VS. FRACTURE FLOW, MATRIC POTENTIAL, ETC.
- RN SOLUBILITY, COLLOID FORMATION
- RN DIFFUSION RATE, OSMOTIC POTENTIAL (?)
- INTERACTION WITH HOST ROCKS AND FRACTURE LININGS
  - ANION EXCLUSION, COLLOID FILTRATION
  - SORPTION REACTIONS, COPRECIPITATION

MAIN FACTORS THAT CONTROL SORPTION BEHAVIOR OF EACH RN

- TYPES AND ADSORPTION CAPACITIES OF SOLID SURFACES IN ROCKS AND FRACTURES
  - ION EXCHANGE IN ZEOLITES AND CLAYS
  - SURFACE ADSORPTION IN Fe–Mn PHASES, FELDSPARS, SILICA PHASES, GLASS, ETC.
- GROUND-WATER COMPOSITION
  - pH,Eh,m_i,I
- IDENTITIES AND CONCENTRATIONS OF RN
- SORPTION KINETICS
- TEMPERATURE

EXPERIMENTAL R_d DETERMINATIONS

- **BATCH CRUSHED ROCK, SOLID-ROCK WAFERS, CRUSHED–ROCK COLUMNS**
  - OBTAIN R_d's FOR EACH RN UNDER RANGE OF ANTICIPATED CONDITIONS
  - INVESTIGATE SORPTION KINETICS FOR EACH RN

- **VALIDATION AND EXTRAPOLATION OF EXPERIMENTAL R_d DATA**
  - INVESTIGATE POTENTIAL EXPERIMENTAL ARTIFACTS
  - MECHANISTIC STUDIES OF SORPTION ON "KEY MINERALS"

EMPIRICAL (BATCH) APPROACH

SELECT:

(1) ROCK (CRUSHED) SAMPLE

(2) GROUND-WATER COMPOSITION

(3) RADIONUCLIDE SPECIES AND CONCENTRATIONS
- SOLUBILITY CONSTRAINTS

(4) ATMOSPHERE
- pH, Eh CONSTRAINTS

(5) WATER/ROCK RATIO
- UNSATURATED-ZONE DATA
- EXPERIMENTAL CONSTRAINTS

6) EXPERIMENT DURATION – KINETICS

EMPIRICAL (BATCH) APPROACH

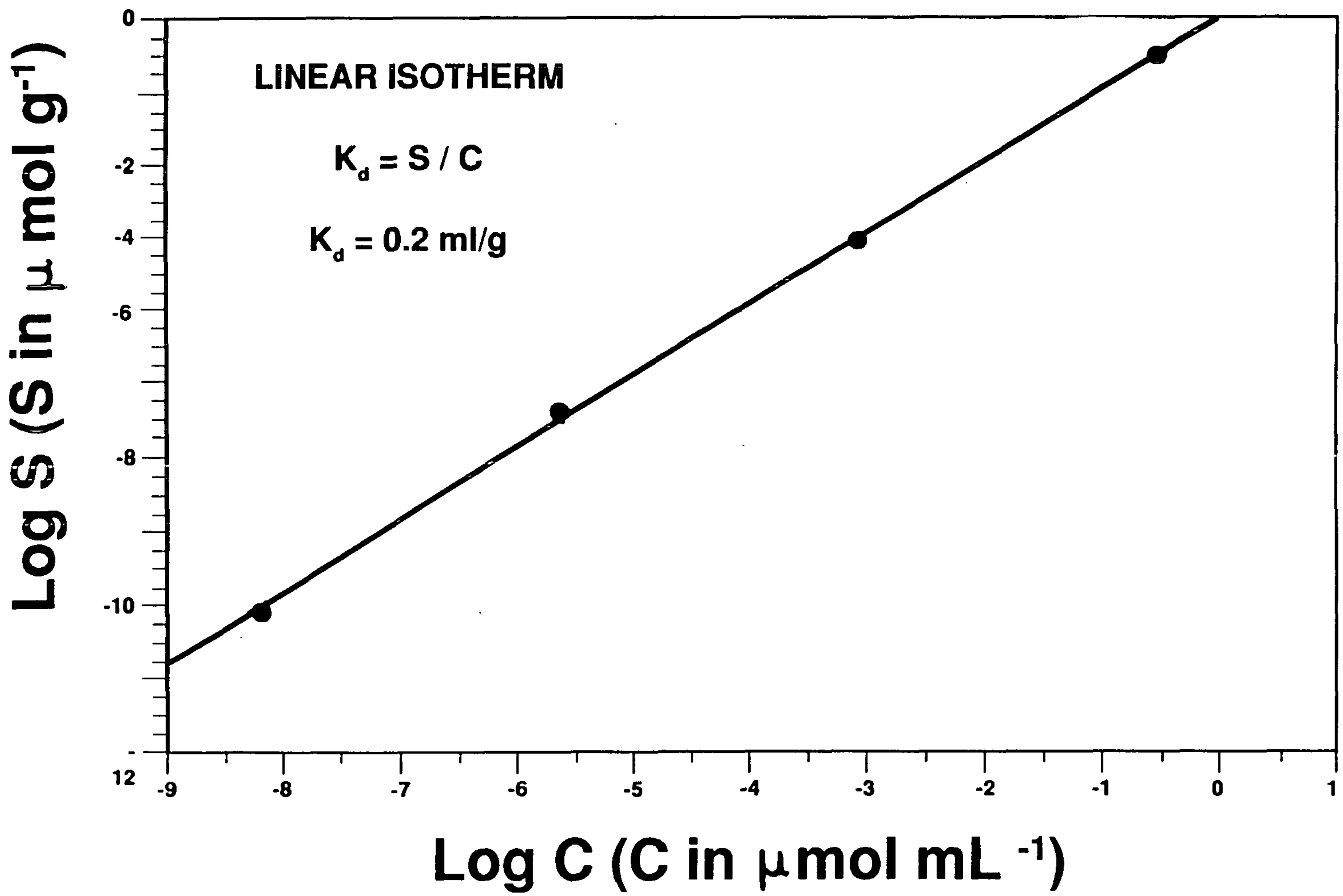
(CONTINUED)

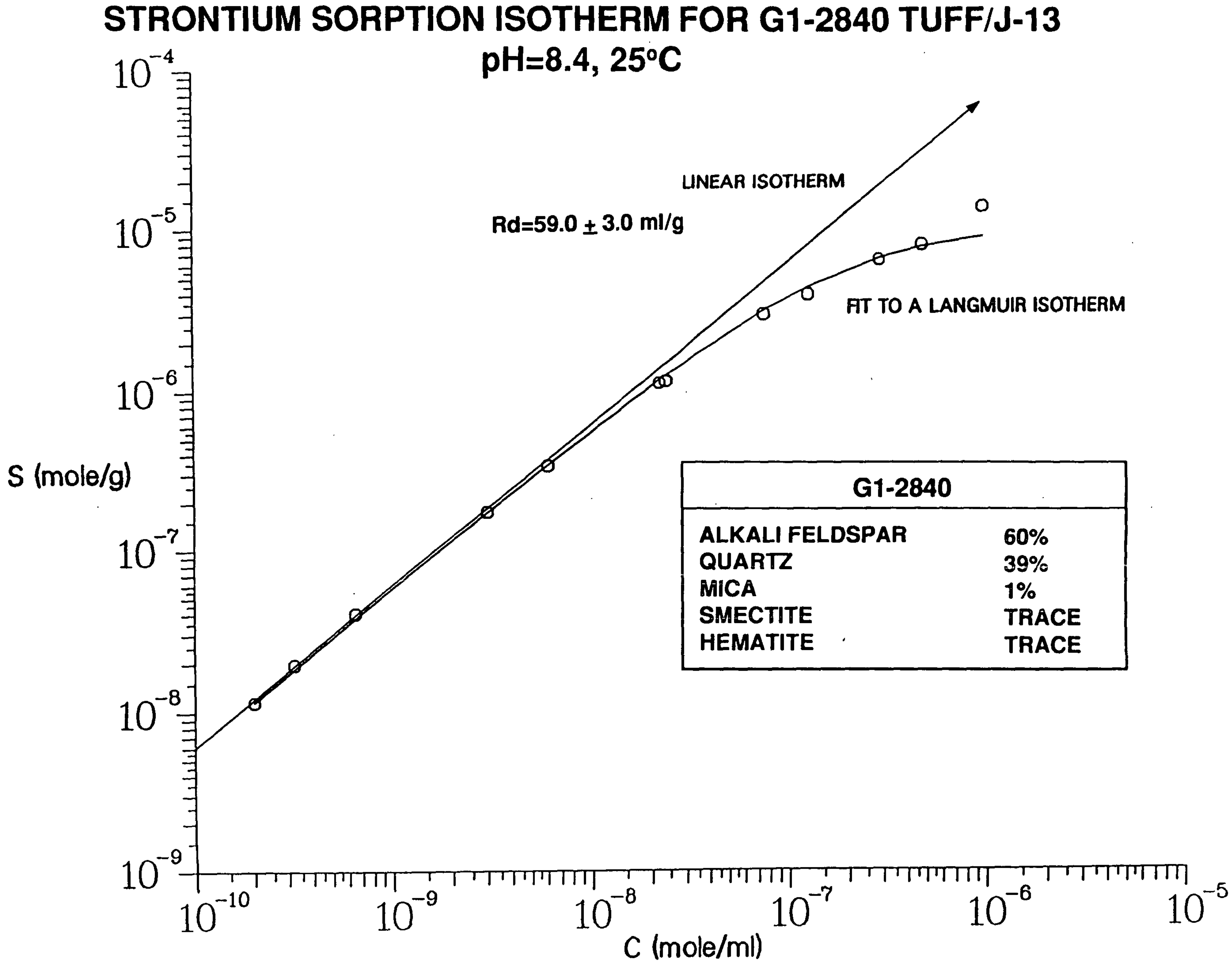
DEVELOP: (1) EXPERIMENTAL TECHNIQUE

OBTAIN: (1) SORPTION RATIOS (R_d)
(2) SORPTION ISOTHERMS

DERIVE: (1) R_d MATRIX FOR HYDROLOGIC UNITS
(2) PREDICTIVE EQUATIONS FOR FRACTURE R_d's

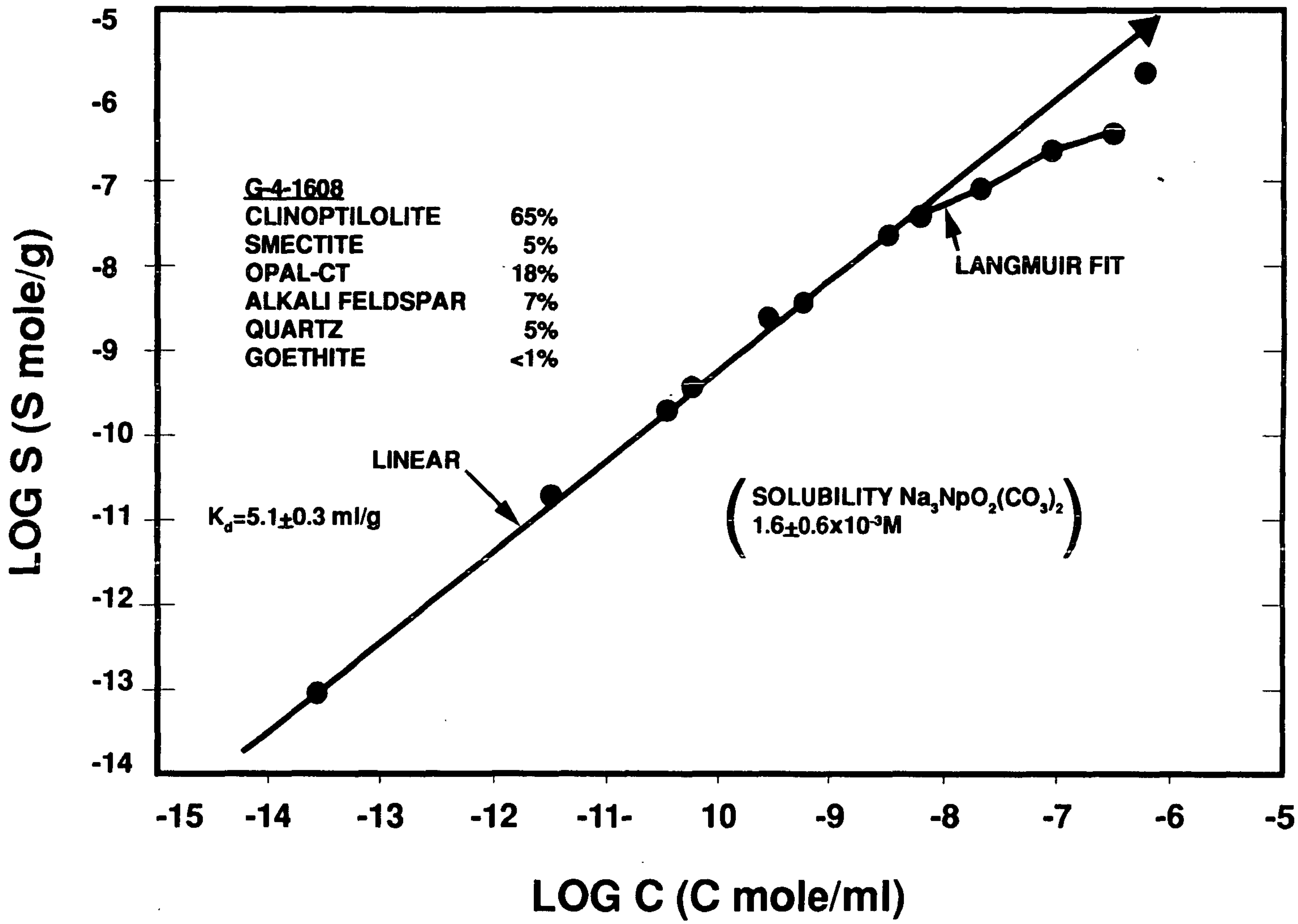
Tc SORPTION ON ZEOLITIC TUFF (AIR)





STRONTIUM SORPTION ISOTHERM FOR G1-2840 TUFF/J-13
pH=8.4, 25°C
LINEAR ISOTHERM
Rd=59.0 ± 3.0 ml/g
FIT TO A LANGMUIR ISOTHERM
S (mole/g)
C (mole/ml)
G1-2840
ALKALI FELDSPAR 60%
QUARTZ 39%
MICA 1%
SMECTITE TRACE
HEMATITE TRACE

Np ON ZEOLITIC TUFF (J-13;5% CO_2)



VALIDATION AND EXTRAPOLATION OF EXPERIMENTAL R_d DATA

- **EXPERIMENTAL ARTIFACTS**
  - ADSORPTION TO WALLS OF CONTAINER
  - OVERSATURATION
  - EFFECTS OF ROCK CRUSHING
  - EXCESSIVE WATER/ROCK RATIOS
  - SOLID/LIQUID SEPARATIONS
  - SPECIES EQUILIBRIUM IN SOLUTION

Am ADSORPTION ON WALLS OF CONTAINER

- GROUND WATER (J–13) + ^{241}Am + TEFLON CONTAINER

TRACED AND ACIDIFIED	TECHNIQUE	CONCENTRATION
IMMEDIATELY	I.D.	7.1×10^{-12} M
1 DAY	I.D.	6.7×10^{-12} M
3 WEEKS	I.D.	4.5×10^{-12} M

- 35% ^{241}Am LOST TO WALLS OF CONTAINER IN 3 WEEKS

Am SORPTION ON DEVITRIFIED TUFF IN J-13 WATER

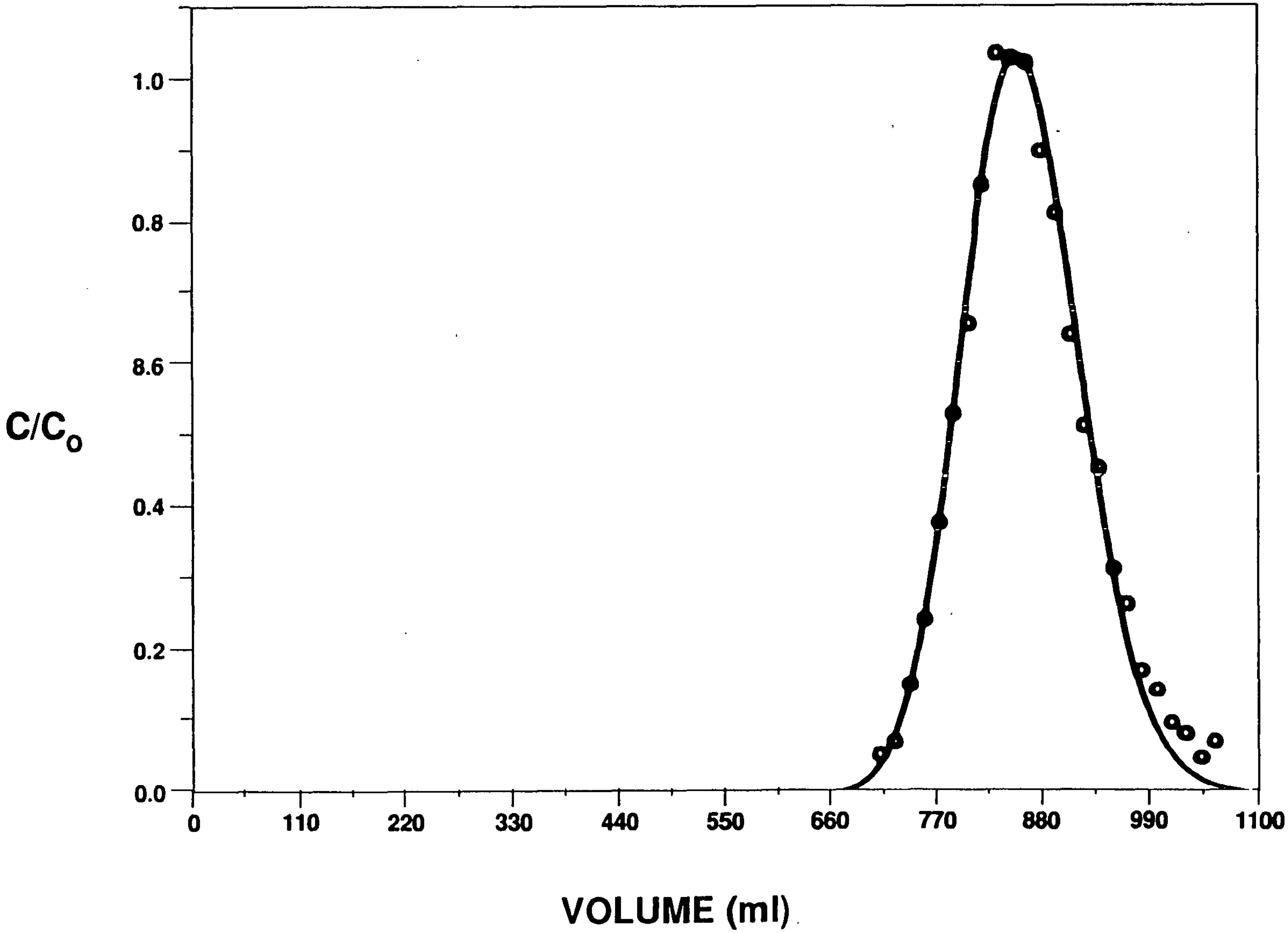
SAMPLE NO.	R_d (SORPTION)	R_d (DESORPTION)	INITIAL CONCENTRATION
GU3-688	14,000		6.9×10^{-12}M
G1-1833	4,200-5,300	5,900-8,900	1.0×10^{-7}M
GU3-433	2,900-3,800	6,000-14,000	2.1×10^{-7}M
JA-32	79-230	1,500-2,800	1.0×10^{-6}M
YM-22	1,100-1,500	1,900-3,100	1.0×10^{-7}M
YM-54	150-160	400-680	1.0×10^{-7}M

SOLUBILITY OF SOLID $AmOHCO_3$ = 10^{-9} TO 10^{-10} M
pH = 8.0-8.5

R_d COMPARISON: TUFF WAFERS vs. CRUSHED TUFF

SAMPLE NO.	ELEMENT	R_d (WAFER) (ml/gm)	R_d (CRUSHED) (ml/gm)
G1-1883 (DEVITRIFIED)	Ba	210	180
	Cs	230	190
	Sr	27	22
G1-1982 (DEVITRIFIED + CLAYS)	Ba	800	800
	Cs	1,000	1,200
	Sr	80	62
G1-1436 (ZEOLITIC)	Cs	14,900	2,400
	Sr	95,500	87,000

G1-3658 CRUSHED-ROCK COLUMN, Sr SPIKE IN CLAY-RICH TUFF (J-13 WATER)



WATER/ROCK RATIO EXPERIMENTS
ZEOLITIC TUFF (G4-1502)

ULTRACENTRIFUGATION EXPERIMENTS
R_d's (ml/g)

W/R RATIO	Ba		Cs		Sr	
5:1	6,970	(2,400)	14,600	(4,200)	>10,500	
10:1	46,700	(14,000)	13,900	(1,400)	>32,400	
20:1	81,100	(3,900)	23,800	(2,200)	>27,900	
30:1	123,000	(25,000)	31,100	(770)	108,000	(40,000)

ULTRAFILTRATION EXPERIMENTS
R_d's (ml/g)

W/R RATIO	Ba		Cs		Sr	
5:1	69,200	(4,900)	17,900	(800)	92,500	(55,900)
10:1	106,000	(25,400)	33,500	(3,100)	169,600	(10,900)
20:1	236,000	(4,100)	43,200	(3,700)	207,900	(9,050)
30:1	433,800	(70,300)	44,700	(2,150)	322,100	(5,100)

"MECHANISTIC" SORPTION STUDIES

- SELECT "KEY" MINERALS
- CHARACTERIZE SURFACE PROPERTIES OF MINERALS SELECTED
- OBTAIN ISOTHERMS FOR "IMPORTANT" RADIONUCLIDES
- INVESTIGATE NATURE OF SORBED SPECIES
- DEVELOP MODELS FOR SORPTION BEHAVIOR

- EVALUATE EXISTING R_d DATABASE
- DEVELOP PREDICTIVE CAPABILITIES BASED ON MODELS OF SORPTION BEHAVIOR AND SITE DATA

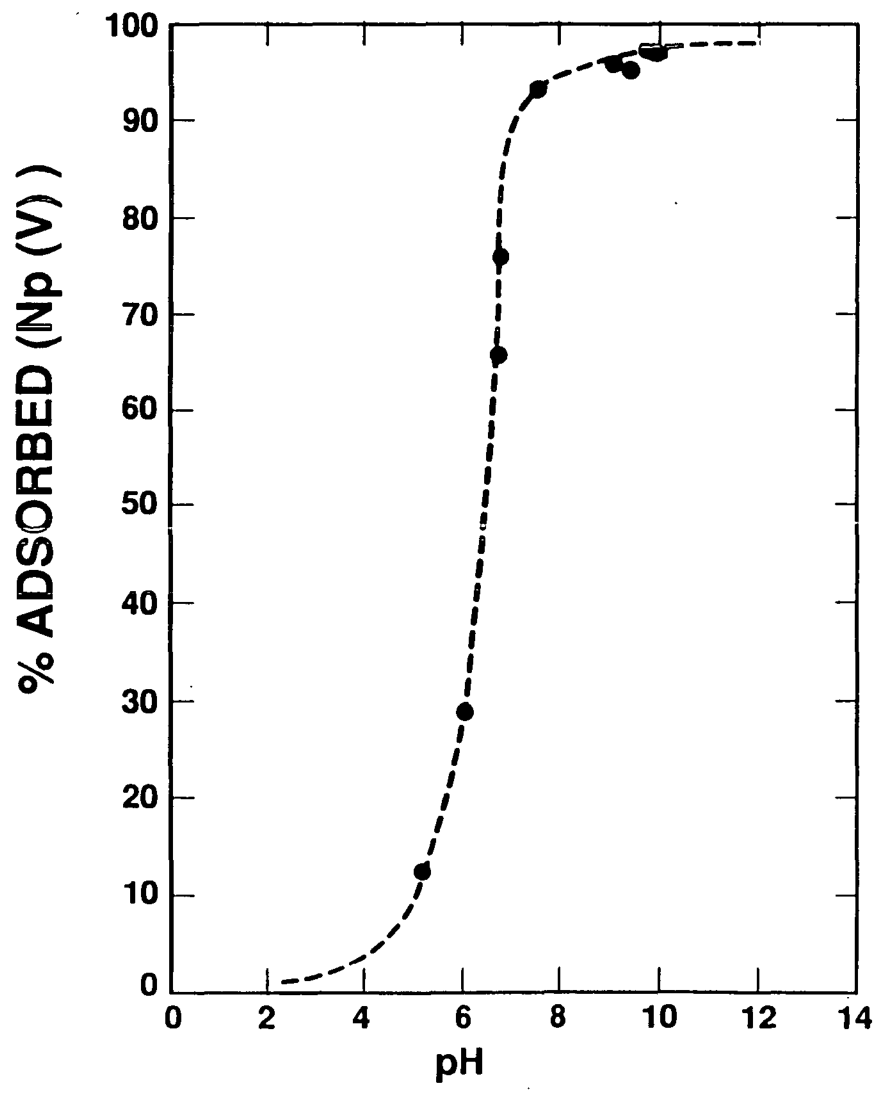
Np PURE MINERAL R_d's

MINERAL	FORMULA	R_d (ml/g)[1,2]
HEMATITE (SYNTHETIC)	Fe_2O_3	5.1×10^4
GOETHITE (SYNTHETIC)	$FeO(OH)$	5.1×10^4
HOLLANDITE	$Ba(Mn^{2+},Mn^{4+})_8O_{16}\cdot xH_2O$	7.8×10^3
ROMANECHITE (NATURAL)	$(Ca,Mn)(Mn^{2+},Mn^{4+})_4O_9\cdot 3H_2O$	1.5×10^3
CALCITE (NATURAL)	$CaCO_3$	390
CALCITE (SYNTHETIC)	$CaCO_3$	21
MONTMORILLONITE	$(Al_{1.37}Fe_{0.19}Mg_{0.46})(Si_{3.84}Al_{0.16})O_{10}(OH)_2$	78
CLINOPTILOLITE	$(Na,K)_6(Al_6Si_{30}O_{72})\cdot 20H_2O$	30

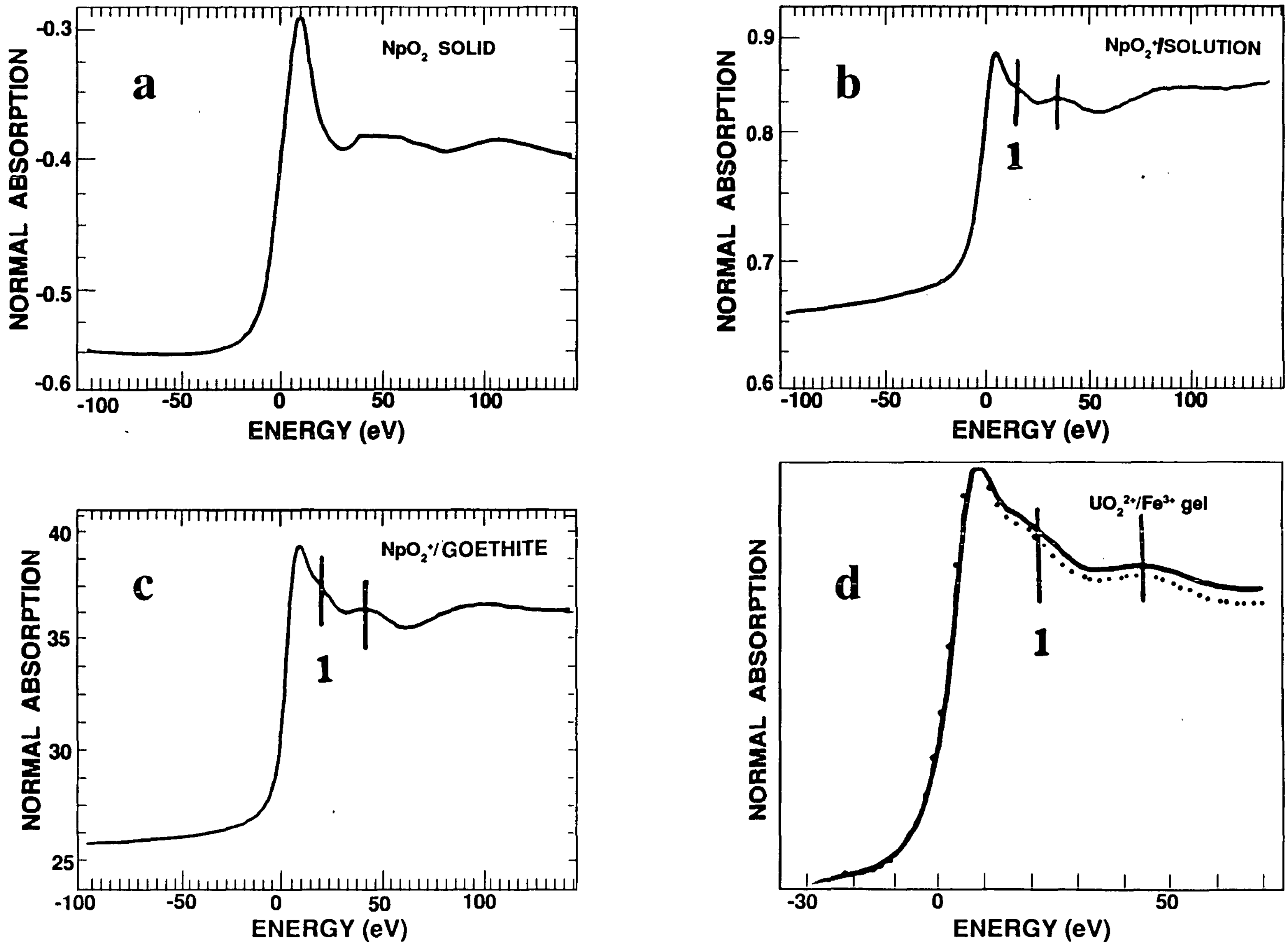
[1] DISTILLED WATER BUFFERED AT pH = 8.5 WITH SODIUM CARBONATE/BICARBONATE

[2] NOT CORRECTED FOR DIFFERENCES IN SURFACE AREAS

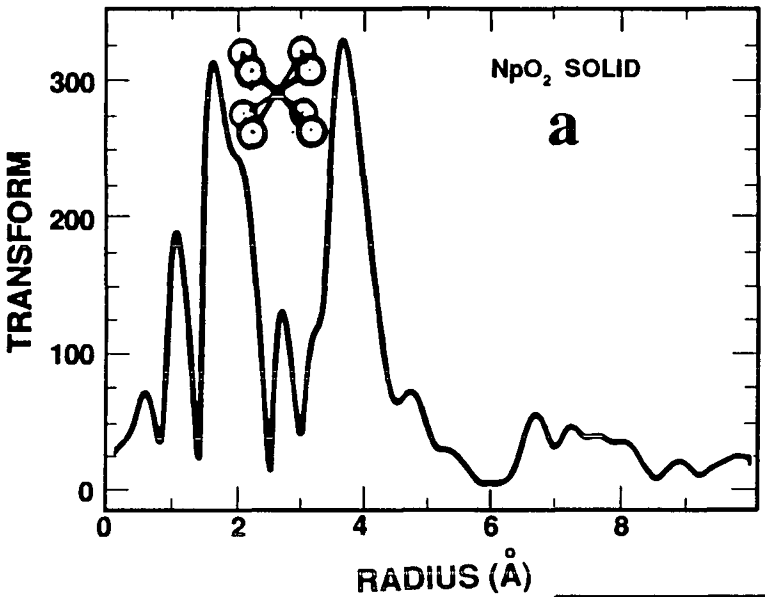
ADSORPTION OF Np (V) ON GOETHITE

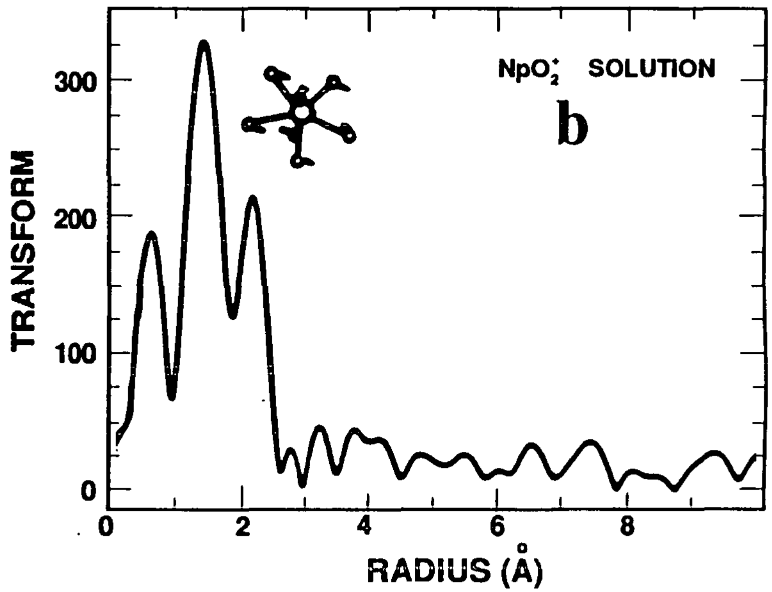


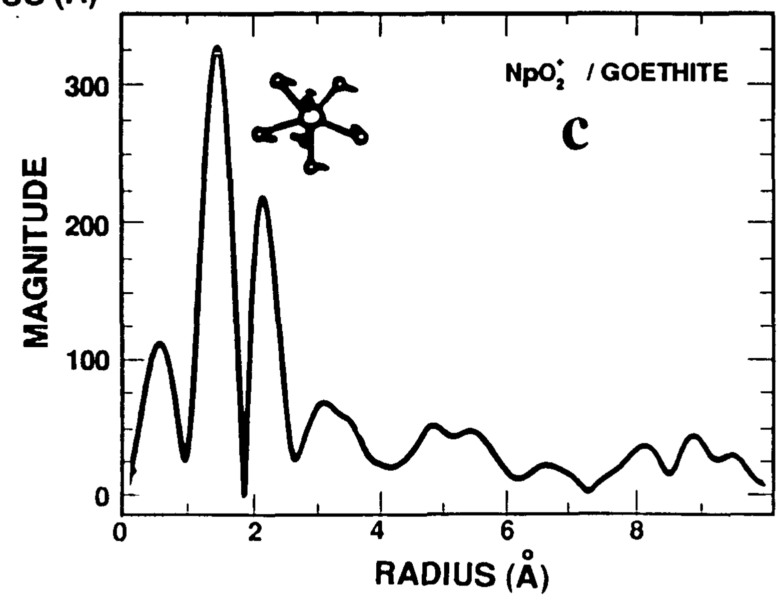
NEXAFS SPECTRA OF Np



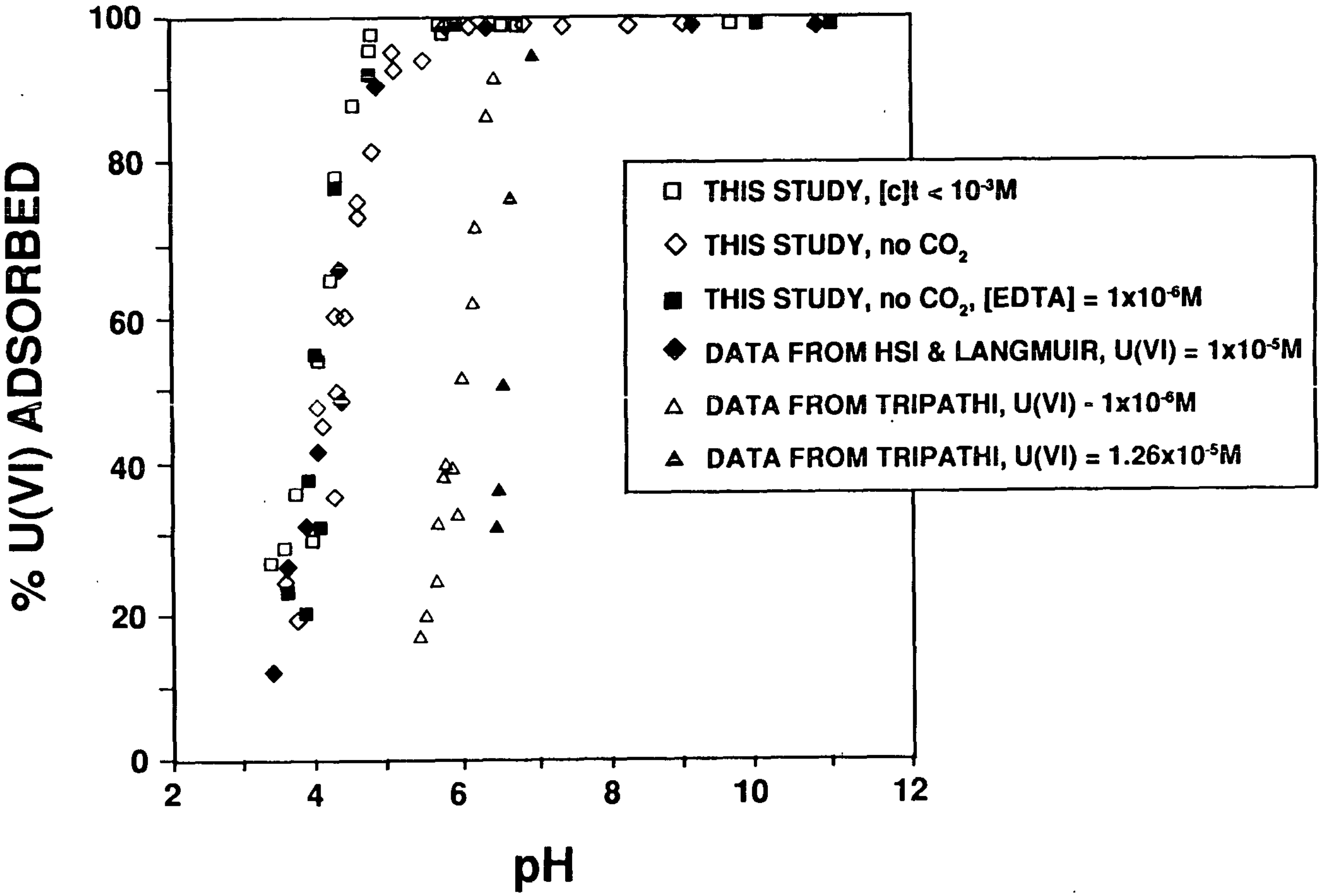
FOURIER TRANSFORM OF NEXAFS SPECTRA OF Np



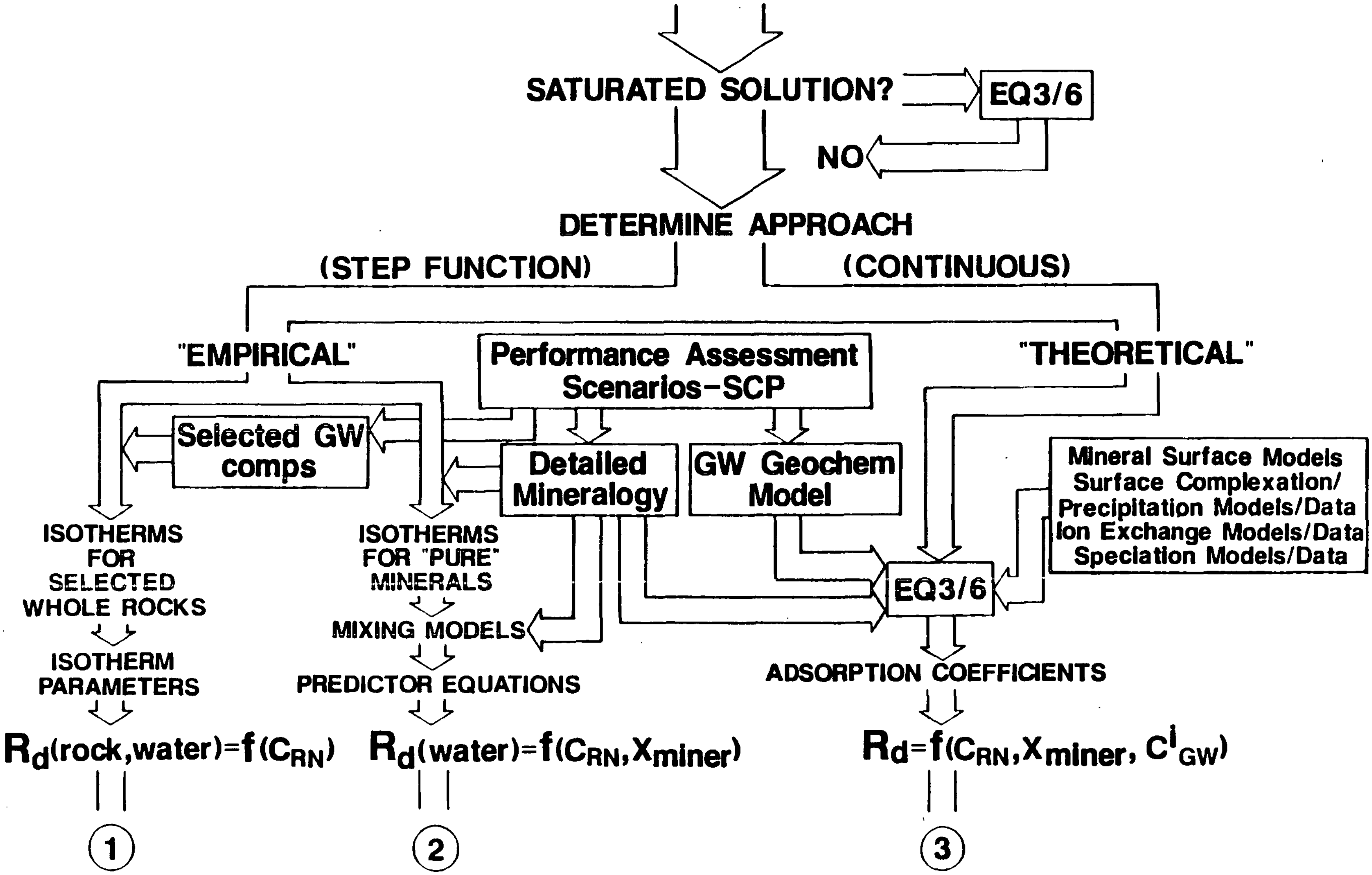




U(VI) - ADSORPTION ONTO GOETHITE
I=0.1M $NaClO_4$, U(VI) = 1.0×10^{-6}M
GOETHITE CONCENTRATION: 1g/l



CONCEPTUAL STRATEGIES FOR OBTAINING Rd's



DYNAMIC TRANSPORT TASK: PURPOSE

- TEST THE VALIDITY OF K_ds FROM BATCH MEASUREMENTS FOR CALCULATING THE RETARDATION OF RADIONUCLIDES BY ADSORPTION ON MINERALS
- MEASURE THE EFFECTS OF DIFFUSION AND DISPERSION ON THE TRANSPORT OF RADIONUCLIDES
- PROVIDE EXPERIMENTAL EVIDENCE FOR SPECIATION AND/OR COLLOID FORMATION
- MEASURE COLLOID FILTRATION COEFFICIENTS IN YUCCA MOUNTAIN TUFF
- STUDY RADIONUCLIDE MIGRATION IN UNSATURATED TUFF

DETERMINATION OF OTHER TRANSPORT PARAMETERS

I. ANION EXCLUSION VOLUMES

II. DISPERSION PARAMETERS FROM SOLID ROCK COLUMNS

III. DISPERSION/R_d RELATIONSHIP

DYNAMIC TRANSPORT TASK: SCOPE

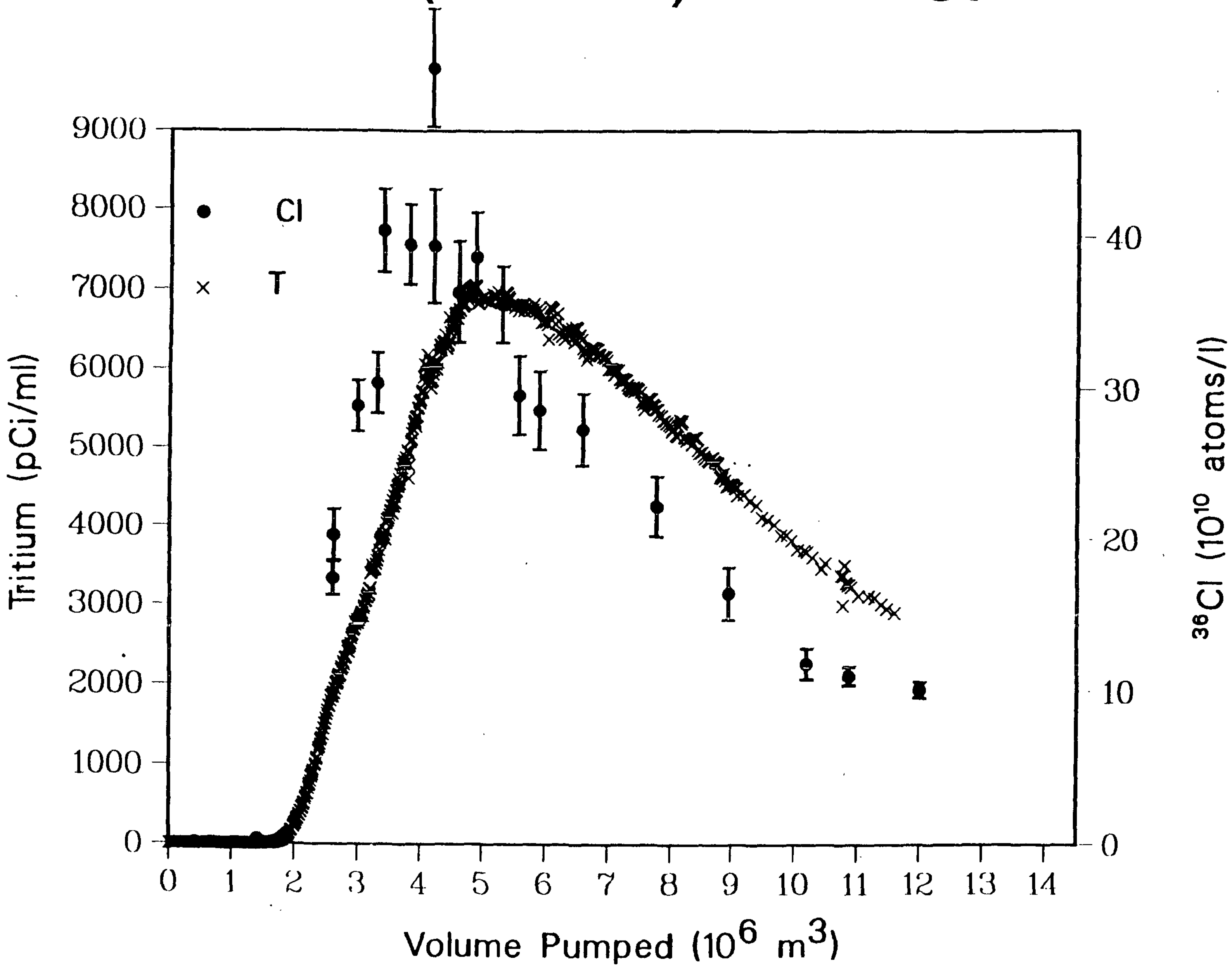
- CRUSHED TUFF COLUMNS
- ADSORPTION KINETICS
- UNSATURATED TUFF COLUMNS
- FRACTURED TUFF COLUMNS
- COLLOID FILTRATION
- DIFFUSION CELLS
- SORPTION KINETICS WITH INTACT TUFF
- UNSATURATED DIFFUSION CELLS

CRUSHED TUFF COLUMNS: CATION SORPTION

COMPARISON OF CRUSHED TUFF COLUMNS WITH BATCH SORPTION EXPERIEMENTS

SAMPLE	ELEMENT	BATCH K_d	R_f (calc.)	R_f (meas.)
1-2334	Sr	180	250	102
	Ba	1,400	1,940	1,180
	Cs	1,200	1,670	1,630
YM-22	Sr	60	128	50
	Ba	890	1,890	723
	Cs	255	540	266
YM-38	Cs	13,000	54,000	49,000
G1-3116	Sr	2,300	9,146	1,065
	Ba	120,000	480,000	8,300
	Cs	5,900	23,000	7,100

OBSERVATION OF ANION EXCLUSION AT RNM-25 (CAMBRIC) FIELD TEST



STRUCTURAL DATA FOR ZEOLITES

<u>ANALCIME</u>

DENSITY	2.24 g/cc
VOID VOLUME	0.18 cc/cc
INTERSTITIAL VOLUME	0.089 cc/g
CHANNEL APERTURE	2.6 Å
KINETIC DIAMETER	2.6 Å

<u>CLINOPTILOLITE</u>

DENSITY	2.16 g/cc
VOID VOLUME	0.34 cc/cc
INTERSTITIAL VOLUME	0.21 cc/g
KINETIC DIAMETER	3.5 Å

<u>MORDENITE</u>

DENSITY	2.13 g/cc
VOID VOLUME	0.28 cc/cc
INTERSTITIAL VOLUME	0.15 cc/g
CHANNEL APERTURE (LARGE)	6.7 x 7.0 Å
CHANNEL APERTURE (SMALL)	2.9 x 5.7 Å
KINETIC DIAMETER	3.9 Å

EFFECTIVE IONIC RADII

ANION	IONIC RADIUS Å
F^-	1.38[7]
Cl^-	1.81[7]
I^-	2.16[7]
NO_3^-	2.68[8]
SO_4^-	2.88[8]
TcO_4^-	3.13[9]

ANION EXCLUSION VOLUMES

SAMPLE IDENTIFICATION	MEASURED (ml/g)	CALCULATED[a] (ml/g)	CALCULATED[b] (ml/g)
USWG2–339	0.056±0.010	0.030±0.006	—
USWG2–1951	0.20±0.03	0.112±0.020	0.145±0.028
USWG2–2017	0.13±0.01	0.109±0.020	0.142±0.025
USWG2–2698	0.069±0.009	0.072±0.008	0.09±0.011
USWG3–1868	0.035±0.001	0.033±0.004	0.035±0.004

[a] BASED ON VOID VOLUME

[b] BASED ON INTERSTITIAL VOLUMES OF DEHYDRATED ZEOLITES

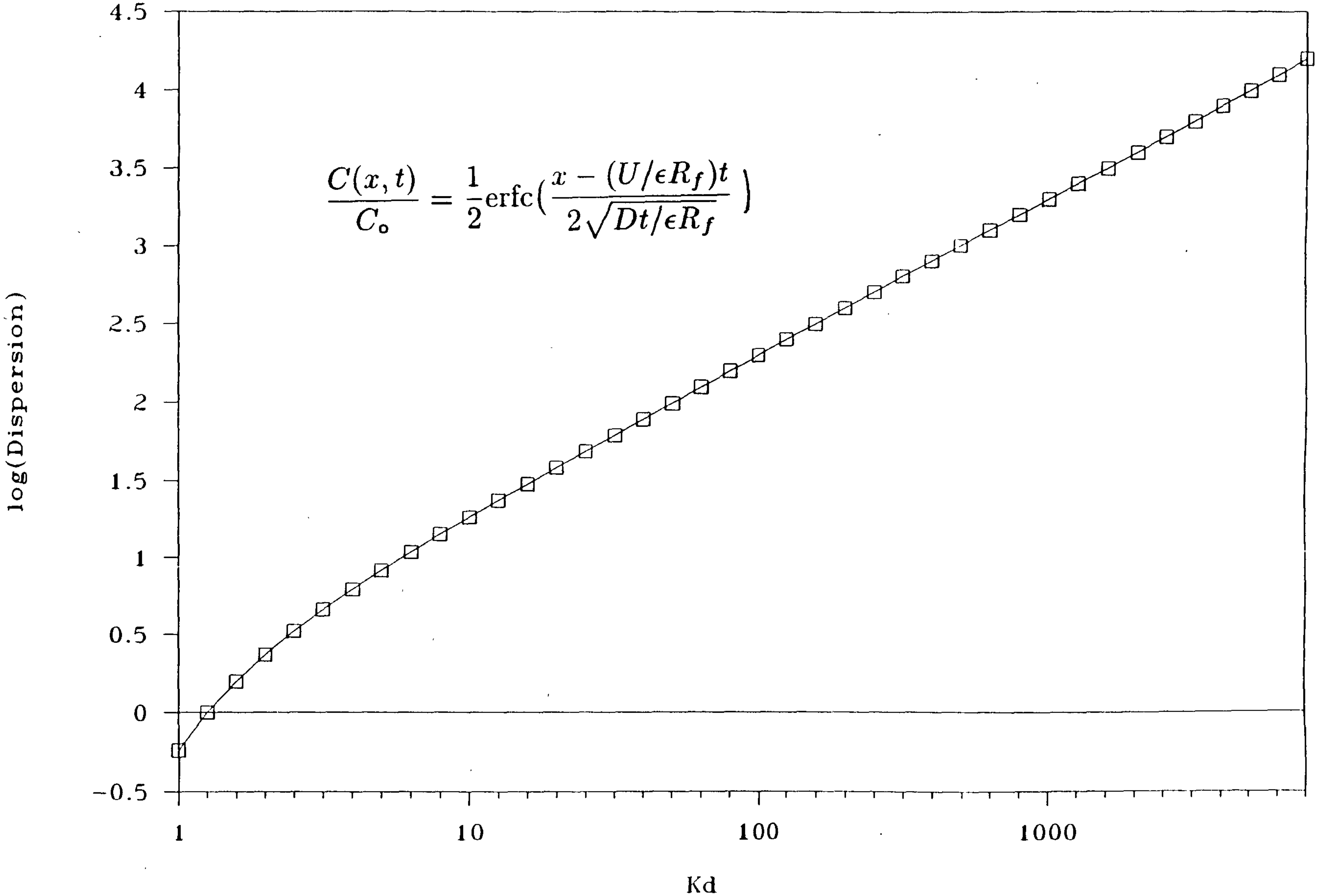
HOW DOES DISPERSION AFFECT THE MIGRATION OF CONTAMINANTS?

- THE BREAKTHROUGH OF CONTAMINANTS IS BROADENED BY DISPERSION. DISPERSIVITY IS EQUIVALENT TO THE HEIGHT OF THEORETICAL PLATE (AS IT IS REFERRED TO IN ANALYTICAL CHEMISTRY)

- A BROADENED BREAKTHROUGH CURVE RESULTS IN THE EARLY ARRIVAL OF A FRACTION OF TOTAL CONTAMINANT

- IF THE DISPERSIVITY IS LARGE, THE PEAK CONCENTRATION OF A CONSERVATIVE TRACER WILL OCCUR AT A TIME EARLIER THAN ANTICIPATED BASED ON THE POROSITY AND FLOW RATE ALONE

DISPERSION vs K_d



COMMON ASSUMPTIONS IN HYDROLOGY

- TRANSPORT OF RADIONUCLIDES IN POROUS MEDIA HAS BEEN CONSIDERED A DIFFUSIVE PROCESS,

$$\mathrm{div}(D\,\mathrm{grad}C - UC) = \frac{\epsilon \partial C}{\partial t}$$

  THIS APPROACH ASSUMES THAT A HETEROGENEOUS AQUIFER CAN BE TREATED AS AN EQUIVALENT HOMOGENEOUS POROUS MEDIUM

- THE EXISTENCE OF A REPRESENTATIVE ELEMENTARY VOLUME, REV. THE PRINCIPLE THAT VARIATIONS IN MACROSCOPIC VARIABLES OCCUR ONLY ON A SMALL SCALE, i.e., THE SCALE OF A PORE DIAMETER

- THAT DISPERSION CAN ALWAYS BE TREATED AS FICKIAN

- THE MIGRATION OF SORBING CONTAMINANTS CAN BE PREDICTED USING THE RETARDATION FACTOR,

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

NEW THEORIES OF CONTAMINANT MIGRATION

- STOCHASTIC MODELS ALLOW ONE TO CONSIDER HETEROGENEITY IN TERMS OF STATISTICAL PROPERTIES (MEAN, VARIANCE, COVARIANCE, ...). A SIMPLE CASE IS A STRATIFIED POROUS MEDIUM WITH FLOW PARALLEL TO THE STRATIFICATION. THE ADVECTION DISPERSION EQUATION IN RANDOM VARIABLES, ξ AND ζ, IS

$$X_t = \xi + \int_0^t u(Z_t)d\tau$$

$$Z_t = \zeta_t$$

- THE EQUIVALENT DISPERSION IN THIS TREATMENT IS

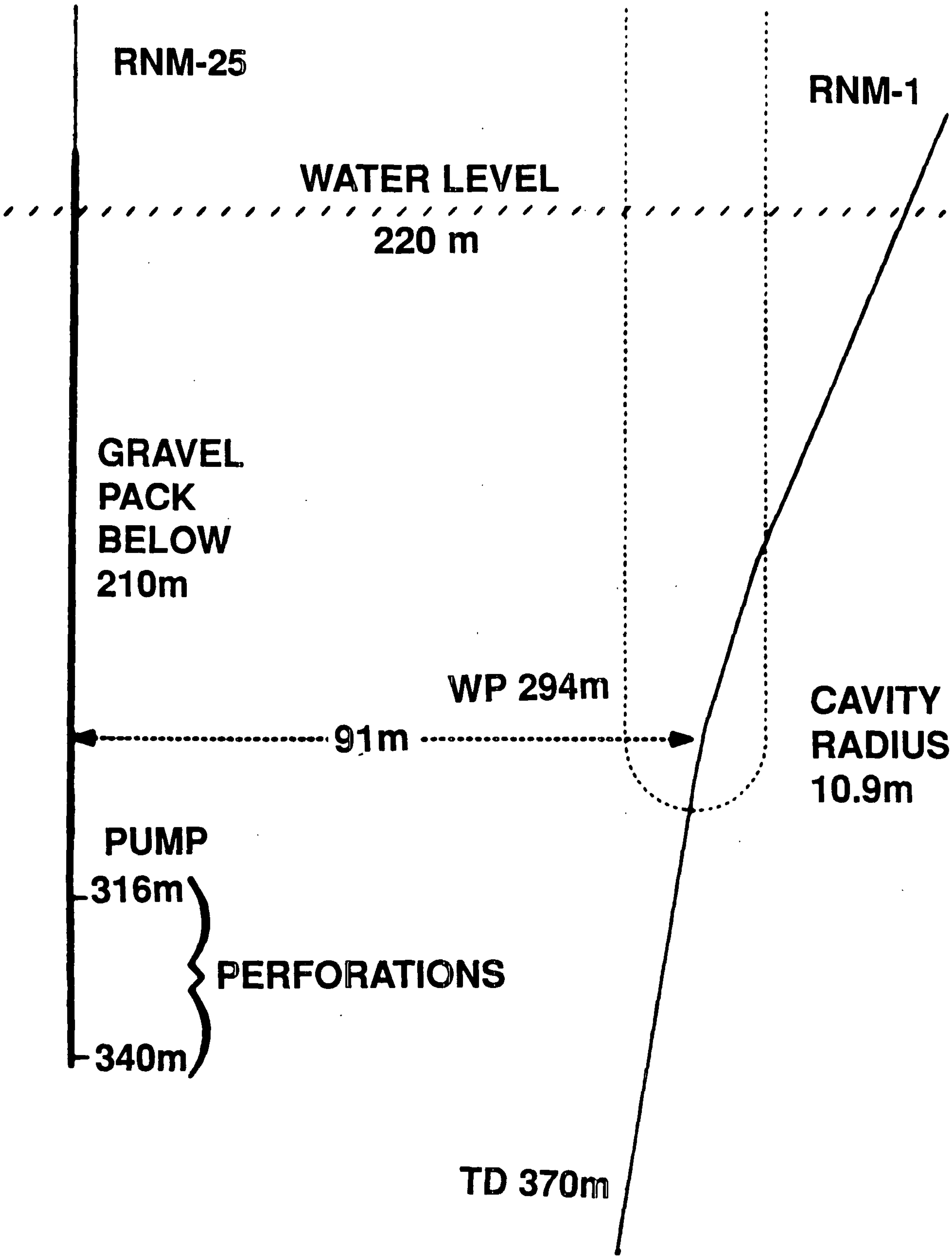
$$D_A = D_L +$$

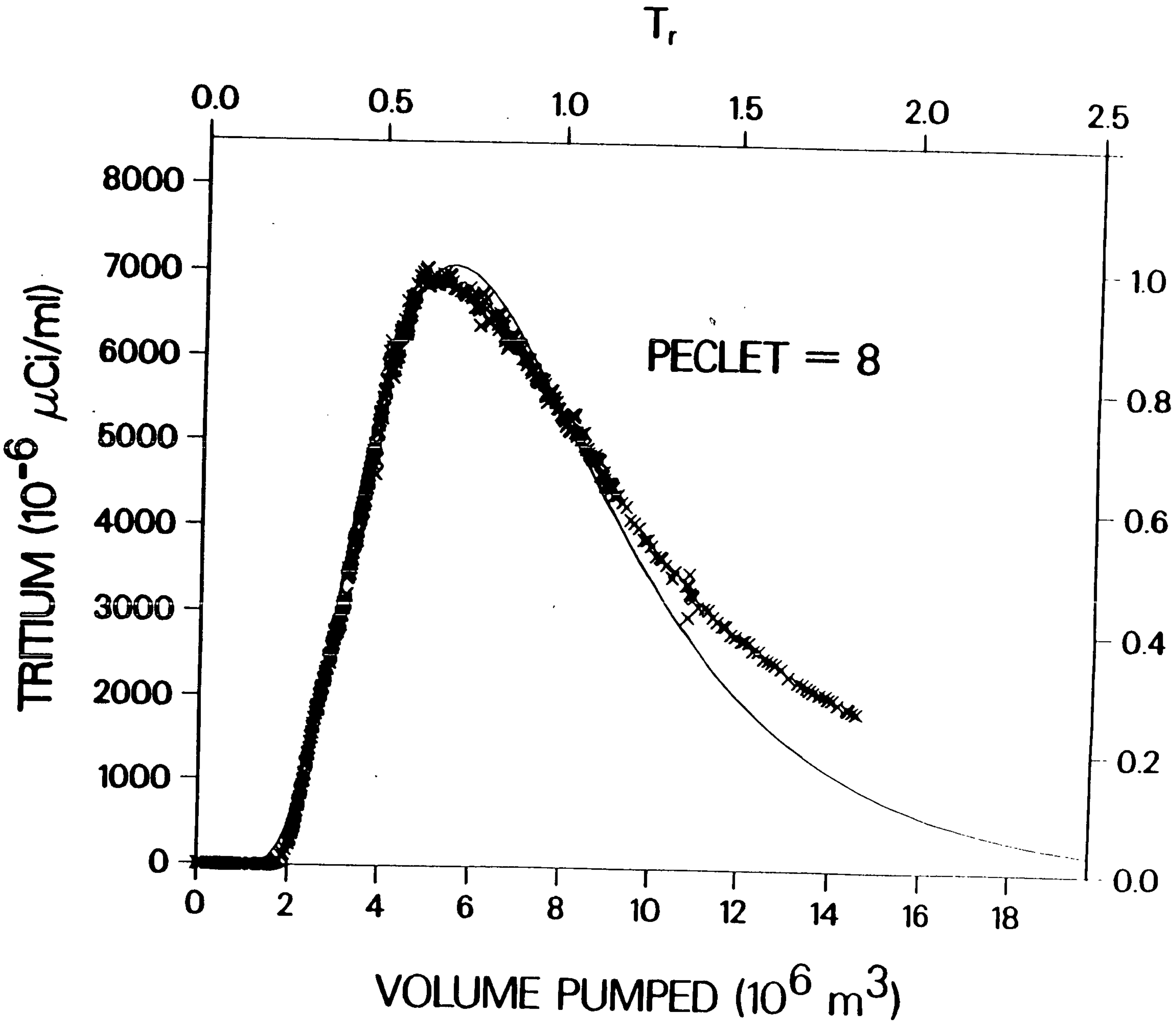
$$t^{-1} \int_0^t (t-\tau)\frac{1}{2(\pi D_T \tau)^{\frac{1}{2}}} \cdot \int_{-\infty}^{+\infty} \exp\left(-\frac{s^2}{4D_T\tau}\right) \mathrm{Cov(s)dsd}\tau$$

- IT CAN BE SHOWN FROM THIS EQUATION THAT DISPERSION IS STRICTLY FICKIAN ONLY WHEN THE COVARIANCE FUNCTION IS EQUAL TO THE FIRST DERIVATIVE OF THE DELTA FUNCTION. THE PORE STRUCTURE WHICH ENABLES THE USE OF REV PRINCIPLE APPROXIMATES THIS COVARIANCE FUNCTION

- THIS STOCHASTIC APPROACH DEMONSTRATES THAT THE CONVENTIONAL DIFFUSION EQUATION IS ONLY APPLICABLE TO A SUBSET OF SPATIAL DISTRIBUTIONS OF PERMEABILITY, i.e., THOSE WHERE THE GRAPH OF CONDUCTIVITY HAS A FRACTAL DIMENSION GREATER THAN 1.5

SCHEMATIC OF CAMBRIC FIELD TEST

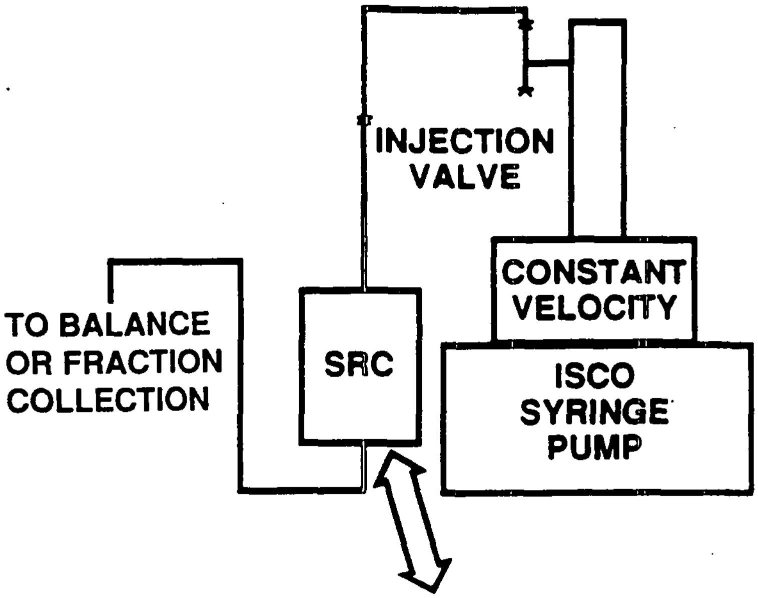


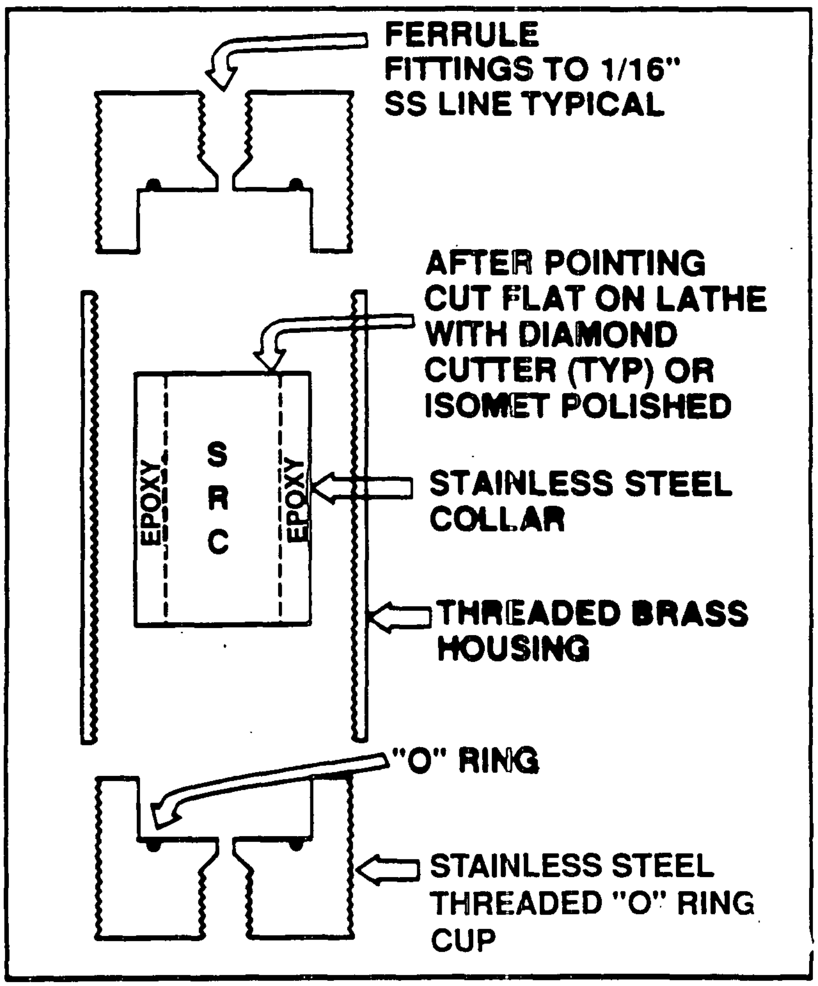


T_r
0.0
0.5
1.0
1.5
2.0
2.5
8000
7000
6000
5000
4000
3000
2000
1000
0
TRITIUM (10^-6 μCi/ml)
PECLET = 8
1.0
0.8
0.6
0.4
0.2
0.0
C_r
0
2
4
6
8
10
12
14
16
18
VOLUME PUMPED (10^6 m^3)

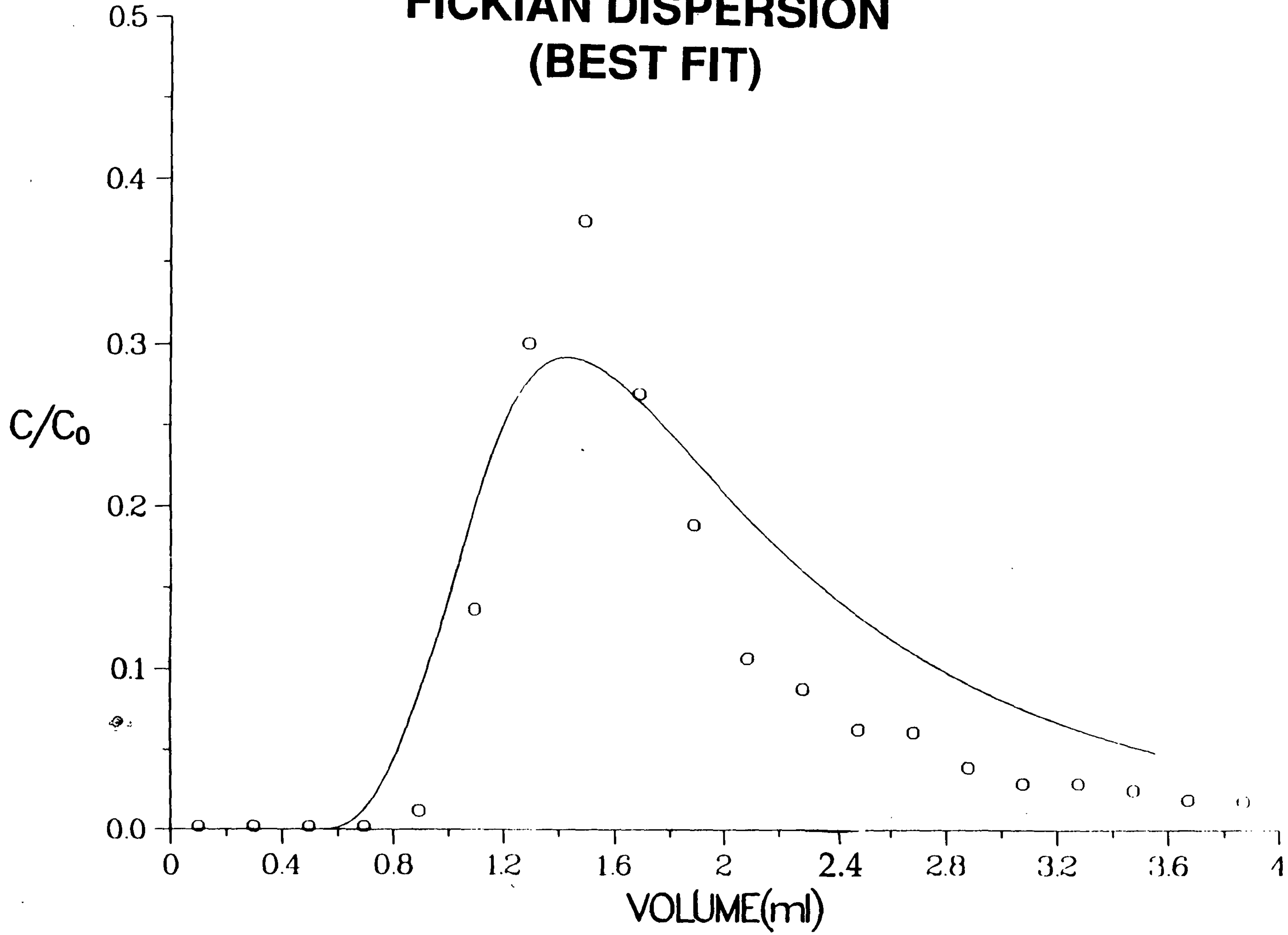
SOLID ROCK COLUMN SET-UP DRAWING

SET UP OF SYRINGE PUMP AND SOLID ROCK COLUMN

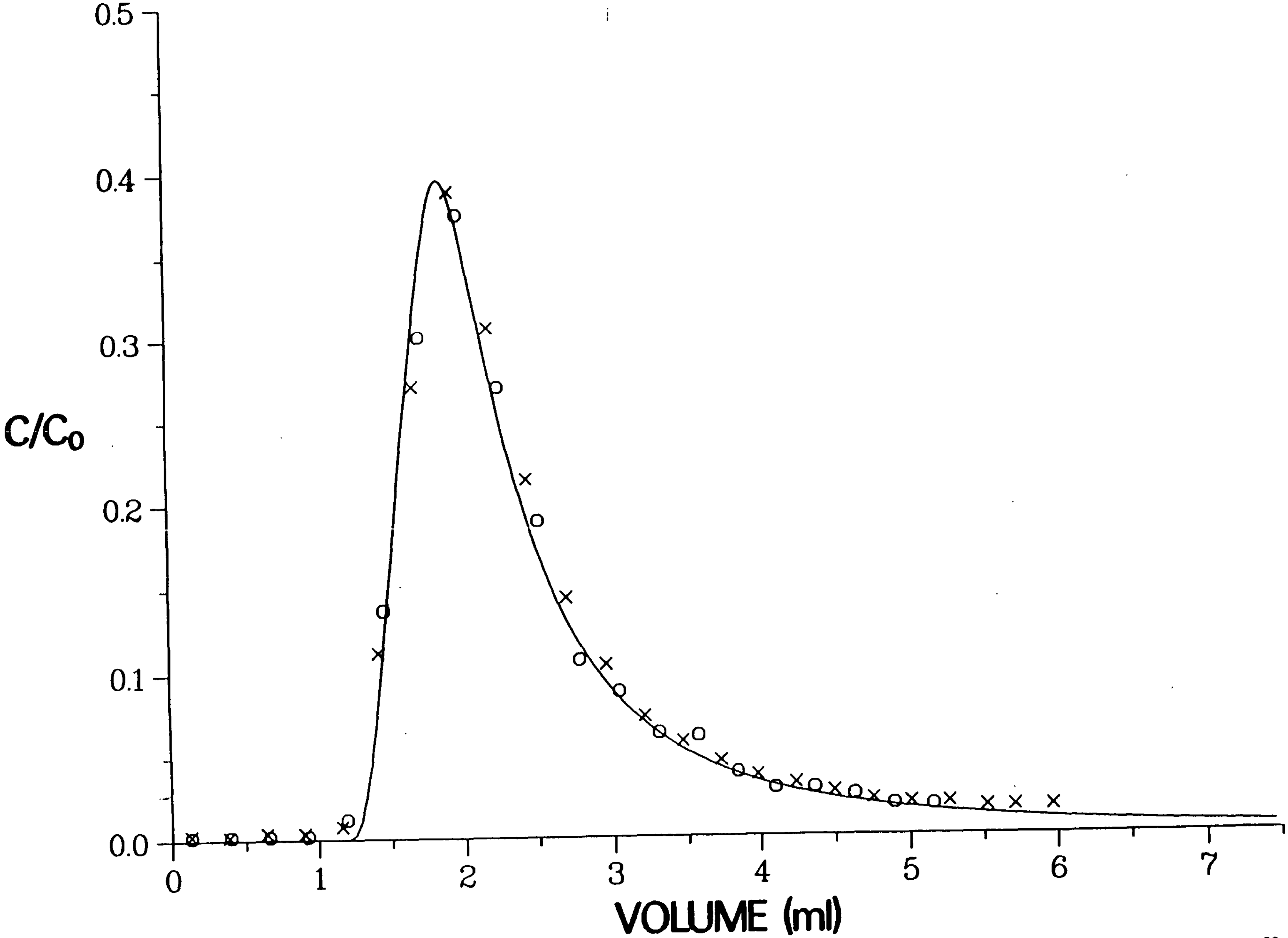




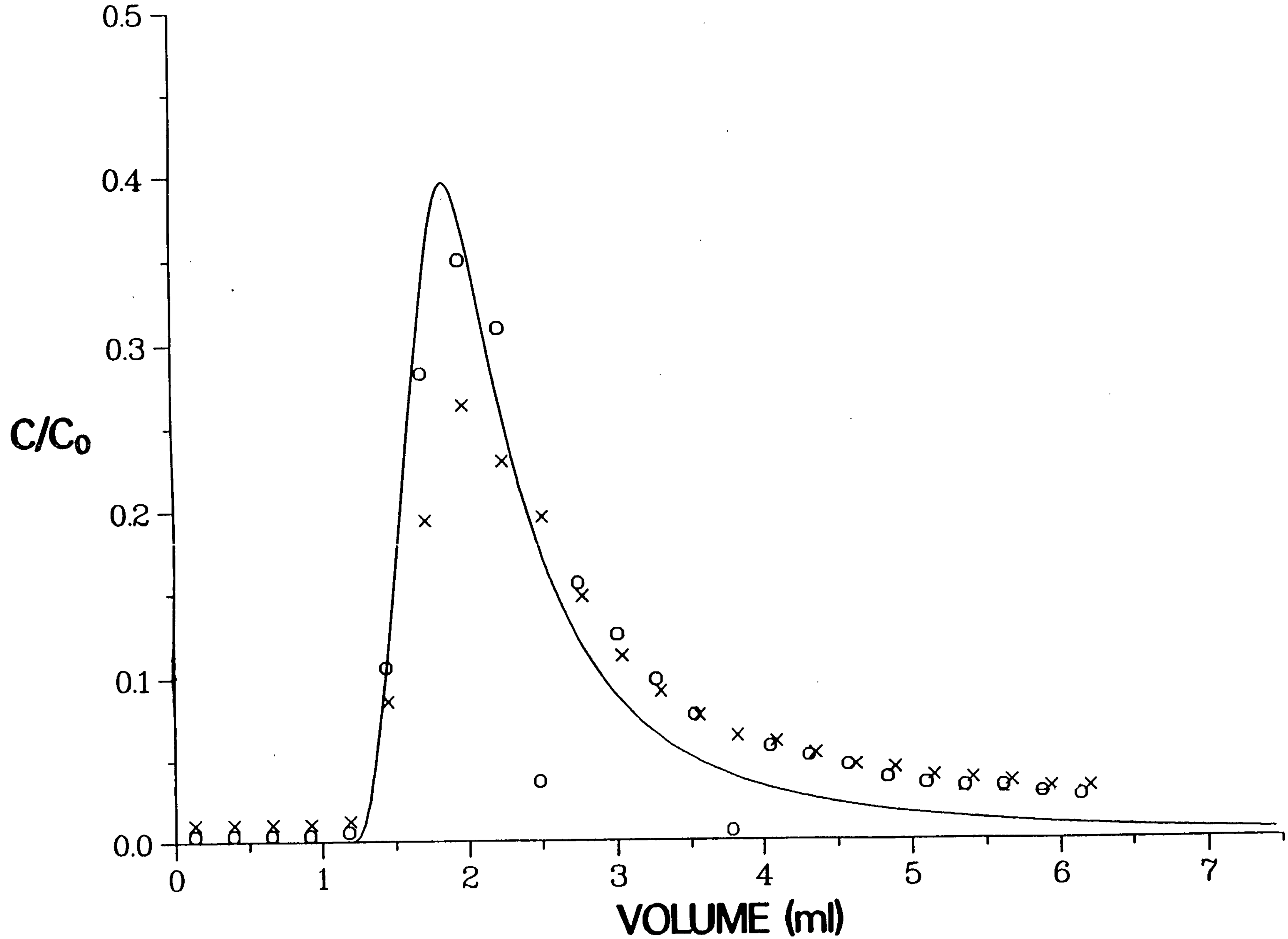
Tpt SRC 1 TRITUM RUN
FICKIAN DISPERSION
(BEST FIT)



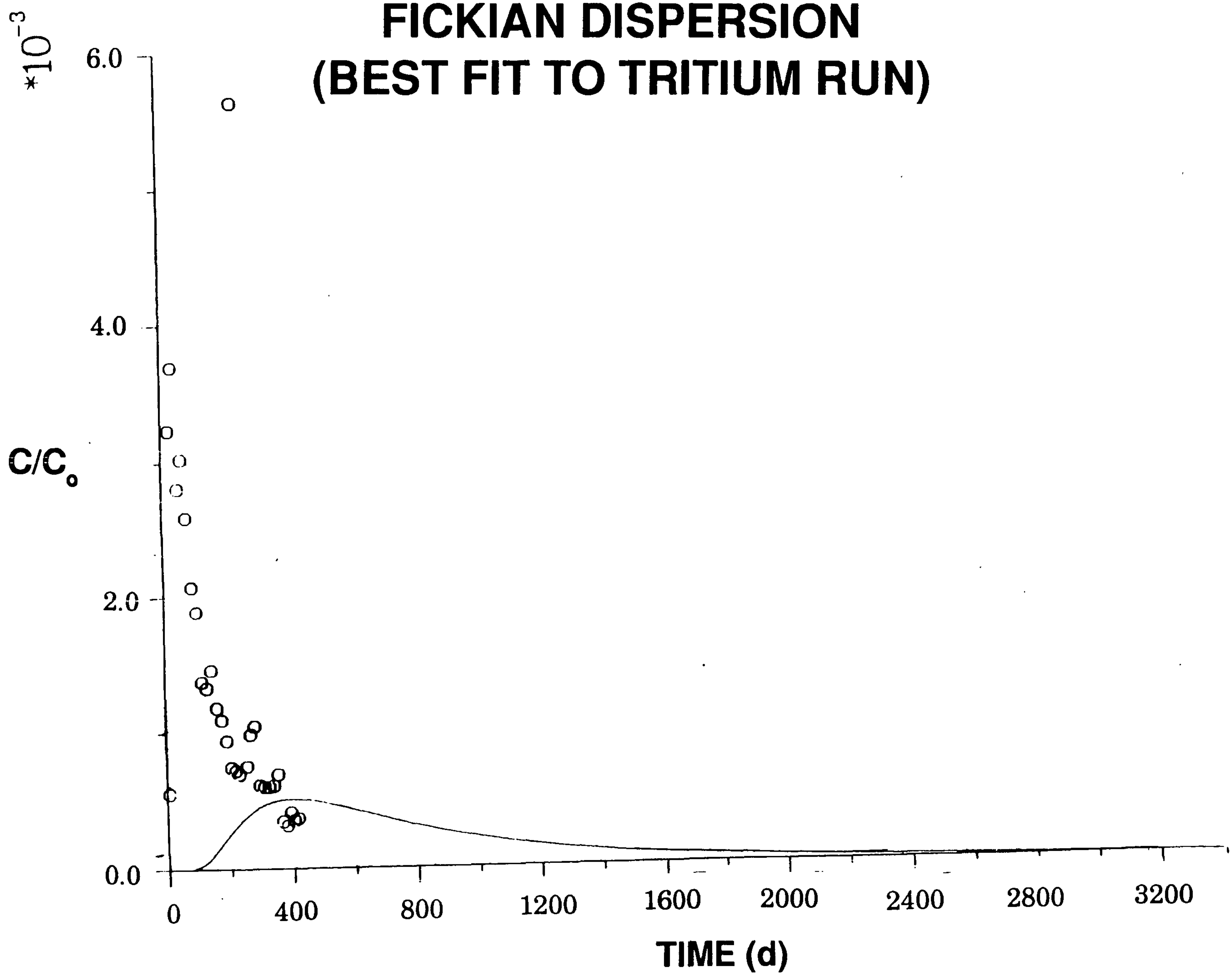
Tpt OUTCROP SRC 1 TRITIATED WATER RUNS
NON-FICKIAN DISPERSION
(BEST FIT)



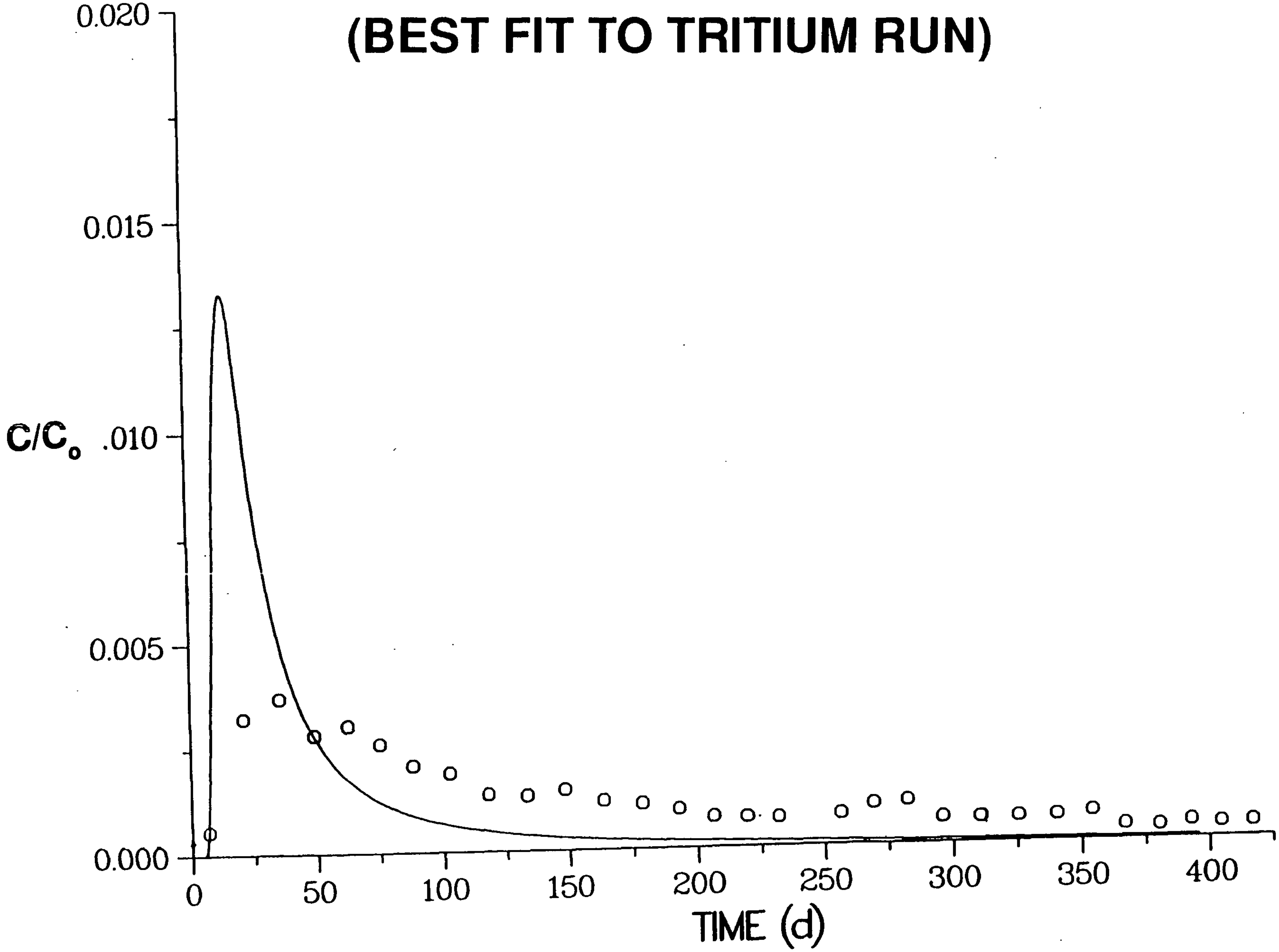
Tpt OUTCROP SRC 1 PERTECHNETATE RUNS



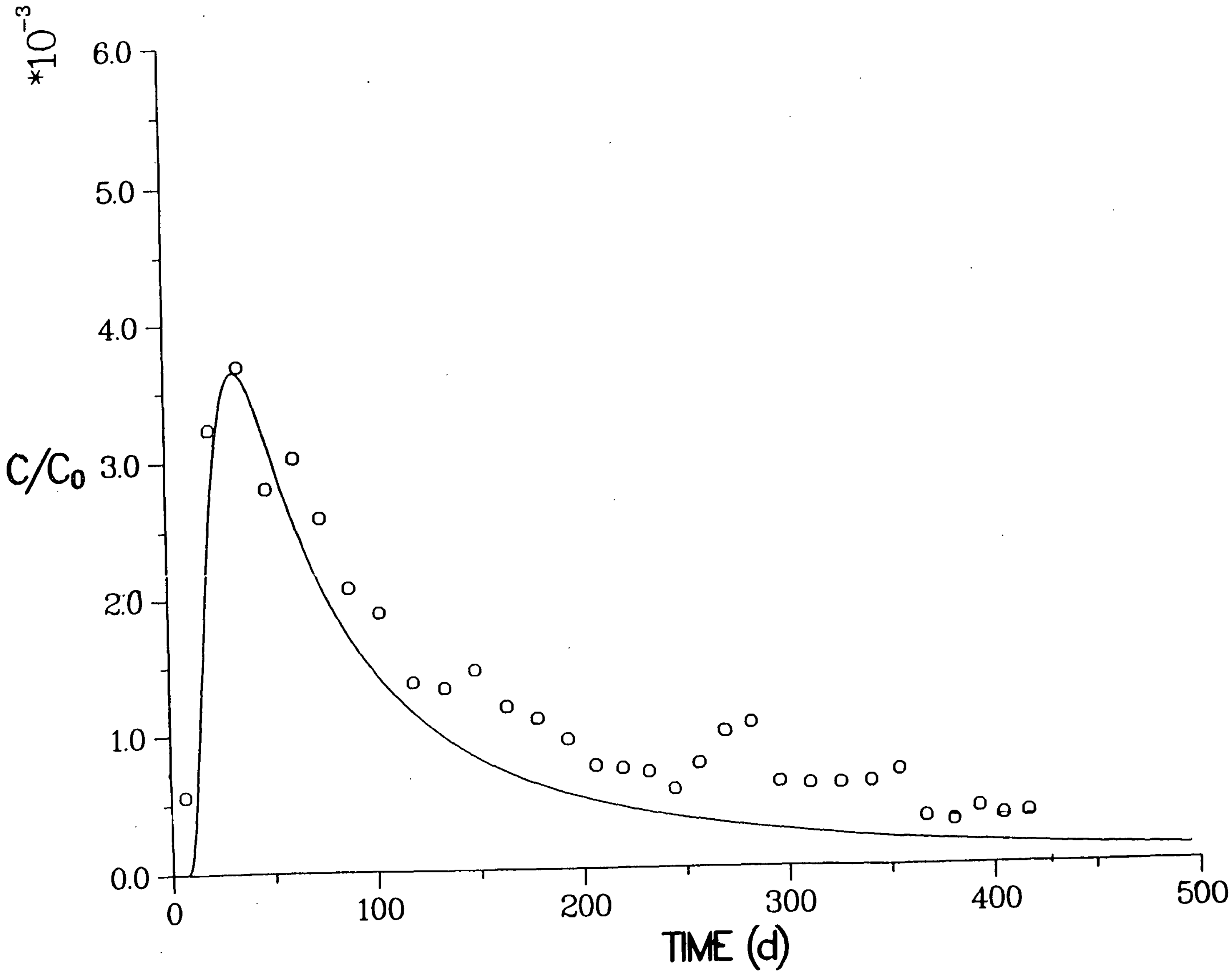
Tpt OUTCROP SRC-1 STRONTIUM RUN FICKIAN DISPERSION (BEST FIT TO TRITIUM RUN)



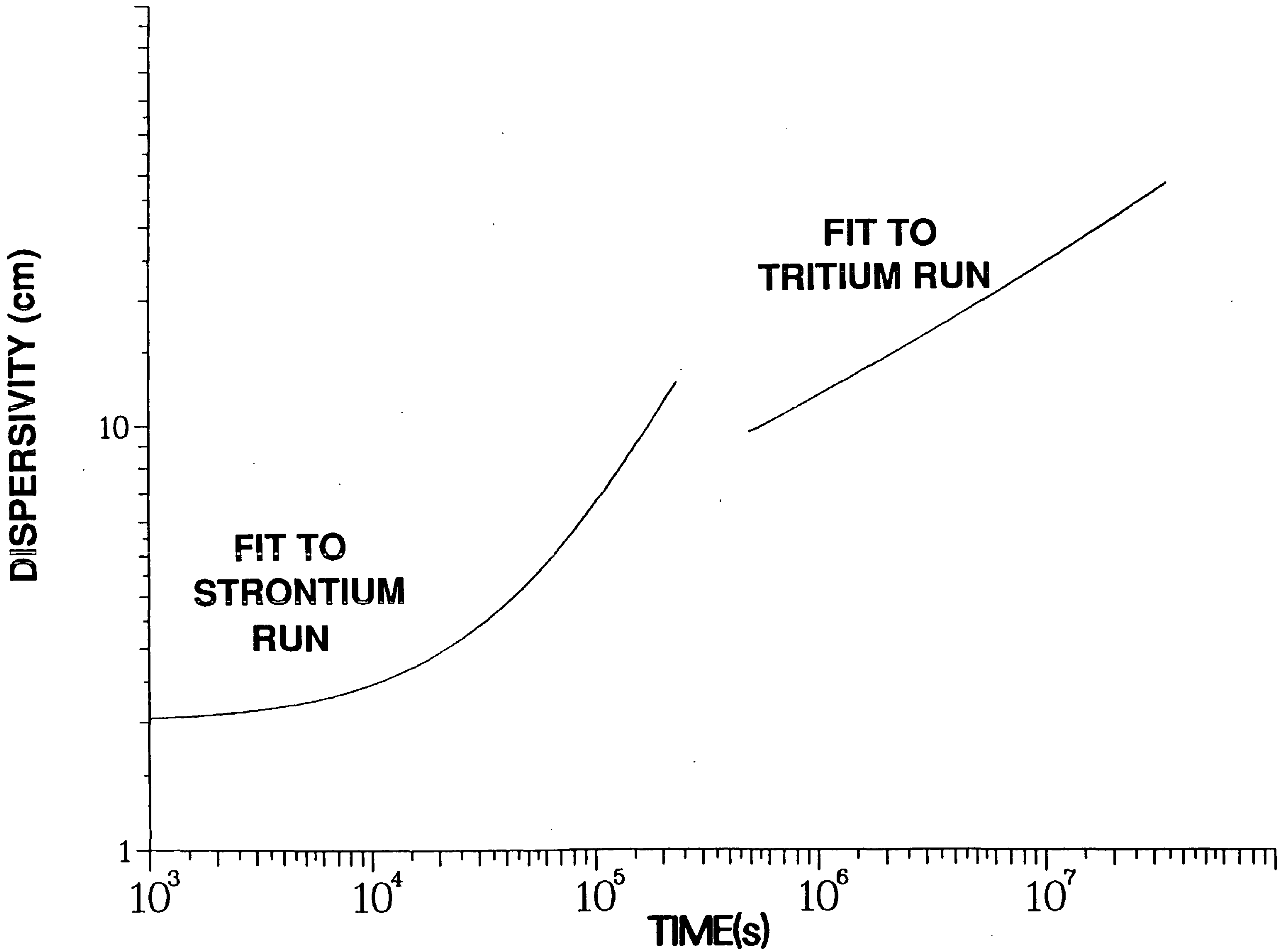
Tpt OUTCROP SRC 1 STRONTIUM RUN NON-FICKIAN DISPERSION (BEST FIT TO TRITIUM RUN)



Tpt OUTCROP SRC 1 STRONTIUM RUN
NON-FICKIAN DISPERSION



DISPERSIVITY vs TIME (TOPOPAH SRC 1)



INTACT TUFF COLUMNS: CONCLUSIONS

- DISPERSIVITIES ARE LARGE AND APPEAR TIME DEPENDENT FOR POROUS FLOW THROUGH INTACT DENSELY WELDED TUFF
- PEAK ARRIVALS FOR SORBING TRACER APPEAR MUCH EARLIER THAN EXPECTED FROM BATCH SORPTION K_ds UNLESS TIME DEPENDENT DISPERSION IS INVOKED
- RADIOASSAYS OF COLUMN SECTIONS EXHIBIT NONUNIFORM SORPTION OF RADIONUCLIDES
- PERTECHNETATE RETAINS THE SAME DISPERSION AS TRITIATED WATER, BUT THERE IS A LOSS OF TRACER IN THE FRAN RIDGE OUTCROP SAMPLES
- PERTECHNETATE HAS A MUCH GREATER DISPERSION THAN TRITIATED WATER, BUT THERE IS NO LOSS OF TRACER IN THE CALICO HILLS SAMPLES
- HETEROGENEITY IS AN IMPORTANT FACTOR EVEN AT THE LABORATORY SCALE

CONCLUSIONS

- BATCH R_d MEASUREMENTS AUGMENTED BY ISOTHERM AND MECHANISTIC STUDIES SHOULD YIELD A DEFENSIBLE DATABASE FOR USE IN PERFORMANCE ASSESSMENT CALCULATIONS
- LARGER SORPTION COEFFICIENTS MAY BE REQUIRED TO MITIGATE THE EFFECTS OF DISPERSION IF THE GEOCHEMICAL BARRIER IS TO FUNCTION EFFECTIVELY